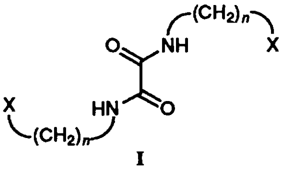
Oxamidato Complexes. Part 6.[1] Complex Formation between Copper(II) and *N,N'*-Bis[2-(dimethylamino)ethyl]oxamide (H_2dmaeoxd). Preparation, Crystal Structure, and Magnetic Properties of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$†

José Antonio Real,[a] Miquel Mollar,[a] Rafael Ruiz,[a] Juan Faus,[a] Francesc Lloret,*,[a] Miguel Julve[a] and Michèle Philoche-Levisalles[b]
[a] *Department de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain*
[b] *Laboratoire de Chimie des Métaux de Transition, URA 419 CNRS, Université Pierre et Marie Curie, 75252 Paris, France*

The protonation and deprotonation of *N,N'*-bis[2-(dimethylamino)ethyl]oxamide (H_2dmaeoxd, H_2L) and its complex formation with Cu^{II} have been investigated by potentiometry in aqueous solution at 25 °C and 0.1 mol dm^{-3} $NaNO_3$. The proton association constants β_j corresponding to the equilibria $L^{2-} + jH^+ \rightleftharpoons H_jL^{(j-2)+}$ were found to be log β_2 = 24.0(2), log β_3 = 32.63(1) and log β_4 = 40.46(1). The values of the stability constants β_{pqr} concerning the equilibria $pCu^{2+} + qL^{2-} + rH^+ \rightleftharpoons [Cu_pL_qH_r]^{[2(p-q)+r]+}$ were log β_{212} = 34.11(8), log β_{211} = 29.52(8), log β_{210} = 24.74(2), log β_{320} =44.87(5), log β_{430} = 64.09(7) and log β_{110} = 16.92(2). The compound of formula $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ has been synthesised and its crystal structure determined by single-crystal X-ray diffraction methods at room temperature. It crystallizes in the monoclinic system, space group $P2_1/a$ and $Z = 2$, with a = 11.589(3), b = 12.456(1), c = 6.771(2) Å, and β = 102.39(2)°. Least-squares refinement gave a final R (R') factor of 0.038 (0.045) for 2249 unique reflections having $I \geqslant 3\sigma(I)$. The structure consists of neutral centrosymmetric oxamidato-bridged dinuclear copper(II) units. The co-ordination geometry around each copper(II) ion is distorted square pyramidal: the equatorial plane comprises the oxygen and nitrogen atoms of the amide, the nitrogen atom of the amine group and the nitrogen atom of the cyanate ligand, whereas the apical position is filled by a water molecule. The intramolecular copper–copper separation is 5.306(1) Å. Variable-temperature magnetic susceptibility measurements (50–300 K) of this complex reveal a strong antiferromagnetic coupling through the oxamidate, the relevant parameters being g = 2.12 and J (singlet–triplet energy gap) = −560 cm^{-1}. The chelating ability of $dmaeoxd^{2-}$ and its ability to transmit electronic effects are discussed and compared to those of related *N,N'*-dialkyloxamidate ligands.

A relatively recent review on the co-ordination chemistry of *N,N'*-bis(substituent)oxamides such as **I** has shown that their co-ordinating ability toward transition-netal ions can be modified and tuned by playing on the nature of the amide substituents.[2] The great variety of co-ordinating groups X which can be used and the fact that both *cis* and *trans* conformations can be adopted in the absence of steric effects make them very suitable as polynucleating ligands. Their remarkable ability to transmit electronic effects when acting as bridges between paramagnetic centres has been explored along four directions: (*i*) the design and synthesis of dinuclear copper(II) complexes for which the singlet–triplet energy gap can be tuned (tunable exchange),[3] (*ii*) the achievement of new topologies in inorganic complexes,[4] (*iii*) the introduction of the idea of irregular spin-state structure,[5] and (*iv*) the design of molecular-based compounds exhibiting a spontaneous magnetization below a critical temperature T_c (molecular-based ferromagnets).[6]

These solid-state investigations in the field of molecular materials have been complemented by solution studies aiming at rationalizing the synthesis of such complex units and characterizing thermodynamically the chelating behaviour of this family of ligands.[1,7–10] The *cis–trans* conformational change of the ligand *N,N'*-bis(3-aminopropyl)oxamidate (apoxd) (n = 3, X = NH_2) in its metal complexes,[8] the behaviour of the complex [Cu(apoxd)] as a ligand to build polynuclear species, the modifications of the complexing ability of *N,N'*-substituted oxamides caused by the occurrence of alkyl substituents on their amine groups and which are exemplified by the Cu^{II}–$mapoxd^{2-}$ {mapoxd = dianion of *N,N'*-bis[3-methylamino)propyl]oxamide; n = 3, X = NHMe} and Cu^{II}–$dmapoxd^{2-}$ {dianion of *N,N'*-bis[3-(dimethylamino)propyl]-oxamide; n = 3, X = NMe_2} systems,[1] and the redox behaviour of the Cu^{III}–Cu^{II} couple in monomeric *N,N'*-bis(substituent)oxamidatocopper(II) complexes[9] were the main objectives of the solution studies.



