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Synthesis, structure and magnetic properties of a mononuclear Cu(II) complex with a NNO donor Schiff base ligand and its oxalato- and oxamidato-bridged dinuclear complexes

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The Schiff base *N*,*N*-dimethyl-*N*′-propylsalicylideneimine (HL) acts as a bidentate as well as a tridentate ligand for copper(II) ions. The mononuclear complex $[(HL)_2Cu](ClO_4)_2$ **1** reacts with oxalate or oxamidate anions to give dinuclear complexes $[(HL)Cu(\mu\text{-}C_2O_4)Cu(HL)](ClO_4)_2$ **2**, $[(HL)Cu(SCN)(\mu\text{-}C_2O_4)(SCN)Cu(HL)]$ **3**, $[LCu(\mu\text{-}C_2O_4)CuL]$ **4**, and $[LCu\{\mu\text{-}(NH)_2C_2O_2\}CuL]$ **5**. Complexes **1**, **3** and **4** have been structurally characterised. Complexes **2** (previously reported) and **3** are found to be essentially square planar and square pyramidal, respectively, whereas complex **4** shows a structure intermediate between square pyramidal and trigonal bipyramidal geometry. Interconversions between **2**, **3** and **4** were observed in water, depending upon the pH of the solutions. The cryomagnetic properties of **3**, **4** and **5** were studied. The magnitude of the exchange coupling has been analysed in the framework of a simple orbital model.

Complexes of copper(II) with tridentate *N*-alkylidene or *N*-arylidene alkanoato Schiff base ligands are of considerable interest due to their structural and magnetic properties, in addition to them being potential models for a number of important biological systems.[1] Several *N*-salicylideneaminoalkanoato complexes exhibit antimicrobial, anti-inflammatory and antipyretic activities,[2] together with an activity similar to superoxide dismutase.[3]

The potentially tridentate NNO donor ligand *N*,*N*-dimethyl-*N*′-propylsalicylideneimine (HL) is known to act as a bidentate ligand for Mn(II).[4] The tertiary amine group is protonated by transfer of the phenolic proton, and remains uncoordinated to the metal ion. The reduced form of the ligand acts as tridentate to the same metal ion. However, various NNO donor ligands are known in the literature, in which all three donor sites coordinate to a metal ion.[5] The plasticity of the coordination sphere of copper(II) allows it to adopt various stereochemical arrangements. We have synthesised the copper(II) mononuclear complex, **1**, with the *N*,*N*-dimethyl-*N*′-propylsalicylideneimine (HL) ligand. Moreover, oxalato- and oxamidato-bridged dinuclear copper(II) complexes were synthesised with *N*,*N*-dimethyl-*N*′-propylsalicylideneimine as a terminal ligand. Previous reports[6–8] show that the singlet–triplet energy gap in oxalato- and oxamidato-bridged dinuclear complexes varies over a wide range of values between 0 and $-385.6\ cm^{-1}$ and is dependent on the nature of the terminal ligands.

We report here the detailed synthesis, structure and magnetic properties of several new complexes, along with the pH-dependent interconversion of the oxalato-bridged complexes **2**, **3** and **4**.

Experimental

Infrared spectra were recorded on a Perkin Elmer 883-IR spectrophotometer from KBr pellets. Electronic spectra were recorded on a Hitachi U-3400 (UV-VIS-NIR) spectrophotometer from samples in solution. Magnetic susceptibility measurements were carried out in the temperature range 40–300 K by means of a Faraday-type magnetometer. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a standard. Corrections for the diamagnetism of the complexes were estimated from Pascal's constants.[9] EPR spectra of the compounds in solution were recorded with a Varian E-9 X-band spectrometer and Varian E-15 Q-band spectrometer equipped with a variable-temperature probe.

