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Interesting copper(II)-assisted transformations of 2-acetylpyridine and 2-benzoylpyridine†

Alexandros A. Kitos,[a] Constantinos G. Efthymiou,[a] Manolis J. Manos,[b,c] Anastasios J. Tasiopoulos,[b] Vassilios Nastopoulos,[a] Albert Escuer*[d] and Spyros P. Perlepes*[a,e]

The reactions of various copper(II) sources with 2-acetylpyridine, (py)(me)CO, and 2-benzoylpyridine, (py)(ph)CO, under strongly basic conditions have been studied and novel ligand transformations have been discovered. Reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ and (py)(me)CO in the presence of NBu^n_4OMe (1:1:1) in $CHCl_3$ gave a mixture of $[Cu_2Cl_2(HL_A)_2](ClO_4)_2$ (1) and $[Cu_2Cl_2(L_B)_2](ClO_4)_2$ (2), where HL_A is 3-hydroxy-1,3-di(pyridin-2-yl)-butane-1-one and L_B the zwitterionic-type ligand 3-hydroxy-1-methyl-3-(pyridin-2-yl)-3H-indolizin-4-ium. The ligand HL_A is formed through an aldol reaction-type mechanism, while the formation of L_B takes place *via* an intramolecular nucleophilic attack of the remote 2-pyridyl nitrogen atom on the positive carbonyl carbon of HL_A, after transformation of the latter through deprotonation and dehydration. The Cu^{II} ions in 1 are bridged by two 2.1111 HL_A ligands resulting in a long $Cu^{II}\cdots Cu^{II}$ distance (5.338 Å); the metal ions in 2 are triply bridged by the alkoxide oxygen atoms of the two 2.21 L_B ligands and one 2.1100 perchlorato group. The absence of *a*-hydrogens in (py)(ph)CO leads the reactivity of this ligand in the presence of Cu^{II} to different pathways. The $Cu(ClO_4)_2 \cdot 6H_2O/(py)(ph)CO/NBu^n_4OMe$ reaction mixture in $MeOH/H_2O$ (25:1 v/v) gave the dinuclear cationic complex $[Cu_2\{(py)(ph)CO\}_2(L_C)_2](ClO_4)_2$ (3), where L_C^- is the anion of (methoxy)(phenyl)(pyridin-2-yl)methanol formed *in situ* via the nucleophilic addition of MeO^- to the carbonyl carbon of (py)(ph)CO upon Cu^{II} coordination. The Cu^{II} ions in the cation are doubly bridged by the deprotonated oxygen atoms of the two L_C^- ligands. Replacement of $Cu(ClO_4)_2 \cdot 6H_2O$ with $Cu(NO_3)_2 \cdot 3H_2O$ and NBu^n_4OMe with NMe_4OH, and decrease of the H_2O concentration in the above reaction system yielded the tetranuclear coordination cluster $[Cu_4(OMe)_2(NO_3)_4\{(py)(ph)CO\}_2(L_C)_2]$ (4). The Cu^{II} centres in this complex define a parallelogram. Two parallel sides of the parallelogram are each supported by deprotonated oxygen atoms belonging to a 2.21 L_C^- ligand and a 2.21 MeO^- group. The metal ions that define each of the other two sides are singly bridged by an oxygen atom of a 2.210 nitrato group. No bridging exists between the Cu^{II} ions that define the two diagonals of the parallelogram. Replacement of MeOH with EtOH in the reaction system that gave 4 resulted in the dinuclear complex $[Cu_2(NO_3)_2(L_D)_2](EtOH)]$ (5), L_D^- being the anion of (ethoxy)(phenyl)(pyridin-2-yl)methanol. The Cu^{II} ions are doubly bridged by the alkoxide oxygen atoms of the two 2.21 L_D^- ligands. The 1:1:1 $Cu(NO_3)_2 \cdot 3H_2O/(py)(ph)CO/NMe_4OH$ reaction system in CH_3NO_2 gave the dinuclear complex $[Cu_2(NO_3)_2(L_E)_2]$ (6), where L_E^- is the anion of 2-nitro-1-phenyl-1-(pyridin-2-yl)ethanol. The OH^- ion abstracts one of the methyl hydrogens of CH_3NO_2, and once the carbanion $^-:CH_2NO_2$ is formed it attacks the positive (δ+) carbonyl carbon of (py)(ph)CO; as the carbanion forms the new C-C bond, the π electrons of the carbonyl group of the original ligand are transferred completely to the oxygen forming the alkoxide-type ligand L_E^-. The Cu^{II} ions are doubly bridged by the alkoxide oxygen atoms of the two 2.21 L_E^- ligands. Simplified mechanistic views for the Cu^{II}-assisted formation of the transformed ligands are proposed. Dc magnetic susceptibility studies in the 2-300 K range for the representative complexes 3-6 reveal the presence of very strong antiferromagnetic $Cu^{II}\cdots Cu^{II}$ exchange interactions in the dinuclear complexes 3, 5, 6 and within the dimeric $\{Cu_2(OMe)(NO_3)\{(py)(ph)CO\}(L_C)\}^+$ subunits of 4. The strong antiferromagnetic coupling is discussed in terms of the large Cu-O-Cu angles (101.0 – 102.9°) in the dinuclear, planar $\{Cu_2O_2\}$ units/subunits of 3-6.

[a] Department of Chemistry, University of Patras, 26504 Patras, Greece. E-mail: perlepes@patreas.upatras.gr; Tel: +30 2610 996780
[b] Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus
[c] Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece
[d] Departament de Quimica Inorganica and Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain. E-mail: albert.escuer@ub.edu; Tel: +34 93 4039141
[e] Institute of Chemical Engineering Sciences, Foundation for Research and Technology-Hellas (FORTH/ICE-HT), Platani, P.O. Box 1414, 26504 Patras, Greece

Introduction

The effect of the ligands upon a transition metal ion is today well understood and can be rather easily quantified; in contrast, the converse effect is not so. There are several reasons for this.[1] Firstly, to a certain extent, the orbitals of the metal ion have many of the properties of hydrogen-like atomic orbitals, whereas the orbitals of the donor atoms of the ligands are also involved in intra-ligand covalent bonding.

Secondly, the ligand orbitals are generally more or less polarisable than metal orbitals. This means that ligand donor orbitals become perturbed, whereas metal d orbitals remain more-or-less recognisable as such in coordination complexes (as seen, for example, from d-d electronic spectra). In particular, the change from lone pair to bonding pair, consequent upon the formation of the coordinate bond, has significant effects upon the other groups which might be bonded to the ligand donor atom(s). A metal ion may alter the properties of a coordinated ligand through conformational, polarisation and π-bonding changes.

Upon coordination of a ligand L to a metal centre M, the ligand's properties (acidity, susceptibility to oxidation or reduction, electrophilic or nucleophilic character, *etc.*) can be significantly modified, thereby enhancing or inhibiting its reactivity.[2] Thus, while metal complexes (mononuclear, polynuclear, polymeric) are most often prepared by the reaction of a metal source and a presynthesized ligand, it is also possible to generate the ligands *in situ* from an easily available organic compound (precursor). This approach allows the reactivity of M to activate a proligand, transforming it through an *in situ* reaction, sometimes providing coordination complexes with ligands not accessible by conventional organic synthesis. Important landmarks in the area of the reactivity of coordinated ligands were the hydrolysis of Pt[II]-bound organonitriles to give the platinum blues[3] in 1907 and the studies of Chugaev who hydrolysed coordinated CNO[-] groups to obtain ammino complexes[2] in 1921. Nowadays, the altered reactivity of ligands as a consequence of their ligation to a M is a "hot" research theme in contemporary transition-metal chemistry,[1,2,4] because it forms the basis for the use of coordination complexes as stoichiometric reagents and also as homogeneous catalysts in organic chemistry. The main factors that affect the L reactivity are the electron-acceptor/donor properties of the individual M and L partners, as well as the nature of any co-ligand. Among the reactions occurring upon coordination[2] are acid-base and related reactions, internal redox reactions between M and L, L coupling, template synthesis, M-induced rearrangements, nucleophilic or electrophilic addition to L, and stabilization of unstable species and protection of functional groups by M centres.[2] The reactions of coordinated organic ligands can be used for M-mediated synthesis of new products upon their elimination from the coordination sphere of a metal complex. However, if we examine the literature we will easily see that the number of new ligands which have been eliminated is still limited; this is due to the fact that often the major driving force for their formation is the high thermodynamic stability of the complexes formed that contain the new (*i.e.,* transformed) ligand.

A large number of reactions of *carbonyl* compounds has been shown to be sensitive to the presence of transition metal ions. Carbonyl compounds are of great importance in the formation of C-C bonds in organic chemistry and metal-ion control of their reactivity offers a means to promote, inhibit or even control such reactions. The coordination of the oxygen atom of a carbonyl compound to a metal centre often modifies
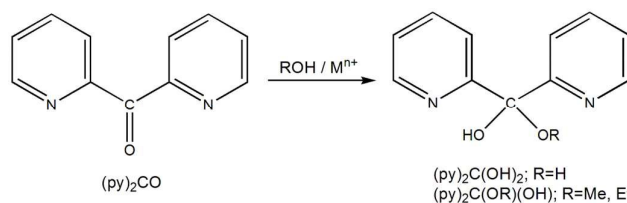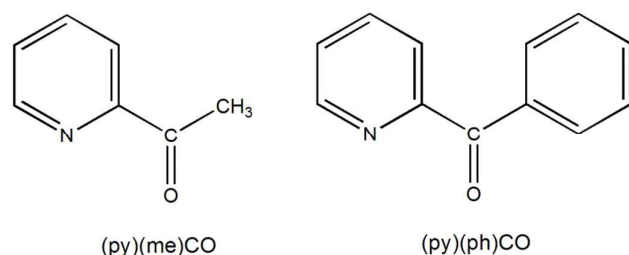

Scheme 1 Di-2-pyridylketone, (py)$_2$CO, and its neutral *gem*-diol, (py)$_2$C(OH)$_2$, and hemiketal, (py)$_2$C(OR)(OH) [R=Me, Et,...], forms. Note that (py)$_2$C(OH)$_2$, (py)$_2$C(OR)(OH) and their anions do not exist as free species but exist only as ligands in their respective metal complexes. M^{n+} is a metal ion and n is normally 2 or 3.

the reactivity of that group.[1] Due to the polarisation effect, the electrophilic character of a carbonyl C atom may be increased by coordination of the O atom to a metal ion, and so reactions in which the rate-determining step is nucleophilic attack upon this site (nucleophilic addition to the carbonyl carbon is a principal reaction of carbonyl compounds) might be accelerated. Similarly, the presence of a positive metal ion coordinated to the O atom might favour enolisation (another important type of reaction commonly associated with carbonyl compounds involves the generation of a nucleophilic enol or enolate ion) and accelerate reactions in which enolisation or reaction of an enolate is rate determining; the pKa of the enol will also be sensitive to coordination of the oxygen, and generation of the enolate may be facilitated.[5] Examples of Cu[II]-ion modification of the reactions of two carbonyl compounds will be presented in this work.

