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Angle isomerism, as exemplified in a five coordinate, dimeric copper(II) Schiff base complex. Observation of Ostwald ripening

Shanti G. Patra [a], Nirmal K. Shee [a], Michael G. B. Drew [b] and Dipankar Datta * [a]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icdd@iacs.res.in*

[b] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*

Abstract

The 1:1 condensate of benzil and 2-hydrazinopyridine is the ligand (LH; H: a dissociable proton) here. Its reaction with $CuCl_2.2H_2O$ in methanol at room temperature in equimolar proportion affords a mixture of two types of dark green (with metallic luster) single crystals – hexagonal (**1a**) and rectangular (**1b**). They were separated mechanically. The yield of **1a** is higher. X-ray crystallography shows that **1a** and **1b** are penta-coordinate, dichloro bridged dimers of the type $Cu_2L_2Cl_2$ with very similar centrosymmetric structures. All the bonding parameters except two mutually dependent bond angles in the N_2OCl_2 coordination sphere of Cu(II) are same. Correspondingly two different minima are located in DFT calculations on **1a** and **1b**. Energetically **1b** is more stable than **1a** in

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the gas phase by 3-4 kcal mol^{-1}. Their X-band EPR spectra in the solid state at 77 K, which are axial, reveal that $(d_{x^2-y^2})^1$ is the ground state in **1a** ($g_{\parallel} > g_{\perp}$) and $(d_{z^2})^1$ in **1b** ($g_{\parallel} < g_{\perp}$). In keeping with Ostwald ripening, the energetically less stable isomer **1a** crystallizes first. As the crystallization time is allowed to be longer, more of **1b** is formed. The transformation of **1a** to **1b** in methanol solution is found to follow the kinetics of a zero order reaction. The reverse transformation is not possible.

1. Introduction

The concept of "isomer" was introduced in chemistry by Berzelius in 1831.[1] In Greek, it means "equal parts". It all started with the observations that despite having the same elemental composition, silver cyanate (AgOCN) and silver fulminate (AgCNO) possess different physicochemical properties.[1] Berzelius argued that the connectivities of the atoms in these two compounds are different. This remarkable idea paved the way for the concept of structure in chemical compounds. It is noteworthy that present day's ball and stick model of a molecule emerges only from Bader's theory of atoms-in-molecules (AIM)[2], since from X-ray crystallography one can know[3] only about the shape of a molecule. Isomers, as now understood, are molecules with the same chemical formula but different structures.

Inorganic complexes are different from organic molecules in many ways. These usually contain a central atom which is surrounded by other neutral molecules or ions. It was Werner who first recognized this type of structure for coordination compounds.[4,5] Prior to Werner, it was assumed that there can be only associative bonds. For example, he showed that in $CoCl_3.6NH_3$, there is an octahedral Co atom with six ammonia molecules bound at the apices and the three chloride ions are free from any type of bonding. Since six ammonia molecules are attached to the central Co^{3+}, the coordination number of cobalt in $CoCl_3.6NH_3$ is six. Ammonia is a "ligand" here and chloride anion is not. In $CoCl_3.4NH_3$, two of the three chlorides behave as ligands giving rise to "cis" and "trans" isomers (geometric), maintaining six coordination for the metal. The number of isomers of an inorganic complex depends on the coordination number of the central atom and the nature of the ligands. Coordination chemistry now is rife with varieties of isomerism.[6] Herein we describe a hitherto undiscovered type of isomers in some five-coordinate copper(II) complexes. In five coordinate complexes, the most characteristic isomerism is the adoption of square pyramidal (SP) and trigonal bipyramid (TBP) geometries. For example, the $CuCl_5^{3-}$ ion in (piperazinium)$_2$CuCl$_6$.CH$_3$OH is square pyramidal[7] but in [Cr(NH$_3$)$_6$][CuCl$_5$] trigonal bipyramidal.[8] In our pair of five-coordinate complexes, all the bonding parameters except two angles are same in their X-ray crystal structures, a feature which we call "angle isomerism". Additionally we point out the relevance of Ostwald ripening in the formation of our isomers.