Copper(II) perchlorate hexahydrate, sodium hydroxide, oxalic acid, oxamide, *N*,*N*-dimethyl-1,3-diaminopropane and salicylaldehyde were of reagent grade quality and were used without further purification. Analytical data (C, H, N) were obtained with a Perkin-Elmer 2400 II elemental analyser. Copper was estimated gravimetrically by using *N*-benzoyl-*N*-phenylhydroxylamine. The perchlorate anion was estimated gravimetrically as tetraphenylarsonium(V) perchlorate.

The ligand LH was synthesised as reported previously.[10]

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts should be prepared and should be handled with great care.

Synthesis of the complexes

$[(HL)_2Cu](ClO_4)_2$ 1. Solid $Cu(ClO_4)_2\cdot 6H_2O$ (0.37g, 1 mmol) was added to a vigorously stirred 20 cm^3 methanol solution of the ligand (HL, 2 mmol). A yellowish-green solid appeared after 5 min, and was recrystallised from a 1 : 1 water–ethanol mixture, yielding yellowish-green needle-shaped crystals, which were filtered off and air-dried. Anal. calc. for $[C_{24}H_{36}N_4O_2Cu](ClO_4)_2$: C, 42.6; H, 5.3; N, 8.3; ClO_4, 29.5; Cu, 9.4. Found: C, 42.8; H, 5.5; N, 8.0; ClO_4, 29.3; Cu, 9.8%.

$[(HL)Cu(\mu\text{-}C_2O_4)Cu(HL)](ClO_4)_2$ 2. This was prepared by the reported method.[10]

$[(HL)Cu(SCN)(\mu\text{-}C_2O_4)(SCN)Cu(HL)]$ 3. A 10 cm^3 aqueous solution of oxalic acid (0.03 g, 0.25 mmol) and NaSCN (0.04g, 0.5 mmol) was added to a 100 cm^3 aqueous solution of **1** (0.37 g, 0.5 mmol) with stirring. The pH of the resulting mixture was adjusted to *ca.* 6 by adding dilute HCl. Green crystals were obtained after 3 days. Anal. calc. for $[C_{28}H_{36}N_6S_2O_6Cu_2]$: C, 45.1; H, 4.8; N, 11.3; Cu, 17.0. Found: C, 45.2; H, 5.0; N, 11.5; Cu, 17.3%.

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Table 1 Crystallographic data and structure refinement of the complexes **1**, **3** and **4**

	1	**3**	**4**
Formula	$C_{24}H_{36}Cl_2CuN_4O_{10}$	$C_{28}H_{36}Cu_2N_6O_6S_2$	$C_{26}H_{34}Cu_2N_4O_6$
M	675.0	743.8	625.7
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pbca$
a/Å	13.3004(9)	9.3820(8)	10.2160(10)
b/Å	23.5227(17)	13.6689(11)	10.9109(10)
c/Å	9.6924(7)	12.2240(10)	23.883(2)
β/°	109.698(2)	99.720(2)	90.0
U/Å^3	2854.9(3)	1545.1(2)	2662.1(4)
Z	4	2	4
D_c/g cm^{-3}	1.570	1.599	1.561
μ/mm^{-1}	1.01	1.56	1.65
Data measured	17498	9342	19991
Unique data	6673	3633	3217
R_{int}	0.0569	0.0189	0.0557
Parameters	374	201	174
R (F, $F^2 > 2\sigma$)	0.0469	0.0251	0.0521
R_w (F^2, all data)	0.1017	0.0688	0.1231

[LCu(μ-C_2O_4)CuL] 4. Oxalic acid (0.03 g, 0.25 mmol), dissolved in the minimum volume of water, was added to a 100 cm^3 aqueous solution of **1** (0.37 g, 0.5 mmol). The pH of the solution was adjusted to *ca.* 9 by adding NaOH solution. On standing, a green powder was obtained. The compound was crystallised from a chloroform–hexane mixture, yielding green crystals. Anal. calc. for [$C_{26}H_{34}N_4O_6Cu_2$]: C, 49.9; H, 5.4; N, 8.9; Cu, 20.3. Found: C, 50.0; H, 5.5; N, 9.0; Cu, 20.4%.