I

In the present contribution we investigate the protonation of the $dmaeoxd^{2-}$ ligand {H_2dmaeoxd = *N,N'*-bis[2-(dimethyl-amino)ethyl]oxamide, H_2L; n = 2, X = NMe_2} and its complex formation with copper(II) in aqueous solution. Knowledge

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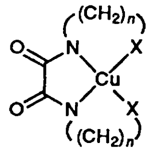
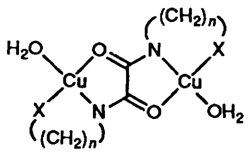
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-S.I. unit employed: emu = SI × $10^6/4\pi$.



II



III

of the behaviour of L^{2-} as ligand, which is close to that of apoxd^{2-}, has allowed us to compare the relative stabilities of copper(II) complexes with *l*-5-*l* (**II**) and *l*-5 (**III**) ($l = n + 3$) member fused chelates and analyse the influence of the alkyl substituents. The structure of the dinuclear complex $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ and its magnetic properties are also reported.

Experimental

Materials.—Copper(II) nitrate trihydrate, sodium cyanate, *N*,*N*′-dimethylethylenediamine and diethyl oxalate were of reagent-grade quality. They were purchased from commercial sources and used as received. Carbonate-free NaOH (0.1 mol dm^{-3}) and HNO_3 (0.1 mol dm^{-3}) were used in the potentiometric titrations. Stock solutions of copper(II) nitrate were prepared in doubly distilled water and the concentration of the metal ion determined by standard methods. All potentiometric measurements were carried out at constant ionic strength, 0.1 mol dm^{-3} $NaNO_3$. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain).

Ligand and Complex Preparations.—The ligand *N*,*N*′-bis[2-(dimethylamino)ethyl]oxamide (H_2dmaeoxd, H_2L), was prepared by using the usual method:[11] a methanolic solution of diethyl oxalate (0.1 mol) was treated with *N*,*N*-dimethylethylenediamine (0.2 mol) at room temperature. The mixture was kept at 80 °C for half an hour under continuous stirring and the white solid was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Analytical data indicated the anhydrous ligand.

Dark blue prismatic crystals of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ were obtained by slow diffusion of aqueous solutions of $[Cu_2(dmaeoxd)]^{2+}$ [stoichiometric amounts of copper(II) nitrate and fully deprotonated dmaeoxd] and cyanate in an H-shaped tube at room temperature. They were collected, washed with cold water and dried over calcium chloride (Found: C, 30.25; H, 4.90; N, 17.55. Calc. for $C_{12}H_{24}Cu_2N_6O_6$ **1**: C, 30.30; H, 5.10; N, 17.70%).

Physical Techniques.—Magnetic susceptibility measurements of the complex $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ were carried out at 50–300 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer[12] equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with $Hg[Co(NCS)_4]$. Corrections for the diamagnetism of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ were estimated from Pascal's constants[13] as -270×10^{-6} emu mol^{-1}. Magnetic susceptibility data were also corrected for temperature-independent paramagnetism (-60×10^{-6} emu per Cu^{II}) and magnetization of the sample holder. X-Band EPR spectra were recorded with a Brüker ER 200D spectrometer at 298–4.2 K.

Electromotive force measurements were performed at 25 °C using a titrating assembly that has been previously described.[14] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titration of known amounts of HNO_3 with CO_2-free NaOH and determining the equivalent point by Gran's method,[15] which gives the standard potential of the cell, $E°$, and the ionic product of water, K_w. Aqueous solutions of H_2L [$c_L = (1\text{–}10) \times 10^{-3}$ mol dm^{-3} previously acidified with HNO_3 and of metal to ligand ratios in the range 0.5–2 : 1 [$c_M = (1.5) \times 10^{-3}$ mol dm^{-3}] were titrated with NaOH (0.1 mol dm^{-3}) to determine the equilibrium constants involved in the deprotonation and complex formation, respectively. The computer programs SUPERQUAD[16] and BEST[17] were used to process electromotive force data from each experiment and calculate the equilibrium constants; 100 experimental points in the range pH 6.5–11.6 (H_4L^{2+}) and 160 in the range pH 4.5–10.0 (Cu^{II}–H_2L) were treated.