Our groups have had a strong interest over many years in the reactivity chemistry of coordinated ligands of the general types X-CO-X, X-CO-CO-X and X-CO-X-CO-X, where X is a donor group.[5,6] The most thoroughly studied such ligand is di-2-pyridyl ketone, (py)$_2$CO (Scheme 1). The particular interest on this ligand stems from the reactivity potential of the carbonyl function which can easily undergo metal ion-assisted hydration or alcoholation (Scheme 1) and subsequent deprotonation of the hydroxyl group(s). Thus, a range of nucleophiles, including H$_2$O and alcohols (ROH), have been shown to add to the carbonyl group *upon coordination of the carbonyl O atom and/or the 2-pyridyl rings in solution* forming the ligands (py)$_2$C(OH)$_2$ [the *gem*-diol form of (py)$_2$CO] and (py)$_2$C(OR)(OH) [the hemiketal forms of (py)$_2$CO], respectively. Sometimes this is a relatively long-range effect because there is often no direct interaction of the carbonyl O atom with M. The deprotonated (py)$_2$C(OH)(O)$^-$, (py)$_2$C(O)$_2$$^{2-}$ and (py)$_2$C(OR)(O)$^-$ forms are flexible and versatile, and can adopt a variety of coordination modes leading to coordination clusters and polymers with interesting structures and properties.[5-7] It has not been proven whether the coordination of the O to M occurs *after* the hydration reaction (in which case we are seeing a polarisation effect of the metal ion upon the hydroxyl group leading to its deprotonation) or *prior* to the reaction, in which case we are facing a direct activation of the carbonyl towards nucleophilic attack,[1] although the existing evidence points towards the latter case.

With our previous experience in mind we sought to modify the possibilities provided by (py)$_2$CO by studying the metal

Scheme 2 (Left) 2-acetylpyridine and (right) 2-benzoylpyridine, the two 2-pyridyl ketones whose Cu^{II} ion-assisted reactivity has been studied in the present work.

ion-assisted reactivity chemistry of (py)COY molecules, where Y is a *non*-donor group. Our goals are to investigate to what extent the use of such ligands might allow metal ion-assisted/promoted reactivity on the carbonyl group and to what extent this might affect the identity of the obtained products compared with (py)$_2$CO. Concerning the first point, the rich reactivity of coordinated (py)$_2$CO is generally attributed[1,5-7] to the electron-withdrawing character of both substituents (the 2-pyridyl rings) on the carbonyl C atom and thus the polarisation of the C-C σ bonds connecting the 2-pyridyl groups to the central C atom is sufficient to increase its electrophilic nature and activate it for further reaction. Concerning the second point, the lack of the second ring N atom was expected to affect the identity of the metal complexes in the case of the (py)COY ligands. We have decided to start our efforts with the simple ligands 2-acetylpyridine, (py)(me)CO, and 2-benzoylpyridine, (py)(ph)CO, see Scheme 2. These ligands offer interesting characteristics which are expected to affect their reactivity. For example: (i) (py)(me)CO is less bulky than (py)$_2$CO, whereas (py)(ph)CO has almost the same size with (py)$_2$CO; (ii) the methyl group is electron-releasing, whereas the phenyl group is electron-withdrawing (albeit less than the 2-pyridyl group); and (iii) the C-H bonds adjacent to the carbonyl group of (py)(me)CO, *i.e.* the C-H bonds of the methyl group, are polar and potential reaction sites,[8] while (py)(ph)CO lacks such acidic *a*-hydrogens. We have already reported that the reaction of Co(ClO$_4$)$_2$·6H$_2$O and (py)(me)CO in acetone at room temperature under aerobic and strongly basic conditions afforded the wheel-shaped, mixed-valence cluster [Co^{III}Co$^{II}_6$(OH)$_6$(L$_1$)$_6$](ClO$_4$)$_3$,[9] where L$_1^-$ is the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one, (py)(me)C(CH$_2$COCH$_3$)(O)$^-$, formed *in situ* through a crossed-aldol reaction (*vide infra*). We report here some interesting transformations observed during the reactions of copper(II) sources with (py)(me)CO and (py)(ph)CO; the resultant complexes were structurally characterized by single-crystal, X-ray crystallography, while the magnetic properties of selected examples will also be described. This work can be considered as a continuation of our interest in metal ion-assisted transformations of organic compounds containing carbonyl[5-7,10] and other[4a,11] functional groups.

Experimental section

Materials and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. *Warning:* Although no such behaviour was observed during the present work, perchlorate salts are potentially explosive; such compounds should be used in small quantities, and treated with utmost care at all times. Elemental analyses (C, H, N) were performed by the University of Patras microanalytical service. FT-IR spectra (4000-400 cm^{-1}) were recorded using a Perkin Elmer 16PC FT-IR spectrometer with samples prepared as KBr pellets and as Nujol or hexachlorobutadiene mulls between CsI plates. Variable-temperature magnetic susceptibility measurements for selected copper(II) complexes were performed using a DSM5 Quantum Design SQUID magnetometer operating at 0.3 T in the 300-30 K range and at 0.02 T in the 30-20 K range to avoid saturation effects. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constant.

Synthetic details

Preparation of [Cu$_2$Cl$_2$(HL$_A$)$_2$](ClO$_4$)$_2$ (1) and [Cu$_2$Cl$_2$(L$_B$)$_2$(ClO$_4$)$_3$]·2CHCl$_3$ (2·2CHCl$_3$) in a mixture, where HL$_A$ and L$_B$ are the neutral organic ligands 3-hydroxy-1,3-di(pyridin-2-yl)-butane-1-one and 3-hydroxy-1-methyl-3-(pyridin-2-yl)-3H-indolizin-4-ium, respectively. To a solution of (py)(me)CO (0.056 mL, 0.50 mmol) in CHCl$_3$ (25 mL) was added a 20% (w/v) solution of NBu$^n_4$OMe in MeOH (0.84 mL, 0.50 mmol). The resulting solution was stirred for 1 h to obtain a pale yellow colour and then solid Cu(ClO$_4$)$_2$·6H$_2$O (0.185 g, 0.50 mmol) was added under vigorous stirring. The solid dissolved and the colour of the solution turned to green. The reaction solution was stirred for a further 1 h, filtered and left undistured in an open flask at room temperature for slow evaporation. X-ray quality, green pisms of **1** and purple plates of **2**·2CHCl$_3$ were obtained in a period of 3-5 d. The crystals were collected by filtration, seperated manually, washed with ice-cooled CHCl$_3$ (2x1 mL), and dried *in vacuo*. Typical yields were in the ranges 45-50% (**1**) and 7-10% (**2**). Analytical data for **1**, calcd for C$_{28}$H$_{28}$Cu$_2$N$_4$O$_{12}$Cl$_4$ (found values in parentheses): C 38.15 (38.40), H 3.21 (3.10), N 6.36 (6.47)%. The purple complex was analysed as lattice solvent-free, *i.e.* as **2**. Analytical data, calcd for C$_{28}$H$_{24}$Cu$_2$N$_4$O$_{10}$Cl$_4$ (found values in parentheses): C 39.77 (39.63), H 2.87 (2.94), N 6.63 (6.39)%. IR bands (KBr, cm^{-1}) for **1**: 3372mb, 3060w, 3024w, 2973w, 1670s, 1602s, 1570m, 1488m, 1440m, 1372s, 1306sh, 1266m, 1224s, 1144sh, 1088sb, 1036m, 954m, 878w, 828w, 780s, 756m, 696w, 660w, 626s, 572m, 558sh, 432m. Selected IR bands (KBr, cm^{-1}) for **2**: 2985m, 1630m, 1599s, 1564m, 1430s, 1400m, 1265m, 1157s, 1129m, 1030s, 1005m, 955s, 632m, 617w, 530m, 459w, 440w.

[Cu$_2${(py)(ph)CO}$_2$(L$_C$)$_2$](ClO$_4$)$_2$·MeOH (3·MeOH), where L$_C^-$ is the anion of methoxy(phenyl)(pyridin-2-yl)methanol. To a solution of (py)(ph)CO (0.092 g, 0.50 mmol) in MeOH (25 mL)/H$_2$O (1 mL) was added a 20% (w/v) solution of NBu$^n_4$OMe in MeOH (0.84 mL, 0.50 mmol). The resulting colourless solution was stirred for 1 h and then solid Cu(ClO$_4$)$_2$·6H$_2$O (0.185 g, 0.50 mmol) was added. The solid soon dissolved and the colour of the solution became blue. The reaction solution

was stirred for a further 1 h, filtered and left undisturbed in an open flask at room temperature for slow evaporation. X-ray quality, blue plates of the product were formed in a period of 5-6 d. The crystals were collected by filtration, washed with cold MeOH (1 mL) and Et$_2$O (3x2 mL), and dried in air. The yield was 35% (based on the (py)(ph)CO initially available). The complex was analysed as lattice MeOH-free, *i.e.* as **3**. Analytical data, calcd for C$_{50}$H$_{42}$Cu$_2$N$_4$O$_{14}$Cl$_2$ (found values in parentheses): C 53.57 (53.74), H 3.78 (3.90), N 5.00 (4.87)%. IR bands (KBr, cm^{-1}): 3100w, 3072w, 2960w, 2932w, 1652s, 1596m, 1572w, 1474w, 1448m, 1324s, 1294w, 1256m, 1244sh, 1226w, 1090sb, 1054sh, 990m, 950m, 818sh, 794sh, 778m, 752m, 700sh, 688s, 652m, 624s, 544w, 505w, 458w, 423w.

[Cu$_4$(OMe)$_2$(NO$_3$)$_4${(py)(ph)CO}$_2$(L$_C$)$_2$] (4). To a solution of (py)(ph)CO (0.092 g, 0.50 mmol) in MeOH (25 mL) was added solid NMe$_4$OH·5H$_2$O (0.091 g, 0.50 mmol). The resulting colourless solution was stirred for 25 min and then solid Cu(NO$_3$)$_2$·3H$_2$O (0.121 g, 0.50 mmol) was added. The solid soon dissolved and the colour of the solution became green. The reaction solution was stirred for a further 30 min, filtered and layered with Et$_2$O (50 mL). Slow diffusion gave turquoise prisms of the product. The crystals were collected by filtration, washed with cold MeOH (3x2 mL) and dried in air. Typical yields were in the 40-50% range. Analytical data, calcd for C$_{52}$H$_{48}$Cu$_4$N$_8$O$_{20}$ (found values in parentheses): C 49.95 (49.69), H 3.57 (3.44), N 8.25 (8.31)%. IR bands (KBr, cm^{-1}): 3058w, 2968w, 2932w, 1658s, 1600m, 1574w, 1448m, 1382s, 1350s, 1324sh, 1288sh, 1254m, 1238w, 1220m, 1172w, 1090m, 1048s, 986m, 948m, 922sh, 805sh, 791sh, 778m, 754m, 706sh, 688s, 650m, 542w, 516w, 458w, 426w.

[Cu$_2$(NO$_3$)$_2$(L$_D$)$_2$(EtOH)] (5), where L$_D$$^-$ is the anion of ethoxy(phenyl)(pyridine-2-yl)methanol. To a solution of (py)(ph)CO (0.092 g, 0.50 mmol) in EtOH (25 mL) was added solid NMe$_4$OH·5H$_2$O (0.091 g, 0.50 mmol) to give a colourless solution. After stirring for 20 min, solid Cu(NO$_3$)$_2$·3H$_2$O (0.121 g, 0.50 mmol) was added which soon dissolved to give a green solution. The reaction solution was stirred for a further 25 min, filtered and layered with Et$_2$O (45 mL). Slow mixing gave blue prisms of the product, which were collected by filtration, washed with cold EtOH (2x2 mL) and Et$_2$O (3x2 mL), and dried in air. The yield was 48%. Analytical data, calcd for C$_{30}$H$_{34}$Cu$_2$N$_4$O$_{11}$ (found values in parentheses): C 47.80 (47.94), H 4.56 (4.51), N 7.43 (7.59)%. IR bands (KBr, cm^{-1}): 3548sh, 3440sb, 3070w, 2970w, 2928w, 2874w, 1606m, 1570w, 1542sh, 1488s, 1438m, 1384s, 1302s, 1284sh, 1240sh, 1216m, 1158m, 1110m, 1088sh, 1038s, 1006sh, 968m, 918w, 876w, 798sh, 776m, 754w, 700m, 656m, 560m, 512w, 468w, 422w.