[LCu{μ-$(NH)_2C_2O_2$}CuL] 5. A suspension of oxamide (0.05 g) in acetone (15 cm^3) was treated with NaOH (0.07 g) with vigorous stirring to obtain a clear solution. A slight excess of NaOH was added, then the solution was added to 0.37 g of **1**, suspended in 30 cm^3 of acetone, with vigorous stirring. The solution was filtered and green crystals appeared after 24 h; they were collected and air-dried. Anal. calc. for [$C_{26}H_{36}N_6O_4Cu_2$]: C, 50.0; H, 5.7; N, 13.5; Cu, 20.4. Found: C, 49.8; H, 5.5; N, 14.0; Cu, 19.4%.

X-Ray crystallography

The details of structure solution and refinement are given in Table 1. Cell dimensions and intensity data for all three crystals were measured at 160 K on a Bruker AXS SMART CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å. Cell parameters were refined from the observed ω angles of all strong reflections in the complete data set. Semi-empirical absorption corrections were applied, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2. Anisotropic displacement parameters were refined for all non-hydrogen atoms, and isotropic hydrogen atoms were included with riding model constraints.

Programs were standard Bruker AXS control (SMART) and integration (SAINT) software,[11] SHELXTL,[12] and local programs.

CCDC reference numbers 189451–189453.

See http://www.rsc.org/suppdata/dt/b2/b206076k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Infrared spectra and crystallographic study of **1** revealed protonation of the $-CH_2-CH_2-CH_2-NMe_2$ arm, which remains uncoordinated to copper(II). Treatment of an aqueous solution of **1** with a dilute aqueous solution of NaOH (10%), followed by slow evaporation, gives a green solid **1a**. The infrared absorptions for perchlorate anion ($\nu = 1090$ and 625 cm^{-1}) were absent in **1a**, indicating that the tertiary nitrogen is no longer protonated. The analytical results suggest that the chemical formula for **1a** is [L_2Cu]. The electronic spectrum of **1a** does not show any significant change in its d–d transition peak compared with **1** ($\lambda_{max} = 637$ nm, $\varepsilon = 337$ L mol^{-1} cm^{-1}); thus the tertiary nitrogen still remains uncoordinated in **1a**. However, reduction of the imine bond of the ligand HL by sodium borohydride and subsequent reaction of the reduced ligand (HL′) with $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol gives deep green crystals of **1b**. There is a considerable change in the d–d absorption position ($\lambda_{max} = 683$ nm, $\varepsilon = 102$ L mol^{-1} cm^{-1}) relative to **1**, indicating a six-coordinate complex. The analytical data and other spectroscopic results support the formulation [L'_2Cu], where the tertiary nitrogen atoms are coordinated to the metal centre. These observations are in consonance with previously reported work.[4]

The mononuclear species **1** reacts with oxalate anion at a pH ≈ 6 to give the oxalato-bridged dinuclear complex **2**. The parent ligand (HL) acts as a bidentate ligand, with elimination of one ligand (HL) molecule from each copper centre of complex **1**. However, in basic aqueous medium (pH ≈ 9), **2** gives another oxalato-bridged complex, **4**, in which the ligand acts as a tridentate one. The metal centre in compound **2** possesses square planar geometry, whereas **4** has an intermediate geometry between square pyramidal and trigonal bipyramidal. This change in stereochemistry between **2** and **4** consequently generates a different orientation of the resulting magnetic orbitals and the magnitude of the antiferromagnetic interaction varies.

