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# Magnetic superexchange interactions: trinuclear bis(oxamidato) versus bis(oxamato) type complexes $\dagger$ 

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#### Abstract

The diethyl ester of o-phenylenebis(oxamic acid) (opbaH $\mathrm{Et}_{2}$ ) was treated with an excess of $\mathrm{RNH}_{2}$ in MeOH to cause the exclusive formation of the respective 0 -phenylenebis( $N(\mathrm{R})$-oxamides) (opboH $\mathrm{H}_{4} \mathrm{R}_{2}, \mathrm{R}=$ $\mathrm{Me} \mathbf{1}$, $\mathrm{Et} \mathbf{2},{ }^{n} \mathrm{Pr} 3$ ) in good yields. Treatment of 1-3 with half an equivalent of $\left[\mathrm{Cu}_{2}\left(\mathrm{AcO}_{4}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ or one equivalent of $\left[\mathrm{Ni}(\mathrm{AcO})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]$ followed by the addition of four equivalents of $\left[{ }^{n} \mathrm{Bu} \mathrm{H}_{4} \mathrm{~N}\right] \mathrm{OH}$ resulted in the formation of mononuclear bis(oxamidato) type complexes [ $\left.{ }^{n} B U_{4} N\right]_{2}\left[M\left(o p b o R_{2}\right)\right](M=N i, R=M e 4, ~ E t 5$, ${ }^{n} \operatorname{Pr}$ 6; $\left.M=C u, R=M e 7, E t 8,{ }^{n} \operatorname{Pr} 9\right)$. By addition of two equivalents of $\left[C u(p m d t a)\left(\mathrm{NO}_{3}\right)_{2}\right]$ to MeCN solutions of $\mathbf{7 - 9}$, novel trinuclear complexes $\left[\mathrm{Cu}_{3}\left(\mathrm{opboR} \mathrm{R}_{2}\right)(\mathrm{L})_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{~L}=\right.$ pmdta, $\mathrm{R}=\mathrm{Me} 10$, Et 11, ${ }^{\mathrm{n}} \mathrm{Pr}$ 12) could be obtained. Compounds $\mathbf{4 - 1 2}$ have been characterized by elemental analysis and NMR/IR spectroscopy. Furthermore, the solid state structures of $\mathbf{4 - 1 0}$ and 12 have been determined by single-crystal X-ray diffraction studies. By controlled cocrystallization, diamagnetically diluted $\mathbf{8}$ and $\mathbf{9}(1 \%)$ in the host lattice of $\mathbf{5}$ and $\mathbf{6} \mathbf{9 9 \%}$ ) (8@5 and $\mathbf{9} @ 6$ ), respectively, in the form of single crystals have been made available, allowing single crystal ESR studies to extract all components of the $g$-factor and the tensors of onsite ${ }^{{ }^{C u} A} A$ and transferred ${ }^{{ }^{N} A}$ hyperfine (HF) interaction. From these studies, the spin density distribution of the $[$ Cu(opboEt 2$)]^{2-}$ and $\left[C u\left(o p b o^{n} \mathrm{Pr}_{2}\right)\right]^{2-}$ complex fragments of $\mathbf{8}$ and 9 , respectively, could be determined. Additionally, as a single crystal ENDOR measurement of $\mathbf{8}$ © $\mathbf{5}$ revealed the individual HF tensors of the N donor atoms to be unequal, individual estimates of the spin densities on each $N$ donor atom were made. The magnetic properties of $10-12$ were studied by susceptibility measurements versus temperature to give $J$ values varying from $-96 \mathrm{~cm}^{-1}(10)$ over $-104 \mathrm{~cm}^{-1}(11)$ to $-132 \mathrm{~cm}^{-1}(12)$. These three trinuclear $\mathrm{Cu}^{\prime \prime}$-containing bis(oxamidato) type complexes exhibit $J$ values which are comparable to and slightly larger in magnitude than those of related bis(oxamato) type complexes. In a summarizing discussion involving experimentally obtained ESR results (spin density distribution) of $\mathbf{8}$ and $\mathbf{9}$, the geometries of the terminal $[\mathrm{Cu}(\mathrm{pmdta})]^{2+}$ fragments of 12 determined by crystallographic studies, together with accompanying quantum chemical calculations, an approach is derived to explain these phenomena and to conclude if the spin density distribution of mononuclear bis(oxamato)/bis(oxamidato) type complexes could be a measure of the $J$ couplings of corresponding trinuclear complexes.


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## Introduction

Over the past three decades, the diethyl ester of $N, N^{\prime}$-alkylene or arylene bis(oxamic acid) (type I) has been extensively used for the synthesis of mononuclear bis(oxamato) type IV complexes, $c f$. Scheme 1. ${ }^{1}$ The flexidentate properties of the type IV complexes paved the way for, e.g., the preparation of their corresponding trinuclear type VII complexes, which are excellently suited to study magnetic superexchange phenomena. ${ }^{1,2}$

On the other hand, mono- N - (type II) and di- N -substituted (type III) type I compounds and, thus, their subsequent mononuclear type V and VI complexes, cf. Scheme 1, have received less attention. ${ }^{3-6}$ Due to this, a limited number of corresponding trinuclear type VIII and IX complexes, cf. Scheme 1, have been reported so far. ${ }^{7,8 a}$

As reported by Kahn, ${ }^{9}$ a slight tuning of the ligand skeleton that bridges neighbouring metals, mainly the replacement of the Lewis-basic heteroatoms of the oxamato fragments with less electronegative ones, can induce higher $J$ couplings between neighbouring, e.g. $\mathrm{Cu}^{\text {II }}$ ions, as shown for a number of binuclear complexes.

In a recent study, we observed a direct proportionality between the spin density distribution of a type $\mathbf{V}$ complex, namely $\quad\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}[\mathrm{Cu}($ opooMe) $]$ (opooMe $=o$-phenylene( $N^{\prime}$-methyl oxamidato)(oxamato)) (13), and the magnetic superexchange interactions of its corresponding trinuclear type VIII complex, namely $\left[\mathrm{Cu}_{3}(\right.$ opooMe $\left.)(\text { pmdta })_{2}\right]\left(\mathrm{NO}_{3}\right)_{2} \cdot 3 \mathrm{MeCN}(14) .{ }^{8 a}$ These results support the assumption, on the one hand, that the spin density distribution of mononuclear type IV and/or $\mathbf{V}$ complexes is a measure of the magnitude of $J$ values of corresponding trinuclear type VII/VIII complexes. ${ }^{8 a, 10}$

On the other hand, the asymmetric type VIII complex 14 has been synthesized to verify whether the magnetic superexchange interactions between its oxamato or oxamidato bridged $\mathrm{Cu}^{\text {II }}$ ions are different or not. However, only one experimental $J$ value of $-130 \mathrm{~cm}^{-1}$ was determined, although, for example, from DFT calculations two different $J$ values ( $-84 \mathrm{~cm}^{-1} /-72 \mathrm{~cm}^{-1}$ via the oxamidato/oxamato bridging unit) were derived. ${ }^{8 b}$ This observation agrees with the statement made by Kahn on how to induce higher $J$ couplings. ${ }^{9}$ For example, we have already reported on the conversion of $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}[\mathrm{Cu}($ opba $)] \quad(15)$ to $\left[\mathrm{Cu}_{3}(\right.$ opba $\left.)(\text { pmdta })_{2}\left(\mathrm{NO}_{3}\right)\right]-$ $\left(\mathrm{NO}_{3}\right) \cdot 2 \mathrm{MeCN}(16$, opba $=o$-phenylenebis(oxamato)) or the
conversion of $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}[\mathrm{Cu}(\mathrm{obbo})]$ (17) to $\left[\mathrm{Cu}_{3}(\mathrm{obbo})-\right.$ (pmdta) $\left.)_{2}\left(\mathrm{NO}_{3}\right)\right]\left(\mathrm{NO}_{3}\right) \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot \mathrm{H}_{2} \mathrm{O} \quad(18, \quad$ obbo $=o$-benzylbis(oxamato)) with $J=-89 \mathrm{~cm}^{-1}$ and $J=-111 \mathrm{~cm}^{-1}$, respectively. ${ }^{11,12}$ However, additional studies are required to verify this finding.

In order to elaborate further the interplay between the spin density distribution of mononuclear type IV-VI complexes and the magnetic superexchange interactions of their corresponding trinuclear type VII-IX complexes, we report here on the synthesis of the mononuclear type VI complexes $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{M}\left(\mathrm{opboR}_{2}\right)\right]\left(\mathrm{M}=\mathrm{Ni}^{\mathrm{II}}, \mathrm{R}=\mathrm{Me}(4)\right.$, Et (5), ${ }^{n} \operatorname{Pr}(\mathbf{6}) . \mathrm{M}=$ $\mathrm{Cu}^{\text {II }}, \mathrm{R}=\mathrm{Me}$ (7), Et (8), $\left.{ }^{n} \operatorname{Pr}(9)\right)$. Diamagnetically diluted single crystals of 8@5 and 9@6 were prepared to estimate the spin density distributions of 8 and 9 from the HF tensors determined by ESR spectroscopy. From $\mathbf{7 - 9}$, the corresponding type IX complexes $\left[\mathrm{Cu}_{3}\left(\mathrm{opboR}_{2}\right)(\mathrm{L})_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~L}=$ pmdta, $\mathrm{R}=\mathrm{Me}(\mathbf{1 0})$, Et (11), ${ }^{n} \operatorname{Pr}(\mathbf{1 2 )})$ were synthesized to determine their magnetic properties. The results obtained thereof are reported here, together with supporting DFT calculations.

## Results and discussion

## Synthesis

The synthesis of compounds $\mathbf{1 - 1 2}$ is shown in Scheme 2. 1-3 were synthesized according to a procedure reported by Ruiz et al. ${ }^{3}$ by the condensation reactions of opbaH ${ }_{2} \mathrm{Et}_{2}$ with an excess of alkylamines (1: $\mathrm{MeNH}_{2}$, 2: $\mathrm{EtNH}_{2}$, 3: ${ }^{n} \mathrm{PrNH}_{2}$ ) in MeOH. Compounds 1-3 were separated from the reaction mixture by filtration.

For the synthesis of the mononuclear type VI complexes 4-9, a hot MeOH solution of $\left[\mathrm{Cu}_{2}(\mathrm{OAc})_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ or $\left[\mathrm{Ni}(\mathrm{OAc})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]$, respectively, was added to a suspension of either 1-3 in MeOH. ${ }^{13}$ Then, four equivalents of $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OH}$ were added, causing the complete dissolution of all suspended materials and the reaction mixture was stirred for 15 min at $60^{\circ} \mathrm{C}$. Complexes 4-9 were isolated after appropriate workup as yellow and red powders. ${ }^{13}$

The trinuclear type IX complexes $\mathbf{1 0} \mathbf{- 1 2}$ were synthesized conveniently according to Scheme 2 in MeCN. After reducing the volume of the reaction mixtures, the desired complexes were precipitated by the addition of THF. The purification was effectively achieved by re-dissolving the crude material in



$\mathbf{X}=\mathbf{Y}=$ OEt (type $\mathbf{I})$
$\mathbf{X}=\mathbf{Y}=\mathbf{O}$ (type IV)
$\mathbf{X}=\mathbf{Y}=\mathbf{O}$ (type VII)
$\mathbf{X}=\mathbf{O E t}, \mathbf{Y}=$ RNH (type II)
$\mathbf{X}=\mathbf{O}, \mathbf{Y}=$ RN (type $\mathbf{V}$ )
$\mathbf{X}=\mathbf{O}, \mathbf{Y}=$ RN (type VIII)
$\mathbf{X}=\mathbf{Y}=$ RNH (type III)
$\mathbf{X}=\mathbf{Y}=$ RN (type VI)
$\mathbf{X}=\mathbf{Y}=$ RN (type $\mathbf{I X}$ )

Scheme 1 Chemical structures of type I-IX compounds.


Scheme 2 Synthetic strategy to achieve the mononuclear 4-9 and trinuclear 10-12 complexes.

MeCN and precipitation by the addition of THF. This method was satisfactory to produce analytically pure complexes, $c f$. the Experimental part.

## Structural descriptions

The mononuclear type VI complexes 4-9. The solid state structures of these complexes were determined by single crystal X-ray crystallographic studies, whereby 5 forms crystals of the composition $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Ni}\left(\right.\right.$ opboEt $\left.\left._{2}\right)\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}\left(5^{\prime}\right)$ and 8 forms $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Cu}\left(\right.\right.$ opboEt $\left.\left._{2}\right)\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}\left(8^{\prime}\right)$. The molecular structures of the dianionic complex fragments of the $\mathrm{Ni}^{\mathrm{II}} / \mathrm{Cu}^{\mathrm{II}}$ con-
taining type VI complexes are shown in Fig. 1 and 2, respectively, selected bond lengths and angles are given in Table 1 and crystal/structural refinement data are summarized in Table 3. The dianionic complex fragments $\left[\mathrm{M}\left(\mathrm{opboR}_{2}\right)\right]^{2-}$ are denoted in the following as follows: $\mathrm{M}=\mathrm{Ni}^{\mathrm{II}}, \mathrm{R}=\mathrm{Me}(\mathbf{4 A})$, Et (5A), ${ }^{n} \operatorname{Pr}(\mathbf{6 A})$ and $\mathrm{M}=\mathrm{Cu}^{\mathrm{II}}, \mathrm{R}=\mathrm{Me}(\mathbf{7 A})$, Et (8A), ${ }^{n} \operatorname{Pr}(\mathbf{9 A})$.

For 6 the asymmetric unit comprises two crystallographically different $\left[\mathrm{Ni}\left(\mathrm{opbo}\left({ }^{n} \mathrm{Pr}\right)_{2}\right)\right]^{2-}$ dianionic complex fragments, denoted as 6A (comprising Ni1) and 6B (comprising Ni2). Related bond lengths and angles of $\mathbf{6 A}$ and $\mathbf{6 B}$ show differences of up to $c a .2 \%$ and $c a .6 \%$, respectively. Additionally, in


Fig. 1 ORTEP diagrams of the molecular structures of 4A,5A and 6A (left to right) at 50,50 and 25\% ellipsoid probability. Above: top view. Below: side view. All hydrogen atoms are omitted for clarity. The sign $\varangle$ refers to calculated interplanar angles between differently coloured mean planes. With hdp the atom having the highest deviation from planarity of calculated mean planes is indicated. Symmetry operation for ' $A$ ' $5 A$ : $-x, y,-z+\frac{1}{2}$.