2. Results and discussion

The ligand involved here is the 1:1 Schiff base of benzil and 2-hydrazinopyridine (LH where H is a dissociable proton). It has been first reported by Chiswell et al in 1964.[9] It can exist in two forms – keto and enol. In its X-ray crystal structure, reported very
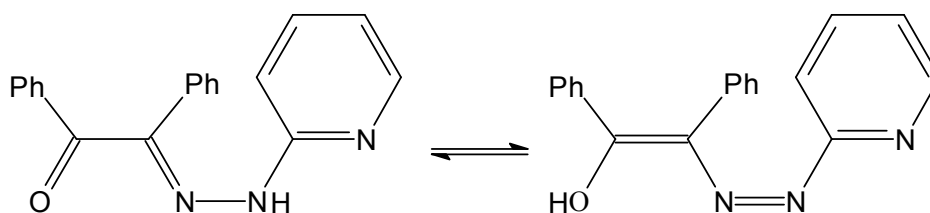

Chart 1. Tautomers of the ligand LH

recently by Hu et al,[10] the keto form is observed. This is commensurate with our DFT calculations. At the BP86/LanL2DZ level, the keto form is found to be more stable than the enol form by 27.96 kcal mol^{-1} and at the B3LYP/6-311++G(2d,p) level, 21.39 kcal mol^{-1}. Crucial bond distances in the tautomers of LH are given in Table 1. The bond

Table 1 Selected bond distances (in Å) in the two tautomers of LH[a]

Bond	Keto form			Enol form	
	X-ray[b]	BP86	B3LYP	BP86	B3LYP
C-O	1.239	1.277	1.221	1.403	1.359
C(Ph)-C(Ph)	1.496	1.503	1.495	1.401	1.366
C(Ph)-N(NH)	1.301	1.338	1.295	1.413	1.391
N-N	1.328	1.362	1.328	1.320	1.260

[a] The basis set used in conjunction with the BP86 functional is LanL2DZ and that with B3LYP functional 6-311++G(2d,p).

[b] From ref. 10.

distances calculated for a particular tautomer at two different levels of DFT are comparable. As expected, the N-N bond is much shorter in the enol form than in the keto form as it assumes the character of a double bond in the enol form. Similarly, the C-O bond is much longer in the enol form than in the keto form as its bond order is two in the keto form but one in the enol form. The copper(II) complex CuLCl has been reported by Chiswell et al.[9] And the use of LH as a very sensitive colorimetric detector for the Cu^{2+} ion has been described by Hu et al[10] where the related copper(II) complex in solution is CuL_2. It is argued qualitatively that LH prefers to bind to a metal in the anionic enolate form as a tridentate N,N,O donor ligand.[9,10] But till date there is no X-ray crystal structure available for any of its metal complexes.

We have found that LH reacts with $CuCl_2.2H_2O$ in methanol at room temperature in equimolar proportion to yield a mixture of two types of single crystals (Fig. 1) – hexagonal (**1a**) and rectangular (**1b**) which are dark green with metallic sheen. On crushing, they become red powder. This, we believe, is an optical phenomenon. The colour of their solutions is deep red. The two types of crystals were separated mechanically. They both
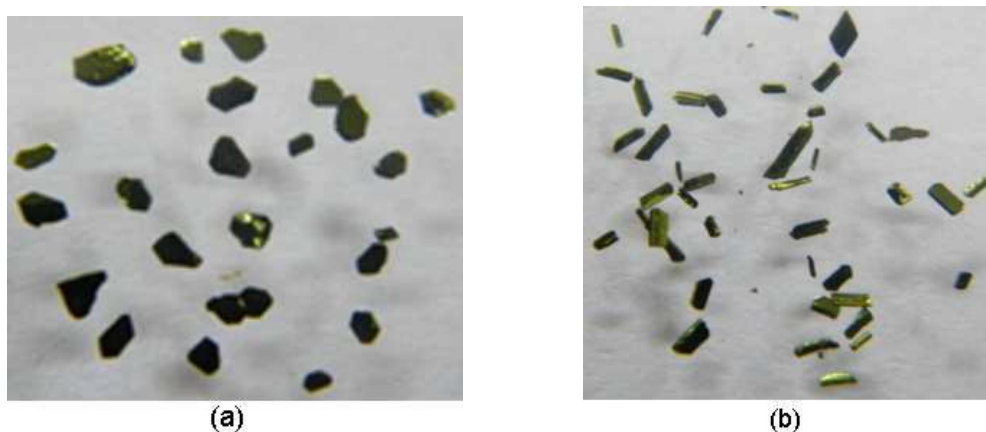