Interconversion between 2, 3 and 4 in H_2O

The electronic absorption spectrum of [LCu(μ-C_2O_4)CuL] **4** in H_2O at a neutral pH shows two well separated peaks at 620 and 820 nm. The absorbances at 620 and 820 nm are attributable to the d–d transitions of **2** and **4**, respectively, as found in CH_2Cl_2. With decreasing pH, the absorbance at 620 nm increases and that at 820 nm decreases (shown in Fig. 1). At *ca.* pH 5, the absorbance at 820 nm completely disappears. On the other hand, on increasing the pH to about 9, the absorbance at 820 nm increases, with complete disappearance of the peak at 620 nm. There is an isosbestic point at 750 nm. Such a spectral change is reasonably explained by the equilibrium between **2** and **4**. The shift of λ_{max} towards shorter wavelength (620 nm) is associated with the formation of **2** at a pH lower than 7, and towards higher wavelength (820 nm) due to the formation of **4** at a pH higher than 7. The two absorbances at 620 and 820 nm in neutral solution are attributable to the coexistence of both **2** and **4**. An addition of a 10 molar excess of NaSCN to an aqueous solution of **2** at pH < 7 results in the appearance of a new absorption band at 640 nm, which is essentially consistent with that of [(HL)Cu(SCN)(μ-C_2O_4)(SCN)Cu(HL)] **3** in CH_2Cl_2.

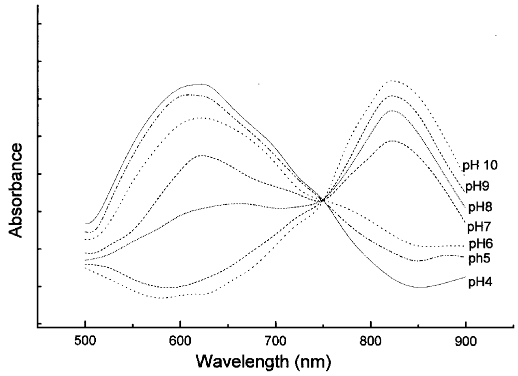

Fig. 1 Plots of absorbance *vs.* wavelength (nm) at different pH values.

The electronic spectrum of **4** at pH *ca.* 9 was not changed, even by the addition of a 100 molar excess of NaSCN. On the other hand, a basic solution of **3** shows an absorption at 820 nm, attributable to the absorption due to **4**, indicating that the tertiary amine group easily substitutes the SCN^- ligand of **3**. Thus the apical position of **2** is easily occupied by NCS^-, while **4** is inert towards the dissociation of the tertiary amine. Loss of thiocyanate from **3** is observed, but it is not incorporated when added to **4**.

Description of the molecular structures

The crystal structure of **2** has been reported earlier.[10] The structures of **1**, **3** and **4** are shown in Figs. 2, 3 and 4, respectively. Selected bond distances and angles are given in Table 2.

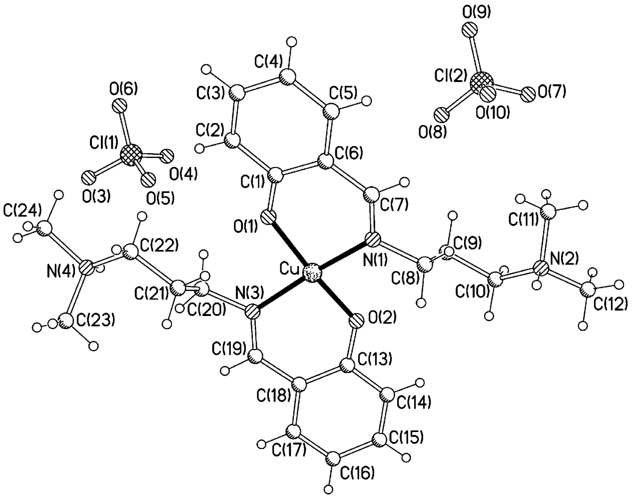

Fig. 2 Complete asymmetric unit of complex **1**.

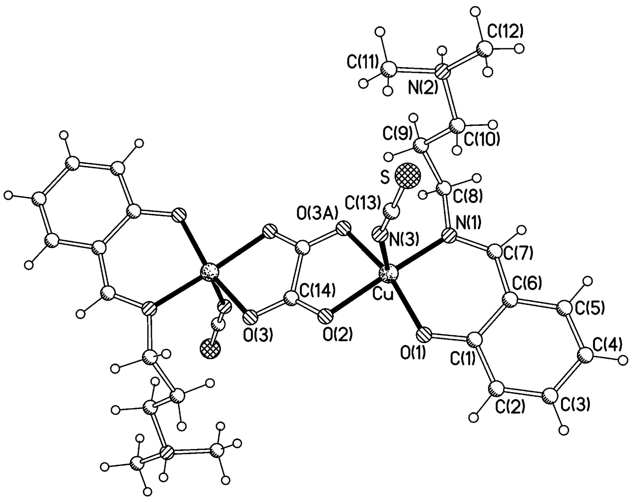

Fig. 3 Structure of the dinuclear complex **3**.

