mononuclear complexes that we have isolated as tetra- and pentahydrate sodium salts, respectively.

The synthesis of M_2L complexes was carried out in the light of the respective distribution diagrams based on fitted equilibrium constants (Figures 4 and 5). In order to obtain single crystals of such species, aqueous solutions of copper(II) nitrate (nickel(II) nitrate) and H_4L in a 2:1 molar ratio were prepared at pH = 3. In the case of copper(II), the slow polymerization of $Cu(H_2L)$ leads to the insoluble polymeric complex **1**. Nevertheless, $Cu_2L\cdot 6H_2O$ can be isolated as a powder in weakly acidic aqueous solutions. The nonpolymerization of the $Ni(H_2L)$ species allows in this case the formation of single crystals of the insoluble complex **2** in nearly neutral aqueous solutions.

Conclusions. The versatility of N,N'-disubstituted oxamides has allowed the synthesis of mono-, di-, and polynuclear complexes. Strong antiferromagnetic coupling is observed in the μ-oxamidato polynuclear compounds. This work shows how one must be careful when using the $n^2|J|$ values to estimate the magnitude of the exchange coupling in binuclear nickel(II) complexes from the known values for the corresponding copper(II) complexes through a given bridge. Although nickel(II)-oxamide complexes are usually diamagnetic, paramagnetic nickel(II) species can be obtained by tuning the strength of the ligand field using as tools appropriate N-substituted derivatives and angular strain. Finally, this report provides a new example of complementarity between solution and solid-state studies, showing how solution data can orientate the synthetic work in order to obtain the desired products.

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Registry No. **1**, 138490-13-8; **2**, 138490-14-9; H_4L, 23354-00-9; $Cu_2L(H_2O)_6$, 138490-15-0; $Ni(H_2L)(H_2O)_3$, 138516-45-7.

Supplementary Material Available: For **1** and **2**, stereoviews showing the crystal packing and listings of crystallographic data (Table S1), anisotropic thermal parameters (Tables S2a and S2b), bond distances and angles involving hydrogen atoms (Tables S3a and S3b), hydrogen-bonding data (Tables S4a and S4b), and torsional angles (Tables S5a and S5b) (11 pages); listings of calculated and observed structure factors (Tables S6a and S6b) (25 pages). Ordering information is given on any current masthead page.

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Oxamidato Complexes. 3. A Study of the Formation of Homo- and Heteropolymetallic Cu(II)–H_2apox–M(II) Complexes (H_2apox = *N*,*N*'-Bis(3-aminopropyl)oxamide; M(II) = Mn, Co, Ni, Cu, Zn, Cd). Synthesis and Crystal Structure of $[Cu_2(apox)(NCO)_2]$

Francesc Lloret,*[1a] Miguel Julve,[1a] Juan Faus,[1a] Rafael Ruiz,[1a] Isabel Castro,[1a] Miquel Mollar,[1a]
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Potentiometric studies on the quaternary system Cu^{2+}–M^{2+}–$apox^{2-}$–H^+ (M = Mn, Co, Ni, Zn, Cd; $apox^{2-}$ = dianion of *N*,*N*'-bis(3-aminopropyl)oxamide, $C_8H_{18}N_4O_2$ (L^{2-})) have been carried out at 25 °C and 0.1 mol dm^{-3} $NaNO_3$. The proton association constants corresponding to the equilibria $L^{2-} + jH^+ \leftrightarrow H_jL^{(j-2)+}$ (β_j) were found to be log β_2 = 24.0 (2), log β_3 = 34.15 (2), and log β_4 = 43.60 (2). The values of the stability constants related to the equilibria $pCu^{2+} + qL^{2-} \leftrightarrow [Cu_pL_q]^{2(p-q)+}$ (β_{pq}) were log β_{11} = 20.33 (2), log β_{21} = 28.15 (2), log β_{32} = 51.68 (4), and log β_{43} = 74.35 (7), and those concerning the equilibria $pM^{2+} + qCu^{2+} + rL^{2-} \leftrightarrow [M_pCu_qL_r]^{2(p+p-r)+}$ (β_{pqr}) were log β_{111} = 23.86 (2) (Mn), 24.31 (2) (Co), 24.86 (2) (Ni), 24.87 (2) (Zn), and 23.80 (2) (Cd); log β_{122} = 46.79 (3) (Mn), 47.77 (3) (Co), 48.70 (4) (Ni), 48.81 (4) (Zn), and 46.90 (3) (Cd); and log β_{133} = 69.58 (3) (Mn), 70.66 (4) (Co), 72.30 (5) (Ni), 72.04 (5) (Zn), and 69.60 (3) (Cd). Since the ligand L^{2-} can exhibit both cis and trans conformations in its metal complexes, we have carried out an ab initio calculation to determine the energy involved in such conformational change using $(CH_3NCO)_2^{2-}$ as a model system. The trans conformation is predicted to lie 2.25 kcal below the cis one. Both the sign and magnitude of this result are in good agreement with our experimental data, and this result accounts for the anomalies observed in the values of the stepwise stability constants. The molecular structure of the complex $[Cu_2L(NCO)_2]$ has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13.237 (3) Å, b = 7.715 (3) Å, c = 7.161 (3) Å, β = 94.02 (1)°, and Z = 2. Refinement of the atomic parameters by least-squares techniques gave a final R factor of 0.036 (R_w = 0.039) for 1101 unique reflections having $I \geq 3\sigma(I)$. The structure consists of neutral one-dimensional chains of copper(II) ions bridged alternatively by the oxamidato and cyanato groups. The former acts as a bis-terdentate bridge whereas the latter is bound through nitrogen in an end-on fashion. The copper environment can be described as square pyramidal: the equatorial plane is defined by the oxygen and nitrogen atoms of the amide, the nitrogen atom of the amine group, and the nitrogen atom of the cyanato ligand whereas the apical position is filled by a nitrogen atom of another cyanato group. The values of the stability constants of the system Cu^{2+}–M^{2+}–L^{2-} are compared and discussed in light of the available structural data.

Introduction

For more than a decade, the design and synthesis of heteropolymetallic complexes have been a challenging field for inorganic chemists.[2] In general, the strategies to synthesize these species are based (i) on the use of dissymmetric polynucleating ligands,[3] (ii) on the use of both the kinetic and thermodynamic stability "self-assembly method",[4] or (iii) on working step by step by using "complexes as ligands".[5] A nice example of this latter case is represented by the (oxamidato)copper(II) complexes.[6] Although

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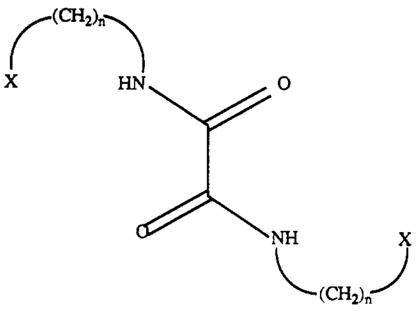
the chelating properties of oxamidate are similar to those of oxalate, the simultaneous presence of nitrogen and oxygen donor atoms in the former offers the possibility of synthesizing heteropolymetallic complexes very easily in contrast to the latter case. *N,N'*-Bis(coordinating group substituted)oxamides (I) are more



H_2apox (X = NH_2 , n = 3)

I

reluctant to hydrolyze and are much more soluble. Moreover, if the substituted oxamide can form a five- or six-membered chelate ring, in the presence of metal ions, the amide dissociates and coordinates simultaneously in an unexpectedly low pH range.[6] (Oxamidato)copper(II) complexes have been used to design and synthesize new topologies in inorganic complexes,[7] high-spin molecules with an irregular spin structure,[8] and also the very exciting molecular-based ferromagnets.[9]