[Cu$_2$(NO$_3$)$_2$(L$_E$)$_2$]·2MeNO$_2$ (6·2MeNO$_2$), where L$_E$$^-$ is the anion of 2-nitro-1-phenyl-1-(pyridin-2-yl)ethanol. To a solution of (py)(ph)CO (0.092 g, 0.50 mmol) in MeNO$_2$ (25 mL) was added solid NMe$_4$OH·5H$_2$O (0.091 g, 0.50 mmol). The resulting colourless solution was stirred for 30 min and then solid Cu(NO$_3$)$_2$·3H$_2$O (0.121 g, 0.50 mmol) was added. The solid dissolved upon stirring for 30 min to give a green solution, which was filtered and layered with Et$_2$O (40 mL). Slow mixing gave blue prisms of the product, which were collected by filtration, washed with MeNO$_2$ (3x2 mL) and dried in air. The

yield was 45%. Analytical data, calcd for C$_{28}$H$_{28}$Cu$_2$N$_8$O$_{16}$ (found values in parentheses): C 39.11 (38.87), H 3.29 (3.33), N 13.04 (12.85)%. IR bands (KBr, cm^{-1}): 3060w, 2955w, 2845w, 1608m, 1556s, 1508s, 1442w, 1384s, 1276s, 1188w, 1164w, 1100m, 1080w, 1062w, 994m, 928w, 896w, 806m, 768m, 702m, 652m, 598wb, 525w, 478w, 452w.

Single-crystal X-ray crystallography

Suitable single crystals covered with paratone-N oil were attached on the tip of glass fibers. X-ray diffraction data were collected (ω-scan) with a SuperNova A Oxford Diffraction diffractometer under a flow of nitrogen gas at 100(2) K using Mo Kα radiation (λ = 0.7107 Å). Data were collected and processed by the CRYSALIS CCD and RED software,[12] respectively. The reflection intensities were corrected for absorption by the multi-scan method. The structures were solved using SIR92[13] and refined by full-matrix least-squares techniques on F^2 using the latest version of SHELXL (2014/7).[14] All non-H atoms were refined anisotropically and carbon-bound H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. The hydroxyl H atoms of HL$_A$ in **1** and the EtOH ligand in **5** were located in difference Fourier maps and refined isotropically applying soft distance restraints. The two ClO$_4$$^-$ counterions in the structure of **1** are orientationally disordered about a two-fold axis and the structure contains a small area of disordered solvent (a water molecule). Attempts to model it with a chemically reasonable geometry were unsuccessful; therefore, the SQUEEZE procedure of PLATON[15] was employed to remove the contribution of the electron density associated with this water molecule from the intensity data. The Cl2O7O8O9O10 perchlorate counterion in **3**·MeOH, orientationally disordered about a center of symmetry, has been modelled over two sites with a 50:50 domain ratio. A disordered phenyl ring in complex **6**·2MeNO$_2$ has been modelled over two orientations (50:50).

Geometric/crystallographic calculations were carried out using PLATON,[15] OLEX2,[16] and WINGX[17] packages; molecular/packing graphics were prepared with DIAMOND[18] and MERCURY.[19]

Important crystallographic data are listed in Table 1. Full details can be found in the CIF files.

Results and discussion

Synthetic comments and IR spectra

Our approach to activate the proligands 2-acetylpyridine, (py)(me)CO, and 2-benzoylpyridine, (py)(ph)CO, for further reactivity was to treat a copper(II) salt with (py)(me)CO or py)(ph)CO (Scheme 2) *under strongly basic conditions*. A variety of such reaction systems involving different inorganic anions, bases, solvent media and crystallisation techniques were systematically studied in arriving at the optimised procedures described in the experimental section.

Treatment of Cu(ClO$_4$)$_2$·6H$_2$O with (py)(me)CO and NBu$^n_4$OMe (1:1:1) in CHCl$_3$ at room temperature under aerobic conditions gave a green solution from which was isolated a

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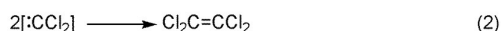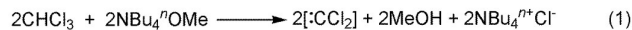**Table 1** Crystallographic data for compounds **1**, **2**·2CHCl₃, **3**·MeOH, **4**, **5** and **6**·2CH₃NO₂

Compound	1	2·2 CHCl₃	3·MeOH	4	5	6·2CH₃NO₂
Formula	$C_{28}H_{28}Cl_2Cu_2N_4O_4$·$2(ClO_4)$	$C_{28}H_{24}Cl_4Cu_2N_4O_{10}$·$2(CHCl_3)$	$C_{50}H_{42}Cu_2N_4O_6$·$2(ClO_4)$·$(MeOH)$	$C_{52}H_{48}Cu_4N_8O_{20}$	$C_{30}H_{34}Cu_2N_4O_{11}$	$C_{26}H_{22}Cu_2N_6O_{12}$·$2(CH_3NO_2)$
Fw	881.42	1084.13	1152.90	1359.14	753.69	859.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1/c$	$I2/a$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.9015(2)	18.5412(5)	14.9187(3)	11.7946(2)	10.8067(1)	8.1588(2)
b/Å	11.5144(2)	10.7733(3)	15.1684(4)	17.9549(3)	17.0394(3)	10.3914(3)
c/Å	14.4136(3)	20.6281(5)	23.0231(5)	13.2815(2)	17.1831(2)	20.3706(5)
β/º	99.328(2)	100.364(3)	90.537(2)	107.407(2)	90.295(1)	98.962(2)
V/Å³	1785.3(6)	4053.2(19)	5209.7(2)	2683.8(8)	3164.1(7)	1705.9(8)
Z	2	4	4	2	4	2
ρ_{calcd}/g cm⁻³	1.640	1.777	1.470	1.682	1.582	1.674
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Radiation/μ (mm⁻¹)	Mo Kα/1.555	Mo Kα/1.767	Mo Kα/0.990	Mo Kα/1.651	Mo Kα/1.411	Mo Kα/1.334
Reflns collected/unique	14559/4299	32039/9221	20502/5902	26859/6063	29897/6841	11182/3680
No. of parameters	253	507	347	381	430	276
R_1 [$I > 2\sigma(I)$], wR_2 (all data)	0.0388, 0.1024	0.0559, 0.1593	0.0677, 0.2059	0.0312, 0.0695	0.0361, 0.0842	0.0317, 0.0768
GOF (F^2)	1.093	1.046	1.051	1.060	1.057	1.070
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å⁻³)	0.991/-0.607	1.808/-1.589	2.536/-1.992	0.494/-0.347	0.400/-0.384	0.503/-0.344
CCDC number	1429519	1429520	1429521	1429522	1429523	1429524

mixture of green and purple crystals of complexes $[Cu_2Cl_2(HL_A)_2](ClO_4)_2$ (**1**) and $[Cu_2Cl_2(L_B)_2(ClO_4)_2]$·2CHCl₃ (**2**·2CHCl₃), respectively; due to the sharp colour difference, the crystals were separated manually and characterized by microanalyses, IR spectroscopy and single-crystal X-ray crystallography. HL_A and L_B are the neutral ligand 3-hydroxy-1,3-di(pyridin-2-yl)-butane-1-one and the zwitterionic-type molecule 3-hydroxy-1-methyl-3-(pyridin-2-yl)-3H-indolizin-4-ium, respectively (Schemes 3 and 4). The purple compound is clearly a byproduct of the reaction since its yield never exceeded 10%. Although we performed hundreds of reactions, we have not been able to prepare **1** and **2** alone in a pure form.

Simplified mechanisms for the formation of HL_A and L_B are proposed in Scheme 3. The carbon-oxygen double bond of (py)(me)CO is a strong electron-withdrawing group and polarises the adjacent carbon-hydrogen bonds, making the methyl *a*-hydrogens weakly acidic. Strong bases, such as MeO⁻ used here, can abstract an *a*-hydrogen, forming an equilibrium with the corresponding carbanion. Once formed, the carbanion is resonance-stabilised. The negative charge is not concentrated on one atom but delocalized between the *a*-carbon and the carbonyl oxygen; this charge dispersal stabilizes the carbanion. Note that only the resonance form with the negative charge on the oxygen atom is shown in Scheme 3. This is due to the fact that the electronegative

oxygen is more able to accommodate a negative charge than is carbon; thus the resonance hybrid is more like this resonance form than the one with the negative charge on the carbon. As a result this anion (referred to as an enolate ion) is more like an alkoxide ion than a carbanion, even though it is formed by abstraction of a hydrogen from the *a*-carbon (the methyl carbon). The ligand HL_A has been formed through an aldol reaction-type mechanism.[8] Once the carbanion $(py)C(O)CH_2^-$ is formed, it attacks the positive (δ+) carbonyl carbon of another (py)(me)CO molecule by a nucleophilic addition mechanism in an effort to neutralize itself. As the carbanion forms the new C-C bond, the π electrons of the carbonyl group of neutral (py)(me)CO are transferred completely to the oxygen, forming an alkoxide ion. The alkoxide ion is neutralised by a MeOH molecule forming HL_A (step 1 in Scheme 3). We want to emphasize that the reaction that leads to HL_A is *not* an aldol *condensation*.[8] In organic chemistry, the products of the described reactions (aldols) are easily dehydrated, because the resulting double bond is conjugated with the carbonyl group, which creates an extended system of overlapping *p* orbitals, that is, a resonance-stabilised structure. A possible reason for the non-condensation of HL_A is the stabilisation of the alcohol function by the Cu^{II} ion; the latter also possibly stabilises the above mentioned resonance-stabilised enolate intermediate.[20] The formation of the zwitterionic-type ligand L_B takes place *via* an intramolecular nucleophilic attack of the remote 2-pyridyl

nitrogen atom on the positive carbonyl carbon of HL_A, after transformation of the latter through deprotonation and dehydration (step 2 in Scheme 3). Another interesting feature in the preparation of **1** and **2** is the presence of two terminal chloro ligands in their structures which derive from $CHCl_3$ under the strongly basic conditions, eqns (1) and (2).[21]

$$2CHCl_3 + 2NBu^n_4OMe \longrightarrow 2[:CCl_2] + 2MeOH + 2NBu_4^{n+}Cl^- \quad (1)$$

$$2[:CCl_2] \longrightarrow Cl_2C=CCl_2 \quad (2)$$

The observed transformations of (py)(me)CO to HL_A and L_B during the preparation of **1** and **2** are novel. The reactivity chemistry of this ligand in the presence of metal ions has been examined before by two groups[22] and our group,[9] and the coordination modes of the resulting ligands are shown in Scheme 4. Table 2 lists the structurally characterised metal complexes that contain transformed ligands derived from (py)(me)CO during the reactions.

