

Contribution from the Departament de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100-Burjassot València, Spain, and Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, 75252 Paris, France

Oxamidato Complexes. 5. Influence of the Steric Constraints on the Complex Formation between Copper(II) and N,N' -(Alkyl-substituted)oxamides. Synthesis and Crystal Structure of $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ ($\text{H}_2\text{mapox} = N,N'$ -Bis[3-(methylamino)propyl]oxamide)

Francesc Lloret,^{*1a} Miguel Julve,^{1a} José Antonio Real,^{1a} Juan Faus,^{1a} Rafael Ruiz,^{1a} Miquel Mollar,^{1a} Isabel Castro,^{1a} and Claudette Bois^{1b}

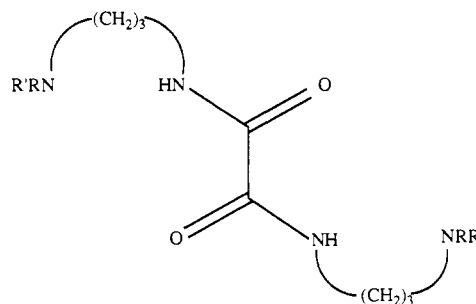
Received December 4, 1991

Potentiometric studies on the ternary systems $\text{Cu}^{2+}\text{-mapox}^{2-}\text{-H}^+$ and $\text{Cu}^{2+}\text{-dmapox}^{2-}\text{-H}^+$ where mapox^{2-} and dmapox^{2-} are the dianions of N,N' -bis[3-(methylamino)propyl]oxamide and N,N' -bis[3-(dimethylamino)propyl]oxamide, respectively, have been carried out at 25 °C and 0.1 mol dm^{-3} NaNO_3 . The proton association constants corresponding to the equilibria $\text{L}^{2-} + j\text{H}^+ \rightleftharpoons \text{H}_j\text{L}^{(2-j)+}$ were found to be $\log \beta_2 = 24.0$ (2), $\log \beta_3 = 34.31$ (1), and $\log \beta_4 = 44.06$ (1) for $\text{L} = \text{mapox}$ and $\log \beta_2 = 24.0$ (2), $\log \beta_3 = 33.49$ (1), and $\log \beta_4 = 42.34$ (1) for $\text{L} = \text{dmapox}$. The values of the stability constants related to the equilibria $p\text{Cu}^{2+} + q\text{L}^{2-} + r\text{H}^+ \rightleftharpoons [\text{Cu}_p\text{L}_q\text{H}_r]^{(2p-q)+r+}$ were $\log \beta_{212} = 36.70$ (8), $\log \beta_{211} = 31.70$ (8), $\log \beta_{210} = 26.41$ (1), $\log \beta_{320} = 47.28$ (2), $\log \beta_{430} = 67.53$ (2), and $\log \beta_{110} = 17.09$ (1) for $\text{L} = \text{mapox}$ and $\log \beta_{212} = 34.64$ (9), $\log \beta_{211} = 29.12$ (5), $\log \beta_{210} = 23.24$ (1), $\log \beta_{21-1} = 14.66$ (1), and $\log \beta_{21-2} = 4.88$ (1) for $\text{L} = \text{dmapox}$. The molecular structure of the complex $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 11.439$ (3) Å, $b = 10.522$ (1) Å, $c = 7.376$ (1) Å, $\beta = 106.47$ (4)°, and $Z = 2$. Refinement of the atomic parameters by least squares gave a final R factor of 0.052 ($R_w = 0.059$) for 1036 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 azido groups. The former acts as a bis-terdentate ligand whereas the latter is bound through a nitrogen in an asymmetrical end-on fashion. Copper environment can be best 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 a nitrogen atom of the azide ligand whereas the apical position is filled by a nitrogen atom of another azide group. The ligand dmapox presents only the trans conformation in its metal complexes, whereas the ligand mapox can adopt either the cis or trans conformations. The greater flexibility of mapox allows the formation of mono-, di-, tri-, and tetranuclear complexes, in contrast to the restriction to the dinuclearity imposed by the trans configuration in dmapox . The values of the stability constants of these systems and the different chelating capabilities of N,N' -bis(alkyl-substituted)oxamidate ligands are analyzed and discussed in the light of the available structural data and steric effects caused by the presence of methyl substituents on amine groups.