Crystal Structure Determination and Refinement.—Diffraction data for $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ were collected at 291 K with a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). Crystal parameters and pertinent refinement results are listed in Table 1. The unit-cell parameters were determined from least-squares refinement of the 25 well centred reflections in the range θ 14–15°. Examination of two standard reflections, monitored every 2 h, showed no sign of crystal deterioration. The space group $P2_1/a$ was deduced from systematic absences. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was performed by the use of DIFABS.[18]

The structure was solved by Patterson methods with the program CRYSTALS[19] followed by successive Fourier syntheses and least-squares refinements in three blocks (157 parameters). All non-hydrogen atoms were treated anisotropically. All hydrogen atoms were found on a ΔF map and were included in the refinement with an overall isotropic thermal parameter [$U_{iso} = 0.056(4)$ Å^2]. A secondary extinction coefficient was introduced in the final stage of the refinement. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and each reflection was assigned a unit weight. Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 19. The refinement converged at R and R' values of 0.038 and 0.045, respectively. The goodness of the fit is 1.8. The final Fourier-difference map showed residual maxima and minima of 0.43 and -0.46 e Å^{-3}. All crystallographic calculations were performed on a VAX 725 computer and the molecular plot was drawn with the ORTEP[20] program. The final atomic coordinates for non-hydrogen atoms and interatomic bond lengths and angles are listed in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Description of the Structure.—The structure of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ consists of neutral centrosymmetric dinuclear copper(II) units in which dmaeoxd and cyanate groups act as bis(terdentate) and unidentate ligands, respectively. A perspective view of the dinuclear entity with the atomic numbering scheme is depicted in Fig. 1. An analysis of the crystal packing revealed no features of chemical relevance except the occurrence of hydrogen bonding between coordinated water and amide-oxygen and cyanate-oxygen atoms from two neighbouring units (see end of Table 3).

Each copper atom is surrounded by three nitrogen atoms [N(1), N(2) and N(3)] and two oxygen atoms [O(1) and O(3)] occupying the vertices of a square-based pyramid. The basal plane is built by the carbonyl oxygen O(1), amide N(1) and amine N(2) nitrogen atoms of the oxamidate ligand and the cyanate-nitrogen N(3) atom whereas the apical position is filled by the oxygen O(3) atom of a water molecule. The four equatorial atoms are practically coplanar with deviations from the least-squares planes lower than 0.075 Å, the copper atom being pulled out of this plane toward the apical site by 0.185 Å. The three copper–oxamide bond distances [1.928(2), 2.079(3)

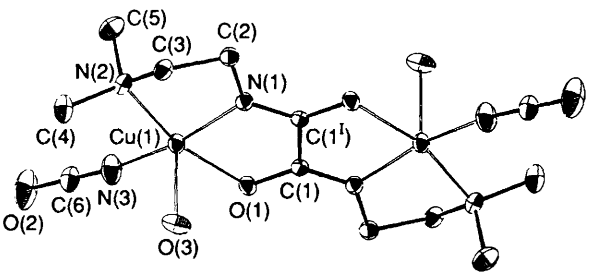


Fig. 1 An ORTEP view of [Cu_2(dmaeoxd)$(NCO)_2(H_2O)_2$] showing the atom labelling. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms have been omitted for clarity

Table 1 Summary of crystal data, intensity-data collection and structure refinement for [Cu_2(dmaeoxd)$(NCO)_2(H_2O)_2$]

Formula	$C_{12}H_{24}Cu_2N_6O_6$
M	475.4
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	11.589(3)
b/Å	12.456(1)
c/Å	6.771(2)
β/°	102.39(2)
U/Å^3	954.6(4)
Z	2
D_c/g cm^{-3}	1.82
F(000)	488
Crystal size/mm	0.55 × 0.45 × 0.30
μ(Mo-Kα)/cm^{-1}	22.7
Scan type	ω–2θ
Scan width	1.20 + 0.34 tan θ
θ range/°	1–30
No. of measured reflections	2559
No. of unique reflections[a]	2249
No. of refined parameters	157
$R\{=[\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]\}$	0.038
$R'\{=[\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$[b]	0.045

[a] $I \geqslant 3\sigma(I)$. [b] Unit weights.