In contrast to the great efforts devoted to the study of oxamidato complexes in the solid state,[6–11] studies concerning their formation in solution are uncomprehensibly scarce.[6b,c,12] In fact, knowledge of the existing species in solution is very important in order to synthesize both mononuclear and polynuclear species.[13]

In this paper, we investigate the protonation of the ligand apox^{2-} (dianion of *N,N'*-bis(3-aminopropyl)oxamide, H_2L) and its complex formation with copper(II) in aqueous solution. Some years ago, it was observed that the mononuclear [CuL] complex could act as a bidentate chelating agent toward a second metal ion to form homo and hetero di-, tri-, and tetranuclear complexes.[14–16] Consequently, we have investigated the formation of these polynuclear species in the system M^{2+}–Cu^{2+}–L^{2-}–H^+ (M = Mn, Co, Ni, Zn, Cd) by potentiometry. The structure of the complex $[Cu_2L(NCO)_2]$ is also reported herein, and as far as we are aware, it is the first structure reported in which the apox^{2-} ligand exhibits the trans conformation. We have estimated the energy involved in the cis–trans conformational change of apox^{2-} by an ab initio calculation.

Table I. Structural Parameters for the Cis[a] and Trans[b] Conformations

Bond Distances (Å)

	cis	trans		cis	trans
C(1)–C(8)	1.49	1.51	C(1)–N(3)	1.30	1.30
C(1)–O(2)	1.29	1.28	N(3)–C(4)	1.46	1.47

Bond Angles (deg)

	cis	trans
O(2)–C(1)–C(8)	116.0	117.7
N(3)–C(1)–C(8)	116.0	114.5
C(1)–N(3)–C(4)	118.0	118.0

[a] Structural parameters from CuL fragment of the trinuclear $[Cu_3L_2](ClO_4)_2$ complex. [b] Average values from the dinuclear $[Cu_2L(NCO)_2]$ and $[Cu_2L(NCS)_2]\cdot H_2O$ complexes (see text).

Experimental Section

Materials. All chemicals were of reagent grade quality and were obtained from commercial sources. They were used without further purification. Carbonate-free NaOH (0.1 mol dm^{-3}) and HNO_3 (0.1 mol dm^{-3}) were used in the potentiometric titrations. All potentiometric measurements were carried out in 0.1 mol dm^{-3} $NaNO_3$ as background electrolyte.

Ligand and Complex Preparations. The ligand *N,N'*-bis(3-aminopropyl)oxamide (H_2L)[17] and its metal complexes [CuL],[14] $[Cu_3L_2](ClO_4)_2$,[15] $[NiCu_2L_2(H_2O)_2](ClO_4)_2$,[15] $[ZnCu_2L_2(H_2O)_2](ClO_4)_2$,[15] $[MCu_3L_3](ClO_4)_2\cdot 2H_2O$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+})[9] were synthesized by following the procedures described in the literature.

$[Cu_2L(NCO)_2]$ was obtained as follows: Aqueous solutions of copper(II) perchlorate (1 mmol, 10 mL) and [CuL] (1 mmol, 50 mL) were mixed with stirring. The resulting blue solution was filtered, and a blue precipitate separated upon slow addition of an aqueous solution of NaNCO (2 mmol, 20 mL). The solid was filtered off, washed with water, and dried in a desiccator over silica gel. Anal. Calc for $C_{10}H_{16}Cu_2N_6O_4$: C, 29.20; H, 3.92; N, 20.43. Found: C, 29.11; H, 3.98; N, 20.35. Blue single crystals of $[Cu_2L(NCO)_2]$ were obtained by slow diffusion of aqueous solutions of $[Cu_2L]^{2+}$ and cyanate in an H-shaped tube.

Physical Techniques. IR spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets. UV–vis solution spectra as well the reflectance spectra of the complexes as Nujol mulls on filter paper were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, microcomputer, etc.) that has been previously described.[6b] The temperature of all solutions was held at 25.0 °C by circulating constant-temperature water through the water-jacketed titration cell. The standard potential of the cell, *E*°, was determined by the Gran method.[18] The computer programs SUPERQUAD[19] and BEST[20] were used to process emf data from each experiment and calculate the equilibrium constants. In all the cases, both computer programs provided very close results in their refinement processes. The slight differences observed can be attributed to the different weighting schemes. So, the constants reported herein are the mean values.

Ab Initio Calculations. Theoretical ab initio calculations to evaluate the energy gap associated with the cis–trans conformational change of L^{2-} were performed on the model system *N,N'*-dimethyloxamidate(2–), $(CH_3NCO)_2{}^{2-}$. This model along with the atom-numbering scheme is shown in II. Only twisting around the C–C bond was considered in the calculations (i.e. varying the internal dihedral angle β between 0 and

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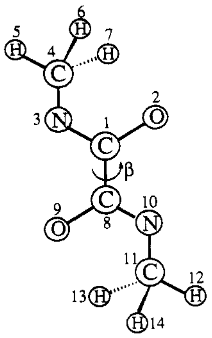

II

180°). The rest of the molecule was treated as rigid. Atoms 1–5 define one plane, while the other one comprises atoms 8–12. The geometrical data used to set up the Cartesian coordinates of the model are gathered in Table I. As far as the cis conformation is concerned, the values of the C—C, C═O, and C—N bond lengths and amide angles were taken from X-ray data for the Cu(apox) fragment in the trimer $[Cu_3L_2](ClO_4)_2$.[15] For the trans conformation, the values used were the mean ones for the dimeric complexes $[Cu_2L(NCO)_2]$ (vide infra) and $[Cu_2L(NCS)_2(H_2O)]$.[21] The standard bond length value of 1.10 Å was used for the C-H bond. The H-C-N angle was treated as tetrahedral.

The sophistication of the method was restricted to the SCF level of approximation without including a CI analysis (vide infra). The SCF calculations were performed with the minimal STO-3G and the split-valence 4-31G basis of Pople[22] (i.e. 46 and 84 base functions, respectively). The computations were performed on a VAX-3600 computer using a standard Gaussian 86 package of programs.[23] We took advantage of symmetry considerations to reduce the number of calculations (i.e. C_{2v} and C_{2h} for the cis and trans conformers, respectively).

Crystallographic Data Collection and Refinement of the Structure. A prismatic crystal of $[Cu_2L(NCO)_2]$ with approximate dimensions 0.45 × 0.40 × 0.30 mm was mounted on a Philips PW1100 diffractometer and used for data collection. Intensity data were collected by using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) with the θ–2θ scan technique where the scan width was $(1.3 + 0.34 \tan\theta)°$. Accurate unit-cell dimensions were obtained from least-squares refinement of 25 reflections in the 15–16° θ range. A summary of the crystallographic data is reported in Table II. A full-length table of crystallographic data is given as supplementary material (Table S1). The intensities of two standard reflections measured every 2 h showed no systematic variation. Intensities were corrected for Lorentz, polarization, and absorption effects, the transmission factors ranging between 0.85 and 1.00 (an absorption correction was applied by use of DIFABS[24]). Of the 1232 measured independent reflections, 1101 were unique with $I \geq 3\sigma(I)$ and were used for the structure refinement.