Introduction

The oxamide dianion can act as a chelating or a bis-chelating ligand like the parent oxalate dianion to yield monomeric, dimeric and one-dimensional complexes with first row transition-metal ions.² Moreover, its strong electron-donating capability due to the presence of deprotonated N-amide atoms stabilizes high oxidation states.³ However, the low solubility of oxamide in common solvents and its hydrolytic decomposition in alkaline solution preclude an exhaustive exploration of its coordination chemistry. These difficulties can be overcome by using N,N' -bis(coordinating group substituted)oxamides.⁴ They are more reluctant to undergo the hydrolytic reaction and their solubility can be much increased by choosing the appropriate substituent. Furthermore, in the presence of transition-metal ions and if the oxamide has another coordinating group at a position which can form a five- or six-membered chelate, the amide deprotonates and coordinates simultaneously in a low pH range, as shown recently.⁴⁻⁶

In the framework of our current solution and solid-state research work concerning the N,N' -bis(substituent)oxamides,⁶⁻⁹ we have investigated the complex formation between copper(II) and N,N' -bis[3-(methylamino)propyl]oxamide (H_2mapox) and N,N' -bis[3-(dimethylamino)propyl]oxamide (H_2dmapox) aiming at both characterizing the chelating ability of these ligands and rationalizing the synthesis of their mononuclear and polynuclear metal complexes.



$\text{R} = \text{R}' = \text{H}; \text{H}_2\text{apox}$

$\text{R} = \text{H}, \text{R}' = \text{CH}_3; \text{H}_2\text{mapox}$

$\text{R} = \text{R}' = \text{CH}_3; \text{H}_2\text{dmapox}$

In this paper we report on the complexing ability of mapox^{2-} and dmapox^{2-} ligands toward hydrogen ions and copper(II) in aqueous solution. The crystal structure of the first mapox -containing copper(II) complex of formula $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ is also reported. Finally, a discussion on the steric constraints induced

- (1) (a) Universitat de València. (b) Université Pierre et Marie Curie.
- (2) (a) Kuroda, Y.; Kato, M.; Sone, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 877. (b) Armendarez, P. X.; Nakamoto, K. *Inorg. Chem.* **1966**, *5*, 796. (c) Nonoyama, K.; Ojima, H.; Ohki, K.; Nonoyama, M. *Inorg. Chim. Acta* **1980**, *41*, 155. (d) Sletten, J. *Acta Chem. Scand.* **1982**, *A36*, 345. (e) Sletten, J. *Acta Chem. Scand.* **1985**, *A39*, 475. (f) Verdager, M.; Kahn, O.; Julve, M.; Gleizes, A. *Nouv. J. Chim.* **1985**, *9*, 325. (g) Okawa, H.; Matsumoto, N.; Koikawa, M.; Takeda, K.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1990**, 1383.
- (3) Bour, J. J.; Birker, P. J. M. W. L.; Steggerda, J. J. *Inorg. Chem.* **1971**, *10*, 1202.
- (4) Ojima, H.; Nonoyama, K. *Coord. Chem. Rev.* **1988**, *92*, 85, and references therein.
- (5) (a) Sprta, F.; Bartusek, M. *Collect. Czech. Chem. Commun.* **1974**, *39*, 2023. (b) Votava, J.; Havel, J.; Bartusek, M. *Chem. Zvesti* **1975**, *29*, 734.
- (6) (a) Lloret, F.; Julve, M.; Faus, J.; Journaux, Y.; Philoche-Levisalles, M.; Jeannin, Y. *Inorg. Chem.* **1989**, *28*, 3702. (b) Lloret, F.; Sletten, J.; Ruiz, R.; Julve, M.; Faus, J.; Verdager, M. *Inorg. Chem.* **1992**, *31*, 778. (c) Lloret, F.; Julve, M.; Faus, J.; Ruiz, R.; Castro, I.; Mollar, M.; Philoche-Levisalles, M. *Inorg. Chem.* **1992**, *31*, 784.