(a)　　　　　　　　　　　　　(b)

Fig. 1 Morphology of the single crystals of **1a** (a) and **1b** (b).

analysed as CuLCl. Their FTIR spectra in KBr, devoid of an N-H peak, are essentially similar. It is clear from their electronic spectra that these two are different species. The ligand is light yellow in colour in methanol showing strong absorptions at 333 and 234 nm together with a shoulder at 257 nm (Fig. 2). The band at 333 nm ($\varepsilon = 34,300$ dm^3 mol^{-1} cm^{-1}) has been assigned to the n $\rightarrow$ $\pi*$ transition of the carbonyl group by Bahgat[11]

from DFT calculations. This band upon complexation shifts to a longer wavelength at 506 nm in **1a** and **1b** giving rise to their intense red colour in solution (Fig. 2). The ε of
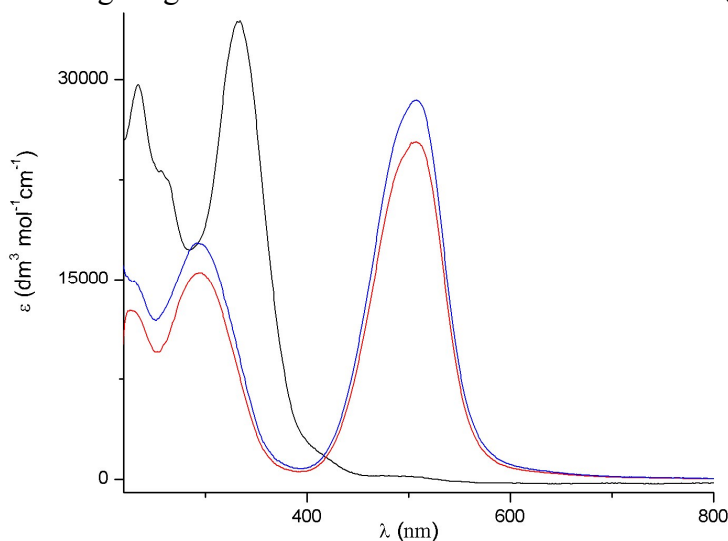

Fig. 2 Electronic spectra of LH (black), **1a** (blue) and **1b** (red) in methanol. The intensity ε for **1a** and **1b** shown are per copper.

this band in **1b** is 25,300 dm^3 mol^{-1} cm^{-1}. It is 90% of that in **1a**. Interestingly, the other strong band observed at 294 nm in the copper(II) complexes has an ε of 15,600 dm^3 mol^{-1} cm^{-1} in **1b** which is also 90% of that in **1a**.

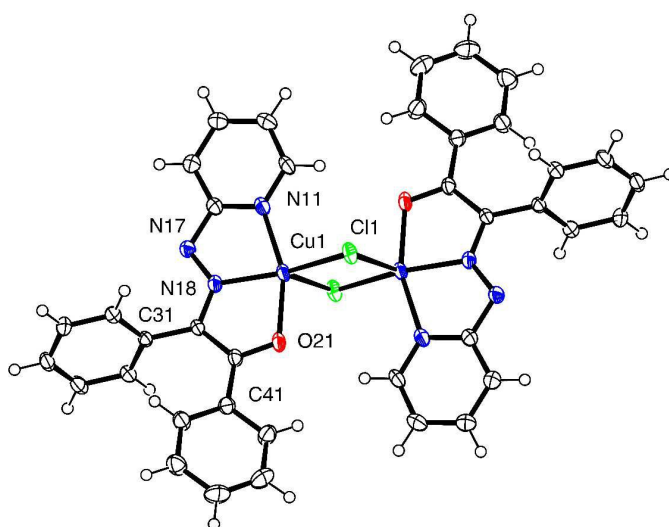The crystal structure of **1a** shown in Fig. 3. The x-ray structure of **1b** is similar.

Fig. 3 The centrosymmetric structure of **1a** with ellipsoids at 50% probability.