Table 2 Final atomic coordinates for [Cu_2(dmaeoxd)$(NCO)_2(H_2O)_2$] with standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cu(1)	0.137 60(3)	0.107 49(3)	−0.197 50(6)
O(1)	−0.036 4(2)	0.064 8(2)	−0.237 8(3)
O(2)	0.116 0(3)	0.340 3(3)	−0.659 7(6)
O(3)	0.169 2(3)	−0.045 9(2)	−0.364 1(4)
N(1)	0.147 4(2)	0.038 0(2)	0.060 0(4)
N(2)	0.313 6(2)	0.142 4(2)	−0.072 8(4)
N(3)	0.116 0(3)	0.208 4(3)	−0.416 8(5)
C(1)	−0.052 1(2)	0.008 7(2)	−0.087 8(4)
C(2)	0.261 8(3)	0.032 9(3)	0.199 3(5)
C(3)	0.352 8(3)	0.054 0(3)	0.074 1(5)
C(4)	0.391 5(4)	0.148 5(4)	−0.219 5(7)
C(5)	0.317 6(4)	0.247 0(3)	0.033 1(8)
C(6)	0.116 1(3)	0.272 9(3)	−0.534 1(5)

Table 3 Interatomic distances (Å) and angles (°) for [Cu_2(dmaeoxd)-$(NCO)_2(H_2O)_2$] with e.s.d.s in parentheses[a]

Copper environment			
Cu(1)–O(1)	2.046(2)	Cu(1)–N(3)	1.920(3)
Cu(1)–N(1)	1.928(2)	Cu(1)–O(3)	2.288(3)
Cu(1)–N(2)	2.079(3)		
O(3)–Cu(1)–O(1)	85.0(1)	O(1)–Cu(1)–N(1)	82.49(9)
O(3)–Cu(1)–N(1)	95.0(1)	O(1)–Cu(1)–N(2)	164.01(9)
O(3)–Cu(1)–N(2)	97.4(1)	N(1)–Cu(1)–N(2)	82.2(1)
O(3)–Cu(1)–N(3)	100.0(1)	N(1)–Cu(1)–N(3)	165.0(1)
O(1)–Cu(1)–N(3)	96.1(1)	N(2)–Cu(1)–N(3)	97.5(1)
dmaeoxd ligand			
C(1)–O(1)	1.278(3)	C(1)–C(3)	1.511(4)
C(1)–C(1^{I})	1.518(5)	C(3)–N(2)	1.489(4)
C(1^{I})–N(1)	1.297(4)	N(2)–C(5)	1.483(5)
N(1)–C(2)	1.455(4)	N(2)–C(4)	1.481(5)
C(1)–O(1)–Cu(1)	109.9(2)	C(2)–C(3)–N(2)	110.7(3)
O(1)–C(1)–C(1^{I})	118.4(3)	C(3)–N(2)–C(5)	110.7(3)
O(1)–C(1)–N(1^{I})	129.2(3)	C(3)–N(2)–C(4)	122.9(3)
C(3)–N(3)–C(4)	115.9(3)	N(1)–C(4)–N(3)	110.1(3)
C(1^{I})–C(1)–N(1^{I})	112.4(3)	C(3)–N(2)–Cu(1)	104.4(2)
C(1^{I})–N(1)–Cu(1)	116.5(2)	C(5)–N(2)–C(4)	108.6(3)
C(1^{I})–N(1)–C(2)	124.9(3)	C(5)–N(2)–Cu(1)	107.8(2)
C(2)–N(1)–Cu(1)	118.3(2)	C(4)–N(2)–Cu(1)	115.1(2)
N(1)–C(2)–C(3)	106.1(2)		
Cyanate ligand			
O(2)–C(6)	1.195(4)	N(3)–C(6)	1.130(4)
N(3)–C(6)–O(2)	179.4(5)	C(6)–N(3)–Cu(1)	171.6(3)

Hydrogen bonds[b]

A	D	H	A···D	A···H–D
O(1)	O(3^{II})	H(2^{II})	2.812(3)	166(4)
O(2)	O(3^{III})	H(1^{III})	2.839(4)	171(4)

[a] Symmetry translations: I $-x, -y, -z$; II $-x, -y, -z - 1$; III $\frac{1}{2} - x, \frac{1}{2} + y, -z - 1$. [b] A = Acceptor, D = donor atom.

and 2.046(2) Å for Cu(1)–N(1), Cu(1)–N(2) and Cu(1)–O(1), respectively] are very similar to those found in the parent [Cu_2(dmaeoxd)$(NCS)_2(dmf)_2$](dmf = dimethylformamide).[21] The difference between the Cu(1)–N(1) and Cu(1)–N(2) bond lengths reflects the different basicities of the amine and deprotonated amide nitrogen atoms (see below). The copper–nitrogen (cyanate) bond distance [1.920(3) Å for Cu(1)–N(3)] compares well with those observed in other copper(II) complexes containing terminally *N*-bonded cyanate.[8,22] The axial Cu(1)–O(3) (water) bond distance [2.288(3) Å] is slightly elongated compared with the Cu–O (dmf) bond length (2.217 Å) of the thiocyanate salt. The value of the τ index[23] is 0.02.