(7) Nakatani, K.; Carriat, Y.; Journaux, Y.; Kahn, O.; Lloret, F.; Renard, J. P.; Pei, Yu; Sletten, J.; Verdager, M. *J. Am. Chem. Soc.* **1989**, *111*, 5739.

(8) Lloret, F.; Journaux, Y.; Julve, M. *Inorg. Chem.* **1990**, *29*, 3967.

(9) Soto, J.; Payá, J.; Martínez-Mañez, R.; Lloret, F.; Julve, M. *Transition Met. Chem. (Weinheim, Ger.)*, in press.

Table I. Crystallographic Data for $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$

chem formula	$\text{C}_{10}\text{H}_{20}\text{Cu}_2\text{N}_{10}\text{O}_2$	space group	$P2_1/n$
fw	439.4	$T, ^\circ\text{C}$	18
$a, \text{\AA}$	11.439 (3)	$\lambda, \text{\AA}$	0.71073
$b, \text{\AA}$	10.522 (1)	$\rho_{\text{calcd}}, \text{g cm}^{-3}$	1.71
$c, \text{\AA}$	7.376 (1)	μ, cm^{-1}	26.1
β, deg	106.47 (4)	transm coeff	0.74-1
$V, \text{\AA}^3$	851.3 (3)	$R = \sum \Delta F /\sum F_o $	0.052
Z	2	$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.059

^aUnit weights.

by the presence of methyl substituents on the amine groups and their influence on the adoption of cis and/or trans conformations of such ligands is carried out in the light of both solution and solid-state studies.

Experimental Section

Materials. Copper(II) nitrate trihydrate, sodium azide, *N*-methyl-1,3-propanediamine, *N,N*-dimethyl-1,3-propanediamine, and diethyl oxalate were of reagent grade quality. They were purchased from commercial sources and used without further purification. Carbonate-free NaOH (0.1 mol dm⁻³) and HNO₃ (0.1 mol dm⁻³) were used in the potentiometric titrations. The stock solution of copper(II) nitrate was prepared in doubly distilled water and the concentration of the metal ion determined by standard methods. All potentiometric measurements were carried out in 0.1 mol dm⁻³ NaNO₃ as background electrolyte.

Ligands and Complex Preparations. The ligands *N,N*-bis[3-(methylamino)propyl]oxamide (H₂mapox) and *N,N*-bis[3-(dimethylamino)propyl]oxamide (H₂dmapox) were prepared by using the usual method.¹⁰ A methanolic solution of diethyl oxalate (0.1 mol) was treated with either *N*-methyl-1,3-propanediamine (0.2 mol) (H₂mapox) or *N,N*-dimethyl-1,3-propanediamine (0.2 mol) (H₂dmapox) at room temperature. The mixture was kept at 80 °C for half an hour with stirring and the white precipitate was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Analytical data (C, H, N) agree for the anhydrous ligands.

$[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ was obtained as follows: aqueous solutions of copper(II) nitrate (2 mmol, 10 mL) and H₂mapox (1 mmol, 50 mL) were mixed with stirring and neutralized by adding lithium hydroxide (2 mmol) dissolved in a minimum amount of water. The resulting blue solution was filtered and a dark green precipitate separated when adding slowly an aqueous solution of NaN₃ (2 mmol, 20 mL). The solid was filtered, washed with water, and dried in a desiccator over silica gel. Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{Cu}_2\text{N}_{10}\text{O}_2$: C, 27.33; H, 4.55; N, 31.85. Found: C, 27.30; H, 4.45; N, 31.90. Single crystals of $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ were obtained by slow diffusion of aqueous solutions of $[\text{Cu}_2(\text{mapox})]^{2+}$ and azide in an H-shaped tube.

Physical Techniques. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, microcomputer, etc.) that has been previously described.^{6a} 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.¹¹ The computer programs SUPERQUAD¹² and BEST¹³ 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.