The structure was solved by Patterson methods and subsequent Fourier maps. Full-matrix least-squares refinements were carried out (102 parameters) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located from a ΔF map, except those of C(3) and C(4), which were geometrically positioned because of the rather high thermal agitation of these carbon atoms. Hydrogen atom positions were not refined, and they were assigned an overall isotropic thermal parameter. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Each reflection was assigned a unit weight. The scattering factors of all atoms and the anomalous dispersion correction term for Cu were taken from ref 25. The computer program CRYSTALS[25] was used in the crystallographic calculations. The final values of the discrepancy indices, R and R_w were 0.036 and 0.039, respectively. The final difference-Fourier map shows residual maxima and minima of 0.61 and −0.59 e Å^{-3}, the maxima of electronic density being located in the vicinity of C(3) and C(4). We tried to solve the disorder problem concerning C(3) and C(4), but it was not possible to find (after isotropic refinement) other positions giving a reasonable geometry, in order to introduce atoms with various occupancy factors. The goodness of fit is 1.49. The final atomic coordinates for non-hydrogen atoms and bond distances and angles are listed in Tables III and IV, respectively. Crystallographic calculations were performed on a VAX725 computer, and figures for the crystal structure were drawn by the ORTEP[26] program. Anisotropic thermal parameters, positional parameters for hydrogen atoms, least-squares planes, and observed and

Table II. Crystallographic Data for $[Cu_2(apox)(NCO)_2]$

chem formula	$C_{10}H_{16}Cu_2N_6O_4$
mol wt	411.4
space group	$P2_1/n$
a, Å	13.237 (3)
b, Å	7.715 (3)
c, Å	7.161 (3)
β, deg	94.02 (1)
V, Å^3	729.5 (7)
Z	2
temp, °C	18
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.87
μ, cm^{-1}	29.5
transm coeff	0.85–1.00
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.036
$R_w{}^a = [\sum w(\Delta F)^2/\sum wF_o{}^2]^{1/2}$	0.039

[a] Unit weights.

Table III. Atomic Coordinates and Thermal Parameters[a,b] for Non-Hydrogen Atoms of $[Cu_2(apox)(NCO)_2]$

Atom	x/a	y/b	z/c	10^4U_{eq}, Å^2
Cu(1)	−0.07972 (4)	0.02922 (8)	−0.34392 (8)	324
O(1)	−0.0023 (3)	−0.1463 (4)	−0.1891 (4)	354
O(2)	−0.1558 (4)	−0.3314 (7)	−0.7809 (7)	727
N(1)	−0.0758 (3)	0.1612 (5)	−0.1103 (5)	323
N(2)	−0.1465 (3)	0.2159 (6)	−0.5007 (6)	459
N(3)	−0.0953 (3)	−0.1353 (6)	−0.5497 (6)	422
C(1)	0.0202 (3)	−0.0876 (6)	−0.0235 (6)	290
C(2)	−0.1169 (4)	0.3339 (7)	−0.0764 (8)	426
C(3)	−0.1413 (9)	0.430 (1)	−0.252 (1)	799
C(4)	−0.1837 (9)	0.371 (1)	−0.411 (1)	792
C(5)	−0.1265 (4)	−0.2305 (7)	−0.6619 (8)	432

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

Table IV. Bond Lengths (Å) and Angles (deg) for $[Cu_2(apox)(NCO)_2]$[a,b]

	Bond Distances		
Cu(1)–N(1)	1.956	C(1)–N(1)	1.297 (6)
Cu(1)–N(2)	1.994 (4)	N(1)–C(2)	1.466 (6)
Cu(1)–N(3)	1.945 (4)	C(2)–C(3)	1.480 (9)
Cu(1)–O(1)	1.989 (3)	C(3)–C(4)	1.31 (1)
Cu(1)–N(3)^{ii}	2.620 (4)	C(4)–N(2)	1.464 (9)
O(1)–C(1)	1.284 (5)	O(2)–C(5)	1.198 (7)
C(1)–C(1)^{i}	1.501 (9)	C(5)–N(3)	1.144 (6)
	Bond Angles		
N(1)–Cu(1)–O(1)	84.0 (1)	O(1)–C(1)–C(1)^{i}	117.5 (5)
N(1)–Cu(1)–N(2)	95.2 (2)	N(1)–C(1)–C(1)^{i}	114.9 (5)
N(2)–Cu(1)–N(3)	91.4 (2)	O(1)–C(1)–N(1)	127.6 (4)
N(3)–Cu(1)–O(1)	90.1 (2)	C(1)–N(1)–C(2)	118.2 (4)
N(1)–Cu(1)–N(3)	169.4 (2)	Cu(1)–N(1)–C(2)	128.8 (3)
N(2)–Cu(1)–O(1)	175.2 (2)	N(1)–C(2)–C(3)	112.2 (5)
N(1)–Cu(1)–N(3)^{ii}	96.6 (1)	C(2)–C(3)–C(4)	128.2 (8)
N(2)–Cu(1)–N(3)^{ii}	88.7 (2)	C(3)–C(4)–N(2)	121.9 (7)
N(3)–Cu(1)–N(3)^{ii}	91.8 (2)	C(4)–N(2)–C(1)	119.6 (4)
O(1)–Cu(1)–N(3)^{ii}	86.7 (1)	Cu(1)–N(3)–C(5)	164.8 (4)
Cu(1)–O(1)–C(1)^{i}	110.6 (3)	Cu(1)–N(3)–Cu(1)^{ii}	88.1 (3)
Cu(1)–N(1)–C(1)	112.6 (3)	N(3)–C(5)–O(2)	177.7 (6)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (i) $-x, -y, -z$; (ii) $-x, -y, -1 - z$.

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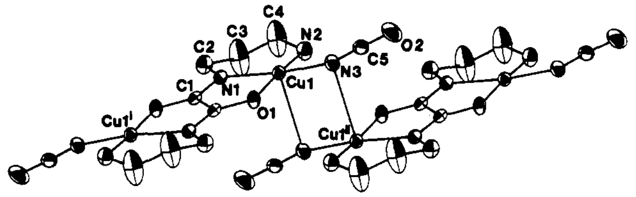

Figure 1. ORTEP view of the asymmetric unit and of three symmetry-related units of $[Cu_2(apox)(NCO)_2]$. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are not shown for simplicity.

calculated structure factors (Tables S2–5) are available as supplementary material.

Results and Discussion

Description of the Structure. The structure of $[Cu_2L(NCO)_2]$ consists of neutral zigzag chains of copper(II) ions bridged by both $apox^{2-}$ and cyanato groups. The former acts as a bis-terdentate ligand whereas the latter bridges copper atoms in an asymmetrical end-on fashion. A perspective view of the asymmetric unit along with the atom-labeling scheme and of three symmetry-related units is depicted in Figure 1. Inversion centers stand at the middle of the $C(1)-C(1)^{i}$ bond and $Cu(1)\cdots Cu(1)^{ii}$ distance. The packing of the chains parallel to the *c* axis is illustrated by means of a stereoview (supplementary material).