Fig. 2 ORTEP diagrams of the molecular structures of 7A, 8A and 9A (left to right) at 50, 50 and 25\% ellipsoid probability. Above: top view. Below: side view. All hydrogen atoms are omitted for clarity. The sign $\varangle$ refers to calculated interplanar angles between differently coloured mean planes. Symmetry operation for ' $A$ ' 8A: $-x, y,-z+\frac{1}{2}$.
the case of $\mathbf{6 A}$ an anti-conformation of the ${ }^{n} \mathrm{Pr}$ groups with respect to their orientation to the almost planar $\{\mathrm{Ni}(\mathrm{opbo})\}$ unit is observed, whereas for 6B a syn-conformation is found. Despite this, only data of $\mathbf{6 A}$ will be discussed. For completeness and comparison, Table 1 gives bond lengths and angles of both 6A and 6B. Fig. S1 $\dagger$ displays the molecular structures of $\mathbf{6 A}$ and $\mathbf{6 B}$. The 1D chains formed by $\mathbf{5}^{\prime}$ and $\mathbf{8}^{\prime}$ due to intermolecular hydrogen bonds are illustrated in Fig. S2 and S3, $\dagger$ while selected bond lengths and angles of these hydrogen bonds are given in Tables S1 and S2, $\dagger$ respectively.

For $\mathbf{5 A}$ and $\mathbf{8 A}$ crystallographically imposed $C_{2}$ symmetry is observed. The $C_{2}$ axes pass the M1 atom and the middle of the C3/C3A bond, cf. Fig. 1 and 2. In contrast, all other herein discussed $\left[\mathrm{M}\left(\mathrm{opboR}_{2}\right)\right]^{2-}$ fragments exhibit $C_{1}$ symmetry. Moreover, as revealed by entries in Table 3, related pairs of $\mathrm{Ni}^{\text {iI }} / \mathrm{Cu}^{\text {II }}$ containing complexes ( $\mathbf{4}$ and 7, 5 and 8, 6 and 9) can be regarded as isomorphic to each other. In the case of the related $\mathrm{Ni}^{\mathrm{II}} / \mathrm{Cu}^{\text {II }}$ pair of $6\left(\mathrm{Ni}^{\mathrm{II}}\right.$, monoclinic, $\left.P 2(1)\right)$ and $9\left(\mathrm{Cu}^{\mathrm{II}}\right.$, monoclinic, $P 2(1) / c$ ), unit cell parameters are in good agreement with each other, although the determined space group is different. It is verified that a solution/refinement of 6 in the space group $P 2(1) / c$ and of 9 in $P 2(1)$, respectively, is not possible. Responsible for this observation is the orientation of the ${ }^{n} \operatorname{Pr}$ groups with respect to the planar $\{\mathbf{M}(\mathrm{opbo})\}$ units, $c f$.
above. Despite this, the isomorphism of corresponding pairs indicates that a co-crystallization of them should be possible, $c f$. the Experimental part.

A common feature of $\mathbf{4 A} \mathbf{- 9 A}$ is the coordination of the respective opboR ${ }_{2}{ }^{4-}$ ligands to the metal ions by their four deprotonated amido nitrogen atoms N1-N4, forming planar $\mathrm{MN}_{4}$ coordination units, $c f$. Fig. 1 and 2 . The metal ions are located $0.004(1) \AA(4 A), 0.000 \AA(5 A), 0.006(5) \AA(6 A), 0.001(1) \AA$ $(7 \mathbf{A}), 0.0002(10) \AA(\mathbf{8 A})$ and $0.003(3) \AA(9 A)$, respectively, above/ below the calculated mean planes of atoms N1-N4 with root mean square deviations (rmsd) from planarity of $0.033 \AA(4 \mathrm{~A})$, $0.047 \AA(5 A), 0.001 \AA(6 A), 0.055 \AA(7 \mathrm{~A}), 0.081 \AA(8 \mathbf{A})$ and $0.023 \AA(9 \mathbf{A})$, respectively. The planarity of the $\mathrm{MN}_{4}$ coordination units is indicated further by the sum of the four bond angles around the metal ions of $360.05(14)^{\circ}$ for $\mathbf{4 A}, 360.14(17)^{\circ}$ for 5A, 360.0(7) ${ }^{\circ}$ for 6A, $360.18(14)^{\circ}$ for 7A, $360.41(16)^{\circ}$ for 8A and $360.1(6)^{\circ}$ for $\mathbf{9 A}$, respectively. As observed and discussed for the related type IV complexes, $c f$. Scheme $1,{ }^{14}$ a unique feature of planar complexes possessing 5-5-5 fused chelate rings around the respective metal ion is that three of the bond angles are rather small, whereas the fourth one is substantially larger. Indeed, this situation is observed as well for $\mathbf{4 A}-\mathbf{9 A}$ with the bond angles N1-M1-N3, N1-M1-N2 and N3-M1-N4 being in the range from $80.8(3)^{\circ}(\mathbf{9 A})$ to $86.3(4)^{\circ}(\mathbf{6 A})$ compared to

Table 1 Selected bond lengths $(\AA \AA)$ and angles $\left({ }^{\circ}\right)$ of 4A-9A and of the $\left[C u\left(o p b o R_{2}\right]^{2-}\right.$ fragments of 10A/10B and 12A

|  | $4 A^{a}$ | $\mathbf{5} \mathbf{A}^{a, b}$ | 6A/6B ${ }^{a, c}$ | $7 \mathrm{~A}^{\text {d }}$ | $8 \mathbf{A}^{\text {b,d }}$ | $9 \mathrm{~A}^{d}$ | 10A/10B ${ }^{c, d}$ | $12 A^{d}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Bond lengths |  |  |  |  |  |  |  |  |
| N1-M1 | 1.8485(16) | 1.8546(15) | 1.855(7)/1.864(6) | 1.938(16) | 1.9374(17) | $1.934(6)$ | 1.953(9)/1.946(16) | 1.953(11) |
| N2-M1 | 1.9033(16) | 1.9130(16) | 1.879(6)/1.877(6) | 1.952(17) | 1.9645(18) | 1.967 (7) | 1.985(7)/1.952(16) | 1.986(13) |
| N3-M1 | $1.8508(15)$ | 1.8546(15) | 1.879(7)/1.855(8) | 1.938(17) | 1.9374(17) | $1.936(7)$ | 1.926(9)/1.918(14) | $1.933(11)$ |
| N4-M1 | $1.8989(16)$ | 1.9130(16) | 1.919(8)/1.950(6) | 1.953(17) | 1.9645(18) | 1.942 (7) | 1.991(7)/1.948(17) | $1.992(12)$ |
| C1-O1 | 1.237 (2) | 1.247(2) | 1.250(8)/1.267(9) | 1.239(2) | 1.244(3) | 1.244 (3) | 1.294(13)/1.28(4) | $1.297(17)$ |
| C2-O2 | 1.247 (2) | 1.255(2) | 1.275(8)/1.274(8) | 1.251(2) | 1.258(3) | 1.240 (7) | 1.297(13)/0.93(5) | 1.278(19) |
| C3-O3 | 1.239(2) | 1.247(2) | 1.217(12)/1.243(11) | 1.243(2) | 1.244(3) | 1.171(8) | 1.43(3)/1.198(13) | $1.262(16)$ |
| C4-O4 | 1.245(2) | 1.255(2) | 1.312(15)/1.263(9) | 1.250 (3) | 1.258(3) | 1.312(10) | 1.296(14)/1.206(14) | $1.300(17)$ |
| C1-C2 | 1.544(3) | 1.539(3) | 1.524(11)/1.493(12) | 1.545(3) | 1.551(3) | 1.561(11) | 1.527(17)/1.34(4) | 1.47(2) |
| C3-C4 | 1.541(3) | 1.539(3) | 1.44(2)/1.424(14) | 1.548(3) | 1.551(3) | 1.559(14) | 1.525(14)/1.396(13) | 1.47(2) |
| Bond angles |  |  |  |  |  |  |  |  |
| N1-M1-N3 | 84.76(7) | 84.26(9) | 82.4(3)/84.2(3) | 82.20(7) | 81.97(10) | 80.8(3) | 81.3(3)/80.6(6) | 80.5(5) |
| N2-M1-N4 | 106.16(7) | 108.24(10) | 107.7(3)/104.8(3) | 111.18(7) | 112.38(11) | 111.9(3) | 110.3(3)/108.1(6) | 112.9(5) |
| N1-M1-N2 | 84.66(7) | 83.82(7) | 83.6(3)/85.8(3) | 83.30(7) | 83.03(7) | 83.2(3) | 83.9(3)/85.5(6) | 83.6(5) |
| N3-M1-N4 | 84.47(7) | 83.82(7) | 86.3(4)/85.2(3) | 83.50(7) | 83.03(7) | 84.2(3) | 84.5(3)/85.9(6) | 83.4(5) |
| N1-M1-N4 | 169.09(7) | 167.67(6) | 168.7(3)/168.8(3) | 165.23(7) | 164.04(7) | 164.9(3) | 165.8(3)/166.3(6) | 162.8(5) |
| N2-M1-N3 | 169.21(7) | 167.67(6) | 166.0(3)/169.9(3) | 165.05(7) | 164.04(7) | 163.9(3) | 165.1(3)/165.9(6) | 163.2(5) |
| O1-C1-N1 | 128.27(19) | 128.22(18) | 126.4(7)/123.8(9) | 128.7(2) | 128.4(2) | 128.2(10) | 131.3(14)/120(3) | 127.1(13) |
| O1-C1-C2 | 121.98(17) | 121.40(18) | 123.2(6)/122.5(7) | 120.50(18) | 120.22(19) | 121.1(6) | 115.3(11)/124(2) | 119.0(13) |
| N1-C1-C2 | 109.75(16) | 110.38(16) | 110.3(6)/113.6(7) | 110.79(18) | 111.38(18) | 110.7(7) | 113.4(11)/116(3) | 113.7(13) |
| O2-C2-N2 | 126.97(19) | 128.00(19) | 127.8(7)/129.1(8) | 126.2(2) | 127.2(2) | 127.6(9) | 126.6(11)/126(4) | 124.2(15) |
| $\mathrm{O} 2-\mathrm{C} 2-\mathrm{C} 1$ | 119.29(18) | 119.27(18) | 119.0(6)/118.1(8) | 118.68(19) | 118.5(2) | 117.4(7) | 115.7(9)/114(3) | 117.7(13) |
| N2-C2-C1 | 113.70(16) | 112.72(17) | 113.1(6)/112.7(6) | 115.10(18) | 114.31(18) | 115.0(6) | 117.6(11)/120(3) | 118.1(15) |
| O3-C3-N3 | 128.47(18) | 128.22(18) | 127.1(14)/121.6(11) | 128.3(2) | 128.4(2) | 132.8(13) | 129.5(14)/127(2) | 127.3(15) |
| O3-C3-C4 | 121.69(17) | 121.40(18) | 120.9(11)/127.2(9) | 120.31(19) | 120.22(19) | 117.7(10) | 118.2(9)/119.4(18) | 119.8(12) |
| N3-C3-C4 | 109.84(16) | 110.38(16) | 111.8(9)/111.2(7) | 111.42(18) | 111.38(18) | 109.4(7) | 112.2(11)/113.7(17) | 112.9(11) |
| O4-C4-N4 | 127.21(19) | 128.00(19) | 115.8(15)/121.1(9) | 126.3(2) | 127.2(2) | 122.1(13) | 127.1(11)/115.0(19) | 124.5(13) |
| O4-C4-C3 | 119.43(17) | 119.27(18) | 126.4(11)/119.4(8) | 119.0(2) | 118.5(2) | 122.0(8) | 114.5(9)/126(2) | 117.2(12) |
| N4-C4-C3 | 113.33(16) | 112.72(17) | 117.7(9)/118.8(7) | 114.74(18) | 114.31(18) | 115.9(8) | 118.4(10)/118.9(17) | 118.1(12) |

the N2-M1-N4 bond angles in the range from $106.16(7)^{\circ}(4 A)$ to $112.38(11)^{\circ}(\mathbf{8 A})$.

The $\mathrm{M}-\mathrm{N}$ bonds can be divided into $\mathrm{M}-\mathrm{N}_{\text {aryl }}$ and $\mathrm{M}-\mathrm{N}_{\mathrm{alkyl}}$ bonds with respect to the substituents at the N donor atoms. Especially for $\mathrm{Ni}^{\mathrm{II}}$-containing $\mathbf{4 A}$ and $\mathbf{5 A}$ the $\mathrm{M}-\mathrm{N}_{\text {aryl }}$ bond lengths (range: $1.8485(16) \AA(4 A)$ to $1.8546(15) \mathrm{A}(5 A)$ ) are significantly shorter compared to the $\mathrm{M}-\mathrm{N}_{\text {alkyl }}$ ones, although for $\mathbf{6 A}$ and the $\mathrm{Cu}^{\mathrm{II}}$-containing complex fragments $\mathbf{7 A} \mathbf{- 9 A}$ this difference is not significant. The $\mathrm{M}-\mathrm{N}_{\text {aryl }}$ bond lengths of 7A9A (range: $1.934(6) \AA(\mathbf{9 A})$ to $1.967(7) \AA(9 \mathbf{A})$ exceed those of $\mathbf{4 A -}$ 6A (range: $1.8485(16) \AA(4 \mathrm{~A})$ to $1.879(7) \AA(\mathbf{6 A})$ ) dramatically, whereas a comparison of the $\mathrm{M}-\mathrm{N}_{\text {alkyl }}$ bond lengths reveals minor differences only, $c f$. Table 1. Such differences have been observed for pairs of $\mathrm{Ni}^{\mathrm{II}} / \mathrm{Cu}^{\mathrm{II}}$-containing related type IV complexes as well and could be explained by the shorter ion radii of $\mathrm{Ni}^{\text {II }}$ ( 63 pm ) compared to that of $\mathrm{Cu}^{\mathrm{II}}(71 \mathrm{pm})$ in quadratic planar coordination environments. ${ }^{15}$
The trinuclear type IX complexes 10 and 12. The solid state structures of the trinuclear type $\mathbf{I X}$ complexes $\mathbf{1 0}^{\prime}$, cf. the Experimental part, and of $\mathbf{1 2}$ in the form of $\left[\mathrm{Cu}_{3}\left(\mathrm{opbo}^{n} \mathrm{Pr}_{2}\right)\right.$ (pmdta) $\left.)_{2}\right]\left(\mathrm{NO}_{3}\right)_{2} \cdot 1 / 2 \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 3 / 4 \mathrm{Et}_{2} \mathrm{O} \quad\left(\mathbf{1 2}{ }^{\prime}\right)$, have been determined by single crystal X-ray crystallographic studies.