X-ray Structure Determination. The intensity data were collected on a Philips PW1100 diffractometer with monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) by using the ω - 2θ scan technique. The air-stable crystal selected for X-ray analysis had roughly a rhombohedral shape with approximate dimensions 0.45 × 0.40 × 0.15 mm. Unit-cell parameters were obtained by least squares from the setting angles of 25 reflections in the 15–16° θ . The crystallographic data, conditions employed for the intensity data collection and some features of the structure refinement are listed in Table I. The intensities of two standard reflections measured every 2 h showed no significant variations. Intensity data were

Table II. Atomic Coordinates and Thermal Parameters^{a,b} for Non-Hydrogen Atoms of $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$

atom	x/a	y/b	z/c	$10^4 U_{\text{eq}}, \text{\AA}^2$
Cu(1)	0.02310 (9)	0.9010 (1)	0.1855 (1)	390
O(1)	0.0999 (5)	1.0374 (5)	0.3646 (8)	414
N(1)	-0.0686 (6)	0.8693 (6)	0.3675 (9)	409
N(2)	-0.043 (1)	0.749 (1)	0.020 (2)	731
N(3)	0.1292 (7)	0.9479 (9)	0.026 (1)	568
N(4)	0.2278 (7)	0.9933 (8)	0.085 (1)	551
N(5)	0.3227 (8)	1.040 (1)	0.133 (1)	798
C(1)	0.0490 (7)	1.0481 (7)	0.497 (1)	350
C(2)	-0.165 (1)	0.772 (1)	0.360 (2)	558
C(3)	-0.163 (2)	0.670 (2)	0.230 (2)	870
C(4)	-0.138 (1)	0.672 (1)	0.064 (2)	781
C(5)	-0.022 (1)	0.693 (1)	-0.081 (2)	815

^aEstimated standard deviations in the last significant digits are given in parentheses. ^b $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i a_j a_i a_j$.

Table III. Bond Lengths (Å) and Angles (deg)^{a,b} for $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$

Bond Distances			
Cu(1)–O(1)	1.980 (5)	N(1)–C(2)	1.50 (1)
Cu(1)–N(1)	1.952 (7)	C(2)–C(3)	1.44 (2)
Cu(1)–N(2)	2.024 (9)	C(3)–C(4)	1.33 (2)
Cu(1)–N(3)	1.976 (8)	C(4)–N(2)	1.47 (1)
Cu(1)–N(3) ⁱ	2.542 (9)	N(2)–C(5)	1.33 (1)
O(1)–C(1)	1.274 (9)	N(3)–N(4)	1.19 (1)
C(1)–C(1) ⁱⁱ	1.52 (1)	N(4)–N(5)	1.15 (1)
C(1) ⁱⁱ –N(1)	1.30 (1)		
Bond Angles			
N(1)–Cu(1)–O(1)	83.6 (2)	N(1) ⁱⁱ –C(1)–O(1)	129.3 (7)
N(2)–Cu(1)–O(1)	174.1 (4)	C(1) ⁱⁱ –N(1)–C(2)	116.8 (7)
N(2)–Cu(1)–N(1)	95.7 (3)	C(2)–N(1)–Cu(1)	128.8 (6)
N(3)–Cu(1)–O(1)	89.1 (3)	C(4)–N(2)–Cu(1)	118.5 (7)
N(3)–Cu(1)–N(1)	172.6 (3)	N(1)–C(2)–C(3)	112.3 (9)
N(3)–Cu(1)–N(2)	91.5 (4)	N(2)–C(4)–C(3)	125.1 (11)
N(3) ⁱ –Cu(1)–O(1)	93.1 (3)	C(2)–C(3)–C(4)	130.9 (13)
N(3) ⁱ –Cu(1)–N(1)	97.0 (3)	C(5)–N(2)–C(4)	116.6 (10)
N(3) ⁱ –Cu(1)–N(2)	92.8 (4)	C(5)–N(2)–Cu(1)	120.9 (8)
N(3) ⁱ –Cu(1)–N(3)	84.7 (3)	Cu(1)–N(3)–Cu(1) ⁱ	95.3 (3)
C(1)–O(1)–Cu(1)	111.2 (5)	N(4)–N(3)–Cu(1)	124.1 (7)
C(1) ⁱⁱ –N(1)–Cu(1)	114.1 (5)	N(4)–N(3)–Cu(1) ⁱ	112.8 (7)
C(1) ⁱⁱ –C(1)–O(1)	117.8 (9)	N(5)–N(4)–N(3)	176.2 (10)
C(1)–C(1) ⁱⁱ –N(1)	112.9 (9)		