Both are centrosymmetric dimers, $Cu_2L_2Cl_2$, with equivalent connectivities but have slightly different geometries. Selected crystallographic data are given in Table 2 and the dimensions are compared in Table 3. LH does bind the copper atoms in the anionic mode and behaves as a tridentate (N,N,O) ligand. Bond lengths from the metal to the three donor atoms in the ligand are very similar in **1a** and **1b**. Slight difference is observed in

Table 2 Some crystallographic data for the complexes **1a** and **1b**

	1a	1b
Colour	dark green with metallic luster	same as **1a**
Formula	$C_{38}H_{28}N_6Cu_2Cl_2O_2$	$C_{38}H_{28}N_6Cu_2Cl_2O_2$
M	798.64	798.64
Space group	monoclinic, $C2/c$	triclinic, P-1
Cell dimensions (Å, º)		
a	21.798(3)	7.1801(6)
b	9.7924(9)	10.2796(7)
c	17.180(3)	12.3788(8)
β	111.803(18)	95.428(6)
U (Å^3)	3404.9(8)	846.66(11)
Z, d_{calc} (g cm^{-3})	4, 1.558	1, 1.566
μ (mm^{-1})	1.451	1.459
$F(000)$	1624	406
Unique reflections	4801	4734
Observed reflections [$I > 2\sigma(I)$]	3459	4115
Parameters	226	226
R_1, wR_2 [$I > 2\sigma(I)$]	0.0619, 0.1515	0.0356, 0.0858
R_1, wR_2 (all data)	0.0788, 0.1635	0.0432, 0.0899
Largest peak/hole (e Å^{-3})	1.460/-1.556	0.400/-0.669

Table 3 Experimental (X-ray) and calculated (by DFT using BP86 functional and LanL2DZ basis set) dimensions (Å, °) in the metal coordination spheres of **1a** and **1b**[a]

	1a		1b	
	X-ray	DFT	X-ray	DFT
Cu(1)-Cl(1)	2.266(1)	2.379	2.242(1)	2.397
Cu(1)-Cl(1)$1	2.575(1)	2.619	2.614(1)	2.567
Cu(1)-N(18)	1.938(2)	2.011	1.955(2)	2.011
Cu(1)-N(11)	1.996(3)	2.014	1.983(2)	2.005
Cu(1)-O(21)	1.996(2)	2.038	1.988(1)	2.043
Cl(1)-Cu(1)-Cl(1)$1	92.86(3)	93.89	95.75(2)	94.47
Cl(1)-Cu(1)-N(11)	99.71(8)	98.25	100.84(5)	98.11
Cl(1)-Cu(1)-N(18)	155.94(9)	164.06	171.57(5)	153.86
Cl(1)-Cu(1)-O(21)	97.20(6)	99.69	97.70(4)	98.33
Cl(1)$1-Cu(1)-N(11)	96.41(9)	97.05	95.96(5)	97.77
Cl(1)$1-Cu(1)-N(18)	111.19(9)	102.04	92.65(5)	111.67
Cl(1)$1-Cu(1)-O(21)	94.90(8)	96.27	94.05(5)	94.77
N(11)-Cu(1)-N(18)	79.07(10)	79.28	78.97(7)	79.46
N(11)-Cu(1)-O(21)	159.11(9)	156.81	157.90(6)	158.43
N(18)-Cu(1)-O(21)	80.48(9)	79.43	80.93(6)	79.61
Cu-Cl(1)-Cu	87.14(3)	86.11	84.26(2)	85.53

[a] Symmetry operation $1: 1-x, 1-y, 1-z in **1a** and 2-x, 1-y, 1-z in **1b**. For the atom labeling scheme, see Fig. 3. Note that the optimized structures from DFT showed very small deviations in the last digit between dimensions in the two halves of the molecule so only dimensions in one half of the molecule are given.

the metal-chlorine bonds with Cu(1)-Cl(1) 2.266(1), 2.242(1) Å in the equatorial plane. The metal atom is 0.168(1) Å from the plane in **1a** and 0.295(1) Å in **1b**. The Cu…Cu distances in **1a** and **1b** are 3.269(1) and 3.344(1) Å respectively. In the two complexes, the bonds of the ligand fragment listed in Table 1 are found to be closer to the enol form of LH. For example, experimental N-N bond lengths in **1a** and **1b** are 1.304 Å and 1.298 Å respectively. On the other hand, this bond in the enol form of LH is calculated to be

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1.260 Å at the B3LYP/6-311++G(2d,p) level and found to be 1.328 Å in the X-ray crystal structure of LH which, as pointed out above, is essentially the keto form of LH.