The coordination environment around the copper atoms can be described as a distorted square pyramid. The equatorial plane is defined by the oxygen (O(1)) and nitrogen (N(1)) atoms of the amide, the amine (N(2)) nitrogen, and the nitrogen (N(3)) atom of the cyanato ligand. The mean displacement of the four atoms from this plane is 0.11 Å. The N(1)–Cu(1)–N(3) and N(2)–Cu(1)–O(1) angles are 169.4 (2) and 175.2 (2)°, respectively. The axial coordination site is occupied by another nitrogen $(N(3)^{ii})$ atom of a cyanate group which is equatorially bound to the neighboring copper $(Cu(1)^{ii})$ atom. Each copper atom is displaced out of the equatorial plane toward the axial nitrogen by 0.033 Å. The two copper–nitrogen (cyanato) bonds are markedly different from each other, the equatorial being 1.945 (4) Å and the axial 2.620 (4) Å. The other three equatorial distances (1.956 (4), 1.989 (3), and 1.994 (4) for Cu(1)–N(1), Cu(1)–O(1), and Cu(1)–N(2), respectively) are close to those found in other analogous copper(II) complexes with oxamides.[6b,10,11,27-30]

The least-squares plane through the four closest donor atoms of Cu(1)(N(1)N(2)N(3)O(1)) forms a dihedral angle of 6.9° with the oxamidato plane $(O(1)N(1)C(1)O(1)^{i}N(1)^{i}C(1)^{i})$. The bis-tridentate character of the L^{2-} ligand produces one five- and one six-membered chelate metal cycle on each copper atom, the latter being markedly larger (95.2 (2)° for N(1)–Cu(1)–N(2)) than the former (84.0 (1)° for N(1)–Cu(1)–O(1)). The distance between the mean plane Cu(1)O(1)N(1)N(2)N(3) and the symmetry-related one of the $Cu(1)^{ii}$ atom is 2.524 Å. Mean planes Cu(1)O(1)N(1)N(2)N(3) and $Cu(1)N(3)Cu(1)^{ii}N(3)^{ii}$ form a dihedral angle of 90.7°. Cyanato bridges are quasi-linear (N(3)–C(5)–O(2) = 177.7 (6)°), whereas the Cu(1)–N–C(O) linkage is bent (Cu(1)–N(3)–C(5) = 164.8 (4)°). These structural features have been observed recently in end-on cyanato-bridged nickel(II)[31] and copper(II)[32] dinuclear complexes.

The copper⋯copper separations through L^{2-} and cyanato bridges are 5.240 (1) $(Cu(1)\cdots Cu(1)^{i})$ and 3.212 (1) Å $(Cu(1)\cdots Cu(1)^{ii})$. The shortest interchain copper⋯copper distance is 6.153 (1) Å $(Cu(1)\cdots Cu(1)^{iii}$ and $Cu(1)\cdots Cu(1)^{v}$ where *iii* and v denote the symmetry operations $-^1/_2 - x, -^1/_2 + y, -^1/_2 - z$ and $-^1/_2 - x, ^1/_2 + y, -^1/_2 - z$, respectively). An interchain hydrogen bond occurs between O(2) and $N(2)^{iv}$ $(O(2)\cdots N(2)^{iv} = 2.976$ (7) Å, $O(2)\cdots H(1)^{iv} = 2.1$ Å, and $O(2)\cdots H(1)^{iv}-N(2)^{iv} = 160°$, iv being the symmetry operation $-x - ^1/_2, y - ^1/_2, -z - ^3/_2$).

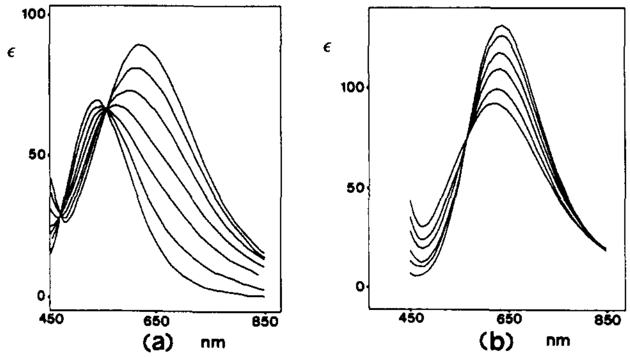

Figure 2. Visible absorption spectra of aqueous solutions of [Cu(apox)] $(2 \times 10^{-3}$ mol $dm^{-3})$ and variable amounts of copper(II) nitrate: (a) 0 ≤ [Cu(II)]/[Cu(apox)] ≤ 0.5; (b) 0.5 < [Cu(II)]/[Cu(apox)] ≤ 1.

Infrared Spectrum. The lack of the intense absorption located at 3290 cm^{-1} (amide N–H stretching vibration) and the position of the amide I band (1620 cm^{-1}) in the infrared spectrum of $[Cu_2L(NCO)_2]$ are a diagnostic of the occurrence of a bridging oxamidato group.[6a] In fact, the amide I band in the IR spectra of polynuclear complexes containing [CuL] as a ligand[16] is located at 1600 cm^{-1}. Therefore, the position of this amide band can be used to distinguish between cis and trans oxamidato bridging. A sharp and intense absorption at 2215 cm^{-1} and two medium-intensity peaks at 610 and 630 cm^{-1} are attributed to the asymmetric stretching vibration ν_1 (ν_{CN}) and bending mode ν_2 (δ_{NCO}) of the cyanate ligand. The shift toward higher frequencies of ν_1 stretching in $[Cu_2L(NCO)_2]$ when compared to the free-ion value (2170 cm^{-1} for ν_1 in KNCO)[33] and the splitting of ν_2 are consistent with the presence of the end-on cyanato bridge.[34-36] All these spectral features agree with the structure described above.

Electronic Spectra: A Spectrophotometric Study. The electronic absorption spectrum of aqueous solutions of [CuL] displays a weak d–d band in the visible range (ν = 18 600 cm^{-1}, ϵ = 69.5 dm^3 mol^{-1} cm^{-1}) which obeys the Lambert–Beer law. A change of color from purple to blue occurs upon addition of copper(II) to these solutions, the absorption maximum being shifted to lower frequencies. The electronic absorption spectra of a series of aqueous solutions containing [CuL] $(2 \times 10^{-3}$ mol $dm^{-3})$ and variable amounts of copper(II) nitrate (0 ≤ [Cu(II)]/[CuL] ≤ 0.5) are shown in Figure 2a. The presence of two isosbestic points at 21 300 and 18 000 cm^{-1} suggests the existence of only two absorbing species. Moreover, the position of the maximum is shifted from 18 600 to 16 300 cm^{-1}. The disappearance of the foregoing isosbestic points together with a progressive shift to lower frequencies and the appearance of a new isosbestic point is observed for greater [Cu(II)]/[CuL] molar ratios (Figure 2b). Any further change is observed in the resulting spectrum for [Cu(II)]/[CuL] > 1. These spectral features show that only a 1:2 Cu(II):CuL species (eq i) is formed in the range 0 ≤ [Cu(II)]/[CuL] ≤ 0.5, whereas

$$2[CuL] + Cu^{2+} \leftrightarrow [Cu_3L_2]^{2+} \qquad (i)$$

a 1:1 Cu(II):CuL complex (eq ii) appears at 1 ≥ Cu(II)/[CuL]