As mentioned in Introduction, L_1^- is formed *in situ* through a crossed-aldol reaction[8] between (py)(me)CO and the carbanion of acetone (used as solvent) in the presence of Co^{II} under aerobic and basic conditions.[9] The formation of coordinated L_2^- is interesting. Ten years ago, Drew, Datta and coworkers[22a] attempted to grow single crystals of $[Cu^I\{(py)(me)CO)\}_2](ClO_4)$ by allowing Et_2O diffusion into its reddish solution in MeOH, but they obtained dark green crystals of $[Cu^{II,II}_2(L_2)_2](ClO_4)_2$ instead; the Cu^{II}_2 complex could also be prepared by oxidizing the mononuclear Cu^I precursor with H_2O_2 in MeOH. The proposed mechanism involves attack of the generated, coordinated $(py)COCH_2^-$ carbanion on the carbonyl carbon of another coordinated (py)(me)CO molecule, followed by nucleophilic attack of MeOH on the carbonyl carbon that formerly belonged to the carbanion and subsequent deprotonation of its hydroxyl group.[22a] The formation of HL_3 and L_3^- is another crossed-aldol addition of acetone to the Re^I tricarbonyl complex of (py)(me)CO.[22b]

Table 2 Structurally characterised coordination complexes derived from reactions of (py)(me)CO with various metal sources and containing transformed derivatives of the carbonyl ligand

Complex[a]	Ref.
$[Co^{III}Co^{II}_6(OH)_6(L_1)_6](ClO_4)_3$	9
$[Cu^{II,II}_2(L_2)_2](ClO_4)_2$	22a
$[Re^I(CO)_3(HL_3)]X^b$	22b
$[Re^I_2(CO)_6(L_3)(HL_3)][B\{3,5-(CF_3)_2C_6H_3\}_4]^c$	22b
$[Cu^{II,II}_2Cl_2(HL_A)_2](ClO_4)_2$ (**1**)	this work
$[Cu^{II,II}_2Cl_2(L_B)(ClO_4)_2]$ (**2**)	this work

[a] For the structural formulae of ligands L_1^-, L_2^-, HL_3, L_3^-, HL_A and L_B (derived from (py)(me)CO) and their coordination modes, see Scheme 4. [b] $X^- = CF_3SO_3^-$, $[B\{3,5-(CF_3)_2C_6H_3\}_4]^-$. [c] The molecule HL_3 and its anion L_3^- can be considered together as a strongly H-bonded bis-tridentate ligand that bridges two Re^I atoms; the H bond, which is formed between the hydroxy group of HL_3 and the alkoxide oxygen of L_3^-, is extremely strong based on the distance between the oxygen atoms (2.391 Å), the O-H⋯O angle (174.0°) and the ^1H NMR shift of that hydrogen atom ($\delta = 16.05$ ppm).
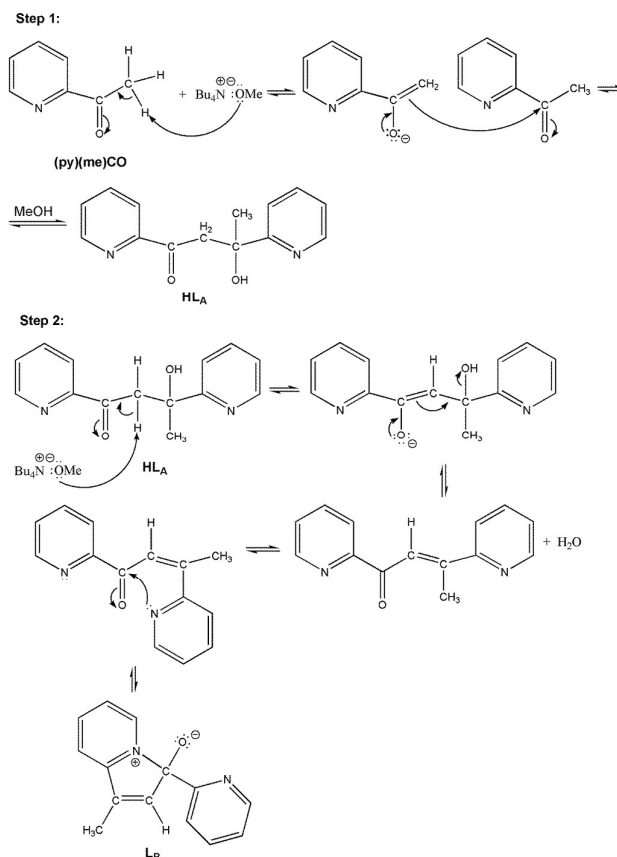

Scheme 3 Proposed simplified mechanisms that lead to the transformed molecules HL_A and L_B that are present as ligands in complexes **1** and **2**.

We do believe that the formation of HL_A and L_B in **1** and **2**, respectively, is Cu^{II}-promoted (or assisted). We have failed to date to synthesize the free ligands (these compounds are not known in organic chemistry) by the reactions of (py)(me)CO and a variety of strong bases, in the absence of Cu^{II}, under several reaction conditions (reaction times, temperatures, solvents, reactant ratios and concentrations of the reaction solutions). We have also failed to isolate the free compounds HL_A and L_B or their salts by treatment of **1** and **2** with dilute hydrochloric, hydrobromic and perchloric acids.

The absence of *a*-hydrogens in (py)(ph)CO led the reactivity of this ligand in the presence of Cu^{II} to different pathways. The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, (py)(ph)CO and NBu^n_4OMe (1:1:1) in $MeOH/H_2O$ (25:1 v/v) gave a blue solution that upon slow evaporation at room temperature gave blue crystals of $[Cu_2\{(py)(ph)CO\}_2(L_C)_2](ClO_4)_2 \cdot MeOH$ (**3·MeOH**) in moderate yield, where L_C^- is the anion of (methoxy)(phenyl)(pyridin-2-yl)methanol (Scheme 5). The dinuclear cation contains both the initially employed, unchanged 2-benzoylpyridine ligand and the anion of its hemiketal form. The latter has been formed *in situ via* the addition of MeOH to the carbonyl carbon atom upon Cu^{II} coordination of the carbonyl oxygen atom and/or the 2-pyridyl nitrogen atom in solution under the strongly basic conditions; this behaviour is similar to that frequently observed with $(py)_2CO$ (Scheme 1).[5,6] In an attempt to obtain products containing coordinated inorganic anions,
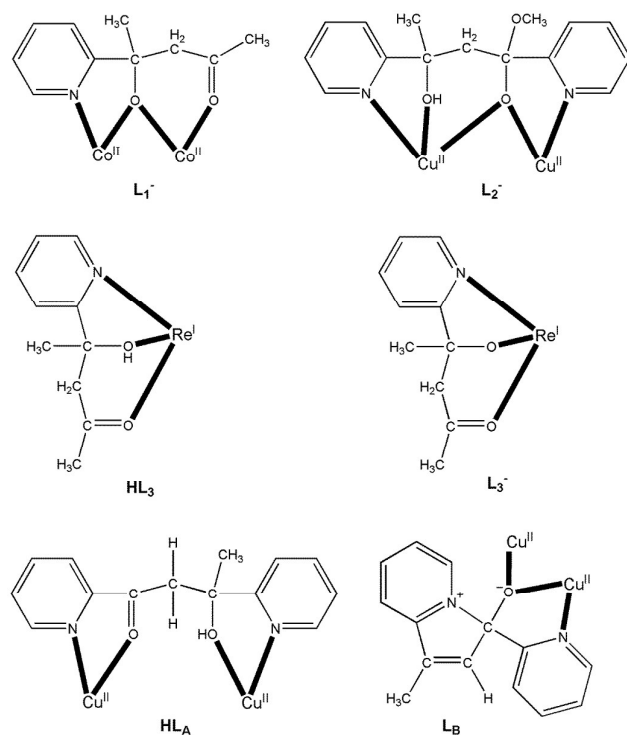
Scheme 4 Structural formulae, abbreviations and coordination modes of ligands resulting from the up to now studied metal ion-assisted reactivity of (py)(me)CO; the formation of HL_A and L_B are described in the present work.
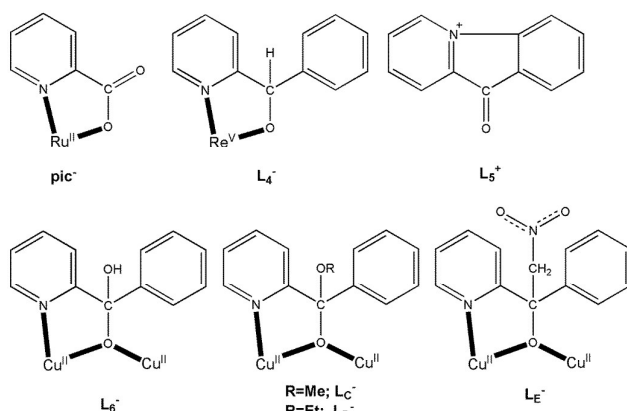

Scheme 5 Structural formulae, abbreviations and coordination modes of ligands resulting from the up to now studied metal ion-assisted reactivity of (py)(ph)CO; the formation of L_C^-, L_D^- and L_E^- are described in the present work. The cation L_5^+, also derived from (py)(ph)CO, is counterion in anionic polymeric complexes of Cu^I (see also Table 3).

we replaced $Cu(ClO_4)_2 \cdot 6H_2O$ with $Cu(NO_3)_2 \cdot 3H_2O$ in the above reaction system. To improve the crystallinity of the obtained microcrystalline product, we used $NMe_4OH \cdot 5H_2O$ (instead of NBu^n_4OMe) as base, eliminated the small amount of H_2O present in MeOH and changed the crystallisation method (liquid Et_2O diffusion instead of solvent evaporation); single-crystal X-ray crystallography revealed the turquoise product to be the tetranuclear cluster
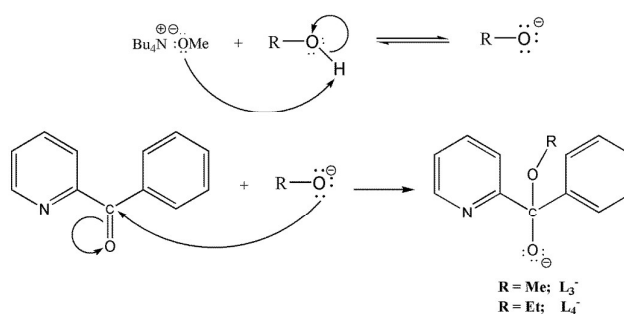
Scheme 6 The proposed simplified mechanism that leads to the transformed anions L_C^- and L_D^- that are present as ligands in complexes **3-5**. The base shown is NBu^n_4OMe (used to obtain single crystals of **3**·MeOH), but NMe_4OH can also be used; the latter was used for the growth of single crystals of **4** and **5**.
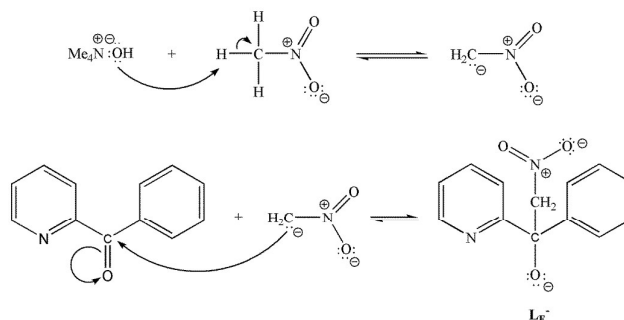
Scheme 7 The proposed simplified mechanism that leads to the transformed anion L_E^- that is present as ligand in complex **6**·2MeNO$_2$.

$[Cu_4(OMe)_2(NO_3)_4\{(py)(ph)CO\}_2(L_C)_2]$ (**4**). In a next step we sought the preparation of a copper(II) complex possessing the anion of (ethoxy)(phenyl)(pyridin-2-yl)methanol (L_D^-, Scheme 5) as ligand. Thus, we replaced MeOH with EtOH in the reaction system that gave **4**. Rather surprisingly, the outcome of the crystallisation procedure (which was again liquid Et_2O diffusion) was the dinuclear complex $[Cu_2(NO_3)_2(L_D)_2(EtOH)]$ (**5**), and not the expected tetranuclear cluster $[Cu_4(OEt)_2(NO_3)_4\{(py)(ph)CO\}_2(L_D)_2]$, emphasizing the important role of the solvent in such reactions. The different nature of **4** and **5** might be related to the slightly different pK_a values of MeOH and EtOH, and the better bridging ability of MeO^- than EtO^- towards Cu^{II} ions, but further discussion would be speculative. A simplified mechanism of the formation of L_C^- and L_D^- that are present as ligands in **3-5** is shown in Scheme 6.