The molecular structures of the dicationic complex fragments $\left[\mathrm{Cu}_{3}\left(\mathrm{opboR}_{2}\right)(\mathrm{pmdta})_{2}\right]^{2+}$ of $\mathbf{1 0}^{\prime}$ and $\mathbf{1 2}^{\prime}$ (denoted in the
following as 10A and 12A) are displayed in Fig. 3. Selected bond lengths and angles of the $\left.\left[\mathrm{Cu}(\mathrm{opboR})_{2}\right)\right]^{2-}$ and $[\mathrm{Cu}(\text { pmdta })]^{2+}$ fragments of $\mathbf{1 0 A}$ and $\mathbf{1 2 A}$ are given in Tables 1 and 2, respectively. As described in the Experimental part, the trinuclear and dicationic complex fragment 10A has been refined as a whole disordered at two positions. Thus, the fragment with the major occupation factor is referred to as 10A, and the other as 10B. In the following we will describe 10A only, although Tables 1 and 2 refer to data of both 10A and 10B. In Table 4 selected crystallographic and structural refinement data of $1 \mathbf{1 0}^{\prime}$ and $\mathbf{1 2}^{\prime}$ have been summarized.

The central $\mathrm{Cu}^{\text {II }}$ ions of $\mathbf{1 0 A}$ and $\mathbf{1 2 A}$ are all coordinated by four deprotonated amide N donor atoms to form $\mathrm{CuN}_{4}$ coordination units. The $\mathrm{CuN}_{4}$ units can be regarded as planar-quadratic, as calculations of mean planes of the N1-N4 atoms give the rmsd/hdp values as follows: 10A/12A (rmsd, hdp) = $0.0005 \AA, \mathrm{~N} 1$ with $0.0005(4) \AA / 0.004 \AA / \mathrm{N} 1$ with $0.086(7) \AA$, respectively, with the Cu1 atoms placed nearly in the plane of the calculated $\mathrm{N}_{4}$ mean planes (10A: $0.007(3) \AA .12 \mathrm{~A}: 0.008(7)$ A). Additionally, the sum of bond angles of the $\mathrm{CuN}_{4}$ units amounts to $360.0(6)^{\circ}(\mathbf{1 0 A})$ and $360.4(10)^{\circ}(\mathbf{1 2 A})$, which indicates the $\mathrm{CuN}_{4}$ units to be planar.

As observed and discussed for $\mathbf{4 A} \mathbf{4 A}$, three bond angles of the $\mathrm{CuN}_{4}$ units are rather small; whereas the fourth one is sub-


Fig. 3 ORTEP diagrams ( $25 \%$ ellipsoid probability) of the molecular structures of 10A (top) and 12A (down). All hydrogen atoms are omitted for clarity. The sign $\varangle$ refers to calculated interplanar angles between differently coloured mean planes.
stantially larger as described for 7A-9A, $c f$. above. This difference is not significant for 10A and 12A, $c f$. Table 1.

The central $\mathrm{CuN}_{4}$ units of $\mathbf{1 0 A}$ and $\mathbf{1 2 A}$ are obviously planar, although only the $\left\{\mathrm{Cu}_{3}\right.$ (opbo) $\}$ fragment of $\mathbf{1 0 A}$ is planar in contrast to $\mathbf{1 2 A}, c f$. Fig. 3. The deviation from planarity of the $\left\{\mathrm{Cu}_{3}\right.$ (opbo) \} fragment of $\mathbf{1 2 A}$ is not induced by the coordination of either counter anions and/or solvent molecules to the central Cu 1 atoms. Indeed, for solvent free $\mathbf{1 0}^{\prime}$ any coordination of the $\left[\mathrm{BPh}_{4}\right]^{-}$anions is certainly not expected. Even in the case of $\mathbf{1 2}^{\prime}$ no coordination of any species to the central Cu1 atoms is observed. It should be mentioned additionally that in the crystal structures of $\mathbf{1 0}^{\prime}$ and $\mathbf{1 2}^{\prime}$ no further intermolecular interactions are observed.

The terminal $\mathrm{Cu}^{\text {II }}$ ions of $\mathbf{1 0 A}$ and $\mathbf{1 2 A}$ are each coordinated by two O donor atoms of the respective oxamidato group as well as the three N donor atoms of the pmdta ligands, forming thus $\mathrm{CuN}_{3} \mathrm{O}_{2}$ coordination units. The geometries of these units are, with respect to their averaged $\tau$ parameters $\langle\tau\rangle,{ }^{16} c f$. Table 2, closer to the ideal trigonal-bipyramidal (10A) or to the ideal square-pyramidal coordination geometry (12A).

A further feature of these $\mathrm{CuN}_{3} \mathrm{O}_{2}$ coordination units needs to be discussed. For the related type VIII complex $\mathbf{1 4}^{8 a}$ it is
observed that the largest bond angle of the $\mathrm{CuN}_{3} \mathrm{O}_{2}$ unit at the "oxamidato side" involves the O donor atom of the $\mathrm{O} \cdots \mathrm{C} \cdots \mathrm{N}_{\text {alkyl }}$ function and the middle N donor atom of the pmdta ligands. For the related $\mathrm{CuN}_{3} \mathrm{O}_{2}$ unit at the "oxamato side" the situation is different. Here, the largest bond angle involves the O donor atom of the $\mathrm{O} \cdots \mathrm{C} \cdots \mathrm{N}_{\text {aryl }}$ function. This specific feature is furthermore usually observed for type VII complexes, as already explained along with the structural discussion of $14 .{ }^{8 a}$ For $\mathbf{1 0 A}$ and $\mathbf{1 2 A}$ it is then exclusively observed that the largest bond angles of the terminal $\mathrm{CuN}_{3} \mathrm{O}_{2}$ units involve the O donor atom of the $\mathrm{O} \cdots \mathrm{C} \cdots \mathrm{N}_{\text {alkyl }}$ function and the middle N donor atom of the pmdta ligands, cf. Fig. 3 and Table 2.

In summary it can be ruled out that a replacement of the two O donor atoms involved in the coordination of the central $\mathrm{Cu}^{\text {II }}$ ions of type VII complexes by $\mathrm{N}(\mathrm{R})$ donor atoms to give the corresponding type IX complexes leads to such trinuclear $\left\{\mathrm{Cu}_{3}\right.$ (opbo) $\}$ fragments of which the central $\mathrm{Cu}^{\text {III }}$ ions are not coordinated by further co-ligands. Furthermore, this replacement rearranges the geometries of the terminal $\mathrm{CuN}_{3} \mathrm{O}_{2}$ units. Both observations compare well with the related type VIII complex 14, ${ }^{8 a}$ although certainly additional work is required to figure out if they are universally valid.

Table 2 Selected bond lengths ( $(\AA)$, angles $\left({ }^{\circ}\right)$ and $\langle\tau\rangle$ parameters ${ }^{16}$ of the terminal $[\mathrm{Cu}(\mathrm{pmdta})]^{2+}$ fragments of $10 \mathrm{~A} / 10 \mathrm{~B}$ and 12 A

|  |  |  |
| :--- | :--- | :--- |
|  | $\mathbf{1 0 A} / \mathbf{1 0 B}$ |  |
| Bond lengths |  |  |
| Cu2-O1 | $1.946(16) / 1.97(3)$ | $2.174(8)$ |
| Cu2-O2 | $2.030(10) / 2.31(3)$ | $1.982(9)$ |
| Cu2-N5 | $2.046(8) / 2.06(3)$ | $2.032(10)$ |
| Cu2-N6 | $2.031(8) / 2.007(19)$ | $2.004(10)$ |
| Cu2-N7 | $2.195(6) / 2.076(10)$ | $2.056(10)$ |
| Cu3-O3 | $2.043(12) / 2.02(3)$ | $2.179(8)$ |
| Cu3-O4 | $1.957(14) / 2.15(4)$ | $1.987(8)$ |
| Cu3-N8 | $1.992(9) / 2.208(16)$ | $2.058(10)$ |
| Cu3-N9 | $2.050(7) / 2.05(2)$ | $1.994(11)$ |
| Cu3-N10 | $2.209(8) / 1.963(13)$ | $2.077(11)$ |
|  |  |  |
| Bond angles | $83.3(4) / 77.7(8)$ | $81.3(3)$ |
| O1-Cu2-O2 | $140.6(7) / 126.2(12)$ | $107.8(4)$ |
| O1-Cu2-N5 | $99.6(4) / 113.9(9)$ | $103.1(4)$ |
| O1-Cu2-N6 | $97.9(6) / 109.8(7)$ | $98.9(4)$ |
| O1-Cu2-N7 | $88.0(4) / 82.2(12)$ | $92.8(4)$ |
| O2-Cu2-N5 | $173.7(4) / 166.8(11)$ | $175.6(4)$ |
| O2-Cu2-N6 | $98.4(3) / 93.8(10)$ | $93.2(4)$ |
| O2-Cu2-N7 | $86.2(4) / 85.8(12)$ | $85.8(4)$ |
| N5-Cu2-N6 | $121.5(3) / 121.0(10)$ | $153.2(4)$ |
| N5-Cu2-N7 | $86.8(3) / 87.9(7)$ | $86.2(4)$ |
| N6-Cu2-N7 | $86.5(7) / 72.0(17)$ | $80.7(3)$ |
| O3-Cu3-O4 | $127.8(7) / 132.1(13)$ | $106.8(4)$ |
| O3-Cu3-N8 | $99.4(7) / 101.3(11)$ | $102.5(4)$ |
| O3-Cu3-N9 | $105.7(6) / 98.5(9)$ | $98.7(4)$ |
| O3-Cu3-N10 | $89.8(4) / 86.5(18)$ | $92.3(4)$ |
| O4-Cu3-N8 | $173.9(5) / 159.0(15)$ | $176.8(4)$ |
| O4-Cu3-N9 | $92.4(5) / 108.3(12)$ | $93.0(4)$ |
| O4-Cu3-N10 | $88.1(4) / 83.7(12)$ | $86.7(4)$ |
| N8-Cu3-N9 | $126.5(4) / 129.1(9)$ | $154.4(4)$ |
| N8-Cu3-N10 | $84.2(3) / 92.2(8)$ | $86.6(4)$ |
| N9-Cu3-N10 | $<\tau>p a r a m e t e r$ | 0.373 |
|  | $0.644^{a}$ |  |
|  |  |  |
|  |  |  |

${ }^{a}$ The averaged $\langle\tau\rangle$ parameter refers to the combination of 10A/10B.

## ESR spectroscopic investigations

The ESR experiments were performed in order to obtain information on the $g$-factors and the hyperfine (HF) coupling tensor of $\mathrm{Cu}^{\text {II }}$, which are important for the discussion of magnetic properties of the complexes studied in this work, cf. below. The relevant interactions, which determine parameters of the $\mathrm{Cu}^{\text {II }}$ ESR spectrum, are standardly described by the following Hamiltonian:

$$
\begin{equation*}
H=g \mu_{\mathrm{B}} B_{0} S+S A^{\mathrm{Cu}} I^{\mathrm{Cu}}+\sum_{i=1}^{4} S A^{\mathrm{N}_{i}} I^{\mathrm{N}_{i}}+H_{i} \tag{1}
\end{equation*}
$$

Here, the first term represents the Zeeman interaction of an electron spin $S$ with the external magnetic field $B_{0}$, whereas $g$ and $\mu_{\mathrm{B}}$ stand for the $g$-tensor and Bohr magneton, respectively. The HF interaction between the electron spin $S$ of $\mathrm{Cu}^{\text {II }}$ and the ${ }^{63} \mathrm{Cu},{ }^{65} \mathrm{Cu}$ and ${ }^{14} \mathrm{~N}$ nuclear spins $I^{\mathrm{Cu}}$ and $I^{\mathrm{N}}$ is described by the second and the third term, respectively. Here, $A^{\mathrm{Cu}}$ and $A^{\mathrm{N}}$ are the respective HF coupling tensors. Finally, $H_{\mathrm{i}}$ accounts for the nuclear Zeeman, hyperfine, and nuclear quadrupole interactions of further surrounding nuclei, such as, e.g., protons.

The isotropic ESR parameters of 8 and 9 were obtained from measurements of 1 mM acetone solutions. In Fig. 4 their ESR spectra are displayed together with the performed simulations. The ESR spectra of both 8 and 9 appear rather similar. Both spectra consist of four lines due to the onsite HF coupling of the electron spin of $\mathrm{Cu}^{\mathrm{II}} S=1 / 2$ to its own nuclear spin $I\left({ }^{63,65} \mathrm{Cu}\right)=3 / 2$. From the modelling of the spectra, cf. Fig. 4, the isotropic $g$-factor, the ${ }^{63} \mathrm{Cu}-\mathrm{HF}$ coupling constants and the ${ }^{14} \mathrm{~N}-\mathrm{HF}$ coupling constants were obtained, respectively. Experimentally determined isotropic ESR parameters are listed in Table 5. We note that in this work in the model calculations of ESR spectra based on the Hamiltonian (1) we took into account only the HF interaction of the electron spin of copper with the spins of the nitrogen nuclei and neglect much weaker interactions with more distant nuclei (the last term in (1)).

In order to obtain anisotropic ESR parameters, the angular dependence of the ESR spectra of a single crystal of 9@6 at $f=$ 9.56 GHz at room temperature was measured by rotation of the magnetic field $B_{0}$ in the plane perpendicular to the molecular plane. For a single crystal of 8@5, the extreme orientations of the spectrum corresponding to the principal axes of the $g$ - and HF-tensors were determined by measuring the angular dependence of the $g$-factor by rotating around an arbitrary axis and searching the direction of $B_{0}$ for the minimum $g$-factor. This direction was chosen as a new axis about which the angular dependence of the $g$-factor and HF-coupling constants was measured. Finally, to check the correctness of the procedure, the direction of the maximum $g$-factor was chosen as the rotation axis and indeed no angular dependence is found. In this experiment the spectra were recorded with a rotation interval of $15^{\circ}$. Representative ESR spectra of a single crystal of 8@5 and 9@6, respectively, together with their simulation, are shown in Fig. 5.

Both spectra consist of two quartet groups of lines owing to the HF-coupling with the ${ }^{63,65} \mathrm{Cu}$ nuclear spin $I\left({ }^{63,65} \mathrm{Cu}\right)=3 / 2$. Each group further represents a subset of lines. They arise due to transferred HF-coupling with the ${ }^{14} \mathrm{~N}$ nuclear spins $I\left({ }^{14} \mathrm{~N}\right)=$ 1 of the four N donor atoms which can be, cf. Fig. 6, classified into two equivalent groups. When the magnetic field is parallel to the normal of the molecular plane $n\left(B_{0} \| n\right)$, the largest $g$ value and the largest copper HF constant are obtained. The smallest $g$ value is obtained when the magnetic field lies in the molecular plane $\left(B_{0} \perp n\right)$. For this field geometry the line groups overlap because of the small ${ }^{63,65} \mathrm{Cu}-\mathrm{HF}$ coupling constant $A_{\perp}^{\mathrm{Cu}}$ in this direction. Therefore the extraction of the coupling parameters becomes very difficult.