Distortion of the metal environment is evident from the somewhat depressed values found for the N(1)–Cu(1)–N(2) and N(1)–Cu(1)–O(1) angles [82.2(1) and 82.49(9)°, respectively] which belong to two adjacent five-membered chelate rings.

The deprotonated dmaeoxd^{2-} ligand exhibits the *trans* conformation with an inversion centre at the middle of the C(1)–C(1^{I}) bond. It forms two five-membered chelate rings around each metal ion. These chelate rings are far from planar, the maximum deviations from the average planes being 0.292 Å [C(3)] for Cu(1)N(1)C(2)C(3)N(2) and 0.034 Å [N(1)] for Cu(1)O(1)C(1)C(1^{I})N(1). The three atoms around N(1) lie in a plane with bond angles of 124.9(3), 118.3(2) and 116.5(2)° for C(1^{I})–N(1)–C(2), C(2)–N(1)–Cu(1) and C(1^{I})–N(1)–Cu(1), respectively. This fact together with the value of the C(1^{I})–N(1) bond length [1.297(4) Å] and the planarity of the oxamidato bridge support the sp^2 hybridization for N(1) and π bonding in the NCO (amide) fragment. These structural features have been observed in other oxamidato-bridged copper(II) complexes and are the reason for the remarkable efficiency of the oxamidate group to transmit a strong antiferromagnetic coupling between paramagnetic centres at distances greater than 5 Å.[1,6c,8,10,21,24] Mean planes through N(1)O(1)N(3)N(2) and N(1)C(1^{I})O(1^{I})-C(1)O(1)N(1^{I}) form a dihedral angle of 4.04°. The value of the C(1)–C(1^{I}) bond length [1.518(5) Å] is as expected for a single carbon–carbon bond. The cyanate group is practically linear [179.4(5)° for N(3)–C(6)–O(2)] whereas the Cu(1)–N(3)–C(6) linkage is somewhat bent [171.6(3)°]. The cyanate dimensions [1.195(4) and 1.130(4) Å for C(6)–O(2) and C(6)–N(3)] agree with those in other structurally characterized *N*-bonded

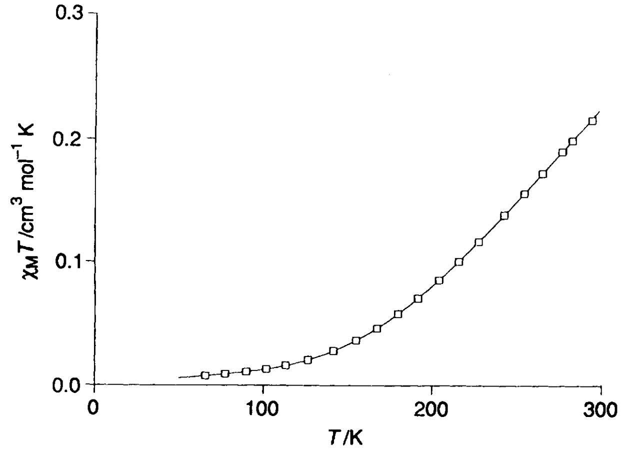


Fig. 2 Temperature dependence of the molar magnetic susceptibility for $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$; ——, theoretical

Table 4 Equilibrium data* for basicity and formation of copper(II) complexes with L^{2-} in aqueous solution at 25 °C and I = 0.1 mol dm^{-3} $NaNO_3$

Equation	Reaction	log β
(i)	$2H^+ + L^{2-} \rightleftharpoons H_2L$	24.0(2)
(ii)	$H^+ + H_2L \rightleftharpoons H_3L^+$	8.63(1)
(iii)	$2H^+ + H_2L \rightleftharpoons H_4L^{2+}$	16.46(1)
(iv)	$2Cu^{2+} + H_2L \rightleftharpoons [Cu_2(H_2L)]^{4+}$	10.11(3)
(v)	$2Cu^{2+} + H_2L \rightleftharpoons [Cu_2(HL)]^{3+} + H^+$	5.52(2)
(vi)	$2Cu^{2+} + H_2L \rightleftharpoons [Cu_2L]^{2+} + 2H^+$	0.74(1)
(vii)	$3Cu^{2+} + 2H_2L \rightleftharpoons [Cu_3L_2]^{2+} + 4H^+$	−3.13(1)
(viii)	$4Cu^{2+} + 3H_2L \rightleftharpoons [Cu_4L_3]^{2+} + 6H^+$	−7.91(2)
(ix)	$Cu^{2+} + H_2L \rightleftharpoons [CuL] + 2H^+$	−7.08(1)

* Values in parentheses are standard deviations in the last significant digit.