Studies in the last 10 years have shown that attack by nucleophiles other than H_2O and alcohols on the carbonyl C atom of (py)$_2$CO,[5,20,23] (py)(me)CO[9,22b] or (py)(ph)CO[24] (see later), in the presence of divalent metals, generates interesting ligands which can be considered as a second generation family of ligands derived from (py)$_2$CO and (py)(R)CO (R=Me, Ph,...). Since the hydrogens of nitromethane, CH_3NO_2, are weakly acidic, we were interested in investigating whether (py)(ph)CO would be capable of undergoing reactivity towards $^-$:CH_2NO_2 in the presence of Cu^{II}; such studies had not been performed in the coordination chemistry of (py)$_2$CO, (py)(me)CO and (py)(ph)CO. The 1:1:1 $Cu(NO_3)_2 \cdot 3H_2O$/(py)(ph)CO/ $NMe_4OH \cdot 5H_2O$ reaction mixture in $MeNO_2$ gave a green

solution, from which were subsequently isolated blue crystals of $[Cu_2(NO_3)_2(L_E)_2]\cdot2MeNO_2$ (**6**·2MeNO$_2$) in moderate yield (~45%) upon layering with Et$_2$O; L$_E^-$ is the anion of 2-nitro-1-phenyl-1-(pyridin-2-yl)ethanol (Scheme 5). The OH$^-$ ion abstracts one of the methyl hydrogens of MeNO$_2$ which is in equilibrium with the corresponding, resonance-stabilised carbanion. Once the carbanion $^-$:CH$_2$NO$_2$ is formed, it attacks the positive (δ+) carbonyl carbon atom of (py)(ph)CO. As the carbanion forms the new C-C bond, the π electrons of the carbonyl group of (py)(ph)CO are transferred completely to the oxygen, forming an alkoxide ion (Scheme 7). The Cu^{II} ion most probably polarises further the carbonyl group of (py)(ph)CO by coordination in solution (making it more susceptible to nucleophilic attack by the nitromethane ion) and stabilises the final L$_E^-$ ligand.

The reactivity chemistry of (py)(ph)CO in the presence of metal ions has been examined before by several groups[24] and is being examined by our group in this work. The coordination modes of the resulting ligands are shown in Scheme 5; also shown in this scheme is the structural formula of a cation, derived from (py)(ph)CO, that counterbalances the anionic charge of two Cu^I polymers.[24c,d] Table 3 lists the structurally characterised metal complexes that contain transformed ligands and counterions derived from (py)(ph)CO during the reactions. Complex [Ru^{II}Cl(CO)(pic)(PPh$_3$)$_2$] was obtained from the reaction of [Ru^{II}HCl(CO)(PPh$_3$)$_2$] and (py)(ph)CO in dimethoxyethane under atmospheric conditions; the ligand is oxidised to the coordinated 2-pyridinecarboxylate(-1) anion (picolinate, pic$^-$).[24a] Complexes [Re^{V}OX$_2$(L$_4$)(PPh$_3$)], obtained from the reactions of [Re^{V}OX$_3$(PPh$_3$)$_2$] and (py)(ph)CO in refluxing EtOH, contains the anion (L$_4^-$) of the 2-electron reduced form of the original ligand.[24b] The anionic polymeric complexes {(L$_5$)[Cu^{I}I$_2$]}$_n$[24c] and {(L$_5$)[Cu^I(SCN)$_2$]}$_n$[24d] have the 9-oxo-indolo[1,2-a]pyridinium cation (L$_5^+$) which neutralises the anionic charge; this cation derives from an intramolecular oxidative cyclisation of (py)(ph)CO. Complex [Cu$_2${(py)(ph)CO}$_2$(L$_6$)$_2$(H$_2$O)](ClO$_4$)$_2$[24e,f] contains the bridging monoanion L$_6^-$ of the *gem*-diol form of (py)(ph)CO, produced *in situ* by the nucleophilic addition of H$_2$O on the electrophilically activated (by coordination of the carbonyl oxygen and/or the pyridyl ring) carbonyl carbon atom and subsequent deprotonation. Perusal of Table 3 and Scheme 5 reveals that the observed transformations of (py)(ph)CO during the preparation of complexes **3**-**6** are all new. The transformations of (py)(ph)CO to the hemiketalate ligands L$_C^-$ and L$_D^-$ in **3**-**5** are similar (but not identical) with the transformation to L$_6^-$ in [Cu$_2${(py)(ph)CO}$_2$(L$_6$)$_2$(H$_2$O)](ClO$_4$)$_2$,[24e,f] the only difference being the nature of the nucleophile (alcohols *vs* H$_2$O).

As in the case of (py)(me)CO, we have failed to date to synthesize the free ligands HL$_C$, HL$_D$ and HL$_E$ (these compounds are not known in organic chemistry) using conventional organic synthesis and by reacting **3**-**6** with dilute acids; these failures let us believe that the anions L$_C^-$, L$_D^-$ and L$_E^-$ exist only in the presence of Cu^{II}, *i.e.*, as ligands.

In the IR spectra of **1** and **5**, the medium- to strong-intensity broad bands at ~3370 and 3440 cm^{-1} are assigned to

Table 3 Structurally characterised coordination complexes derived from the reactions of (py)(ph)CO with various metal sources and containing transformed derivatives of the carbonyl ligand

Complex^a	Ref.
[Ru^{II}Cl(CO)(pic)(PPh$_3$)$_2$]	24a
[Re^{V}OX$_2$(L$_4$)(PPh$_3$)]^b	24b
{(L$_5$)[Cu^{I}I$_2$]}$_n^c$	24c
{(L$_5$)[Cu^I(SCN)$_2$]}$_n^c$	24d
[Cu$_2${(py)(ph)CO}$_2$(L$_6$)$_2$(H$_2$O)](ClO$_4$)$_2^e$	24e^d, 24f^d
[Cu$_2${(py)(ph)CO}$_2$(L$_C$)$_2$](ClO$_4$)$_2$ (**3**)^e	this work
[Cu$_4$(OMe)$_2$(NO$_3$)$_4${(py)(ph)CO}$_2$(L$_C$)$_2$] (**4**)^e	this work
[Cu$_2$(NO$_3$)$_2$(L$_D$)$_2$(EtOH)] (**5**)^e	this work
[Cu$_2$(NO$_3$)$_2$(L$_E$)$_2$] (**6**)^e	this work

^{a} For the structural formulae of ligands pic$^-$, L$_4^-$, L$_6^-$, L$_C^-$, L$_D^-$ and L$_E^-$ (derived from (py)(ph)CO) and their coordination modes, see Scheme 5. ^{b} X=Cl, Br. ^{c} The cation L$_5^+$, also shown in Scheme 5, is the counterion in these anionic polymeric complexes. ^{d} These references describe the structure of the same compound. ^{e} All complexes contain Cu^{II}.

the v(OH) vibration of the hydroxyl group of HL$_A$ and coordinated EtOH, respectively. The relatively low wavenumber and broadness of the former band are both indicative of H bonding.[9] We assign the strong band at 1670 cm^{-1} in the spectrum of **1** to v(C=O) of coordinated HL$_A$.[9] The IR spectra of **3** and **4** exhibit a strong band at ~1655 cm^{-1} attributed to the stretching vibration of the carbonyl group, v(C=O), of the (py)(ph)CO ligands that are present in the complexes. Due to coordination of the carbonyl oxygen, this band has been shifted to lower wavenumbers compared with the corresponding vibration in the spectrum of free (py)(ph)CO (1668 cm^{-1}).[25] The strong band at 1556 cm^{-1} in the spectrum of **6**·2MeNO$_2$ is assigned[26] to the v_{as}(NO$_2$) vibration of L$_E^-$ and lattice MeNO$_2$; as expected, this band is absent from the spectra of **3**-**5**. The spectra of **1** and **3** exhibit two strong bands at ~1090 cm^{-1} and ~625 cm^{-1}, due to the $v_3(F_2)[v_d(Cl\text{-}O)]$ and $v_4(F_2)[\delta_d(OClO)]$ modes, respectively, of the uncoordinated T_d ClO$_4^-$ counterions.[27] Complex **2** possesses both monodentate and bidentate bridging perchlorato ligands (*vide infra*). The coordination of ClO$_4^-$ to metal ions decreases the symmetry of the group and the above mentioned v_3 and v_4 modes are split.[27] Furthermore, the Raman-active $v_1(A_1)$ stretching [v_s(Cl-O)] and $v_2(E)[\delta_d(OClO)]$ modes of the free tetrahedral ClO$_4^-$ become IR-active upon coordination, *i.e.*, once the symmetry is lowered. In the case the ClO$_4^-$-site symmetry is lowered from T_d to C_{3v} (monodentate coordination), both v_1 and v_2 appear in the IR spectrum with weak to medium intensity, while v_3 and v_4 each splits into two IR bands.[27] In the case the ClO$_4^-$-site symmetry is lowered from T_d to C_{2v} (bidentate chelating or bidentate bridging coordination), again both v_1 and v_2 appear in the IR spectrum, while v_3 and v_4 each splits into three IR-active vibrations.[27] The great number of bands attributed to v_1 and v_3 (1265, 1157, 1129, 1030, 1005, 955 cm^{-1}), as well as v_2 and v_4 (632, 617, 530, 479, 459, 440 cm^{-1}) modes reflects the presence of both C_{3v} and C_{2v} perchlorato ligands in **2**.

In the IR spectra of complexes **5** and **6**, the bands at 1488/1508, 1302/1276 and 1038/1062 cm^{-1} are assigned[27] to

the $v_1(A_1)[v(N=O)]$, $v_5(B_2)[v_{as}(NO_2)]$ and $v_2(A_1)[v_S(NO_2)]$ vibrational modes, respectively, of the bidentate (C_{2v}) nitrato group. The separation of the two highest-frequency stretching bands is larger than 180 cm^{-1}, a typical value of bidentate nitrates.[27] The KBr IR spectra of these complexes exhibit a strong band at 1384 cm^{-1}, characteristic of the $v_3(E')[v_d(N-O)]$ mode of the D_{3h} ionic nitrates;[27] such nitrates are absent in the crystal structures of the complexes. The appearance of this band suggests[28] that a certain amount of nitrato ligands are replaced by bromides that are present in excess in the spectroscopic KBr matrix (this replacement is facilitated by the pressure used for the preparation of the pellet), thus generating ionic nitrates (KNO$_3$); in accordance with this conclusion, the 1384 cm^{-1} is absent from the mull spectra of the two complexes.[28b] In the IR spectrum of complex **4** (this compound contains simultaneously monodentate and bridging-chelating nitrates), the bands at 1448 and 1324 cm^{-1} are assigned[27] to the $v_5(B_2)[v_{as}(NO_2)]$ and $v_1(A_1)[v_S(NO_2)]$ modes, respectively, of the monodentate nitrato group (the highest-frequency NO stretching band of the nitrato complexes belongs to the B_2 species in the monodentate complexes, whereas it belongs to the A_1 species in the bidentate ones). The separation of the two highest-wavenumber bands is only 124 cm^{-1}, typical of monodentate nitrato ligands.[27] The bands at 1574, 1350 and 1324 cm^{-1} (the latter two are absent from the spectra of **5** and **6**) are tentatively assigned to the bridging-chelating nitrato groups.[27] Again the appearance of the $v_3(E')$ mode of the ionic nitrates (explained[28] as above) renders exact assignments difficult.

Description of structures

Partially labelled plots of the molecular structures of **1**, **2**·2CHCl$_3$, **3**·MeOH, **4**, **5** and **6**·2MeNO$_2$ are shown in Figs. 1, 3, 5, 6, 7 and 8, respectively. The supramolecular networks of **1** and **2**·2CHCl$_3$ are shown in Figs. 2 and 4, respectively. Selected interatomic distances and angles are listed in the caption of the figures.