The angles around the metal are very similar in the two structures, within 3° as shown in Table 3, apart from Cl(1)-Cu(1)-N(18) 155.94(9), 171.57(5)° and Cl(1)$1-Cu(1)-N(18) 111.19(9), 92.65(5)° in **1a** and **1b** respectively. Interestingly, the sum of these two angles remain same (155.94° +111.19° = 267.13° and 171.57° + 92.65° = 264.22°). This comes about to maintain the angle Cl(1)-Cu(1)-Cl(1)$1 same in **1a** and **1b** (within 3°; 92.86(3)° and 95.75(2)°). Since all the bonding parameters except two mutually dependent angles are same, we call the relation between **1a** and **1b** as angle isomerism. In a much broader sense, they are manifestations of polymorphism which is "the ability of a compound to crystallize in more than one crystal structure".[12] The most enigmatic example of polymorphism is possibly aspirin.[13,14] Aspirin crystallizes in the space group P2₁/c which gives a wide choice of spatial arrangements in the solid.[15] The polymorphs can have difference in their energies as low as 0.50 kcal mol⁻¹. But isomers can have much larger energy differences between them, as found here.

A further feature should be mentioned here, namely the interaction in the dimer between an ortho proton of the pyridine ring of the ligand and O(21)$1. Dimensions for H…A, D…A, D-H…A (D = donor, A = acceptor O(21)$1) are 2.79, 3.518Å, 136° in **1a** and 3.16, 3.604Å, 111° in **1b**, showing a much larger interaction in the former. While this difference is significant, it seems likely to be a consequence of the angle isomerism rather than the driving force behind it, particularly as the interactions can be considered as weak.

In order to show that they are two distinct species, we have examined the two structures via DFT calculations at BP86/LanL2DZ and BP86/6-31G(2d,p) levels in quest of two different minima. Spin multiplicity is taken as 3. Single point energies show **1b** to have energy lower than **1a** by 6.37 kcal mol⁻¹ using LanL2DZ basis set and 3.78 kcal mol⁻¹ with the larger basis set. Upon geometry optimisation, this difference changes to 3.21 kcal mol⁻¹ at BP86/LanL2DZ level but the structures do not converge to the same one. The difference comes out as 4.49 kcal mol⁻¹ at BP86/6-31G(2d,p)// BP86/LanL2DZ level. That the two optimized structures correspond to true minima has been established by frequency calculations. No imaginary frequency is encountered. Theoretically

determined bond parameters are close to the experimental values (Table 3). Particularly the two Cl-Cu-N(18) angles retain the differences, as observed in the X-ray crystal structures.

The X-band EPR spectra of **1a** and **1b** are shown in Fig. 4. They are axial. They reveal that $(d_{x^2-y^2})^1$ is the ground state for **1a** ($g_\parallel > g_\perp$) and $(d_{z^2})^1$ for **1b** ($g_\parallel < g_\perp$). It is remarkable to find that such a small difference in the structures of the metal coordination spheres in **1a** and **1b** affects the electronic nature of the ground state so dramatically. Very few examples of such effects are known.[16] The $A_\parallel$ value in **1a** is unusually small. While the normal mononuclear copper(II) complexes show it around 16 mT, it is only
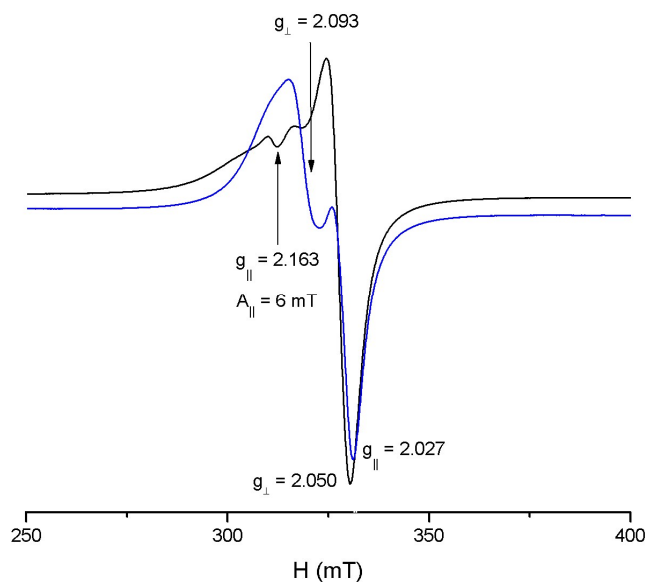

Fig. 4 Solid state X-band EPR spectra of **1a** (black) and **1b** (blue) at 77 K.