Owing to the above described difficulties, the values of $A_{\perp}^{\mathrm{Cu}}$ and $A_{\|}^{\mathrm{N}}$ were estimated with the aid of the isotropic values using the relation $A_{\text {iso }}=\left(2 A_{\perp}+A_{\|}\right) / 3$. For the investigated complexes, the following assumptions are taken:

$$
\begin{equation*}
g_{x}=g_{y}=g_{\perp}, g_{z}=g_{\|}, A_{x}=A_{y}=A_{\perp}<A_{z}=A_{\|} \tag{2}
\end{equation*}
$$

Principal values of $g, A^{\mathrm{Cu}}$ and $A^{\mathrm{N}}$ of 8 and 9 obtained from modeling of the ESR spectra are listed in Table 5. In general,

Table 3 Crystal and structural refinement data of 4, 5', 6, 7, 8' and 9

|  | 4 | 5' | 6 | 7 | $8^{\prime}$ | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chemical formula | $\mathrm{C}_{44} \mathrm{H}_{82} \mathrm{~N}_{6} \mathrm{NiO}_{4}$ | $\mathrm{C}_{46} \mathrm{H}_{90} \mathrm{~N}_{6} \mathrm{NiO}_{6}$ | $\mathrm{C}_{48} \mathrm{H}_{90} \mathrm{~N}_{6} \mathrm{NiO}_{4}$ | $\mathrm{C}_{44} \mathrm{H}_{82} \mathrm{CuN}_{6} \mathrm{O}_{4}$ | $\mathrm{C}_{46} \mathrm{H}_{90} \mathrm{CuN}_{6} \mathrm{O}_{6}$ | $\mathrm{C}_{48} \mathrm{H}_{90} \mathrm{CuN}_{6} \mathrm{O}_{4}$ |
| Formula weight ( $\mathrm{g} \mathrm{mol}^{-1}$ ) | 817.87 | 881.95 | 873.95 | 822.70 | 886.78 | 878.80 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P \overline{1}$ | C2/c | P2(1) | $P \overline{1}$ | C2/c | P2(1)/c |
| Unit cell dimensions ( $\mathrm{A},{ }^{\circ}$ ) | $a=10.7141(4)$ | 24.3834(7) | 13.5126(5) | 10.583(13) | 24.396(5) | 13.4875(6) |
|  | $b=14.4059(5)$ | 13.4528(3) | 14.7246(4) | 14.534(3) | 13.432(3) | 14.6748(7) |
|  | $c=15.4535(6)$ | 15.9421(4) | 25.4056(7) | 15.609(15) | 15.919(3) | 25.6140 (12) |
|  | $\alpha=99.540$ (3) | 90 | 90 | 98.444(11) | 90.0 | 90 |
|  | $\beta=90.910$ (3) | 110.328(3) | 95.567(3) | 91.564(9) | 109.80(3) | 95.346(4) |
|  | $\gamma=102.522(3)$ | 90 | 90 | 102.014(12) | 90.0 | 90 |
| Volume ( $\AA^{3}$ ) | 2292.92(15) | 4903.7(2) | 5031.0(3) | 2318.8(5) | 4908.4(19) | 5047.6(4) |
| Measurement temperature (K) | 110 | 110 | 110 | 100 | 100 | 100 |
| Radiation source | Cu K $\alpha$ | Mo K $\alpha$ | $\mathrm{Cu} \mathrm{K} \alpha$ | $\mathrm{Cu} \mathrm{K} \alpha$ | Mo K $\alpha$ | Cu K $\alpha$ |
| Wavelengths ( A ) | 1.54184 | 0.71073 | 1.54184 | 1.54184 | 0.71073 | 1.54184 |
| $Z$ | 2 | 4 | 4 | 2 | 4 | 4 |
| Density (calculated) ( $\mathrm{Mg} \mathrm{m}^{-3}$ ) | 1.185 | 1.195 | 1.154 | 1.178 | 1.200 | 1.156 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 0.962 | 0.446 | 0.905 | 1.012 | 0.495 | 0.959 |
| $F(000)$ | 896 | 1936 | 1920 | 898 | 1940 | 1924 |
| Reflections collected | 14594 | 10287 | 25119 | 17586 | 21633 | 14520 |
| Independent reflections $/ R_{\text {int }}{ }^{a}$ | 7226, 0.0212 | 4298, 0.0232 | 14 709, 0.0265 | 6824, 0.0325 | 4293, 0.0225 | 7383, 0.0278 |
| Index ranges | $\begin{aligned} & -10 \leq h \leq 12 \\ & -16 \leq k \leq 16 \\ & -16 \leq l \leq 17 \end{aligned}$ | $\begin{aligned} & -28 \leq h \leq 22 \\ & -15 \leq k \leq 15 \\ & -18 \leq l \leq 16 \end{aligned}$ | $\begin{aligned} & -12 \leq h \leq 15 \\ & -16 \leq k \leq 16 \\ & -25 \leq l \leq 29 \end{aligned}$ | $\begin{aligned} & -11 \leq h \leq 11 \\ & -16 \leq k \leq 16 \\ & -17 \leq l \leq 17 \end{aligned}$ | $\begin{aligned} & -28 \leq h \leq 28 \\ & -15 \leq k \leq 15 \\ & -18 \leq l \leq 18 \end{aligned}$ | $\begin{aligned} & -15 \leq h \leq 10 \\ & -16 \leq k \leq 16 \\ & -28 \leq l \leq 25 \end{aligned}$ |
| $\theta$ range for data collection ( ${ }^{\circ}$ ) | 3.19 to 61.99 | 2.96 to 25.00 | 3.47 to 61.98 | 3.91 to 60.63 | 2.96 to 25.00 | 3.29 to 59.99 |
| Data/restraints/parameters | 7226/0/496 | 4298/9/275 | 14 709/479/1094 | 6824/0/496 | 4293/9/274 | 7383/804/715 |
| Goodness-of-fit on $F^{2 b}$ | 1.009 | 1.039 | 0.961 | 0.939 | 1.070 | 0.974 |
| Final $R$ indices $[I>2 \sigma(I)]^{c}$ | $\begin{aligned} & R_{1}=0.0423 \\ & \mathrm{w} R_{2}=0.1171 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0344 \\ & \mathrm{w} R_{2}=0.0927 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0991 \\ & \mathrm{w} R_{2}=0.2531 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0345 \\ & \mathrm{w} R_{2}=0.0850 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0368 \\ & \mathrm{w} R_{2}=0.0933 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0883 \\ & \mathrm{w} R_{2}=0.2625 \end{aligned}$ |
| $R$ indices (all data) ${ }^{\text {c }}$ | $\begin{aligned} & R_{1}=0.0492 \\ & \mathrm{w} R_{2}=0.1195 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0452 \\ & \mathrm{w} R_{2}=0.0950 \end{aligned}$ | $\begin{aligned} & R_{1}=0.1361 \\ & \mathrm{w} R_{2}=0.2794 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0497 \\ & \mathrm{w} R_{2}=0.0892 \end{aligned}$ | $\begin{aligned} & R_{1}=0.0463 \\ & \mathrm{w} R_{2}=0.1013 \end{aligned}$ | $\begin{aligned} & R_{1}=0.1498 \\ & \mathrm{w} R_{2}=0.2980 \end{aligned}$ |
| Flack $x$ parameter | - | - | 0.10(5) | - | - | - |
| Largest diff. peak/hole (e $\AA^{-3}$ ) | 0.452, -0.398 | 0.710, -0.272 | 1.638, -0.301 | 0.226, -0.283 | 1.188, -0.376 | 0.320, -0.407 |

${ }^{a} R_{\text {int }}=\sum \mid F_{\mathrm{o}}{ }^{2}-F_{\mathrm{o}}{ }^{2}($ mean $) \mid / \sum F_{\mathrm{o}}{ }^{2}$, where $F_{\mathrm{o}}{ }^{2}($ mean $)$ is the average intensity of symmetry equivalent diffractions. ${ }^{b} S=\left[\sum \mathrm{w}\left(F_{\mathrm{o}}{ }^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2}\right] /(n-p)^{1 / 2}$, where $n=$ number of reflections, $p=$ number of parameters. ${ }^{c} R=\left[\sum\left(| | F_{\mathrm{o}}\left|-\left|F_{\mathrm{c}}\right|\right) / \sum\left|F_{\mathrm{o}}\right|\right] ; \mathrm{w} R=\left[\sum\left(\mathrm{w}\left(F_{\mathrm{o}}{ }^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2}\right) / \sum\left(\mathrm{w} F_{\mathrm{o}}{ }^{4}\right)\right]^{1 / 2}\right.$.
differences between values reported in Table 5 are not significant; the largest principal values for $A^{\mathrm{Cu}}$ were obtained for 9 .

## Pulse ENDOR study

To obtain additional insights into the HF coupling, pulse Davies ENDOR experiments were performed on a single crystal of 8@5. In Fig. 7 experimental and simulated ENDOR spectra at different orientations of the crystal in the magnetic field are shown. The $0^{\circ}$ orientation corresponds to the direction of $B_{0}$ along the $g_{\|}$-axis of the $g$-tensor, and the $90^{\circ}$ orientation represents the perpendicular direction. The measurements were carried out at the magnetic field value corresponding to the position of the second from the left group of lines in the CW spectrum ( $\sim 310 \mathrm{mT}$ ), $c f$. Fig. 5. In the ENDOR spectra, peaks both from the nitrogen nuclei as well as from protons $\left({ }^{1} \mathrm{H}\right)$ can be identified. The latter ones are located at the low frequency part of the spectrum and are marked correspondingly in Fig. 7. They were not considered in the modeling of the ENDOR spectra. Despite an appreciably lower single-to-noise $(\mathrm{S} / \mathrm{N})$ ratio of the ENDOR spectra as compared to the ESR spectra, the peaks of individual nitrogen nuclei are quite well resolved.

The principal axes of $g$ and $A^{\mathrm{Cu}}$ coincide with their maximum components located perpendicular to the molecular plane. The maximum components of the ${ }^{14} \mathrm{~N}$ hyperfine tensors were found to lie parallel to the $\mathrm{Cu}-\mathrm{N}$ bond vectors as sketched in Fig. 6. The principal values of $g, A^{\mathrm{Cu}}$, and $A^{\mathrm{N}}$ obtained from the ENDOR measurements are shown in Table 6. They agree reasonably well with the ESR data, cf. Table 5. Note that, unlike in the ESR experiment, the better resolution of the ENDOR method enables, with the help of the modeling of the spectra on the basis of (1) and (2), to estimate all four nitrogen HF tensors. They are presented in Table 6 and labeled as A, B, C and D. In agreement with the ESR results, $A_{\perp}^{\mathrm{N}}|<| A_{\| \mid}^{\mathrm{N}}$ has been found for all four tensors. With the parameters listed in Table 6, satisfactory agreement with experimental ENDOR spectra has been achieved. Most optimal fits were obtained close to the orientation of the magnetic field parallel to the normal to the molecular plane, which is due to a better $\mathrm{S} / \mathrm{N}$ ratio for this field geometry. Considering the data in Table 6, the nitrogen HF tensors can be grouped in pairs A-B and C-D with quite close values of the tensor components in each group, respectively. However, the ENDOR measurements indicate some differences in the HF parameters within each group, which is not evident in the

Table 4 Crystal and structural refinement data of 10' and 12'

|  | $10^{\prime}$ | $12^{\prime}$ |
| :---: | :---: | :---: |
| Chemical formula | $\mathrm{C}_{78} \mathrm{H}_{96} \mathrm{~B}_{2} \mathrm{Cu}_{3} \mathrm{~N}_{10} \mathrm{O}_{4}$ | $\mathrm{C}_{150} \mathrm{H}_{290} \mathrm{Cl}_{4} \mathrm{Cu}_{12} \mathrm{~N}_{48} \mathrm{O}_{43}$ |
| Formula weight ( $\mathrm{g} \mathrm{mol}^{-1}$ ) | 1449.89 | 4358.56 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P \overline{1}$ | P2(1)/c |
| Unit cell | $a=13.7472(5)$ | 16.1788(11) |
| dimensions ( $\AA^{\circ},^{\circ}$ ) | $b=14.0699(5)$ | 29.4708(15) |
|  | $c=19.3586(8)$ | 11.2788(7) |
|  | $\alpha=103.343(3)$ | 90.0 |
|  | $\beta=100.238(3)$ | 91.797(7) |
|  | $\gamma=91.599(3)$ | 90.0 |
| Volume ( $\AA^{3}$ ) | 3576.0(2) | 5375.1(6) |
| Measurement temperature (K) | 100 | 100 |
| Radiation source | $\mathrm{Cu} \mathrm{K} \alpha$ | Cu K $\alpha$ |
| Wavelengths (A) | 1.54184 | 1.54184 |
| Z | 2 | 2 |
| Density (calculated) $\left(\mathrm{Mg} \mathrm{~m}^{-3}\right)$ | 1.347 | 1.346 |
| Absorption coefficient $\left(\mathrm{mm}^{-1}\right)$ | 1.483 | 2.338 |
| $F(000)$ | 1526 | 2286 |
| Reflections collected | 21468 | 21200 |
| Independent reflections $/ R_{\text {int }}{ }^{a}$ | 11034, 0.0370 | 11546, 0.1117 |
| Index ranges | $\begin{aligned} & -14 \leq h \leq 14 \\ & -16 \leq k \leq 16 \\ & -22 \leq l \leq 16 \end{aligned}$ | $\begin{aligned} & -18 \leq h \leq 18 \\ & -33 \leq l \leq 34, \\ & -13 \leq k \leq 13 \end{aligned}$ |
| $\theta$ range for data collection ( ${ }^{\circ}$ ) | 3.24 to 62.00 | 4.059 to 63.50 |
| Data/restraints/ parameters | 11 034/434/1238 | 11 546/716/691 |
| Goodness-of-fit on $F^{2 b}$ | 1.039 | 0.939 |
| Final $R$ indices | $R_{1}=0.0987$, | $R_{1}=0.0994$, |
| $[I>2 \sigma(I)]^{c}$ | $\mathrm{w} R_{2}=0.2442$ | $\mathrm{w} R_{2}=0.2628$ |
| $R$ indices (all data) ${ }^{c}$ | $\begin{aligned} & R_{1}=0.1043 \\ & \mathrm{w} R_{2}=0.2479 \end{aligned}$ | $\begin{aligned} & R_{1}=0.1419 \\ & \mathrm{w} R_{2}=0.2894 \end{aligned}$ |
| Largest diff. peak/hole $\left(\mathrm{e}^{\circ}{ }^{-3}\right)$ | 0.713, -0.656 | 1.564, -0.703 |
| ${ }^{a} R_{\mathrm{int}}=\sum \mid{F_{\mathrm{o}}}^{2}-{F_{\mathrm{o}}}^{2}($ mean $) \mid / \sum F_{\mathrm{o}}{ }^{2}$, where $F_{\mathrm{o}}{ }^{2}($ mean $)$ is the average intensity of symmetry equivalent diffractions. ${ }^{b} S=\left[\sum \mathrm{w}\left(F_{\mathrm{o}}{ }^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2}\right] /$ $(n-p)^{1 / 2}$, where $n=$ number of reflections, $p=$ number of parameters.${ }^{c} R=\left[\sum\left(\| \| F_{\mathrm{o}}\left\|-\left\|F_{\mathrm{c}}\right\|\right) / \sum\left\|F_{\mathrm{o}}\right\|\right] ; \mathrm{w} R=\left[\sum\left(\mathrm{w}\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}^{2}\right)^{2}\right) / \sum\left(\mathrm{w} F_{\mathrm{o}}^{4}\right)\right]^{1 / 2} .\right.$ |  |  |

static ESR data. The difference of the HF parameters between the two groups is substantial. The larger values of the HF constants of the group A-B enable to tentatively assign them to the N 1 labeled $\mathrm{N}_{\text {aryl }}$ donor atoms, $c f$. Fig. 6, since these values are closer to those of related type IV Cu ${ }^{\text {II }}$-containing bis(oxamato) complexes comprising only two $\mathrm{N}_{\text {aryl }}$ donor atoms. ${ }^{10}$ The smaller HF constants in the group C-D can then be associated with the N 2 labeled $\mathrm{N}_{\text {alkyl }}$ donor atoms, $c f$. Fig. 6.