Complex **1** cystallises in the monoclinic space group $P2/n$. Its structure consists of dinuclear [Cu$_2$Cl$_2$(HL$_A$)$_2$]$^{2+}$ cations and ClO$_4^-$ counterions in a 1:2 ratio; the latter will not be further discussed. The cation lies on a crystallographic 2-fold axis. The Cu^{II} ions are bridged by two bis-bidentate bridging HL$_A$ ligands (η^1: η^1: η^1: η^1: μ or 2.1111 adopting the Harris notation[29]), Scheme 4; this bridging mode results in the long Cu···Cu' distance of 5.338(1) Å. A terminal chloride (chloro or chlorido ligand) completes 5-coordination at each metal centre. The metal coordination geometry is very distorted. Analysis of the shape-determining angles using the approach of Reedijk and Addison[30] yields a value of trigonality index, τ, of 0.55 (τ=0 and 1.0 for square pyramidal and trigonal bipyramidal geometry, respectively). Thus, the coordination geometry can be either described as distorted trigonal bipyramidal with the two 2-pyridyl nitrogen atoms N1 and N2 (and symmetry equivalents) occupying the axial positions or as distorted square pyramidal with the alkoxido-type oxygen atom O1 (and its symmetry equivalent) occupying the apical position. The C7-O1 and C10-
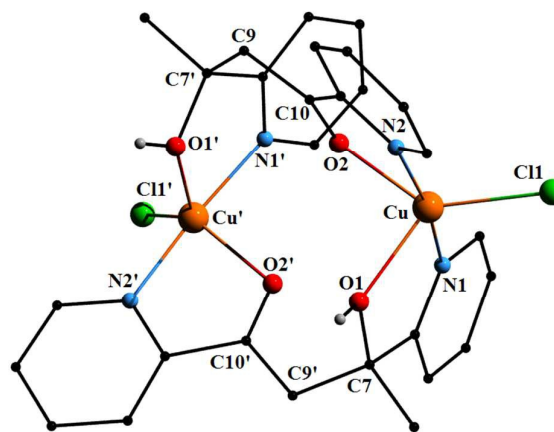

Fig. 1 Partially labelled plot of the molecular structure of the cation [Cu$_2$Cl$_2$(HL$_A$)$_2$]$^{2+}$ that is present in complex **1**. Symmetry operation used to generate equivalent atoms: (') –x + 1/2, y, -z + 3/2. Selected interatomic distances (Å) and angles (°): Cu···Cu' 5.338(1), Cu-N1 1.963(2), Cu-N2 1.979(2), Cu-O1 2.095(2), Cu-O2 2.123(2), Cu-Cl1 2.246(6), C7-O1 1.435(3), C10-O2 1.227(3) Å; N1-Cu-N2 170.9(8), N1-Cu-Cl1 95.1(6), N2-Cu-O1 97.1(8), O1-Cu-O2 93.2(7), O1-Cu-Cl1 129.2(5), O2-Cu-Cl1 137.6(5)°. Colour scheme: Cu, orange; O, red; N, blue; C, black; Cl, green.
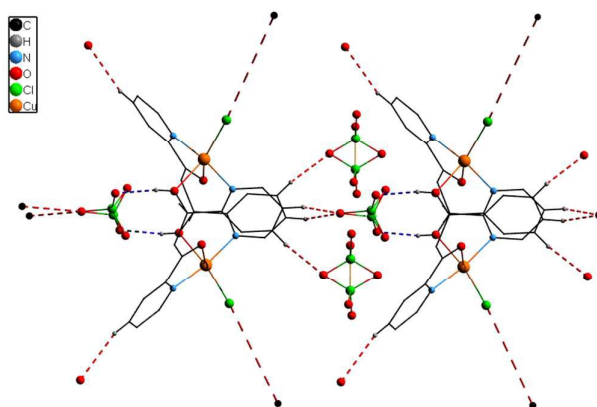

Fig. 2 A portion of the supramolecular network of compound **1** generated by O-H···O(ClO$_4^-$) H bonds (blue dashed lines) and C-H···X (X=O or Cl) interactions (red dashed lines). Only the H atoms involved in these interactions are shown.

O2 bond lengths are 1.435(3) and 1.227(3) Å, respectively, clearly indicating their single- (C7-O1) and double-bond (C10-O2) characters, in agreement with the representation of ligand HL$_A$ in Scheme 4.

Complex **2** crystallises in the monoclinic space group $P2_1/c$. Its structure consists of a dinuclear [Cu$_2$Cl$_2$(L$_B$)$_2$(ClO$_4$)$_2$] molecule and two lattice CHCl$_3$ molecules. The two Cu^{II} ions are triply bridged by the alkoxide oxygen atoms (O1, O2) of the two η^1: η^2: μ (or 2.21) L$_B$ ligands (Scheme 4) and one η^1: η^1: μ (2.1100) perchlorato group. The presence of three bridges, two of which are monoatomic, results in the relatively short Cu1···Cu2 distance of 3.042(6) Å. The approximately square Cu1O1Cu2O2 unit is nearly planar, the four atoms deviating less than 0.02 Å from their best mean plane. A terminal chloro ligand (Cl1), the available for ligation 2-pyridyl nitrogen atom (N1) of one L$_B$ and a monodentate ClO$_4^-$ complete a Jahn-Teller
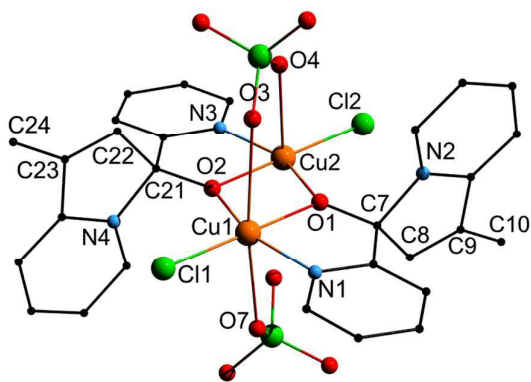
Fig. 3 Partially labelled plot of the structure of the molecule [Cu$_2$Cl$_2$(L$_B$)$_2$(ClO$_4$)$_2$] that is present in complex **2**. Selected interatomic distances (Å) and angles (°): Cu1···Cu2 3.042(6), Cu1-O1 1.944(2), Cu1-O2 1.946(2), Cu1-N1 1.988(3), Cu1-O7 2.687(3), Cu1-O3 2.706(3), Cu1-Cl1 2.195(1), Cu2-O1 1.942(3), Cu2-O2 1.946(2), Cu2-N3 1.981(3), Cu2-O4 2.633(3), Cu2-Cl2 2.202(1), C7-O1 1.370(5), C21-O2 1.365(5) Å; Cu1-O1-Cu2 103.0(1), Cu1-O2-Cu2 102.8(1), O1-Cu1-Cl1 178.0(1), O2-Cu1-N1 158.1(1), O3-Cu1-O7 166.9(1), O4-Cu2-O1 84.2(1), O4-Cu2-O2 85.3(1), O4-Cu2-N3 95.7(1), O4-Cu2-Cl2 93.7(1), O1-Cu2-N3 158.0(1), O2-Cu2-Cl2 178.5(1)°. Colour scheme as in Fig. 1.
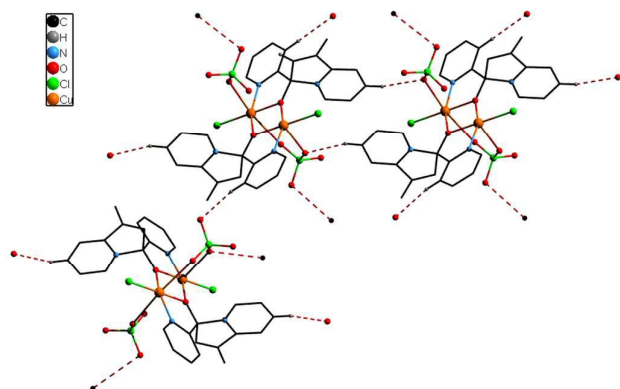

Fig. 4 A portion of the supramolecular network of compound **2**·2CHCl$_3$ generated by C-H···O H-bonding interactions (red dashed lines). Only the H atoms involved in these interactions are shown.

distorted octahedral geometry at Cu1, the *trans* Cu1-O3 and Cu1-O7 distances being long (2.706(3) and 2.687(3) Å, respectively). A terminal chloride (Cl2) and the available for ligation 2-pyridyl nitrogen atom (N3) of the second L$_B$ ligand complete 5-coordination at Cu2. The coordination geometry at Cu2 is well described as distorted square pyramidal (τ=0.34) with the perchlorato oxygen atom O4 occupying the apical position. As expected, the axial bond at Cu2 is the longest (Cu2-O4 = 2.633(3) Å). The C7-O1 and C21-O2 bond lengths are 1.370(5) and 1.365(5) Å, respectively, indicating their single-bond character. The angles around C7 and C21 are in the "tetrahedral" area 99.3(3)-115.3(4) and 99.5(3)-116.8(4)°, respectively, confirming the sp^3 character of these carbon atoms. Furthermore the C8-C9/C22-C23 distances of 1.314(6)/1.320(6) Å and the C7-C8/C21-C22 distances of 1.563(6)/1.555(6) Å, respectively, indicate double C8-C9 and C22-C23 bonds, and single C7-C8 and C21-C22 bonds. All these experimental facts are in agreement with the formulation of
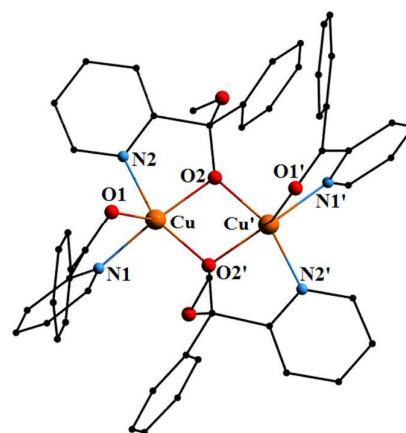

Fig. 5 Partially labelled plot of the molecular structure of the cation [Cu$_2${(py)(ph)CO}$_2$(L$_C$)$_2$]$^{2+}$ that is present in complex **3**·MeOH. Symmetry operation used to generate equivalent atoms: (') −x + 3/2, y, -z. Selected interatomic distances (Å) and angles (°): Cu···Cu' 2.996(8), Cu-O1 2.373(3), Cu-O2 1.917(2), Cu-O2' 1.931(3), Cu-N1 1.984(3), Cu-N2 1.979(3), C7-O1 1.230(5), C19-O2 1.393(4) Å; Cu-O2-Cu' 102.3(1), O1-Cu-O2 111.3(1), O1-Cu-O2' 98.0(1), O1-Cu-N1 75.4(1), O1-Cu-N2 88.8(1), O2-Cu-N1 172.8(1), O2'-Cu-N2 159.0(1), O2-Cu-O2' 77.5(1)°. C7 and C19 are the carbonyl carbon atom of (py)(ph)CO and the central sp^3 carbon atom of L$_C$, respectively, not labelled above. Colour scheme as in Fig. 1.

ligand L$_B$ in Scheme 4. Under this formulation, the medium-intensity band at 1630 cm^{-1} in the IR spectrum of **2** can be assigned[26] to the stretching vibration of the double carbon-carbon bond, v(C=C), of the coordinated L$_B$ ligand.