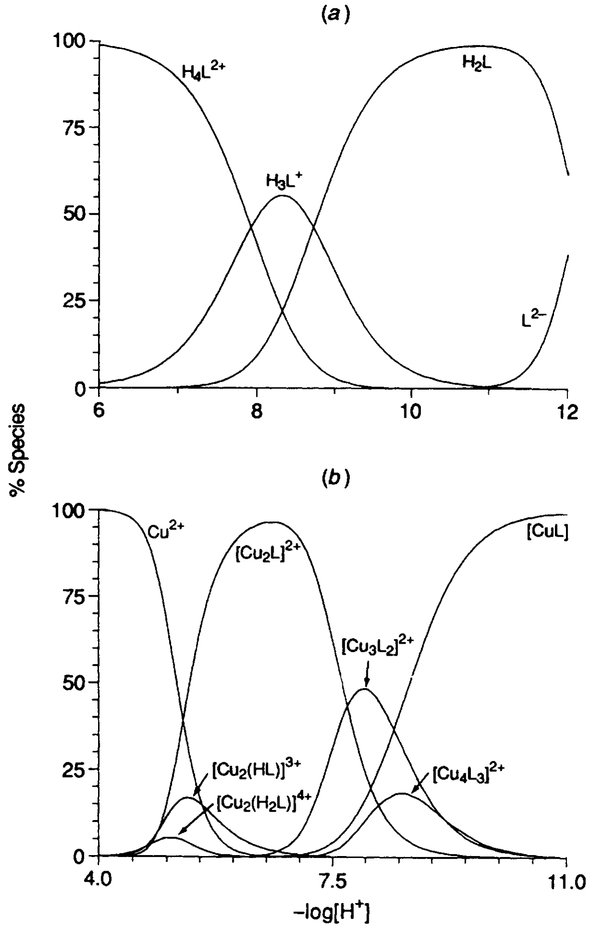


Fig. 3 Calculated distribution diagram for systems H^+–L^{2-} (*a*) and H^+–L^{2-}–Cu^{2+} (*b*) as a function of pH ($c_M = c_L = 5 \times 10^{-3}$ mol dm^{-3})

cyanate complexes.[8,22,25] It is relevant that the value of the cyanate C–N distance tends toward what would be expected for a carbon–nitrogen triple bond. The intramolecular Cu(1) ··· Cu(1^I) separation is 5.306(1) Å whereas the shortest intermolecular metal–metal distance is slightly longer [5.340(1) Å for Cu(1) ··· Cu(1^{II})]. This latter interaction involves the hydrogen bond between O(1) and O(3^{II}).

Magnetic Properties and ESR Spectrum.—The temperature dependence of the molar magnetic susceptibility (χ_M) of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ in the form $\chi_M T$ *versus* T is shown in Fig. 2. The reduced value of the magnetic moment at room temperature (1.36) is indicative of a strong antiferromagnetic coupling between copper(II) ions and the magnetic behaviour with temperature confirms this situation. According to its crystal structure, the magnetic simulation was carried out by a simple Bleaney–Bowers equation[26] (1). In this

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[3 + \exp(-J/kT)]^{-1} \qquad (1)$$

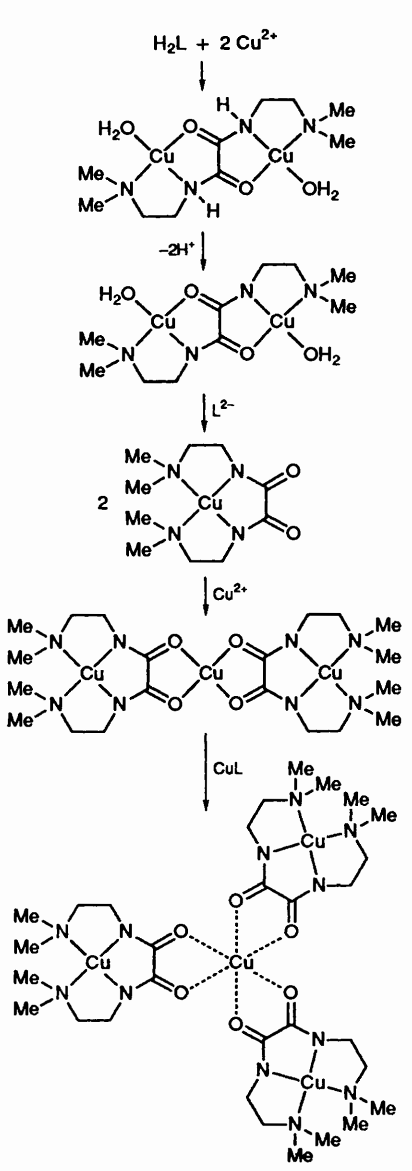
expression N, g, β, k and T have their usual meanings and J is the singlet–triplet energy gap. A least-squares fit of the experimental data led to $J = -560$ cm^{-1}, $g = 2.12$ and $R = 1.0 \times 10^{-5}$ where R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$.