Fig. 4 Experimental (E) and simulation (S) X-band ESR spectrum of 8 (up) and 9 (bottom) in acetone at $f=9.8 \mathrm{GHz}$ (X-band) at room temperature.

## Analysis of the HF tensors

Two models introduced by Maki and McGarvey ${ }^{17}$ and Morton and Preston ${ }^{18}$ were used to calculate the spin density from experimentally obtained HF coupling constants of $\mathrm{Cu}^{\mathrm{II}}$ ions and N donor atoms. According to Maki and McGarvey, ${ }^{17}$ the $\mathrm{Cu}-\mathrm{HF}$ coupling constants can be expressed as:

$$
\begin{gather*}
A_{\|}=P\left(-\kappa-\frac{4}{7} \alpha^{2}+\Delta g_{\|}+\frac{3}{7} \Delta g_{\perp}\right)  \tag{3}\\
A_{\perp}=P\left(-\kappa+\frac{2}{7} \alpha^{2}+\frac{11}{14} \Delta g_{\perp}\right) \tag{4}
\end{gather*}
$$

In these expressions $P_{\kappa}$ is the Fermi contact term with $P\left({ }^{63} \mathrm{Cu}\right)=\mu_{\mathrm{B}} g_{\mathrm{e}} \mu_{n} g_{n} \times\left\langle r^{-3}\right\rangle=1164 \mathrm{MHz}$, that is, the dipolar HF coupling parameter of the unpaired electron, ${ }^{19}$ and $\Delta g_{\|, \perp}=$ $g_{\|, \perp}-2.0023$. The parameter $\alpha^{2}$ is a covalency parameter, which describes the in plane metal-ligand $\sigma$ bonding. The value of $\alpha^{2}$ can be determined by using eqn (3) and (4), cf. above, and the experimental $\mathrm{Cu}-\mathrm{HF}$ coupling constants. The following normalization condition was used to determine $\alpha^{\prime}$ :

$$
\begin{equation*}
\left(\alpha^{2}+\alpha^{\prime 2}-2 \alpha \alpha^{\prime} S=1\right) \tag{5}
\end{equation*}
$$

For the complexes under study, the $\alpha^{2}$ and $\left(\alpha^{\prime} / 2\right)^{2}$ values are given in Table 7. The values of $\alpha^{2}$ and $\left(\alpha^{\prime} / 2\right)^{2}$ represent then the spin density on the $\mathrm{Cu}^{\text {II }}$ ion $\left(\rho_{\mathrm{Cu}}\right.$ (total)) and on the N -donor atom $\left(\rho_{\mathrm{N}}(\right.$ total $)$ ), respectively.

Table 5 Principal values of $g, A^{\mathrm{Cu}}(\mathrm{MHz})$ and $A^{\mathrm{N}}(\mathrm{MHz})$ of 8 and 9 from ESR measurements

| Complex | $g_{\perp}$ | $g_{\\|}$ | $g_{\text {iso }}$ | $A_{\perp}^{\mathrm{Cu}}$ | $A_{\\|}^{\mathrm{Cu}}$ | $A_{\text {iso }}^{\mathrm{Cu}}$ | $A_{\perp}^{\mathrm{N}}$ | $A_{\\|}^{\mathrm{N}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{8}$ | 2.036 | 2.162 | 2.082 | 43.4 | 611 | 225.8 | 36.9 | 50.2 |
| $\mathbf{9}$ | 2.04 | 2.159 | 2.086 | 54.9 | 622.5 | 237.9 | 37.6 | 48.8 |
| iso |  |  |  |  |  |  |  |  |



Fig. 5 Experimental (E) and simulation (S) X-band ESR spectrum of a single crystal of 8@5 (left) and 9@6 (right) at $f=9.56 \mathrm{GHz}$ (X-band) at room temperature. The magnetic field is oriented parallel to the symmetry axis of the $\mathrm{CuN}_{4}$ unit, cf. Fig. 6 .



Fig. 6 Left: chemical structure of the studied complexes. Right: scheme of the principal axes of the Cu and N hyperfine tensors of the $\mathrm{CuN}_{4}$ unit.


Fig. 7 Experimental (E) and simulated (S) Davies-ENDOR spectra of 8@5 (X-band, $T=20 \mathrm{~K}$ ) at six different orientations of the single crystal in the external magnetic field. The $0^{\circ}$ orientation corresponds to the direction of $B_{0}$ along the $g_{\|}$axis of the $g$ tensor, and the $90^{\circ}$ orientation represents the perpendicular direction.

Table 6 Principal values of $g, A^{\mathrm{Cu}}(\mathrm{MHz})$, and $A^{\mathrm{N}}(\mathrm{MHz})$ of 8 from an ENDOR measurement

| $g_{\perp}$ | $g_{\\|}$ |  | $A_{\perp}^{\mathrm{Cu}}$ | $A_{\\|}^{\mathrm{Cu}}$ |
| :--- | :--- | :--- | :--- | :--- |
| 2.016 |  | 2.144 |  | 49 |
|  | A |  | B | C |
| $A_{\\|}^{\mathrm{N}}$ | 51.2 |  | 51.8 | 42.2 |
| $A_{\perp}^{\mathrm{N}}$ | 40.4 |  | 42.6 | 36.6 |

Furthermore, the values obtained for the spin density on the $\mathrm{Cu}^{\text {II }}$ ion were compared with those deduced by the procedure of Morton and Preston. ${ }^{18}$ This approach was also used to calculate the spin density on the N donor atoms. According to this approach, the spin density $\rho(\mathrm{s})$ and $\rho(\mathrm{p})$ on the s and p orbitals (d orbitals for Cu ) are proportional to the isotropic or Fermi contact contribution $A_{\text {iso }}$ and the dipolar HF coupling constant $A_{\text {dip }}=A_{\text {iso }}-A_{\perp}$, respectively. The proportionality constants for many abundant nuclei can be found in the litera-

Table 7 Spin density (in \%) for Cu and N of 8 and 9 in comparison with $13^{8 a}$ and $15^{10}$

|  | $\rho_{\mathrm{Cu}}{ }^{a}$ <br> Complex | total $)=\alpha^{2}$ | $\rho_{\mathrm{Cu}}{ }^{b}$ <br> (total) | $\rho_{\mathrm{N}}{ }^{b}$ <br> (total) | $\rho_{\mathrm{N}}{ }^{b}(\mathrm{~s})$ | $\rho_{\mathrm{N}}{ }^{b}(\mathrm{p})$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | | $\rho_{\mathrm{N}}{ }^{a}$ |
| :--- |
| $($ total $)=\left(\alpha^{\prime} / 2\right)^{2}$ |

${ }^{a}$ According to eqn (2)-(4). ${ }^{b}$ According to ref. 18.
ture. ${ }^{18}$ Spin densities calculated according to Morton and Preston ${ }^{18}$ are also reported in Table 7. A more detailed description of these two models can be found in our previous work and Table 7 refers then additionally to corresponding data obtained for 13 and $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}[\mathrm{Cu}(\mathrm{opba})](\mathbf{1 5}) \cdot{ }^{8 a, 10}$ To make a direct comparison possible, the spin densities on the s orbital of the N donor atom of $\mathbf{1 3}$ and $\mathbf{1 5}$ are recalculated with the isotropic N HF coupling constant for unit spin density taken from ref. 18.

Very similar spin densities on the $\mathrm{Cu}^{\mathrm{II}}$ ion and N donor atoms of $\mathbf{8}$ and 9 are obtained, $c f$. Table 7. As observed earlier for $13^{8 a}$ and $15,{ }^{10}$ the unpaired electron is mainly localized on the $\mathrm{Cu}^{\text {II }}$ ion in both 8 and 9. Additionally, the averaged spin density on one individual N donor atom of $\mathbf{8}$ and $\mathbf{9}$ compares with that for $13^{8 a}$ and $15 .{ }^{10}$ However, experimentally obtained data reported here for 8 and 9 do not follow the expected tendency that a replacement of O versus N donor atoms results in a lower spin density on $\mathrm{Cu}^{\mathrm{II}}$ and higher spin densities on the N donor atoms ${ }^{9}$ when compared with $\mathbf{1 3}{ }^{8 a}$ and $\mathbf{1 5},{ }^{10}$ vide infra.

Furthermore, since ENDOR measurements on 8@5 have enabled to resolve individual HF tensors A-D of the N donor atoms, the spin density on them was estimated according to the approach by Morton and Preston. ${ }^{18}$ The respective values are listed in Table 8.

One might expect the larger HF parameters of tensors A-B as compared with C-D to be reflected in larger spin densities $\rho$. This expectation is only partially met, since the value of $\rho$ (total) for D appears to be the same as that for A-B. Most likely this is related to a limited accuracy of the ENDOR experiment for the field direction close to the molecular plane, which has led to an overestimate of the anisotropy $\left(A_{\|}-A_{\perp}\right)$ of tensor D and consequently to an overestimate of the partial spin density on the p orbital $\rho(\mathrm{p})$. To remind, in the model of Morton and Preston, ${ }^{18} \rho(\mathrm{p})$ is directly proportional to $\left(A_{\|}-\right.$ $\left.A_{\perp}\right)$. Remarkably, the partial spin density on the s orbital $\rho(\mathrm{s})$, which is determined by the isotropic part of the HF coupling
$A_{\text {iso }}=\left(A_{\|}+2 A_{\perp}\right) / 3$, is similar for C and D and both are smaller compared to A and B , as expected.

Generally, the spin density on each N-donor atom, as estimated from ESR and ENDOR data, is smaller than those obtained from DFT calculations. However, an inequality of the HF tensors obtained from the ENDOR measurement is compatible with the DFT calculation data based on the structural data from crystallographic characterization and yield different spin densities on all four N -donor atoms, cf. below. Apparently, the different spin densities on the N atoms reflect their different local geometries, as revealed by different HF tensors.

## Magnetic properties

The temperature dependence of the inverse static magnetic susceptibility $\chi_{\mathrm{m}}{ }^{-1}=H / M$ of $\mathbf{1 0 - 1 2}$ together with the corresponding $\chi_{\mathrm{m}} T$ dependence is presented in Fig. 8. The $\chi_{\mathrm{m}}{ }^{-1}(T)$ dependence shows a strong non-linearity at $T$ below 100 K which is typical for an antiferromagnetic interaction between the spins, see, e.g., ref. 20. The experimental data were fitted on the basis of the following Hamiltonian using the simulation software package julX: ${ }^{21}$

$$
\begin{equation*}
H=\sum_{i=1}^{3} \mu_{\mathrm{B}} g_{i} B_{0} S_{i}+J_{12} S_{1} S_{2}+J_{13} S_{1} S_{3} \tag{6}
\end{equation*}
$$

Here $J_{12}$ and $J_{13}$ denote the exchange integrals between the central and the terminal $\mathrm{Cu}^{\mathrm{II}}$ spins and the first term stands for the Zeeman interaction. The values of $J_{23}$ (the exchange integral between the two terminal $\mathrm{Cu}^{\text {II }}$ ions) in all investigated complexes were assumed to be negligibly small due to the large distance between the Cu 2 and Cu 3 atoms, $c f$. Fig. 3, and the large number of orbitals involved in the corresponding superexchange interaction between them. The analysis yields the best possible fit with the values $J_{12}=J_{13}$ as shown in Fig. 8.

The $J$ values of the type IV complexes 10-12 are with -96 to $-132 \mathrm{~cm}^{-1}$, cf. Fig. 8, comparable with and even slightly larger in magnitude than $J$ values of related type VII complexes such as, for example, those of $16 / 17\left(-89 \mathrm{~cm}^{-1} /-111 \mathrm{~cm}^{-1}\right)^{11,12}$ and those of $\mathbf{1 4}\left(-130 \mathrm{~cm}^{-1}\right),^{8 b}$ a type VIII complex. According to Kahn ${ }^{9}$ and others, ${ }^{22,23}$ a substitution of electronegative oxygen atoms $v s$. less electronegative nitrogen atoms should result in increased $J$ couplings, the question arises whether the, in magnitude, somewhat larger $J$ values reported here for the type IV complexes $\mathbf{1 0 - 1 2}$ as compared with the related type VII complexes are due to this mechanism. We will continue this discussion after displaying next the results obtained from accompanying DFT studies.

Table 8 Spin density (in \%) for the N donor atoms of 8 derived ${ }^{18}$ from an ENDOR measurement

| A |  |  | B |  |  | C |  |  | D |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\rho(\mathrm{s})$ | $\rho(\mathrm{p})$ | $\rho$ (total) | $\rho(\mathrm{s})$ | $\rho(\mathrm{p})$ | $\rho$ (total) | $\rho(\mathrm{s})$ | $\rho(\mathrm{p})$ | $\rho($ total $)$ | $\rho(\mathrm{s})$ | $\rho(\mathrm{p})$ | $\rho$ (total) |
| 2.43 | 6.48 | 8.91 | 2.52 | 5.58 | 8.1 | 2.12 | 3.42 | 5.54 | 1.9 | 6.48 | 8.38 |



Fig. 8 Temperature dependence of the inverse magnetic susceptibility $\chi_{\mathrm{m}}{ }^{-1}$ of 10-12. Symbols represent experimental data and solid lines correspond to the fitting results (see the text). Inset: plot of $\chi_{m} T$ as a function of $T$.