$$[Cu_3L_2]^{2+} + Cu^{2+} \leftrightarrow 2[Cu_2L]^{2+} \qquad (ii)$$

> 0.5. The trinuclear species was isolated a few years ago as a

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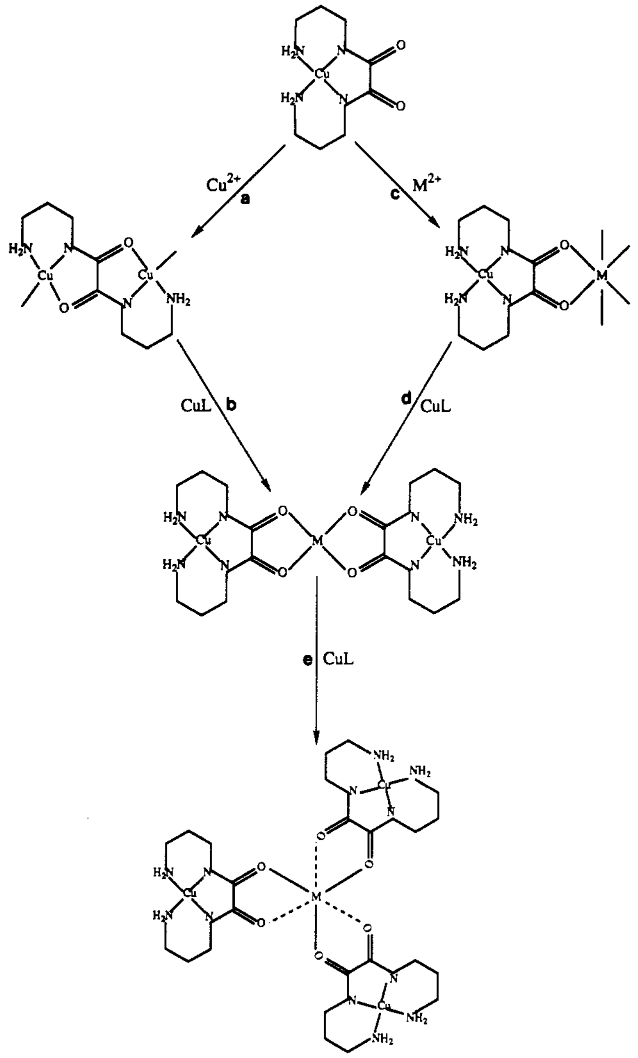
Scheme I



perchlorate salt by reaction of stoichiometric amounts of [CuL] and copper(II) perchlorate, and it was structurally characterized by X-ray diffraction on single crystals.[15] In this compound, each CuL fragment coordinates to a central copper(II) ion using its two carbonyls groups in the α-position. The binuclear species is isolated from its aqueous solutions by addition of NaNCO (present work) or KNCS,[21] and its molecular structure shows that the oxamidato ligand adopts the trans conformation with an inversion center at the middle of the carbon–carbon (amide) bond (see Scheme I).

In these complexes, the copper(II) ion exhibits different chromophores and consequently different ligand fields. A CuN_4 chromophore with two amino and two amido nitrogen donors is present in the mononuclear complex [CuL], the ligand L^{2-} adopting the cis conformation. The ν_{d-d}^{max} for this compound appears in an unusually high wavenumber region (ca. 19 000 cm^{-1}), at a greater value than those of the corresponding amine complexes, revealing that a square-planar environment and a strong ligand field are achieved. In the binuclear species, the oxamidato ligand exhibits a trans conformation, which leads to a CuN_2O_2 chromophore consisting of one amino and one amido nitrogen atom and two oxygen atoms, one from the oxamidato bridge and the other most probably from a water molecule. The visible spectrum of this complex is very simple because the two copper(II) sites are identical. However, a red shift (ν_{d-d}^{max} at ca. 16 000 cm^{-1}) is observed for this species owing to the weaker ligand field associated with oxygen donor ligands compared to nitrogen ones. Finally, two different ligand fields coexist in the trinuclear $[Cu_3L_2]^{2+}$ complex: two identical CuN_4 chromophores and one CuO_4 chromophore, which lead to two close d–d transitions. In fact, a single and broad absorption band centered at ca. 17 500 cm^{-1} is observed in the visible spectrum of this complex. This value is intermediate between the ones mentioned above, as expected. The value of ν_{d-d}^{max} for CuN_4 in the trimer should be greater than that for CuO_4 but slightly smaller than the one for CuN_4 in free [CuL], due to the loss of electronic density (basicity) of amido nitrogen atoms when the oxamidato group acts as a bridging ligand. In this sense, $\nu_{d-d}^{max}(Cu(II))$ for the complexes $[ZnCu_2L_2(H_2O)_2](ClO_4)_2$[15] and $[MCu_3L_3](ClO_4)_2{\cdot}2H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+})[7] is displaced ca. 1000 cm^{-1} toward lower frequency with respect to the value for mononuclear [CuL] complex. The estimated ν_{d-d}^{max} value for the CuO_4 chromophore would be about 15 000–16 000 cm^{-1}.[37]

The fact that the trinuclear $[M(CuL)_2]^{2+}$ and the tetranuclear $[M(CuL)_3]^{2+}$ complexes show identical absorption spectra precludes a spectrophotometric study of their formation. In this regard, although the absorption spectra in the range $0 \leq [Cu(II)]/[CuL] \leq 0.5$ revealed the existence of two absorbing species (eq i), the tetrameric one $[Cu_4L_3]^{2+}$ is also present (eq iii), as shown by the potentiometric study (vide infra).

$$3[CuL] + Cu^{2+} \leftrightarrow [Cu_4L_3]^{2+} \qquad \text{(iii)}$$

The Cis-Trans Conformational Change. As shown previously, the ligand $apox^{2-}$ can adopt either a cis or a trans conformation in its copper(II) metal complexes. The fact that the equilibria involved in this conformational change (dimer–trimer or monomer–dimer, for instance) are attained instantaneously indicates that it does not present any significant barrier at room temperature. In order to determine the energy gap between both conformers, we carried out an ab initio calculation using $(CH_3NCO)_2^{2-}$ as the model system. The cis isomer lies 2.25 kcal above the trans one at the DZ SCF level of theory. From a comparison with more complete and rigorous studies made on related molecules such as glyoxal, $(HCO)_2$,[38] it seems unlikely that a further extension of the basis set (i.e., to include polarization functions) will significantly affect this SCF cis–trans energetic separation. Identical studies on glyoxal also show that a CI treatment to include correlation effects does not appreciably alter the result, supporting the general view that correlation is irrelevant when single-bond rotational barriers are considered. So, the cis–trans energy separation in $(HCO)_2$ at the DZ SCF level of theory is 5.9 kcal, and this result remains practically unchanged (5.86 kcal) when the larger DZ + P basis set is used. The CI treatment yields an energy separation of 5.5 kcal, a value which is close to the above ones.

Nevertheless, the choice of $(CH_3NCO)_2^{2-}$ as the model system deserves some explanation. Although it is well-known that describing the electronic structure at the SCF level for a given basis set is easier and in general more accurate with cationic systems than with anionic ones, it seems that the model chosen is the one that gives a better representation of the actual situation while being relatively simple in terms of the number of nuclei and electrons involved. At this level of approximation, both the sign and magnitude of the theoretical result for the cis–trans energy separation are in good agreement with the experimental data reported herein (vide infra).

Assuming that the participation of copper(II) in eq iv does not significantly alter the value of the enthalpy of the system ($\Delta H' \sim \Delta H$, eq v) and that $|\Delta S| \ll |\Delta H|$, then $\Delta G \sim \Delta H$ for eq v and a value of $\log K = 1.6$ is easily inferred.