6 mT in **1a**. Such small $A_\parallel$ values occur in blue copper proteins.[17] The magnetic moments of **1a** and **1b** correspond to one unpaired electron per copper at room temperature. In keeping with this, no EPR signals at $g = 4$ are observed for them indicating insignificant coupling between the two unpaired electrons on the metals.[18] Such a situation is indeed expected[19,20] on the basis of the near 90° values of the Cu-Cl-Cu bridge angles (Table 3). This justifies our consideration of $S = 1$ (i.e. triplet ground state) in our DFT calculations on **1a** and **1b**.

The relative yield of the two isomers **1a** and **1b** constitutes an interesting phenomenon; it depends on the time allowed for crystallization. When the allowed crystallization time is less, the yield of **1a** is found to be more than **1b**. When the crystallization is carried with longer time, the relative yield of **1a** and **1b** is reversed. The crystallization time is controlled by varying the volume of the solvent methanol used initially to carry out the reaction of LH with $CuCl_2.2H_2O$. Typically, fixed amounts of the two reagents (maintaining the 1:1 molar proportion) are mixed in methanol which almost instantaneously turns deep red indicating the completion of the reaction. Then the reaction mixture is left for aerial evaporation. Crystals deposit when the volume of the reaction mixture reduces to ~ 5 ml. Thus the more the amount of methanol taken initially, the longer the two species remain in solution. When the synthesis is carried out by taking the amounts of the reagents LH and $CuCl_2.2H_2O$ specified in the experimental section in 10 ml of methanol, hexagonal crystals (**1a**) are obtained after 24 h as almost the sole product. In our DFT calculations we have seen that energetically **1a** is less stable than **1b**. The time dependent pattern of relative yield of **1a** and **1b** indicates that the less stable isomer forms first. This observation is in line with the concept of Ostwald ripening. In 1897, Ostwald observed that the solid first formed on crystallization of a melt or a solution is the least stable polymorph.[21] This can be justified by intricate thermodynamics.[22-24] It should be mentioned that Ostwald's law is concerned only with the order of appearance of polymorphs in a single experiment; the appearance of more stable forms later is a result of transition. We have followed the transformation of **1a** to **1b** by monitoring the absorbance at 506 nm with time t, spectrophotometrically. Since the absorption maxima of both the isomers occurs at the same wavelength with only a 10% difference in the extinction coefficients ε in methanol, we have studied the decrease in the absorbance of a methanolic solution of **1a** in the initial few hours of dissolution to avoid complications. The transformation is found to follow the kinetics of a zero order reaction (Fig. 5).

3. Concluding remarks

Here we have demonstrated a new type of isomerism where all the bonding parameters except two mutually dependent bond angles are same. It is reminiscent of the case of previously reported bond stretch isomerism where all the bonding parameters except one
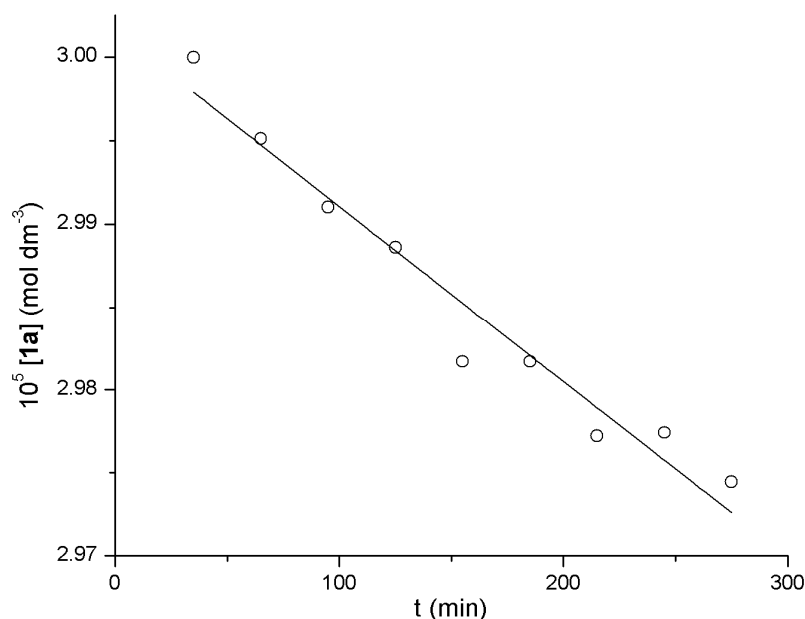