## DFT calculations

Quantum chemical methods as specified in the Experimental section were used to optimize the geometries of the dianionic complex fragments of $\mathbf{7 A} \mathbf{- 9 A}$. Selected bond lengths and bond angles of thus obtained optimized complex fragments, now denoted as $\mathbf{7} \mathbf{A}^{\text {calc }}-\mathbf{9} \mathbf{A}^{\text {calc }}$, are summarized in Table $\mathrm{S} 3 \dagger$ in comparison with related data of 7A-9A. Furthermore, Fig. $\mathrm{S} 4 \dagger$ displays the geometries of $\mathbf{7} \mathrm{A}^{\mathrm{calc}}-\mathbf{9} \mathrm{A}^{\text {calc }}$ in analogy to those shown for $\mathbf{7 A} \mathbf{- 9 A}$ in Fig. 2, cf. above. Besides an elongation of the bond lengths of the $\mathrm{CuN}_{4}$ units of $\mathbf{7} \mathbf{A}^{\text {calc }}-\mathbf{9} \mathbf{A}^{\text {calc }}$ compared to those of 7A-9A, $c f$. Table S3, $\dagger$ no mentionable differences of other related bond lengths and even those of related bond angles are observed. It should be emphasized that an elongation of the bond lengths of the $\mathrm{CuN}_{3} \mathrm{O}$ unit of geometry optimized dicationic 13A compared to data of 13A from crystallographic characterization has already been noticed by us. ${ }^{8 a}$ As observed for $\mathbf{7 A} \mathbf{- 9 A}$, $c f$. Fig. 2, even $\mathbf{7 A}{ }^{\text {calc }}-9 \mathbf{A}^{\text {calc }}$ cannot be considered as planar, cf. Fig. S4, $\dagger$ although deviations from planarity appear to be less dramatic.

Second, the spin density distributions of 7A-9A and $7 \mathbf{A}^{\text {calc }}$ $9 \mathbf{A}^{\text {calc }}$ were calculated and the obtained values are given in Fig. 9. It has to be noticed that related N donor atoms of 7A, 8A and/or 9A do not have identical spin populations. For example, for the $\mathrm{N}_{\text {aryl }}$ donor atoms of 7 A , values of 14.7 and 14.0 were calculated as given in Fig. 9. Such differences are not observed for $\mathbf{7} \mathbf{A}^{\text {calc }} \mathbf{- 9} \mathbf{A}^{\text {calc }}$. The differences observed for $\mathbf{7 A} \mathbf{- 9 A}$ are then attributed to distortions of the molecular geometries,
as outlined above. Additionally, it has to be noticed that generally the spin population at the N donor atoms of $7 \mathrm{~A}-9 \mathrm{~A}$ is larger compared to related atoms of $7 \mathrm{~A}^{\text {calc }}-9 \mathrm{~A}^{\text {calc }}$, whereas the spin population of the Cu atoms is smaller, $c f$. Fig. 9. That is most probably due to overemphasizing long $\mathrm{Cu}-\mathrm{N}$ bond lengths of $\mathbf{7 A}{ }^{\text {calc }}-\mathbf{9 A}{ }^{\text {calc }}$. Eventually, we do not aim to stress this point too much as corresponding data deviate by less than $10 \%$. In the following we refer, however, to calculated data of $7 \mathrm{~A}^{\text {calc }}-9 \mathrm{~A}^{\text {calc }}$ only.

It is certainly of interest to compare the spin density distribution of $\mathbf{7 A}-9 \mathrm{~A}$ with those already reported for $13{ }^{8 a}$ and $\mathbf{1 5 , ~}{ }^{10}$ as done in Fig. 9. With respect to calculated values one can infer from Fig. 9 that the change of the $\mathrm{CuN}_{2} \mathrm{O}_{2}$ unit of $15^{10}$ by a $\mathrm{CuN}_{3} \mathrm{O}$ unit of $13^{8 a}$ and finally by a $\mathrm{CuN}_{4}$ unit of $7 \mathrm{~A}-9 \mathrm{~A}$ results in a decrease of the remaining spin population at the Cu atoms (15: $55 \%, 13: 53.9,7 \mathrm{~A}-9 \mathrm{~A}: 52.2 \%$ on average). This tendency could be expected, as according to Kahn the performed heteroatom substitution should result in a better overlap between the N donor atom orbitals to Cu compared to O donor atom orbitals. ${ }^{9}$ That tendency is, however, not reflected by a clear trend in the spin population at the donor atoms of the Cu atoms. For example, for $15^{10}$ a spin population at the $\mathrm{N}_{\text {aryl }}$ donor atoms of $15 \%$ was calculated, whereas for the $\mathrm{N}_{\text {aryl }}$ donor atoms of $\mathbf{7} \mathbf{A}^{\text {calc }}-\mathbf{9} \mathbf{A}^{\text {calc }}$ this value amounts to $c a$. $13.8 \%$, cf. Fig. 9. Nevertheless, the described tendency for the spin population at the Cu atoms agrees with the expectation. In case there is an interplay between the spin density distribution of mononuclear complexes such as those in Fig. 9 and

${ }^{\text {a) }}$ This work. ${ }^{\text {b) }}$ First/second entry refer to data obtained for geometry optimized complex fragments or to data obtained by using complex geometries from crystallographic characterization, respectively. ${ }^{\text {c) }}$ The first/second entry refers to data obtained according to the approaches by Maki and McGarvey ${ }^{17} /$ Morton and Preston ${ }^{18}$. ${ }^{\text {d) }}$ Data refer to geometry optimized fragments only. For further data of $\mathbf{1 3}$ cf. ref. [8].

Fig. 9 Selected values of the calculated and experimentally obtained spin population of $7 \mathrm{~A}-9 \mathrm{~A}$ together with corresponding values of $13^{8 a}$ and $15 .{ }^{10}$
$J$ values of their corresponding trinuclear complexes, this tendency would indicate higher $J$ coupling for corresponding trinuclear complexes of $\mathbf{7 A} \mathbf{- 9 A}$ compared to related complexes of $13^{8 a}$ and $15 .{ }^{10}$

Finally, the calculated spin density distribution of 7A-9A should be compared with the estimates from the HF tensors. As reported before, ${ }^{8 a}$ the experimental approach according to Morton and Preston ${ }^{18}$ compares much better with calculated values than the Maki and McGarvey approach, ${ }^{17} c f$. Fig. 9. Certainly, the differences of the spin population at the Cu atoms of $\mathbf{8 A} / \mathbf{9 A}$ determined from the HF tensors and calculated values (exp. vs. calc. for $\mathbf{8 A} / \mathbf{9 A}=57.1 / 57.5$ vs. $52.2 / 52.0$ ) are larger than the difference reported for $13^{8 a}$ ( 51 vs. 53.9) and $15^{10}$ (54.6 vs. 55). This could be related to simplifications implicit in the experimental approaches ${ }^{17,18}$ which do not properly account for real local geometries of the complexes in question. In the approach of Maki and McGarvey, ${ }^{17}$ the anisotropic HF coupling constants are calculated for a square planar molecular geometry. In the approach of Morton and Preston, ${ }^{18}$ the HF coupling constants are calculated for a free atom. For both models, this sets a limitation for obtaining precise spin density values due to a deviation from the square planar geometry for the complexes under study. Nevertheless, they still remain reasonable qualitative approaches to obtain insight into the spin density distribution of $\mathrm{Cu}^{\mathrm{II}}$-containing type VI complexes. Furthermore, calculated spin densities of $\mathbf{8 A} / \mathbf{9 A}$ are different when compared to $\mathbf{8} \mathbf{A}^{\text {calc }} / \mathbf{9} \mathbf{A}^{\text {calc }}$, cf. Fig. 9, due to different geometries. The geometry of $\mathbf{8 A}$ in $\mathbf{8 @ 5}$ and of 9A in 9@6 cannot be determined, but it seems likely that both $\mathbf{8 A}$ and 9A do not have identical geometries inside the diamagnetic diluted materials as determined by their crystallographic characterization. Thus, the observed differences of the calculated spin density distribution of 7A-9A compared with those estimated from the HF tensors might be attributed to this effect as well.

Considering that the ESR spectra of type VI complexes reported here are much more complicated compared to type IV and type $\mathbf{V}$ complexes, the spin densities estimated from ESR and calculated spin density distribution reasonably
complement each other. Moreover, the inequality of N donor atoms revealed for 8 in the ENDOR experiment, $c f$. above, is in good qualitative correspondence with the DFT results. Nevertheless, there remains the question whether the increase of the exchange interaction in type IX complexes compared to type VII complexes is related to a smaller electronegativity of N donor atoms. This will be briefly discussed next.

## Discussion

Before starting a discussion it should be pointed out that from the experimental determination of the electron density distribution ${ }^{23}$ and the assignment of spin density maps, ${ }^{22}$ respectively, of the ferrimagnetic chain complex $[\{\mathrm{MnCu}(\mathrm{pba})-$ $\left.\left.(\mathrm{OH}) \cdot 2 \mathrm{H}_{2} \mathrm{O}\right\}_{n}\right]$, the magnetic coupling path of bis(oxamato) type complexes was aimed to be assigned. However, precise statements on the magnetic coupling path were not derived, although it is at least implied that the $\mathrm{N} \cdots \mathrm{C} \cdots \mathrm{O}$ unit of the $\mathrm{C}_{2} \mathrm{NO}_{3}$ containing oxamato bridge contributes to a larger extent to the magnetic superexchange coupling compared to the $\mathrm{O} \cdots \mathrm{C} \cdots \mathrm{O}$ unit. ${ }^{22,23}$ Certainly, polymeric $[\{\mathrm{MnCu}(\mathrm{pba})-$ $\left.(\mathrm{OH}) \cdot 2 \mathrm{H}_{2} \mathrm{O}\right\}_{n}$ ] compares marginally with the situation to be discussed here.

Unfortunately, 10 and 11 cannot be included in the following discussion. In the case of $\mathbf{1 0}$ this is due to the isolation as " $\left[\mathrm{Cu}_{3}(\right.$ opboMe 2$\left.)(\text { pmdta })_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$ ", of which the magnetic properties were measured. As this material could not be characterized crystallographically, it was converted into " $\left[\mathrm{Cu}_{3}\left(\mathrm{opboMe}_{2}\right)\right.$ (pmdta) $\left.)_{2}\right]\left(\mathrm{BPh}_{4}\right)_{2}\left(\mathbf{1 0}^{\prime}\right)$ ) of which crystals were suitable for crystallographic studies. Compound $\mathbf{1 0}^{\prime}$ displays then the same connectivity and coordination mode of the terminal $\mathrm{Cu}($ pmdta) fragments as observed for $\mathbf{1 2}$. However, due to the use of $\mathrm{BPh}_{4}{ }^{-}$anions in the case of $\mathbf{1 0}^{\prime}$ compared to $\mathrm{NO}_{3}{ }^{-}$anions in the case of $\mathbf{1 0}$, especially bond angles are expected to be modified by, for example, packing effects. Of $\mathbf{1 0}^{\prime}$ itself, only very little quantities could be obtained. On the other hand, crystals of $\mathbf{1 1}$ were not suitable to determine the structure reliably, vide supra.


Fig. 10 Representation of the experimentally determined $J$ values of 16 $(\Delta){ }^{11}\left[\mathrm{Cu}_{3}(\right.$ nabo $\left.)(\text { pmdta })_{2}\left(\mathrm{BF}_{4}\right)\right]\left(\mathrm{BF}_{4}\right) \cdot \mathrm{MeCN} \cdot \mathrm{Et}_{2} \mathrm{O}$ (nabo $=2,3$-naphtha-lene-bis(oxamato)) (O) $)^{11}$ and 12 ( $\square$ ) vs. its $\langle\tau\rangle$ parameters of the terminal $\mathrm{Cu}^{\prime \prime}$ ions in comparison with values of related type VII complexes. ${ }^{16,24}$

To identify the reason why the $J$ values of type IX complexes exceed those of type VII complexes the following test should be instructive: supposing that the formerly established nearly linear relationship between $J$ values and $\tau$ parameters of type VII complexes ${ }^{16,24}$ applies to corresponding type IX complexes as well, one could abstract the $J$ value of 12 from Fig. 10 with $-112 \mathrm{~cm}^{-1}$. From now on, we refer to that $J$ value as $J_{\text {abs. }}$. The experimentally determined $J$ value of 12 with $-132 \mathrm{~cm}^{-1}$ exceeds $J_{\text {abs }}$ significantly. From this observation, one could already conclude that for the same $\tau$ parameter, $J$ values of type IX complexes are larger when compared to type VII complexes, although the solid line in Fig. 10 displays an average estimate for type VII complexes. Additional support comes then from the calculated spin density distribution of especially 9A as the precursor of type IX 12 compared to $15^{10}$ as the precursor of type VII $16 .{ }^{11}$ Thereby, the Cu atom of $9 \mathrm{~A}^{\text {calc }}$ exhibits a spin density of $52.0 \%$ compared to $55 \%$ calculated for $15 .{ }^{10}$ This striking difference could indeed be a consequence of the replacement of the O donor atoms of 15 by less electronegative N donor atoms in 9A, as proposed by Kahn. ${ }^{9}$

Unfortunately, up to now, with 12 only one crystallographically characterized type IX complex can be described, the magnetic properties of which were determined. Due to this, it is not yet possible to conclude whether type IX complexes exhibit a related linear $J$ versus $\tau$ dependence as observed for type VII complexes, ${ }^{16,24}$ keeping in mind that the bonding situation of the terminal $\mathrm{CuN}_{3} \mathrm{O}_{2}$ units is different. The different bonding situation of type IX versus type VII complexes might then have an impact on the magnetic superexchange coupling path, which cannot be ruled out here and points out that additional studies are required.