Acidity Constants of H_4L^{2+}. Previously acidified aqueous solutions of H_2L of variable concentration ($c_L = 10^{-2}$–10^{-3} mol dm^{-3}) were investigated by potentiometry by using KOH (0.1 mol dm^{-3}) as titrant. Data processing of 100 experimental points from different series in the pH range 7.6–11.6 allowed us to determine its deprotonation constants. Their values are given in Table V (eqs 1–3) in the form of protonation constants. They show that

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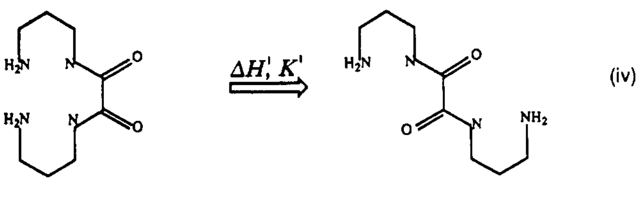
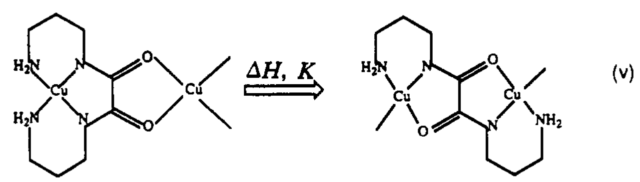


(iv)



(v)

L^{2-} behaves as a relatively strong base in the first two protonation steps (eq 1, Table V) and its basicity decreases slightly in the last two protonation steps. This is consistent with the greater basicity of the deprotonated amide N atoms with regard to the amine N atoms which are involved in such equilibria. The values for the logarithms of the stepwise protonation constants of the amino groups of H_2L are within the range observed for aliphatic amines.[39]

The deprotonation of the amide groups to yield L^{2-} occurs at pH > 11.1. So, the determination of these constants in aqueous solution is not reliable because very basic media are required to deprotonate such groups. In fact, we have not observed any deprotonation of H_2L for pH $\leq$ 11. This observation is general for some N,N'-disubstituted oxamides that we have studied. A detailed analysis of the potentiometric data in the range 11 $\leq$ pH $\leq$ 11.6 reveals that some deprotonation occurs, the emf-computed data being consistent with the simultaneous loss of two protons (log β_{12} = 24.0–24.6). In the present case, a value of 24.0 (2) (eq 1, Table V) was computed. The high value of its standard deviation reflects the low precision which is associated with the determination of this constant due to the low extent of deprotonation (ca. 15%) in a highly basic medium. The very weak basicity of amides makes quantitative equilibrium measurements difficult, and only a few values are reported.[6a,40] The acidity values observed for monoamides varies in the range pK_a = 13–15. Although no acidity constants were reported for oxamides,[6a] a greater acidity would not be expected for them due to the NCO π-delocalization in deprotonated oxamides, as well as to the major electron withdrawal of the other neighboring oxamide group. We have used the value of log β_{12} = 24.0 only to calculate the equilibrium constants of Table VII.

Potentiometric Study of the Cu(II)-H_2L System. Stability Constants. Previously acidified aqueous solutions of copper(II) nitrate and H_2L (c_M = (1–5) × 10^{-3} mol dm^{-3}, c_L/c_M = 0.5–1.5) were titrated with KOH (0.1 mol dm^{-3}) in order to investigate the complex formation. Solutions of [CuL] ((1–5) × 10^{-3} mol dm^{-3}) and $[Cu_3L_2](ClO_4)_2$ ((1–3) × 10^{-3} mol dm^{-3}) wee also titrated with HNO_3 (0.1 mol dm^{-3}). Data processing by the programs SUPERQUAD and BEST of 190 experimental points in the pH range 4.5–9.5 showed the formation of mono-, di-, tri-, and tetranuclear complexes, whose stoichiometries and stability constants are gathered in Table V (eqs 4–7).

The distribution diagram of the system Cu^{2+}–H_2L as a function of pH is depicted in Figure 3a (bottom). The dimeric complex $[Cu_2L]^{2+}$ is the only existing species in the pH range 5.5–6.5. The formation of the trimeric and tetrameric species occurs at pH > 6.5. The mononuclear complex [CuL] is the predominant species at pH > 8.4, becoming the only existing complex at pH > 9.5.

Table V. Equilibrium Data[a] for Basicity and Formation of Cu(II) Complexes with L^{2-} in Aqueous Solution (25 °C in 0.1 mol dm^{-3} $NaNO_3$)

eq no.	reacn	log β
1	$2H^+ + L^{2-} \leftrightarrow H_2L$	24.0 (2)
2	$H^+ + H_2L \leftrightarrow H_3L^+$	10.12 (1)
3	$2H^+ + H_2L \leftrightarrow H_4L^{2+}$	19.57 (1)
4	$Cu^{2+} + H_2L \leftrightarrow [CuL] + 2H^+$	−3.77 (1)
5	$2Cu^{2+} + H_2L \leftrightarrow [Cu_2L]^{2+} + 2H^+$	4.15 (1)
6	$3Cu^{2+} + 2H_2L \leftrightarrow [Cu_3L_2]^{2+} + 4H^+$	3.68 (1)
7	$4Cu^{2+} + 3H_2L \leftrightarrow [Cu_4L_3]^{2+} + 6H^+$	2.35 (3)

[a] Values in parentheses are standard deviations in the last significant digit.

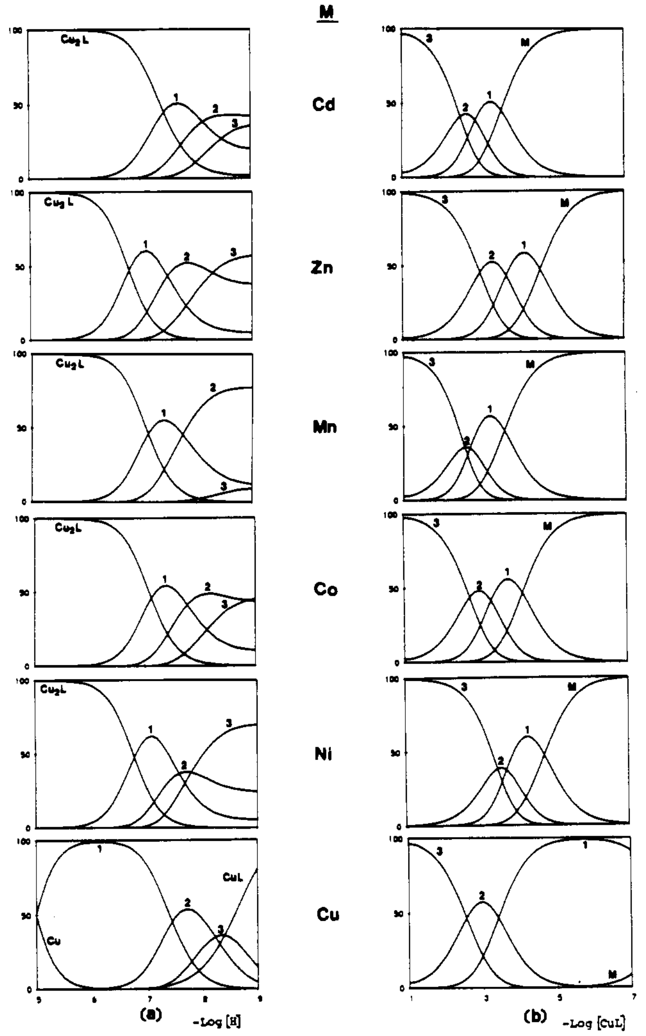


Figure 3. Distribution diagrams for the systems M^{2+}–Cu^{2+}–L^{2-}–H^+ (M = Cd, Zn, Mn, Co, Ni, Cu) as a function of (a) pH and (b) p[CuL]. c_{CuL} = 1 × 10^{-2} mol dm^{-3} and $[CuL]/[M^{2+}]$ = 3 are common to all distribution diagrams except in the case of M = Cu (bottom, part a) for which $c_{Cu^{2+}} = c_{H_2L} = 10^{-2}$ mol dm^{-3}. 1–3 correspond to $[M(CuL)]^{2+}$, $[M(CuL)_2]^{2+}$, and $[M(CuL)_3]^{2+}$, respectively. All the percentages are referred to total concentration of M.