Fig. 5 Variation in the concentration of a 3 x 10^{-5} mol dm^{-3} methanolic solution of **1a** with time t as observed by monitoring the absorbance of the solution at 506 nm. Coefficient of determination $r^2 = 0.952$.

bond length were presumed to be same.[25,26] Anyway, it seems to have been mistaken as no two separate minima could be located clearly on the related potential energy surface. But in **1a** and **1b**, we obtain two distinct minima in our DFT calculations.

We do not understand the reason for the occurrence of angle isomerism in **1a** and **1b**. But a related observation of ours is that replacement of the four phenyl rings in **1a** and **1b** by H atoms leads to the convergence of the two structures to the same structure in DFT where the two relevant Cl-Cu-N(18) angles become 159.2 and 106.7^o with sum of these two angles (265.9^o) almost the same as those obtained in the crystal structures of **1a** and **1b**. Thus the skewness of benzil compared to glyoxal[27] may have a role here.

A remarkable result of our present work is the observation of Ostwald ripening in the formation of isomers **1a** and **1b**. The transformation **1a** to **1b** follows the kinetics of a zero order reaction. It should be noted that the reverse transformation is not possible. Ostwald's law finds practical application in the area of material processing.[28-31] Its present identification is possibly the first in coordination chemistry.

4. Experimental

4.1 Materials and physical measurements

Microanalyses were performed by a Perkin-Elmer 2400II CHNS analyser. Molar conductance was measured by a Syntronics (India) conductivity meter (model 306) in methanol. FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8400S spectrometer and UV-Vis spectra (in CH_3OH) on a Perkin Elmer Lambda 950 spectrophotometer. 500 MHz NMR spectrum of LH was recorded on a Bruker Avance III 500 spectrometer in $CDCl_3$. X-band EPR spectra of the copper(II) complexes were recorded on a JEOL JES-FA200 spectrometer and ESI mass spectra (in CH_3CN) on a Waters Qtof Micro YA263 spectrometer. Room temperature magnetic moments were measured by a magnetic susceptibility balance procured from Sherwood Scientific, UK. The diamagnetic correction was evaluated using Pascal's constants.

4.2 Synthesis of LH

It was prepared by modifying the procedure reported by Chiswell et al[9] in the following manner. 2-Hydrazinopyridine (1.09 g, 10 mmol) was added to a solution of benzil (2.10 g, 10 mmol) in ethanol (40 ml). The resulting orange yellow solution was refluxed for 2 h and then it was left in the air. After 16 h the precipitated light yellow microcrystalline compound was filtered and washed successively with cold ethanol (20 ml) and diethyl ether (25 ml). The compound was dried in air. Yield: 1.8 g (60%). mp 138-141 ^oC (lit. 140 ^oC).[9] Anal. Calc. for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.94 Found: C, 75.59; H, 4.99; N, 13.98 %. ^{1}H NMR δ/ppm: 7.73-7.8 (m, 2H), 7.31-7.39 (m, 8H), 7.19-7.25 (m, 8H), 7.02 (t, 1H). FTIR ν/cm^{-1}: 3315m, 3049w, 1631s, 1595s, 1554s, 1492s, 1440s, 1338s, 1292s, 1265s, 1247s, 1176m, 1081m, 1026w, 929w, 896w, 779m,

698m, 673w, 532m, 445w, 408w. UV-VIS λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}): 234 (29 600), 257 (23 000), 333 (34 500). ESI-MS m/z: 302.20 (LH+H$^+$, 100%).