The EPR spectrum of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ recorded at room temperature shows an asymmetric feature at $g = 2.10$ and no signal at half-field. The spectrum vanishes on lowering the temperature, supporting the triplet nature of the observed feature. The lack of signal at 4.2 K rules out the presence of any copper(II) monomeric impurity.

The obtained J value is close to reported ones for other structurally characterized oxamidato-bridged copper(II) complexes. The singlet–triplet energy separation in this family of complexes falls in the range 488–580 cm^{-1} and the remarkable ability of the oxamidato bridge to transmit the exchange interaction between two copper(II) ions when the magnetic orbitals are in the plane of the oxamidato ligand has been analysed by means of orbital models and extended-Hückel calculations.[3,6c]

Solution Study.—The calculated proton association constants of L^{2-} together with the stability constants of its copper(II) complexes are listed in Table 4. The values of the protonation constants of the ligand show that whereas it behaves as a relatively strong base in the two first protonation steps [equation (i)], its basicity decreases by about six orders of magnitude for the further protonation [equation (iii)]. This different basicity can be understood by taking into account that equation (i) involves the protonation of amide-nitrogen atoms whereas (iii) corresponds to protonation of the amine-nitrogen ones. The distribution diagram for H^+–L^{2-} is depicted in Fig. 3(*a*). The only species at pH < 6 is H_4L^{2+} whereas the triprotonated ligand predominates only in a narrow pH range (7.8–8.8). The neutral species H_2L is the major one at pH > 8.8 and it deprotonates at pH > 11 to yield the fully deprotonated L^{2-} ligand. At the limit of the potentiometric data that we have treated, 20% of L^{2-} is present. The high value of the overall protonation constant concerning the oxamidato group accounts for its great basicity and is identical to those previously

Scheme 1



Scheme 2

reported for the parent *N*,*N*′-substituted oxamides.[1,7,8,10] As far as the protonation of the amine-nitrogen atoms of H_2L is concerned, the calculated value [log β_2 = 16.46(1)] is about two orders of magnitude smaller than that reported for the parent H_2dmapoxd [log β_2 = 18.34(1)].[1] However, the values of the logarithms of the stepwise protonation constants of the amino groups of H_2L are within the range observed for aliphatic amines.[27]

The stability constants corresponding to equations (iv)–(ix) in Table 4 summarize the complex-forming ability of H_2L with regard to Cu^{II}. The distribution diagram of this system as a function of pH is depicted in Fig. 3(*b*). The copper(II) species $[Cu_2(H_2L)]^{4+}$ and $[Cu_2(HL)]^{3+}$ are formed at low pH values and their degrees of formation are not greater than 16%. The dinuclear complex $[Cu_2L]^{2+}$ is the main species under neutral conditions and in a relatively wide pH range (4.2–7.6), whereas the trinuclear $[Cu_3L_2]^{2+}$, tetranuclear $[Cu_4L_3]^{2+}$ and mononuclear [CuL] complexes are sequentially formed at greater pH values. The latter neutral species is the predominant one at pH ⩾ 8.5 and is the only complex at pH ⩾ 10.5. The present pattern of complex formation differs substantially from that previously reported for the related Cu^{II}–H_2dmapoxd system and is identical to that observed for Cu^{II}–H_2apoxd and H_2mapoxd systems.[1] Only dinuclear species are formed in the case of Cu^{II}–H_2dmapoxd because the *cis* conformation of dmapoxd^{2-} is prohibited due to steric hindrance between the methyl amine groups. The fact that *n* = 2 in dmaeoxd^{2-}, increases the separation between the methyl amine groups and allows the adoption of the *cis* conformation in addition to the *trans* one (Scheme 1) and consequently, makes possible the formation of mono-, di, tri- and tetra-nuclear complexes (see Scheme 2). The *trans* conformation of L^{2-} is restricted to the homodinuclear species M_2L^{2+} as illustrated by the structure of $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$. The bis(terdentate) character of L^{2-} is reflected by the high value of the logarithm of the stability constant of $[Cu_2L]^{2+}$[log β = 24.74, equation (2)], although somewhat smaller than those reported