Complex **3**·MeOH is remarkable because it possesses both the original ketone form of the ligand, (py)(ph)CO, and the monoanion of its hemiketal derivative (L$_C$). The compound crystallises in the monoclinic space group *I*2/*a*. Its structure consists of dinuclear [Cu$_2${(py)(ph)CO}$_2$(L$_C$)$_2$]$^{2+}$ cations, ClO$_4^-$ counterions and MeOH lattice molecules in an 1:2:1 ratio; the latter two will not be further discussed. The cation lies on a crystallographic 2-fold axis. The Cu^{II} ions are doubly bridged by the deprotonated oxygen atoms (O2, O2') of two symmetry-related η^1: η^2: μ (or 2.21) L$_C^-$ ligands (Scheme 5). The strictly planar CuO2Cu'O2' unit is close to square (Cu-O2 = 1.917(2) Å, Cu-O2' = 1.931(3) Å, Cu-O2-Cu' 102.3(1)°, O2-Cu-O2' 77.5(1)°). The 2-pyridyl nitrogen atom (N2) of one L$_C^-$ ligand and the donor atoms (the carbonyl oxygen O1 and the 2-pyridyl nitrogen N1) of one bidentate chelating (η^1: η^1 or 1.11) neutral (py)(ph)CO ligand complete 5-coordination at Cu. The intracationic Cu···Cu distance is 2.996(8) Å. The coordination geometry at the Cu^{II} ion is distorted square pyramidal (τ = 0.23). Two of the basal coordination sites are occupied by the deprotonated alkoxo oxygen atoms (O2, O2'), while the other two by two 2-pyridyl nitrogen atoms, one (N1) belonging to (py)(ph)CO and the other (N2) to L$_C^-$. As expected, the axial Cu-O1 bond (2.373(3) Å) is longer than the Cu-O bonds in the basal plane (1.917(2) and 1.931(3) Å). The dihedral angles between the 2-pyridyl and phenyl rings of L$_C^-$ and (py)(ph)CO are 88.7 and 49.0°, respectively.

Compound **4** crystallises in the monoclinic space group *P*2$_1$/*n*. Its structure consists of tetranuclear
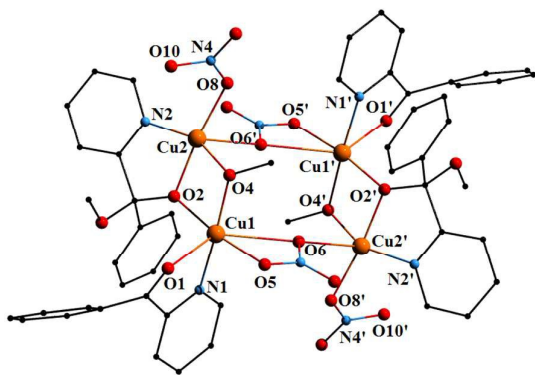
Fig. 6 Partially labelled plot of the structure of the molecule [Cu$_4$(OMe)$_2$(NO$_3$)$_4${(py)(ph)CO}$_2$(L$_C$)$_2$] that is present in complex **4**. Symmetry operation used to generate equivalent atoms: (') –x + 2, -y, -z + 2. Selected interatomic distances (Å) and angles (°): Cu1⋯Cu2 2.982(3), Cu1⋯Cu2' 4.993(3), Cu1⋯Cu1' 5.387(3), Cu2⋯Cu2' 6.216(3), Cu1-O1 2.353(2), Cu1-O2 1.946(2), Cu1-O4 1.917(1), Cu1-O5 1.994(2), Cu1-O6 2.635(2), Cu1-N1 1.998(2), Cu2-O2 1.916(1), Cu2-O4 1.922(1), Cu2-O6' 2.433(1), Cu2-O8 1.954(2), Cu2-N2 1.975(2) Å; Cu1-O2-Cu2 101.1(5), Cu1-O4-Cu2 101.9(5), Cu1-O6-Cu2' 160.4(6), O1-Cu1-O6 136.8(4), O2-Cu1-O5 172.3(6), O4-Cu1-N1 173.4(6), O6'-Cu2-O2 96.2(5), O6'-Cu2-O4 86.3(5), O6'-Cu2-O8 79.1(5), O6'-Cu2-N2 109.8(6), O2-Cu2-O8 173.4(5), O4-Cu2-N2 155.1(6)°. Colour scheme as in Fig. 1.

[Cu$^{II}_4$(OMe)$_2$(NO$_3$)$_4${(py)(ph)CO}$_2$(L$_C$)$_2$] molecules. The Cu^{II} ions define a parallelogram; there is a crystallographically imposed inversion centre at the midpoint of the Cu1⋯Cu1' (and Cu2⋯Cu2') vector and all four metals ions are thus strictly coplanar. The interatomic distances between Cu1 and Cu2, and between Cu1 and Cu2' which constitute the sides of the parallelogram are equal to 2.982(3) and 4.993(3) Å, respectively. The two diagonals of the parallelogram correspond to the interatomic distances Cu1⋯Cu1' and Cu2⋯Cu2' and are equal to 5.387(3) and 6.216(3) Å, respectively. Atoms Cu1 and Cu2 are doubly bridged by deprotonated oxygen atoms (O2, O4) belonging to a η^1: η^2: μ (2.21) L$_C^-$ ligand (Scheme 5) and a 2.2 methoxo group. Atoms Cu1 and Cu2' (and their symmetry equivalents) are singly bridged by an oxygen atom (O6, O6') of a η^1: η^2: μ (2.210) nitrato group. No bridging exists between the symmetrically relevant Cu1/Cu1' and Cu2/Cu2' atoms that define the two diagonals of the parallelogram. Thus, the tetranuclear molecule can be described as two dinuclear {Cu$_2$(OMe)(NO$_3$){(py)(ph)CO}(L$_C$)}$^+$ subunits bridged by two 2.210 nitrato groups. The core of the cluster is therefore {Cu$^{II}_4$(μ-OR)$_2$(μ-OR')$_2$(μ-OR'')$_2$}$^{2+}$, where RO$^-$ = L$_C^-$, R'O$^-$ = MeO$^-$ and R''O$^-$ = O$_2$NO$^-$. The approximately square Cu1O2Cu2O4 subunit (and its symmetry-equivalent) is nearly planar; the largest deviation from their best mean plane is 0.19 Å for O2. The donor atoms (the carbonyl oxygen O1 and the 2-pyridyl nitrogen N1) of a bidentate chelating (η^1: η^1 or 1.11) (py)(ph)CO ligand and the terminally ligated oxygen atom (O5) of a 2.210 nitrato group complete 6-coordination at Cu1, while the 2-pyridyl nitrogen atom N2 of a 2.21 L$_C^-$ ligand and a monodentate nitrato group (O8) complete 5-coordination at Cu2. There is evidence for an additional weak interaction between Cu2 and Cu2' and the "free" nitrato oxygens O10 and O10', respectively. The Cu2⋯O10 distance is 2.840(2) Å and the symmetry related

nitrate groups are clearly tilted towards Cu2 and Cu2' as manifested in the small Cu2-O8-N4 angle of 114.2(6)°. The monodentate NO$_3^-$ N-O distances are shorter for the uncoordinated oxygens (1.231(1) Å) than the N-O distance for the coordinated oxygen (1.291(1) Å). The bridging NO$_3^-$ N-O distances follow the order N-O$_{uncoordinated}$ < N-(μ-O) < N-O(η^1-O), the corresponding bond lengths being 1.226(1), 1.250(1) and 1.286(1) Å, respectively.

The Cu1 atom presents an axially elongated, distorted octahedral geometry; the Jahn-Teller donor sites are defined by O1 and O6. The coordination geometry at Cu2 can be described as distorted square pyramidal (τ = 0.31) with the bridging nitrato oxygen atom O6' occupying the apical position; the latter occupies simultaneously the apical position of the square pyramidal Cu2 and one of the Jahn-Teller sites of the octahedral Cu1'. Assuming, that the Cu2⋯O10 interaction is weakly bonding, the geometry at Cu2 can also be described as axially elongated, distorted octahedral with atoms O6' and O10 occupying the Jahn-Teller positions of Cu2. The dihedral angles between the 2-pyridyl and phenyl rings of L$_C^-$ and (py)(ph)CO are 86.6 and 56.7°, respectively, similar to those observed in the structure of **3**·MeOH.

Compound **5** crystallises in the monoclinic space group $P2_1/c$. Its structure consists of dinuclear [Cu$_2$(NO$_3$)$_2$(L$_D$)$_2$(EtOH)] molecules. The Cu^{II} ions are doubly bridged by the alkoxide oxygen atoms (O1, O2) of the two η^1: η^2: μ (or 2.21) L$_D^-$ ligands (Scheme 5). The Cu1⋯Cu2 distance is 2.997(4) Å. An anisobidentate chelating nitrato group and the 2-pyridyl nitrogen atom N1 of one L$_D^-$ ligand completes 5-coordination at Cu1. The second anisobidentate chelating nitrato group, the 2-pyridyl nitrogen atom N2 of the second L$_D^-$ ligand and a terminal EtOH molecule complete 6-coordination at Cu2. The approximately square Cu1O1Cu2O2 unit is nearly planar, the Cu^{II} and alkoxo oxygen atoms deviating less than 0.03 Å from their best mean plane. The coordination geometry at Cu1 is well described as distorted square pyramidal (τ = 0.25), with the weakly coordinated nitrato oxygen atom O7 (Cu1-O7 = 2.568(2) Å) occupying the apical position. The Cu2 atom presents an axially elongated, distorted octahedral geometry; the Jahn-Teller donor sites are defined by O5 and O10, and the Cu2-O5 and Cu2-O10 bond distances are 2.306(2) and 2.565(2) Å, respectively. The dihedral angles between the 2-pyridyl and phenyl rings of the two L$_D^-$ ligands are 75.5° for the N1-containing ligand and 80.4° for the N2-containing ligand.

Compound **6**·2MeNO$_2$ crystallises in the monoclinic space group $P2_1/c$. Its structure consists of dinuclear [Cu$_2$(NO$_3$)$_2$(L$_E$)$_2$] molecules and lattice MeNO$_2$ molecules in an 1:2 ratio; the latter will not be further discussed. There is a crystallographically imposed inversion centre at the midpoint of the Cu⋯Cu' vector; the Cu⋯Cu' distance is 3.001(5) Å. The Cu^{II} ions are doubly bridged by the alkoxide oxygen atoms (O1, O1') of the two crystallographically equivalent η^1: η^2: μ (or 2.21) L$_E^-$ ligands (Scheme 5). An anisobidentate chelating nitrato group and the 2-pyridyl nitrogen atom N1 complete 5-coordination at Cu. The approximately square CuO1Cu'O1' unit is strictly planar (by symmetry). The two nitrogen-oxygen bonds of the –NO$_2$ group of the L$_E^-$ ligand are nearly equivalent
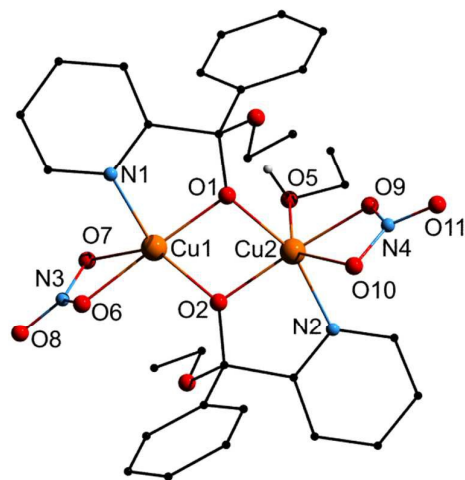
ARTICLE   **Journal Name**