4.3 Syntheses of 1a and 1b

A solution of CuCl$_2$.2H$_2$O (0.034 g, 0.2 mmol) in methanol (10 ml) was added to a solution of the ligand LH (0.060 g, 0.2 mmol) in methanol (10 ml) and stirred for 3 h at room temperature. The reaction mixture was then left in air for slow evaporation. When the volume reduced to ~5 ml, the deposited dark green crystals were filtered and washed with cold methanol (5 ml) and dried in air. Yield: 0.038 g (48 %). Two types of crystals were obtained – hexagonal (**1a**) and rectangular (**1b**). They were separated manually. The crystals were suitable for X-ray crystallography. They both analysed as C$_{38}$H$_{28}$N$_6$O$_2$Cu$_2$Cl$_2$. Anal. Calc. for C$_{38}$H$_{28}$N$_6$O$_2$Cu$_2$Cl$_2$: C, 57.15; H, 3.53; N, 10.52 Found: C, 57.23; H, 3.62; N, 10.45 %. FTIR ν/cm^{-1}: 3053w, 1600m, 1556w, 1515m, 1456m, 1440m, 1359s, 1330s, 1215s, 1176s, 1141s, 1093m, 1070w, 1012m, 931m, 844w, 777m, 689m, 599w, 511w. Λ_M/mho cm^2 mol^{-1} (MeOH): hexagonal (**1a**), 27.4; rectangular (**1b**), 24.5 (non-electrolyte).UV-VIS λ_{max}/nm (ε_{max}/dm^{3}mol^{-1}cm^{-1}): rectangular, 506 (25 300), 294 (15 600), 228 (sh); hexagonal, 506 (28 400), 292 (17 700), 230 (sh). μ_{eff}/μ_B per copper (at 298 K): hexagonal (**1a**), 1.84; rectangular (**1b**), 1.89.

4.4 Computation

DFT calculations were performed using GAUSSIAN 09 suite of programs.[32] Inputs were given from the X-ray crystal structures.

4.5 X-ray crystallography

Data for **1a** and **1b** were collected with MoKα at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD and 321 frames were measured with counting times of 10 s. Data analyses were carried out with the CrysAlis program.[33] Both structures were solved using direct methods with the Shelxs97 program.[34] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the

atom to which they were attached. Absorption corrections were carried out using the ABSPACK program.[35] The two structures were refined using Shelxl97[34] on F^2.

Acknowledgements

Supplementary material available

The cartesian coordinates of the DFT optimized structures of the complexes are given in the ESI. The CCDC 1063592 and 1063593 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Graphical abstract

$g_\perp = 2.093$

$g_{||} = 2.163$

$A_{||} = 6\ mT$

$g_{||} = 2.027$

$g_\perp = 2.050$

H (mT)
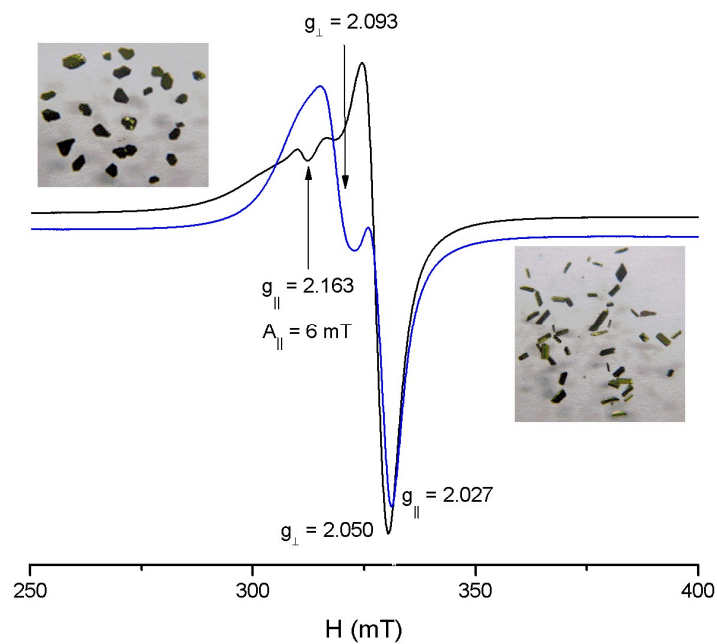
Synopsis

All bonding parameters in the X-ray structures of two forms of a Cu(II) complex are found to be same except two angles. Correspondingly two separate minima are located in DFT.