## Summary and conclusions

Starting from the $o$-phenylenebis $\left(N(\mathrm{R})\right.$-oxamides) $\left(\mathrm{opboH}_{4} \mathrm{R}_{2}\right.$, $\mathrm{R}=\mathrm{Me} 1$, Et 2, ${ }^{n} \operatorname{Pr} 3$ ), achieved in good yields, the corresponding mononuclear $\mathrm{Ni}^{\mathrm{II}}$ and $\mathrm{Cu}^{\mathrm{II}}$ complexes in the form of their tetrabutylammonium salts $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{M}\left(\mathrm{opboR}_{2}\right)\right](\mathrm{M}=\mathrm{Ni}$,

R = Me 4, Et 5, ${ }^{n} \operatorname{Pr} \mathbf{6}$; M = Cu, R = Me 7, Et $\mathbf{8},{ }^{n} \operatorname{Pr} 9$ ) could be successfully synthesized. From 7-9, the trinuclear bis(oxamidato) type complexes $\left[\mathrm{Cu}_{3}\left(\mathrm{opboR}_{2}\right)(\mathrm{L})_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~L}=\mathrm{pmdta}, \mathrm{R}=$ Me 10, Et 11, ${ }^{n} \operatorname{Pr} 12$ ) could be obtained and characterized by, for example, single crystal X-ray diffraction studies in the form of $\left[\mathrm{Cu}_{3}\left(\mathrm{opboMe}_{2}\right)\left(\mathrm{pmdta}_{2}\right]\left(\mathrm{BPh}_{4}\right)_{2}\left(\mathbf{1 0}^{\prime}\right)\right.$ and $\left[\mathrm{Cu}_{3}\left(\mathrm{opbo}^{n} \mathrm{Pr}_{2}\right)-\right.$ (pmdta) $)_{2}\left(\mathrm{NO}_{3}\right)_{2} \cdot 1 / 2 \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 3 / 4 \mathrm{Et}_{2} \mathrm{O}\left(12^{\prime}\right)$.

ESR studies of 8@5 and 9@6 allowed an estimation of the spin density distribution of $\mathbf{8 A}$ and $9 \mathbf{A}$ by two different approaches. Single crystal ENDOR measurements of 8@5 have enabled to resolve individual spin densities of the four N donor atoms of $\mathbf{8 A}$ as individual HF tensors could be observed. The spin densities estimated from HF tensors agree fairly when compared with quantum chemically calculated ones. Especially the inequality of the HF tensors obtained from the ENDOR measurement of $\mathbf{8 @ 5}$ compares well with calculated spin densities of the N donor atoms of $\mathbf{8 \mathbf { A }}$ in case that the crystallographically determined geometry of $\mathbf{8 A}$ is applied for calculation. These results proof at least that the spin densities of the two different types of N donor atoms of $\mathbf{8 A} / \mathbf{9 A}$, namely the $\mathrm{N}_{\text {aryl }}$ and $\mathrm{N}_{\text {alkyl }}$ type atoms, are significantly different.

From susceptibility measurements versus temperature, the $J$ parameters of the trinuclear $\mathrm{Cu}^{\mathrm{II}}$-containing bis(oxamidato) complexes (type IX complexes) $\mathbf{1 0}\left(-96 \mathrm{~cm}^{-1}\right), \mathbf{1 1}\left(-104 \mathrm{~cm}^{-1}\right)$ and $12\left(-132 \mathrm{~cm}^{-1}\right)$ have been determined. They appear larger in magnitude when compared to $J$ values of reported type VII complexes. ${ }^{1}$ Our discussion of the spin density distribution favours the scenario that the enhancement of the exchange coupling $J$ is related to the substitution of the O donor atoms in complexes of type VII by less electronegative N donor atoms in complexes of type IX. To this end, the present work supports earlier studies, ${ }^{8 a, 10}$ in which an interplay between the spin density distribution of mononuclear type IV and VI complexes and magnetic superexchange interactions of trinuclear complexes derived out of them had been proposed.

## Experimental section

## General methods and materials

All chemicals were purchased from commercial sources and used as received without further purification. The solvents were purified according to standard procedures. ${ }^{25}$ NMR spectra were recorded at room temperature with a Bruker Avance III 500 Ultra Shield Spectrometer $\left({ }^{1} \mathrm{H}\right.$ at 500.300 MHz and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ at 125.813 MHz ) in the Fourier transform mode. Chemical shifts are reported in $\delta$ (ppm) vs. $\mathrm{SiMe}_{4}$ with the solvent as the reference signal ( $\left[\mathrm{D}_{6}\right]$-DMSO: ${ }^{1} \mathrm{H}$ NMR, $\delta=2.54$; and $\left.{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}, \delta=40.45\right)$. FT-IR spectra were recorded in the range of $400-4000 \mathrm{~cm}^{-1}$ on a Perkin-Elmer Spectrum 1000 FT-IR spectrophotometer as KBr pellets. Elemental analysis for C, H and N were performed on a Thermo FlashAE 1112 series. The diethyl ester of $N, N^{\prime}-o$-phenylene-bis(oxamic acid) $\left(\mathrm{opbaH}_{2} \mathrm{Et}_{2}\right),{ }^{26}$ compounds $\mathbf{1 - 3},{ }^{3}$ and $\left[\mathrm{Cu}(\mathrm{pmdta})\left(\mathrm{NO}_{3}\right)_{2}\right]^{27}$ were synthesized according to published procedures.

Synthesis of $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Ni}\left(\right.\right.$ opboR $\left.\left._{2}\right)\right], \mathrm{R}=\mathrm{Me}(4)$, Et (5), ${ }^{n} \mathbf{P r}$ (6). A hot solution (ca. $\left.50{ }^{\circ} \mathrm{C}\right)$ of $\left[\mathrm{Ni}(\mathrm{OAc})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]$ ( 0.49 g , $0.002 \mathrm{~mol})$ in $\mathrm{MeOH}(50 \mathrm{~mL})$ was added dropwise with stirring to a hot suspension $\left(c a .50^{\circ} \mathrm{C}\right)$ of $\mathbf{1 , 2}$ or $\mathbf{3}(0.002 \mathrm{~mol})$, respectively, in $\mathrm{MeOH}(50 \mathrm{~mL})$. Then, ${ }^{n} \mathrm{Bu}_{4} \mathrm{NOH}(5.18 \mathrm{~g}, 40 \%$ in $\mathrm{MeOH}, 0.008 \mathrm{~mol})$ was added with continuous stirring. The resulting mixture was stirred at $60^{\circ} \mathrm{C}$ for further 15 minutes, filtered and the solvent evaporated to dryness. The resulting oily material was treated with THF ( 25 mL ) and filtered to eliminate $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OAc}$. The desired complex was precipitated by addition of $\mathrm{Et}_{2} \mathrm{O}(200 \mathrm{~mL})$, as orange powder, filtered and dried in vacuo. Fig. S5-S7† give the ${ }^{1} \mathrm{H}$ NMR and IR spectra of 4-6, respectively.
4. Yield: $1.32 \mathrm{~g}(81 \%)$. Anal. calcd (\%) for $4\left(\mathrm{C}_{44} \mathrm{H}_{82} \mathrm{~N}_{6} \mathrm{NiO}_{4}\right.$, $817.85 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 64.62 , H 10.11, N 10.28; found: C 64.02 , H 10.59, N 9.88. IR: $\nu=2959(\mathrm{~m}), 2870(\mathrm{~m})(\mathrm{CH}) ; 1622(\mathrm{~s}), 1589$ $(\mathrm{s}), 1576(\mathrm{~s})(\mathrm{CO}) .{ }^{1} \mathrm{H}$ NMR: $\delta=0.94\left(\mathrm{t}, 24 \mathrm{H}, \mathrm{H}^{\mathrm{a}}\right), 1.36(\mathrm{~m}, 16 \mathrm{H}$, $\left.\mathrm{H}^{\mathrm{b}}\right), 1.57\left(\mathrm{~m}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{c}}\right), 2.39\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{H}^{1,1^{\prime}}\right), 3.15\left(\mathrm{t}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{d}}\right)$, 6.43 (dd, 2H, H ${ }^{6,6^{\prime}}$ ), 7.95 (dd, 1H, H ${ }^{5,5^{\prime}}$ ).
5. Yield: $1.25 \mathrm{~g}(74 \%)$. Anal. calcd (\%) for $5\left(\mathrm{C}_{46} \mathrm{H}_{86} \mathrm{~N}_{6} \mathrm{NiO}_{4}\right.$, $845.91 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 65.31, H 10.25, N 9.93; found: C 64.96, H 10.40, N 9.90. IR: $\nu=2958(\mathrm{~m}), 2872(\mathrm{~m})(\mathrm{CH}) ; 1619(\mathrm{~s})$, $1587(\mathrm{~m}), 1572(\mathrm{~s})(\mathrm{CO}) .{ }^{1} \mathrm{H}$ NMR: $\delta=0.87\left(\mathrm{t}, 6 \mathrm{H}, \mathrm{H}^{1,1^{\prime}}\right), 0.94$ $\left(\mathrm{t}, 24 \mathrm{H}, \mathrm{H}^{\mathrm{a}}\right), 1.31\left(\mathrm{~m}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{b}}\right), 1.57\left(\mathrm{~m}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{c}}\right), 2.66$ $\left(\mathrm{q}, 4 \mathrm{H}, \mathrm{H}^{2,2^{\prime}}\right), 3.17\left(\mathrm{t}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{c}}\right), 6.41\left(\mathrm{dd}, 2 \mathrm{H}, \mathrm{H}^{7,7^{\prime}}\right), 7.97$ (dd, 2H, H ${ }^{6,6}$ ).
6. Yield: $1.53 \mathrm{~g}(88 \%)$. Anal. calcd (\%) for $6\left(\mathrm{C}_{48} \mathrm{H}_{90} \mathrm{~N}_{6} \mathrm{NiO}_{4}\right.$, $873.96 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 65.97 , H 10.38, N 9.62 ; found: C 65.22 , H 10.50, N 9.79. IR: $\nu=2961(\mathrm{~m}), 2870(\mathrm{~m})(\mathrm{CH}) ; 1618(\mathrm{~s})$, 1584(s), $1570(\mathrm{~s})(\mathrm{CO}) .{ }^{1} \mathrm{H}$ NMR: $\delta=0.77\left(\mathrm{t}, 6 \mathrm{H}, \mathrm{H}^{1,1^{\prime}}\right), 0.95$ $\left(\mathrm{t}, 24 \mathrm{H}, \mathrm{H}^{\mathrm{a}}\right), 1.32\left(\mathrm{~m}, 20 \mathrm{H}, \mathrm{H}^{2,2^{\prime}, \mathrm{b}}\right), 1.58\left(\mathrm{~m}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{c}}\right), 2.55$ $\left(\mathrm{m}, 10 \mathrm{H}, \mathrm{H}^{3,3^{\prime}, \mathrm{DMSO}}\right), 3.17\left(\mathrm{t}, 16 \mathrm{H}, \mathrm{H}^{\mathrm{d}}\right), 6.41\left(\mathrm{dd}, 2 \mathrm{H}, \mathrm{H}^{8,8^{\prime}}\right), 7.97$ (dd, 1H, H $\mathrm{H}^{7,7^{\prime}}$ ).

Synthesis of $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Cu}\left(\right.\right.$ opbor $\left.\left._{2}\right)\right], \mathbf{R}=\mathrm{Me}(7)$, Et (8), ${ }^{n} \mathbf{P r}$ (9). A hot solution $\left(c a .50{ }^{\circ} \mathrm{C}\right)$ of $\left[\mathrm{Cu}_{2}(\mathrm{OAc})_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right](0.39 \mathrm{~g}$, $0.001 \mathrm{~mol})$ in $\mathrm{MeOH}(50 \mathrm{~mL})$ was added dropwise with stirring to a hot suspension $\left(c a .50^{\circ} \mathrm{C}\right)$ of $\mathbf{1 , 2}$ or $\mathbf{3}(0.002 \mathrm{~mol})$, respectively, in MeOH ( 50 mL ). Then, $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OH}(5.18 \mathrm{~g}, 40 \%$ in $\mathrm{MeOH}, 0.008 \mathrm{~mol})$ was added with continuous stirring. The resulting mixture was stirred at $60{ }^{\circ} \mathrm{C}$ for further 15 minutes, filtered and the solvent evaporated to dryness. The resulting oily material was treated with THF ( 25 mL ) and filtered to eliminate $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OAc}$. The desired complexes were precipitated by addition of $\mathrm{Et}_{2} \mathrm{O}(200 \mathrm{~mL})$, as faint red powders, filtered and dried in vacuo. Crystals suitable for X-ray crystallographic studies were grown by slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into MeCN solutions of 7-9. Fig. S8-S10 $\dagger$ give the IR spectra of 7-9, respectively.
7. Yield: 1.26 g (78\%). Anal. Calcd (\%) for $7\left(\mathrm{C}_{44} \mathrm{H}_{82} \mathrm{CuN}_{6} \mathrm{O}_{4}\right.$,
 H 9.97, N 10.13. IR: $\nu=2960(\mathrm{~m})$, 2881(m) (CH); 1616(s), 1587(s), 1568(s) (CO).
8. Yield: $1.44 \mathrm{~g}(85 \%)$. Anal. Calcd (\%) for $8\left(\mathrm{C}_{46} \mathrm{H}_{86} \mathrm{CuN}_{6} \mathrm{O}_{4}\right.$, $849.60 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 65.94, H 10.19, N 9.88; found: C 65.96, H 10.21, 9.68. IR: $\nu=2964(\mathrm{~m}), 2880(\mathrm{~m})(\mathrm{CH}) ; 1614(\mathrm{~s}), 1583(\mathrm{~s})$, 1561(s) (CO).
9. Yield: $1.42 \mathrm{~g}(81 \%)$. Anal. Calcd (\%) for $9\left(\mathrm{C}_{48} \mathrm{H}_{90} \mathrm{CuN}_{6} \mathrm{O}_{4}\right.$, $877.63 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 65.60 , H 10.32, N 9.56; found: C 65.21, H 10.05, N 9.29. IR: $\nu=2963(\mathrm{~m})$, 2890(m) (CH); 1612(s), 1581(s), 1558(m) (CO).
Synthesis of $\left[\mathrm{Cu}_{3}\left(\mathrm{opboR}_{2}\right)(\text { pmdta })_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}, \mathrm{R}=\mathrm{Me}(10)$, Et (11), ${ }^{n} \operatorname{Pr}(12)$. To a solution of 7,8 or $9(0.0006 \mathrm{~mol})$ in MeCN $(50 \mathrm{~mL})$ was added a solution of $\left[\mathrm{Cu}(\mathrm{pmdta})\left(\mathrm{NO}_{3}\right)_{2}\right](0.43 \mathrm{~g}$, 0.0012 mol ) in MeCN ( 25 mL ) dropwise with continuous stirring. After stirring for additional one hour, the resulting reaction mixture was concentrated to approximately 5 mL and $\mathrm{Et}_{2} \mathrm{O}$ ( 100 mL ) was added to precipitate a green powder. The overlaying solvents mixture was removed via a Teflon tube and MeCN ( 5 mL ) was added to dissolve the residue. A mixture of THF$\mathrm{Et}_{2} \mathrm{O}$ 4:1 ( 100 mL ) was added to precipitate the product, which was washed twice with THF ( 100 mL ). After removal of the supernatant, the remaining solid was dried in vacuo. Crystals suitable for X-ray crystallographic studies were grown by slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 12. 10. Yield: $0.50 \mathrm{~g}(90 \%)$. Anal. Calcd (\%) for $10\left(\mathrm{C}_{30} \mathrm{H}_{56} \mathrm{Cu}_{3} \mathrm{~N}_{12} \mathrm{O}_{10}\right.$, $935.48 \mathrm{~g} \mathrm{~mol}^{-1}$ ): C 38.52 , H 6.03, N 17.97; Found: C 38.17, H 5.82, N 17.76. IR: $\nu=2975(\mathrm{~m}), 2936(\mathrm{~m}), 2893(\mathrm{~m})(\mathrm{CH})$; 1621(s), 1615(s) (CO); (1385)(s) ( $\mathrm{N}=\mathrm{O}$ ). 11. Yield: 0.48 g ( $84 \%$ ). Anal. Calcd (\%) for $11\left(\mathrm{C}_{32} \mathrm{H}_{60} \mathrm{Cu}_{3} \mathrm{~N}_{12} \mathrm{O}_{10}, 963.53 \mathrm{~g} \mathrm{~mol}{ }^{-1}\right)$ : C 39.89, H 6.28, N 17.44; found: C 39.59, H 6.06, N 17.12. IR: $\nu=2970(\mathrm{~m}), 2927(\mathrm{~m}), 2890(\mathrm{~m})(\mathrm{CH}) ; 1616(\mathrm{~s}), 1609(\mathrm{~s})(\mathrm{CO}) ;$ (1381)(s) $(\mathrm{N}=\mathrm{O}) .12$. Yield: 0.55 g (93\%). Anal. Calcd (\%) for 12 $\left(\mathrm{C}_{34} \mathrm{H}_{64} \mathrm{Cu}_{3} \mathrm{~N}_{12} \mathrm{O}_{10}, 991.58 \mathrm{~g} \mathrm{~mol}^{-1}\right):$ C 41.18, H 6.51, N 16.95 ; found: C 40.79, H 6.39, N 16.61. IR: $\nu=2972(\mathrm{~m}), 2931(\mathrm{~m})$, 2888(m) (CH); 1620(s), 1612(s) (CO); (1379)(s) (N=O). Fig. S11$\mathrm{S} 13 \dagger$ give the IR spectra of $\mathbf{1 0} \mathbf{- 1 2}$, respectively.