Table 2 Selected bond distance (Å) and angles (°) for the complexes **1**, **3** and **4**

1			
Cu–O(1)	1.8908(19)	Cu–O(2)	1.895(2)
Cu–N(1)	1.992(2)	Cu–N(3)	1.994(2)
O(1)–Cu–O(2)	169.29(9)	O(1)–Cu–N(1)	92.00(8)
O(2)–Cu–N(1)	89.07(9)	O(1)–Cu–N(3)	89.33(9)
N(1)–Cu–N(3)	170.23(9)	O(2)–Cu–N(3)	91.42(9)
3			
Cu–O(1)	1.9134(11)	Cu–N(1)	1.9580(13)
Cu–O(2)	2.0113(11)	Cu–O(3A)	2.0338(11)
Cu–N(3)	2.2158(14)		
O(1)–Cu–N(1)	95.94(5)	O(1)–Cu–O(2)	85.21(5)
O(1)–Cu–O(3A)	158.81(5)	O(2)–Cu–O(3A)	82.21(4)
O(3A)–Cu–N(3)	98.45(5)	O(1)–Cu–N(3)	100.05(5)
O(2)–Cu–N(3)	97.51(5)	N(1)–Cu–O(2)	167.79(5)
N(1)–Cu–O(3A)	92.89(5)	N(1)–Cu–N(3)	94.26(5)
4			
Cu–O(3)	1.917(2)	Cu–O(2A)	2.000(2)
Cu–O(1)	2.160(3)	Cu–N(1)	1.932(3)
Cu–N(2)	2.197(3)		
O(3)–Cu–N(1)	93.85(10)	O(2A)–Cu–N(2)	98.62(10)
O(2A)–Cu–O(1)	80.23(10)	N(1)–Cu–O(2A)	166.54(11)
O(1)–Cu–N(2)	97.37(10)	O(3)–Cu–O(2A)	88.14(10)
N(1)–Cu–N(2)	91.96(11)	N(1)–Cu–O(1)	90.23(10)
O(3)–Cu–O(1)	142.47(10)	O(3)–Cu–N(2)	119.71(10)

Symmetry transformation (inversion) used to generate equivalent atoms for **3** and **4**: $1 - x, 1 - y, 1 - z$.

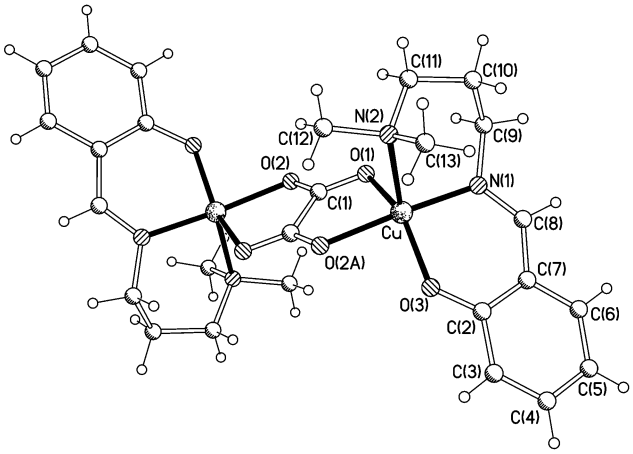

Fig. 4 Structure of the dinuclear complex **4**.