$$2Cu^{2+} + L^{2-} \rightleftharpoons [Cu_2L]^{2+} \qquad (2)$$

for $[Cu_2(apoxd)]^{2+}$ (log β = 28.1) and $[Cu_2(mapoxd)]^{2+}$ (log β = 26.41). The presence of two adjacent five-membered chelate rings around copper(II) in $[Cu_2(dmaeoxd)]^{2+}$ instead of the six- and five-membered fused chelates in the other two complexes on the one hand and the increasing number of methyl amino groups when going from apoxd^{2-} to dmaeoxd^{2-} account for this difference.[2] The great stability of these dinuclear copper(II) species reveals that deprotonated oxamides are highly selective ligands for copper(II). In fact they do not form complexes with other metal ions.

The formation of di-, tri- and tetra-nuclear species starting from the neutral mononuclear [CuL] species can be analysed in the light of the values of the logarithms of the stepwise stability constants corresponding to equations (3)–(5): log K_1 = 7.82,

$$Cu^{2+} + [CuL] \overset{K_1}{\rightleftharpoons} [Cu(CuL)]^{2+} \qquad (3)$$

$$[Cu(CuL)]^{2+} + [CuL] \overset{K_2}{\rightleftharpoons} [Cu(CuL)_2]^{2+} \qquad (4)$$

$$[Cu(CuL)_2]^{2+} + [CuL] \overset{K_3}{\rightleftharpoons} [Cu(CuL)_3]^{2+} \qquad (5)$$

log K_2 = 3.21 and log K_3 = 2.30. Although the trend exhibited by these values is as expected ($K_1 > K_2 > K_3$), too large a difference is observed between the first and second. Such an anomaly can be explained by considering the energetic cost involved in the *cis*–*trans* conformational change for L which is involved in equations (3) and (4). The ligand moves from the *cis* conformation in [CuL] to *trans* in $[Cu_2L]^{2+}$ [equation (3)] and further from the *trans* (dinuclear species) to the *cis* {$[Cu_3L_2]^{2+}$, equation (4)} (see Scheme 2). No conformational change occurs in reaction (5). In this respect, the energy cost of the *cis*–*trans* conformational change (Scheme 1) was estimated as log *K* = 1.6.[8] The corrected values of the stepwise stability constants (log K_1 = 7.82 − 1.6 = 6.22 and log K_2 = 3.21 + 1.6 = 4.81) are closer and fit better the expected trend from a purely statistical viewpoint.

As far as the neutral mononuclear [CuL] complex is concerned, the logarithm of the stability constant for the equilibrium $Cu^{2+} + L^{2-} \rightleftharpoons [CuL]$ (log β = 16.92) is very close to that reported for [Cu(mapoxd)] (log β = 17.09)[1] and three orders of magnitude smaller than that obtained for [Cu(apoxd)] (log β = 20.2).[8] They are very stable species which exhibit 6-5-6 (apoxd and mapoxd) and 5-5-5 (dmaeoxd) member fused chelates around copper(II), the *N*,*N*′-substituted oxamides acting as tetradentate ligands. It seems that the methylation of the amine pendant groups decreases the stability of the resulting mononuclear oxamidato complexes and calorimetric data would be required to analyse this trend.

The distribution diagram of the system Cu^{II}–dmaeoxd^{2-} [Fig. 3(*b*)] provides adequate information to prepare the dmaeoxd-containing copper(II) complexes. The dinuclear $[Cu_2L]^{2+}$ and mononuclear [CuL] complexes are the predominant species over wide pH ranges at $c_M = c_L = 5 \times 10^{-3}$ mol dm^{-3} ($5.5 \leqslant$ pH $\leqslant 7.5$ and pH > 8.5, respectively). In the present work we have isolated the former species as a cyanate complex from aqueous solution containing stoichiometric amounts of copper(II) and dmaeoxd^{2-}. The insolubility of this complex led us to use slow diffusion techniques in order to grow single crystals (see Experimental section). The formation of the trinuclear $[Cu_3L_2]^{2+}$ and tetranuclear $[Cu_4L_3]^{2+}$ complexes is much favoured when using the corresponding stoichiometric c_M/c_L molar ratios and they could be readily isolated from their aqueous solutions as shown recently for L = apoxd.[8]

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