The great stability of $[Cu_2L]^{2+}$ with respect to the other complexes is also illustrated by means of Figure 3b (bottom), which corresponds to the same distribution diagram but as a function of p[CuL]. It can be seen that $[Cu_2L]^{2+}$ is formed quantitatively in the p[CuL] range 5–7. $[Cu_4L_3]^{2+}$ is the predominant species only at high concentrations of [CuL] (>0.1 mol dm^{-3}).

The stability constant of $[Cu_2L]^{2+}$ is 2 orders of magnitude greater than that of its parent $[Cu_2(pmox)]^{2+}$ (log β_{12} = 26.1;[6b] H_2pmox = *N,N'*-bis(2-pyridylmethyl)oxamide) and 6 orders of magnitude greater than that of $[Cu_2(glyox)]^{2+}$ (log β_{12} = 22.0;[6c] H_4glyox = oxamide-*N,N'*-diacetic acid). Both oxamidato ligands in $[Cu_2(pmox)]^{2+}$ and $[Cu_2(glyox)]^{2+}$ form two consecutive five-membered chelate rings around each copper(II) ion whereas the more stable consecutive five- and six-membered fused chelates are present in $[Cu_2L]^{2+}$. Furthermore, the set of donor atoms around copper(II) ($CuNO_2X$) in such dimeric species is different: X = carboxylate O, pyridine N, and amine N for $glyox^{4-}$, $pmox^{2-}$,

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Table VI. Overall (β_n) and Stepwise (K_n) Stability Constants[a] for Complex Formation between [CuL] and M^{2+} in Aqueous Solution (25 °C and 0.1 mol dm^{-3} $NaNO_3$)

	M					
	Mn	Co	Ni	Cu	Zn	Cd
log β_1	3.63 (1)[b]	4.08 (1)	4.63 (1)	7.92 (1)	4.64 (1)	3.57 (1)
log β_2	6.33 (3)	7.31 (2)	8.24 (1)	11.22 (1)	8.35 (1)	6.44 (2)
log β_3	8.89 (3)	9.97 (2)	11.61 (1)	13.66 (3)	11.35 (1)	8.91 (2)
log K_1	3.63[c]	4.08	4.63	7.92	4.64	3.57
log K_2	2.70	3.23	3.61	3.30	3.71	2.87
log K_3	2.26	2.66	3.37	2.44	3.00	2.47

[a] β_n and K_n correspond to the equilibria n[CuL] + M^{2+} ↔ $[M(CuL)_n]^{2+}$ and $[M(CuL)_{n-1}]^{2+}$ + [CuL] ↔ $[M(CuL)_n]^{2+}$, respectively. [b] Values in parentheses are standard deviations in the last significant digit. [c] Calculated values obtained by combining the appropriate equations.

and apox^{2-}, respectively. The lower stability of $[Cu_2(glyox)]^{2+}$ is due to the smaller affinity of carboxylate O for copper(II) with regard to pyridine or amine N.

N,N'-Alkyloxamide ligands form complexes with copper(II) which are very stable. However, this stability is much decreased when copper(II) is replaced by other divalent first-row transition-metal ions. So, the corresponding metal hydroxides precipitate when aqueous solutions of H_2L and M(II) (M = VO^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}) are titrated. Ni^{2+} is the only case for which complex formation has been observed with such ligands,[6c,41] the nickel environment being square planar (diamagnetic). Their stability is much lower than that exhibited by the corresponding copper(II) complexes. For instance, the formation constants of $[Ni_2L]^{2+}$ (log β_{12} = 18.5)[21] and $[Ni_2(glyox)]$ (log β_{12} = 13.1)[6c] are 9 orders of magnitude smaller than those of their Cu(II) homologous complexes log β_{12} = 28.1 and 22.0,[6c] respectively.

Potentiometric Study of the M(II)–Cu(II)–L^{2-} System. Stability Constants of the Heteropolynuclear Complexes $[M(CuL)_n]^{2+}$ (M(II) = Mn, Co, Ni, Zn, Cd). The ability of L^{2-} to form polynuclear species is due to the easy cis–trans conformational change. The trans conformer acts as a bis-terdentate ligand, leading to homodinuclear complexes $[Cu_2(L)^{trans}]^{2+}$, whereas the cis one forms the mononuclear species $[Cu(L)^{cis}]$, which is able to coordinate to metal ions as a bidentate ligand (see Scheme I).

Potentiometric titrations of aqueous solutions of [CuL] and M(II) nitrate (c_M = (1–3) × 10^{-3} mol dm^{-3}, [CuL]/[M(II)] = 2–4), as well as of solutions of $[M(CuL)_3](ClO_4)_2\cdot 2H_2O$ (M(II) = Mn, Co, Ni, Zn, Cd), were carried out using HNO_3 (0.1 mol dm^{-3}) as titrant in order to investigate the complexing ability of [CuL]. Data processing of more than 100 experimental points for each system proved the formation of di-, tri-, and tetranuclear complexes (eq vi, n = 1–3). The computed constants related to

$$n[\mathrm{CuL}] + \mathrm{M}^{2+} \leftrightarrow [\mathrm{M(CuL)}]^{2+} \tag{vi}$$

eq vi are listed in Table VI, and the overall stability constants for this ternary M(II)–Cu(II)–L^{2-} system are listed in Table VII. It is worthwhile noting that although protons do not appear in equation vi, the formation of [CuL] depends on pH. In the presence of M(II), its formation takes place at lower pH values because of the complex formation between [CuL] and M(II).

As indicated above, M(II) ions do not form stable M(II)–L^{2-} binary complexes, except in the case of Ni(II). The stability constants of the Ni(II)–L^{2-} complexes are too low with regard to the those of Cu(II) to allow the formation of these binary species in the presence of Cu(II). Consequently, these equilibria are not considered in the equilibrium scheme of the M(II)–Cu(II)–L^{2-} system during the computational process of the potentiometric data. The protonation constants of L^{2-} and the stability constants for the Cu(II)–L^{2-} system (eqs 1–7, Table VII) were considered as fixed parameters during the refinement process, whereas the three constants corresponding to the formation of the heteropolymetallic species for each M(II) were refined.

The calculated values for eq vi (Table VI) reveal that [CuL] forms complexes which are significantly more stable than the oxalato dianion,[39] especially when the latter acts as a bridging ligand. Studies of complex formation between oxalate and CuL' (L' = bi- or terdentate N-donor ligand) in aqueous solution have shown that oxalato-bridged copper(II) dinuclear complexes do not occur at millimolar concentration.[13a,b,42] Their formation is favored at higher concentrations.[13b,f,g] The greater stability of the complexes of [CuL] with regard to those with oxalate is also evident from the average values of the Cu–O bond distances in μ-oxamidato (1.93 Å)[14,15] and μ-oxalato (2.00 Å)[13f] complexes.