$[(HL)_2Cu](ClO_4)_2$ 1. Complex **1** consists of a $[(HL)_2Cu]^{2+}$ cation and two perchlorate anions. Coordination around the copper(II) ion is by the N_2O_2 donor set of two HL ligands. The salicylideneimine ligand has three potential donor sites, but binds to the copper(II) ion only through the phenolate oxygen and the imine nitrogen. The tertiary nitrogen atom is protonated and does not take part in coordination. In complex **1**, the copper(II) ion lies 0.004 Å out of the coordination plane described by the two imino nitrogen atoms and two phenolate oxygen atoms, and is essentially in a square planar environment. There is, however, a significant twist in the coordination plane, with a dihedral angle of 20.1° between the two six-membered chelate rings. The ligand arrangement is *trans*, and there is an approximate two-fold rotation axis through Cu, except for the orientations of the alkyl side chains. The protonated nitrogen atoms of these form hydrogen bonds with the two perchlorate anions. There are no other significant intermolecular contacts.

[(HL)Cu(SCN)(μ-C_2O_4)(SCN)Cu(HL)] 3. In the precisely centrosymmetric dinuclear species **3**, each Cu(II) ion is in a square pyramidal environment, with two oxalato oxygen atoms, one phenolate oxygen and one imine nitrogen occupying the basal positions, and thiocyanate N at the apical position. The r.m.s. deviation of the basal atoms from their mean plane is 0.054 Å, and Cu lies 0.258 Å out of this plane, displaced towards the apical atom N(3). The tertiary nitrogen atom of HL is protonated and is uncoordinated to copper. The planar oxalato group bridges the two copper ions in the usual bis-(bidentate) fashion. Each copper ion is bound to two oxygen atoms from the two different carboxylate groups, with a copper–copper distance of 5.280 Å across the dinuclear unit. The Cu–O(oxalate) bond lengths are 2.0113(11) and 2.0338(11) Å. The Cu–O(1) and Cu–N(1) bond lengths are 1.9134(11) and 1.9580(13) Å, respectively. The two independent C–O bond lengths of the oxalato bridge are 1.2469(19) and 1.2553(19) Å, essentially identical. The thiocyanate ligand is bent at the coordinating N atom, by 20° from linearity. Each protonated amine N atom forms a bifurcated hydrogen bond to an oxalate O and a phenolic O of a neighbouring molecule.

[LCu(μ-C_2O_4)CuL] 4. The deprotonated ligand L is tridentate in this complex, which is also centrosymmetric with a planar oxalato bridge. The coordination geometry about the five-coordinate Cu(II) ions is best described as intermediate between a square pyramid and a trigonal bipyramid.[13] If the Cu(II) ion coordination geometry is viewed as square pyramidal, the phenolate oxygen atom O(3), the imine nitrogen atom N(1) of the Schiff base ligand, and the oxygen atoms O(2A) and O(1) of the oxalato bridge comprise the basal plane, and the tertiary nitrogen atom N(2) of the ligand is in the apical position. However, the r.m.s. deviation of the basal atoms from their mean plane is 0.217 Å; Cu lies 0.420 Å out of this plane, towards N(2).

The distortion from ideal square pyramidal coordination is a result of the short CH_2–CH_2 tether between the two coordinating N atoms, raising N(1) out of the basal plane. Alternatively, a trigonal bipyramidal description of the Cu(II) ion environment places the atoms N(2), O(3), O(1) in the equatorial plane, with the axial positions occupied by the imine nitrogen atom N(1) of the Schiff base ligand and the oxalate oxygen O(2A). The trigonal axis shows some distortion from linearity, with N(1)–Cu–O(2A) = 166.54(11)°, but the largest deviations from ideal trigonal bipyramidal geometry are in the equatorial angles, with values of 97.37(10), 142.47(10) and 119.71(10)°. The Cu ion lies only 0.076 Å out of the plane of the equatorially coordinating atoms. The intramolecular distance between the two copper ions is 5.407 Å, and the closest intermolecular distances between copper ions are 6.688 and 7.091 Å.