Fig. 7 Partially labelled plot of the structure of the molecule [Cu$_2$(NO$_3$)$_2$(L$_D$)$_2$(EtOH)] that is present in complex **5**. Selected interatomic distances (Å) and angles (°): Cu1···Cu2 2.997(4), Cu1-O1 1.912(2), Cu1-O2 1.912(2), Cu1-O6 1.945(2), Cu1-O7 2.568(2), Cu1-N1 1.954(2), Cu2-O1 1.972(2), Cu2-O2 1.921(2), Cu2-O5 2.306(2), Cu2-O9 1.959(2), Cu2-O10 2.565(2), Cu2-N2 1.979(2), N3-O6 1.291(3), N3-O7 1.234(3), N3-O8 1.234(3), N4-O9 1.298(3), N4-O10 1.250(3), N4-O11 1.217(3) Å; Cu1-O1-Cu2 101.0(1), Cu1-O2-Cu2 102.9(1), O7-Cu1-O1 127.4(1), O7-Cu1-O2 93.3(1), O7-Cu1-O6 55.4(1), O7-Cu1-N1 97.9(1), O1-Cu1-O6 176.8(1), O2-Cu1-N1 161.9(1), O1-Cu2-N2 158.2(2), O2-Cu2-O9 169.3(1), O5-Cu2-O10 145.5(1)°. Colour scheme as in Fig. 1.
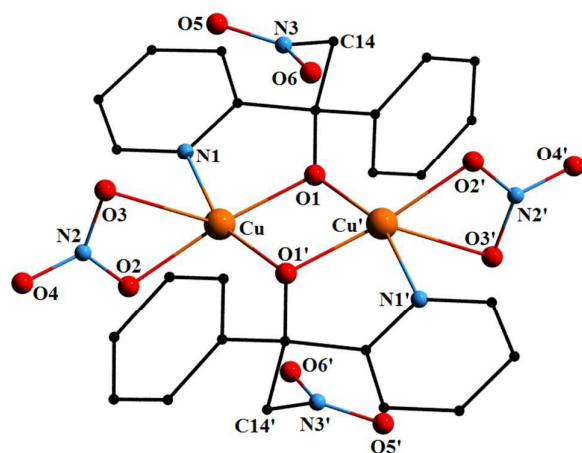

Fig. 8 Partially labelled plot of the structure of the molecule [Cu$_2$(NO$_3$)$_2$(L$_E$)$_2$] that is present in complex **6**·2MeNO$_2$. Only one orientation of the phenyl ring, that belongs to the crystallographically independent L$_E^-$ ligand, is shown, Symmetry operation used to generate equivalent atoms: (') −x + 1, −y, −z + 2. Selected interatomic distances (Å) and angles (°): Cu···Cu' 3.001(5), Cu-O1 1.919(1), Cu-O1' 1.926(1), Cu-O2 1.951(1), Cu-O3 2.563(1), Cu-N1 1.958(2), N2-O2 1.314(2), N2-O3 1.240(2) N2-O4 1.214(2) Å; Cu-O1-Cu' 102.6(1), O3-Cu-O1 132.2(1), O3-Cu-O1' 100.5(1), O3-Cu-O2 55.6(1), O3-Cu-N1 89.9(1), O1-Cu-O2 172.0(1), O1'-Cu-N1 159.0(1), O1-Cu-O1' 77.4(1)°. Colour scheme as in Fig. 1.

(1.227(2), 1.230(2) Å). The metal coordination geometry is distorted square pyramidal (τ = 0.22), with the nitrato oxygen atom O3 occupying the apical position. The dihedral angle between the 2-pyridyl and phenyl rings of L$_E^-$ is 84.3°. The molecular structures of **5** and **6** are similar, the main difference –except the identity of the transformed bridging ligand (L$_D^-$ vs L$_E^-$)- being the presence of a solvate ligand at one Cu^{II} centre in

the former (resulting in different coordination numbers for each metal ion).

At the supramolecular level, the crystal structures of the complexes are organized *via* weak C-H···X (X=O or Cl) H bonds and edge-to-face C-H···π interactions (Fig. 4 for the representative complex **2**·2CHCl$_3$), with the exception of complex **1**, where the presence of the –OH group in HL$_A$ leads to the formation of O-H···O(ClO$_4^-$) motifs (Fig. 2).

Compounds **1**-**6** are the first complexes of any metal containing the neutral or anionic forms of ligands HL$_A$, HL$_C$, HL$_D$ and HL$_E$, and the ligand L$_B$.

Magnetic susceptibility studies

Direct current (dc) magnetic susceptibility data (χ_M) on dried polycrystalline samples of the representative complexes **3**-**6** were collected in the 1.8-300 K range. The data are plotted as $\chi_M T$ product *vs* T in Fig. 9. The tetranuclear cluster **4** was magnetically treated as a dinuclear complex because the Cu1'···Cu2 and Cu1···Cu2' exchange interactions mediated through the monoatomic nitrato bridges O6' and O6, respectively (Fig. 6), which occupy axial/apical positions at both Cu^{II} centres, and involving the non-magnetic 3d_z^2 orbitals of the metal ions are expected to be negligible or very weak in comparison with the Cu1···Cu2 and Cu1'···Cu2' interactions mediated by the alkoxo bridges and involving the magnetic 3$d_{x^2-y^2}$ Cu^{II} orbitals. Thus, any effort to evaluate the Cu1'···Cu2 (and Cu1···Cu2') interaction would be unrealistic.

The room-temperature $\chi_M T$ values for **3** (0.20 cm^3 K mol^{-1}), **4** (0.41 cm^3 K mol^{-1}), **5** (0.37 cm^3 K mol^{-1}) and **6** (0.34 cm^3 K mol^{-1}) are significantly smaller than the expected value for two uncoupled S=1/2 spins (0.75 cm^3 K mol^{-1} for g=2.00), indicative of strong antiferromagnetic coupling operating even at 300 K. The $\chi_M T$ product rapidly decreases with temperature for all complexes, reaching constant values close to diamagnetism below ~100 K (**3**), ~80 K (**5** and **6**) and ~50 K (**4**). The data clearly suggest a well-isolated singlet spin ground state (S=0). No maximum of χ_M is observed in the studied temperature range, in agreement with the very strong antiferromagnetic interactions suggested by the $\chi_M T$ vs T data. Fit of the experimental data was performed by means of the conventional analytical expression derived from the spin Hamiltonian shown in eqn. (3), which also includes the Zeeman term. The best-fit parameters obtained with the PHI program[31] are J=-556 cm^{-1}, g=2.15 for **3**, J=-354 cm^{-1}, g=2.17 for **4**, J=-386 cm^{-1}, g=2.20 for **5** and J=-436 cm^{-1}, g=2.21 for **6**. It should be mentioned at this point that the program uses the -2J convention; however, the fit values were multiplied by 2 according to the -J Hamiltonian.

$$H = -J(\hat{S}_1 \cdot \hat{S}_2) + g\beta H(\hat{S}_1 + \hat{S}_2) \qquad (3)$$

The large intradinuclear Cu-O-Cu angles (102.3° in **3**, 101.1 and 101.9° in **4**, 101.0 and 102.9° in **5**, 102.6° in **6**) are mainly considered to be responsible for the very strong antiferromagnetic coupling.[7b,32,33] Ruiz, Alemany, Alvarez and
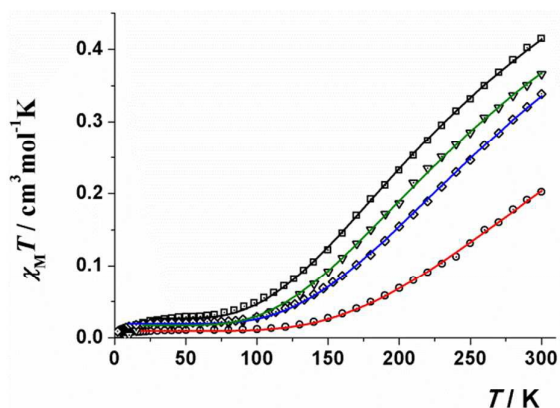
Fig. 9 $\chi_M T$ *vs* T plots of complexes **3** (circles), **4** (squares), **5** (triangles) and **6** (rhombuses); for compound **4**, the plot corresponds to a dinuclear {Cu$_2$(OMe)(NO$_3$){(py)(ph)CO}(L$_C$)}$^+$ subunit of the tetranuclear cluster (see text). The solid lines are the best obtained fits of the data.

Cano have developed an accurate magnetostructural correlation for doubly alkoxo-bridged dinuclear complexes containing planar {Cu$^{II,II}_2$(μ-OR)$_2$}$^{2+}$ units.[32] They compared the calculated and experimental coupling constants for several complexes and proved that the most successful computational strategy is the combination of the B3LYP method with the broken-symmetry approach. Their calculations showed a correlation between the magnetic coupling constant and the Cu-O-Cu bridging angle and with the out-of-plane displacement of the alkoxo groups, in agreement with the experimental data. The larger the Cu-O-Cu angle and the smaller the out-of-plane displacement of the R group, the stronger the antiferromagnetic coupling is.[32] The Cu-O-Cu angles in **3**-**6** (101.0 – 102.9°) are expected[32] to lead to strong antiferromagnetic coupling, which is observed indeed. It is difficult to compare the *J* values observed for **3**-**6** and to correlate them with the two structural parameters mentioned above in a more quantitative way because the *R* groups (which belong to different ligands) are not the same, the distortions of the coordination environment in the equatorial/basal planes are different and the out-of-plane displacement of the R group varies (for example the angle between the C-O vector and the best mean CuO$_2$Cu plane is 79.2° in **3** and 84.3 and 78.6° in **5**).

Conclusions and perspectives

In this report, we have shown that the use (py)(me)CO and (py)(ph)CO in reactions with Cu^{II} sources has led to novel transformations of these ligands under strongly basic conditions, showing that metal-mediated reactions of 2-pyridyl ketones are still in their infancy. The reactivity patterns of the two ligands are different. The observed reactivity of (py)(me)CO, that led to coordinated HL$_A$ and L$_B$ (Scheme 4), is due to the presence of a weakly acidic *a*-hydrogen in the ligand. This characteristic is absent in (py)(ph)CO and its reactivity pattern is dominated by the $\delta+$ character of the carbonyl carbon atom (more positive than that of (py)(me)CO), which is attacked by anionic nucleophiles derived from the

solvent (MeOH and EtOH in complexes **3**-**5**, CH$_3$NO$_2$ in **6**), giving the coordinated ligands L$_C^-$, L$_D^-$ and L$_E^-$ (Scheme 5), the slightly acidic character of CH$_3$NO$_2$ hydrogens playing a decisive role in the formation of L$_E^-$.

We have no reasons to believe that this research area is exhausted of new results. Indeed, ongoing studies in our groups are producing interesting products and transformations from the reactivity of (py)(me)CO and (py)(ph)CO with 3d-metal ions other than Cu^I, Cu^{II} and Co^{II} studied to date (Tables 1 and 2), and our belief is that we have scratched only the surface of the metal ion-assisted reactivity of the two ligands. As far as future perspectives are concerned, variation of the size and electronic properties of the non-pyridyl organic group that is linked to the carbonyl carbon and/or substitutions in the 2-pyridyl group may provide a systematic modification of products (both transformed ligands and complexes), even though their exact structures cannot be *a priori* predicted; we are currently working on this idea and results will be reported soon. In parallel, we have been developing the use of solvents such as Me$_2$CO, MeCN and MeNO$_2$ in the reactions; these solvents can give strongly nucleophilic carbanions under strongly alkaline conditions, favoring formation of unusual ligands when reacting with carbonyl-containing molecules in the presence of metal ions. Finally, we hope that inorganic chemists will be more fascinated in the future by the many and varied reactions that can proceed in the presence of metal ions.

Acknowledgements

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Interesting copper(II)-assisted transformations of 2-acetylpyridine and 2-benzoylpyridine

Alexandros A. Kitos, Constantinos G. Efthymiou, Manolis J. Manos, Anastasios J. Tasiopoulos, Vassilios Nastopoulos, Albert Escuer and Spyros P. Perlepes

Textual Abstract for the Table of Contents
Novel Cu^{II}-assisted transformations have been observed in the reactions of copper(II) sources and 2-pyridyl ketones.

Graphical Abstract for the Table of Contents