Table VII. Species Involved in the Equilibria $pM^{2+} + qCu^{2+} + rL^{2-} + sH^+ \leftrightarrow [M_pCu_qL_rH_s]^{2(p+q-r)+s}$ Considered in the Calculations[a]

eq no.	M^{2+}	Cu^{2+}	L^{2-}	H^+	log K
1	0	0	1	2	24.0
2	0	0	1	3	34.1
3	0	0	1	4	43.6
4	0	1	1	0	20.2
5	0	2	1	0	28.1
6	0	3	2	0	51.7
7	0	4	3	0	74.3
8	1 (Mn)	1	1	0	23.9
9	1 (Mn)	2	2	0	46.8
10	1 (Mn)	3	3	0	69.6
11	1 (Co)	1	1	0	24.3
12	1 (Co)	2	2	0	47.8
13	1 (Co)	3	3	0	70.7
14	1 (Ni)	1	1	0	24.9
15	1 (Ni)	2	2	0	48.7
16	1 (Ni)	3	3	0	72.3
17	1 (Zn)	1	1	0	24.9
18	1 (Zn)	2	2	0	48.8
19	1 (Zn)	3	3	0	72.0
20	1 (Cd)	1	1	0	23.8
21	1 (Cd)	1	1	0	23.8
22	1 (Cd)	3	3	0	69.6

[a] Values at 25 °C and 0.1 mol dm^{-3} $NaNO_3$.

The distribution diagrams illustrating the formation of heteropolymetallic complexes as a function of pH and p[CuL] are shown in Figure 3. The complexes $[M(CuL)_2]^{2+}$ and $[M(CuL)_3]^{2+}$ can be isolated readily by addition of an excess of $NaClO_4$ to aqueous solutions where [CuL]/[M(II)] = 2 and 3. The structural characterization of these compounds has showed that [CuL] acts as a bidentate ligand through the two carbonyl groups in the α-position, the cis conformation of L^{2-} being retained. Although the complex $[M(CuL)]^{2+}$ has not been prepared, the related compounds $[Ni(bpy)_2(CuL)](NO_3)_2$[15] and $[Ni(phen)_2(CuL)](ClO_4)_2\cdot CH_3OH\cdot H_2O$[16] have been isolated and characterized, and [CuL] acts also as a bidentate ligand through its two oxygen atoms. Recently, one of us isolated the complex $[NiCu(obbz)(H_2O)_4]\cdot 2H_2O$[9] (obbz^{4-} = oxamidobis(benzoato)). In this compound the square-planar mononuclear brick $[Cu(obbz)]^{2-}$ acts as a bidentate ligand, similarly to [CuL]. The Ni(II) ion is in an octahedral NiO_6 environment which is formed by four water molecules and the two amide oxygen atoms of obbz^{4-}.

In light of these data, it can be stated that L^{2-} always exhibits a cis conformation in the heteropolymetallic $[Cu^{II}M^{II}]$ species (M ≠ Cu). Nevertheless, such a conformation can be observed also in dinuclear copper(II) complexes if bi- or terdentate N-donor

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(41) Nonoyama, K.; Ojima, H.; Nonoyama, M. *Inorg. Chim. Acta* **1976**, *20*, 127.

(42) Castro, I. Ph.D. Thesis, University of Valéncia, 1991.

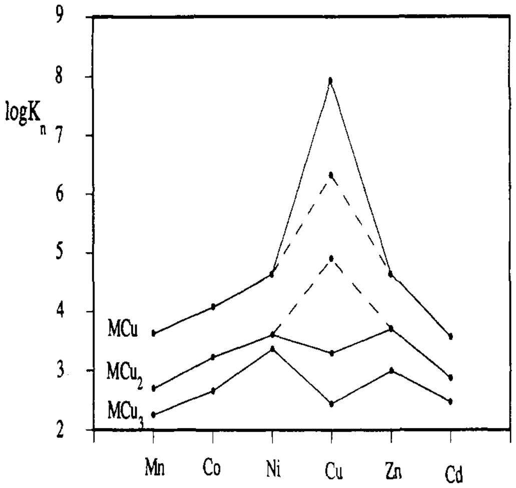

Figure 4. Plot of the stepwise stability constants (log K_n, n = 1–3) for different metal ions: experimental values (solid line); values calculated by taking into account the conformational change (dashed line) (see text).

ligands are used as end-cap ligands of the second copper(II) ion. In this respect, the reactions of $[Cu(bpy)]^{2+}$ and $[Cu(petdien)]^{2+}$ (petdien = *N,N,N′,N″,N″*-pentaethyldiethylenetriamine) with [CuL] lead to the complexes $[(CuL)Cu(bpy)](ClO_4)_2$ and $[(CuL)Cu(petdien)](ClO_4)_2$,[14] where the two copper(II) ions have different environments. However, in both cases [CuL] coordinates to the other metal ion as a bidentate ligand through its two oxygen atoms.

The trans conformation of L^{2-} is restricted to the homodinuclear species without any other ligand, yielding centrosymmetric complexes. This conformational change is responsible for some anomalies in the values of the stability constants given in Table VI. The trend in the values of the stepwise stability constants of the complexes M(II)–[CuL] is shown in Figure 4. The values of the constants increase from Mn(II) to Cu(II) and diminish for Zn(II) (or Cd(II)), as expected for the Irving–Williams series. However, the value of log K_1 for Cu(II)–[CuL] is too high whereas that of log K_2 is too low (even lower than log K_2 for Ni(II)–[CuL]). log K_3 is also very small, and it corresponds to what it could be expected because of the Jahn–Teller effect.

The anomalies observed in log K_1 and log K_2 can be explained by taking into account the cis–trans conformational change of L^{2-} (Scheme I). When 1 mmol of [CuL] is allowed to react with 1 mmol of Cu(II), L^{2-} undergoes a conformational change from cis in [CuL] to trans in $[Cu_2L]^{2+}$ (step a). The trans conformation of L^{2-} in $[Cu_2L]^{2+}$ becomes cis by further coordination of a second [CuL] unit to yield $[Cu_3L_2]^{2+}$ (step b). The higher stability of the trans conformer with regard to the cis one provides an additional stabilization of the dimeric species (step a) and, consequently, a decrease in the stability of the trimer (step b). It is clear that this anomaly disappears in the overall process (steps a + b) as well as in the formation of complexes of [CuL] with M(II) $\neq$ Cu(II) (steps c–e), for which the conformational change of L^{2-} does not occur.

It is interesting to note that if the Jahn–Teller effect was not operative in the Cu(II) complexes, then $K_3 > K_2$ ($K_1 > K_2 < K_3$); i.e., an inversion of constants would take place due to the conformational change with the subsequent decrease of the degree of formation of the trimeric species.

Taking into account the energetic cost of the cis–trans conformational change of L^{2-} in its metal complexes (log K = 1.6 in eq v), we can evaluate the constants of the equilibria:

$$[CuL^{cis}] + Cu^{2+} \leftrightarrow [Cu_2L^{cis}]^{2+} \qquad \log K_1' = 7.9 - 1.6 = 6.3 \tag{vii}$$

$$[Cu_2L^{cis}]^{2+} + [CuL^{cis}] \leftrightarrow [Cu_3L_2{}^{cis}]^{2+} \qquad \log K_2' = 3.3 + 1.6 = 4.9 \tag{viii}$$

These new values fit better the variation of the values of the stepwise stability constants expected for the Irving–Williams series, as shown in Figure 4 (shaded line).

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Registry No. H_2L, 19980-60-0; $Cu_2L(NCO)_2$, 138490-17-2; CuL, 20102-49-2; $(CH_3NCO)_2{}^{2-}$, 138490-16-1.

Supplementary Material Available: A stereoscopic view of the unit cell of $[Cu_2(apox)_2(NCO)_2]$ down the *b* axis, with the *c* axis horizontal (Figure S1), and listings of crystallographic data (Table S1), anisotropic thermal parameters (Table S2), hydrogen atom coordinates (Table S3), and least-squares planes (Table S4) (4 pages); a listing of calculated and observed structure factors (Table S5) (4 pages). Ordering information is given on any current masthead page.