The geometric parameter τ, which is used for five-coordinate structures as an index of the degree of trigonality, within the continuum between trigonal bipyramidal and square pyramidal geometries,[14] is 0.4 for compound **4**. The value of τ for **3** is 0.15, indicating a closer approximation to square pyramidal geometry, for which $\tau = 0$; $\tau = 1$ for an ideal trigonal bipyramid.

Magnetic and EPR results

The magnetic properties of **2** have been described earlier,[10] with a singlet–triplet energy gap of $J = -478$ cm^{-1}, which is larger than other oxalato-bridged copper(II) dinuclear complexes reported earlier.[6,8,15]

The X-band EPR spectrum of **3** in DMSO solution at room temperature has $g_{\parallel} = 2.24$ and $g_{\perp} = 2.06$. A weak absorption at half-field, arising from a $\Delta M_s = 2$ forbidden transition in the populated triplet, is observed at room temperature for the complex. Fig. 5 shows the EPR spectra, (a) for the half-field spectrum, and (b) for the high-field spectrum. On decreasing the temperature the spectrum of the dimeric species reduces in intensity and disappears, in agreement with the expected behaviour, and the spectrum of a monomeric impurity becomes evident.

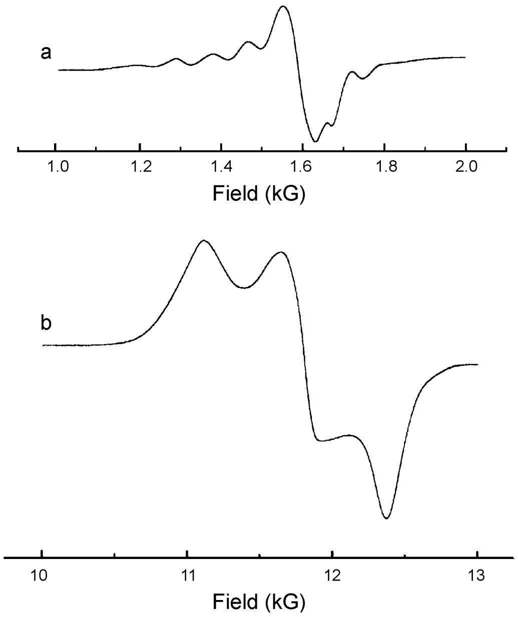

Fig. 5 (a) X-Band EPR spectrum for the half-field transition of complex **3**; (b) high-field X-band EPR spectrum for complex **3**.

The susceptibility data were fitted by the Bleaney–Bowers expression for the magnetic susceptibility of isotropically coupled dinuclear $S = ½$ ions,[16] based on spin Hamiltonian $H = -JS_AS_B$, adding an impurity term defined as the molar fraction of non-coupled species. It is assumed that the impurity obeys the Curie Law and has the same molecular weight and the same g factor as those of the main compound. The criterion of the best fit was the minimum value of $R = \Sigma(\chi_{obs} - \chi_{calc})^2/(\chi_{obs})^2$. The results of the fit for **3** were: $J = -345$ cm^{-1}, $g = 2.15(1)$, $\rho = 0.0013(4)$, with $R = 4.1 \times 10^{-4}$. The J value is similar to that evaluated for oxalato-bridged dinuclear copper(II) complexes characterised by a non-centrosymmetric Cu(C_2O_4)Cu core.[7,8]

A plot of the molar magnetic susceptibility *vs.* temperature for complexes **3**, **4** and **5** is shown in Fig. 6. The Q-band EPR spectrum of **4** in CH_2Cl_2 solution at 120 K shows a high-field signal at $g = 2.020$ and the spectrum is found to be very

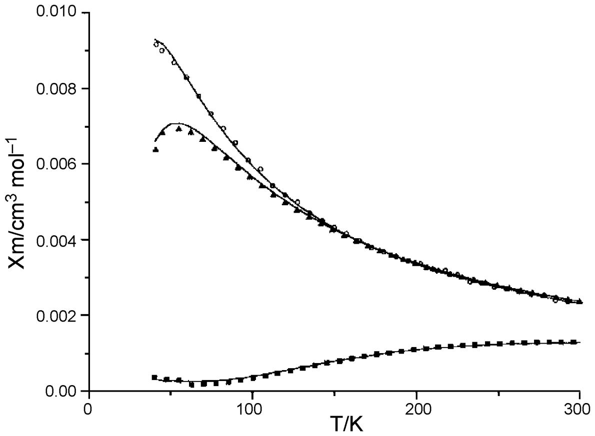

Fig. 6 Experimental (points) and calculated (solid lines) temperature dependence of χ_M for compounds **3** (■), **4** (○) and **5** (▲).