Crystals obtained from slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions of $\mathbf{1 0}$ were of minor quality. Therefore, a metatheses reaction has been carried out. To a solution of $\mathbf{1 0}(0.0002 \mathrm{~mol}$, 0.18 g ) in $\mathrm{MeOH}(25 \mathrm{~mL})$ was added a solution of $\mathrm{NaBPh}_{4}$ $(0.0005 \mathrm{~mol}, 0.17 \mathrm{~g})$ in $\mathrm{MeOH}(25 \mathrm{~mL})$ in one portion with stirring. A pale green powder was precipitated immediately, which was filtered off, washed thoroughly with MeOH and $\mathrm{Et}_{2} \mathrm{O}$ and dried in vacuo. Slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ vapour in a solution of the obtained powder in MeCN-DMF $(1: 1)$ mixture afforded single crystals of $\left[\mathrm{Cu}_{3}\left(\mathrm{opboMe}_{2}\right)\left(\mathrm{pmdta}_{2}\right]\left(\mathrm{BPh}_{4}\right)_{2}\left(\mathbf{1 0}^{\prime}\right)\right.$ suitable for X-ray crystallographic studies after three days. No further characterization of $\mathbf{1 0}^{\prime}$ has been carried out.

Remark for the crystallization of 11: By allowing diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into MeCN solutions of $\mathbf{1 1}$ well shaped single crystals have been obtained. However, these crystals were too weakly diffractive and/or display very diffuse diffraction at higher diffraction angles, independent whether classical sealed-tube or $\mu \mathrm{F} \mathrm{Cu} \mathrm{K} \alpha$ radiation was applied. Due to this, a reliable refinement of the structure of $\mathbf{1 1}$ in the solid state was not possible, even not by treating them as incommensurable modulated. ${ }^{31}$

## Preparation of diamagnetically diluted single crystals (8@5 and 9@6)

To a solution of 5 or $\mathbf{6}(100 \mathrm{mg})$ in $\mathrm{MeCN}(5 \mathrm{~mL})$ was added a solution of $\mathbf{8}$ or $9(1 \mathrm{mg})$, respectively, in MeCN ( 1 mL ) under
stirring. After stirring for additional 24 hours in an open round bottom flask the volume of the mixture reduced to $c a$. 2.5 mL due to slow evaporation of the solvent. The remaining mixture was then transferred to a test tube and the diamagnetically diluted material allowed to crystallize under diffusion controlled conditions against $\mathrm{Et}_{2} \mathrm{O}$. Several orange coloured and non-hygroscopic single crystals with dimensions of $c a$. $0.4 \times 0.2 \times 0.2 \mathrm{~mm}^{3}$ could be isolated after several days.

Any trials to grow sufficiently large single crystals of 7@4 failed, although for both of the individual complexes 4 and 7 comparatively large single crystals could be obtained. The obtained needle-like single crystals of the cocrystallization of 7 and 4 were of dimensions of $c a .0 .1 \times 0.04 \times 0.04 \mathrm{~mm}^{3}$ and were all orange coloured, which indicates that 7@4 was formed. Individual crystals were too small for an ESR characterization and a further characterization of them was not carried out.

## X-ray crystallography

All data were collected on an Oxford Gemini S diffractometer. For data collection, cell refinement and data reduction the software CrysAlisPro was used. ${ }^{28 a}$ All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures on $F^{2}$ using SHELXL-97 as part of the software package SHELXTL. ${ }^{29 a}$ All non-hydrogen atoms were refined anisotropically. All C-bonded hydrogen atoms were refined using a riding model.
Statements for the mononuclear complexes. In the case of 4 a comparatively short distance between the hydrogen atoms of the corresponding carbon atoms C11 and C12 (methyl groups) is observed. The hydrogen atoms were here added on calculated positions as idealised methyl groups in staggered geometries (HFIX 33). The comparatively close vicinity of C11 and C 12 is thus regarded as responsible for this artefact.

In the case of $5^{\prime}$ and $\mathbf{8}^{\prime}$ the positions of O -bonded hydrogen atoms were taken from the difference Fourier map and refined isotropically. Furthermore, for $5^{\prime}$ a comparatively large unrefined electron density peak is observed with $c a .0 .7 \mathrm{e} \AA^{-3}$ at a distance of $c a .1 .8 \AA$ away from O3. This peak might indicate a disorder of the respective water molecule, although this disorder could not be refined reliably.

The absolute structure of 6 was established by anomalous dispersion effects with respect to the absolute structure parameter. ${ }^{30}$ Furthermore, the atoms C11, C13, C14 (0.84/0.16); the atoms C59, C60 (0.43/0.57); the atoms C69-C72 (0.34/0.66) and the atoms C73-C76 (0.72/0.28) are disordered and have been refined to split occupancies given in brackets. Although a number of atoms/groups could be refined disordered, trials to refine more atoms/groups as disordered did fail or gave nonreliable results. This is most probably due to the comparatively low number of observed $v s$. total reflections. The two highest unrefined electron density peaks Q1 $\left(c a .1 .6 \mathrm{e} \AA^{-3}\right)$ and Q2 $(c a$. $1.2 \mathrm{e} \AA^{-3}$ ) are located $c a .1 .1 \AA$ away from Ni2 and $c a .1 .1 \AA$ away from Ni1, respectively.

In the case of 9 the atoms C11, C13, C14 (0.47/0.53); the atoms C17-C20 ( $0.17 / 0.83$ ); the atoms C21-C24 ( $0.32 / 0.68$ ); the
atoms C25-C28 (0.24/0.76); the atoms C33-C36 (0.65/0.35) and the atoms C37-C40 $(0.37 / 0.63)$ are disordered and have been refined to split occupancies given in brackets. Several atoms here do have too large ADP max/min ratios or large Hirshfeld test differences and high $U_{\text {eq }}$ values, respectively, when compared to neighbours. Furthermore, short intra and/or inter $\mathrm{H} \cdots \mathrm{H}$ contacts are observed. Most probably, all of these observations are due to further, but not reliable resolvable, disorder of atoms/groups. Additionally, the best suitable single crystal of 9 was, due to its plate-like shape, weakly diffractive only. Although long measurement times of individual frames have been applied by using $\mathrm{Cu} \mathrm{K} \alpha$ radiation, the ratio between observed/unique reflections is with $c a .45 \%$ still poor. Due to icing problems, the measurement has been stopped at a resolution of $\theta=c a .60^{\circ}$. These reasons might explain why further models of disorder could not be introduced.

Data of 4, $5^{\prime}, 6,7,8^{\prime}$ and 9 have been deposited at the Cambridge Crystallographic Data Centre under CCDC deposition numbers CCDC 1035427-1035432, respectively.

Statements for the trinuclear complexes. In the case of $\mathbf{1 0}^{\prime}$ the trinuclear and dicationic complex fragment has been refined disordered at two positions. This disorder resembles a statistical disorder, whereby the complex fragments are arranged in top versus down orientation with respect to each other. The finally obtained and freely calculated occupation factors amount to 0.68 versus 0.32 . Several atoms appear as further disordered as indicated by high $U_{\text {eq }}$ values and large Hirshfeld test differences when compared to neighbours. Trials to refine with SHELXL-2013 software ${ }^{29 b}$ by applying the RIGU command did not improve this situation. Their disorder could not be solved and refined reliably, which is mostly attributed to the already poor ratio of reflections to parameters.

In the case of $\mathbf{1 2}^{\prime}$ the crystals were twinned. By applying CrysAlisPro version 1.171.37.31 ${ }^{28 b}$ four different domains were applied for data integration. No further domains could be observed, whereby for domains I to IV the ratios $0.36,0.32$, 0.15 and 0.17 , respectively, were finally determined. The SHELXL-2013 software ${ }^{29 b}$ was used for refinement and the command RIGU was applied. The two nitrate anions could be refined disordered over two positions (N11, O5-O7 (0.78/0.22), and N12, O8-O10 (0.34/0.66)). In addition, the atoms C11-C13 of one ${ }^{n} \mathrm{Pr}$ group could be refined disordered with occupations of $0.40 / 0.60$. Furthermore, in the VOIDS one $\mathrm{Et}_{2} \mathrm{O}$ and one $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule could be refined with occupation factors of 0.75 and 0.5 , respectively. Thereby, the $\mathrm{Et}_{2} \mathrm{O}$ molecule was refined disordered over two positions with occupation factors for O11, C36-C39 of 0.52/0.48.

Data of $\mathbf{1 0}^{\prime}$ and $\mathbf{1 2}^{\prime}$ have been deposited at the Cambridge Crystallographic Data Centre under CCDC deposition numbers CCDC 1035433 and 1035435, respectively.

## ESR measurements

The measurements of single crystals of 8@5 and 9@6 as well as liquid solution spectra of 8 and 9 , respectively, were recorded at room temperature on a Bruker EMX spectrometer operating in the X-band with a modulation frequency of 100
kHz. Handling of ESR spectra was carried out using Win-EPR® computer programs, ${ }^{32 a}$ and spectral simulations were performed with the Simfonia program. ${ }^{33}$

Electron Nuclear Double Resonance (ENDOR) experiments were performed with an X-band ESR spectrometer Elexsys E580 (Bruker) at a temperature of 20 K . A standard Davies ENDOR pulse sequence has been used: $\pi_{\mathrm{mw}}-\pi_{\mathrm{rf}}-\pi /$ $2_{\mathrm{mw}}-\pi_{\mathrm{mw}}$-echo. ${ }^{32 b}$ In this pulse protocol the amplitude of the stimulated electron spin echo arising after the application of the microwave (mw) pulses $\pi_{\mathrm{mw}}-\pi / 2_{\mathrm{mw}}-\pi_{\mathrm{mw}}$-echo is recorded as a function of the frequency of the intervening radiofrequency (rf) pulse in the MHz range. To obtain the optimal rf $\pi$-pulse length ( $\pi_{\mathrm{rf}}$ ) the nutation experiments were performed. For all measurements the lengths of the inversion pulse $\pi_{\mathrm{mw}}$, radiofrequency pulse $\pi_{\mathrm{rf}}$ and detection pulses $\pi / 2_{\mathrm{mw}}\left(\pi_{\mathrm{mw}}\right)$ were set to $400 \mathrm{~ns}, 7 \mu \mathrm{~s}$ and $16 \mathrm{~ns}(32 \mathrm{~ns})$, respectively. Simulations of the ENDOR spectra were performed using the EasySpin (version 4.0.0) ${ }^{32 c}$ program of the Matlab 2007a package.

## Magnetic measurements

Static magnetic susceptibility was measured with a 7 T VSM-SQUID magnetometer from Quantum Design at a field of 1 T in a temperature range $2-300 \mathrm{~K}$. In order to ensure the highest possible purity and to avoid any possible influence of partially liberated packing solvent from compounds due to storage, single crystals of $\mathbf{1 0 - 1 2}$ were evacuated for ca. 12 hours in vacuo and the complete loss of all solvent molecules has been ensured by an additional elemental analysis.

## Quantum chemical studies

The density functional theory (DFT) calculations on individual, free molecules were carried out by using revision 2.80 of the ORCA code. ${ }^{34}$ The Def2-TZVPP ${ }^{35,36}$ basis set together with the B3LYP ${ }^{37}$ functional was chosen to obtain a reasonable accuracy in our calculations and to have results comparable to previous investigations. ${ }^{10}$ We used single molecules isolated from the measured X-ray data (where available) as input for our calculations. The counterions were neglected and further geometry optimizations were carried out using a gradient method. To check the optimization result the structures were compared to respective relaxed structures which were initially created from scratch using a molecular editor. We also compared the results to single point calculations using the unaltered crystallographic structures and did not find qualitative disagreement. The spin densities at the different atoms were calculated from the difference of all electron density for minority (spin down) and majority (spin up) electrons followed by a numerical integration within spheres of radius $R$ centred at the respective atoms. The same information was obtained by using Mulliken density analysis ${ }^{38}$ as implemented in the ORCA code. In spite of giving slightly different numerical results for the respective absolute spin densities the results of both methods do agree very well and the same qualitative trends are observed.

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