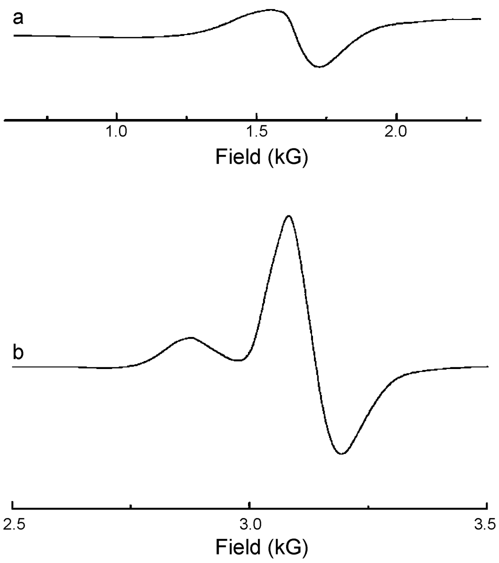

Fig. 7 Low-field sections of (a) the X-band EPR spectrum for **4**; and (b) the Q-band spectrum for **4**.

non-axial, with the other two values at 2.119 and 2.242. This spectrum reflects the appreciable distortion[17] from perfectly square pyramidal or trigonal bipyramidal geometry, in agreement with the structural results. The X-band spectrum under the same conditions shows a $\Delta M_s = 2$ transition with relative intensity *ca.* 0.01 times that of the $\Delta M_s = 1$ transition. At least four hyperfine lines, with a spacing of *ca.* 60 G, are visible in the $\Delta M_s = 2$ resonance. The X-band spectrum for half-field and the high-field Q-band spectrum are shown in Fig. 7(a) and 7(b), respectively.

The magnetic behaviour indicates a weaker interaction for complex **4** than for complexes **2** and **3**. The χ_M *vs.* T data for complex **4** were fitted as for **3**, using the Bleaney–Bowers expression for the magnetic susceptibility of isotropically coupled dinuclear $S = ½$ ions, adding an impurity term defined as the molar fraction of non-coupled species. The criterion of best fit was as before. The result of the fit is shown as the solid line in Fig. 6, where $J = -43\ \text{cm}^{-1}$, $g = 2.13(2)$, $\rho = 0.0080(1)$, with $R = 3.8 \times 10^{-3}$.

The much weaker exchange interaction for **4** than for **2** and **3** can be understood by noting that the geometry for **4** deviates from square pyramidal towards trigonal bipyramidal, but is still intermediate and significantly different from pure trigonal bipyramidal, as shown by the structural results and EPR spectroscopy. With increasing trigonal character of the CuN_2O_3 chromophore, the d_{z^2} character of the magnetic orbital increases and hence a reduction in the exchange interaction is observed. This picture fits very well with previously observed oxalato-bridged complexes.[6,7,13,18]

The μ-oxamidato bridge is more efficient than a μ-oxalato bridge in propagating antiferromagnetic exchange interaction,[19,20] due to the lower electronegativity of nitrogen compared with oxygen. The oxamidato-bridged complex $[LCu\{\mu\text{-}(NH)_2C_2O_2\}CuL]$ **5** shows a higher magnetic interaction, with $J = -56\ \text{cm}^{-1}$ [$g = 2.16(2)$, $\rho = 0.0080(1)$, and $R = 4 \times 10^{-4}$], compared with that of the oxalato-bridged complex **4**.

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