^aEstimated standard deviations in the last significant digits are given in parentheses. ^bRoman numeral superscripts refer to the following equivalent positions relative to x, y, z : (i) $-x, 2 - y, -z$; (ii) $-x, 2 - y, 1 - z$.

collected in the θ range 1–25° with scan speed 1.5° min⁻¹ and scan width (1.2 + 0.34 tan θ)°. The space group $P2_1/n$ was deduced from systematic absences. The intensities were corrected for Lorentz-polarization and absorption effects, the transmission factors varied from 0.74 to 1 (an empirical absorption correction was performed by use of DIFABS¹⁴). No extinction correction was applied. A total of 1488 reflections were collected in the $1 \leq \theta \leq 25^\circ$ range and from these, 1036 were unique with $I \geq 3\sigma(I)$ and were used for the structure refinement.

The copper atom was located on a Patterson map and all other non-hydrogen atoms were found in subsequent Fourier maps. Full-matrix least-squares refinements were carried out (282 parameters) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were neither found in difference maps nor introduced in calculated positions. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and each reflection was assigned a unity weight. The scattering factors of all atoms and the anomalous dispersion correction term for Cu were taken from ref 15. The computer program CRYSTALS¹⁶ was used in the crystallographic calculations. The refinement converged at $R = 0.052$, $R_w = 0.059$. The final difference-Fourier map shows residual maxima and minima of 0.53 and $-0.42 e \text{ \AA}^{-3}$. All crystallographic calculations were

- (10) Ojima, H.; Yamada, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3018.
 (11) (a) Gran, G. *Analyst (London)* **1952**, *77*, 661. (b) Rossotti, F. J.; Rossotti, H. J. *J. Chem. Educ.* **1965**, *42*, 375.
 (12) Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195.
 (13) Martell, A. E.; Motekaitis, R. J. *The Determination and Use of Stability Constants*; VCH Publishers: New York, 1988.

- (14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159.
 (15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–100 and 149.
 (16) Carruthers, J. R.; Watkin, D. W. J. *CRYSTALS, an advanced crystallographic computer program*; University of Oxford, Chemical Crystallographic Laboratory: Oxford, England, 1985.

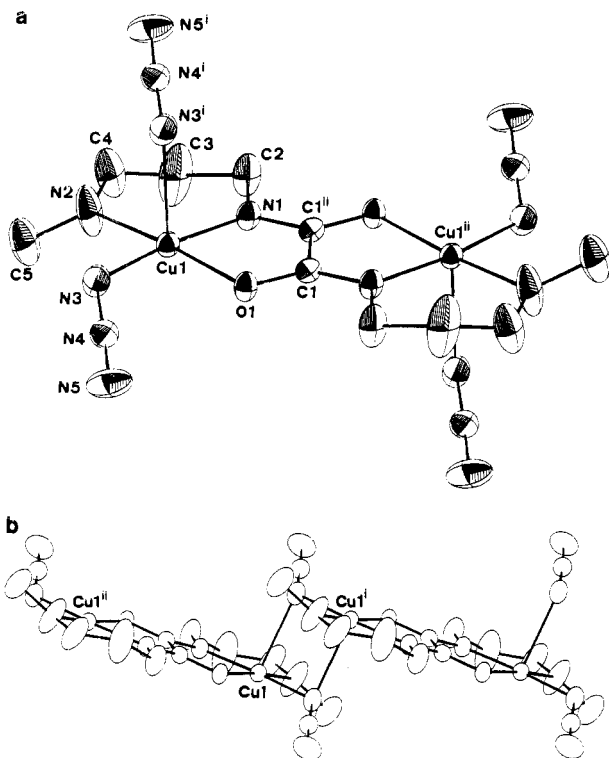


Figure 1. (a) ORTEP view of the binuclear $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]$ unit showing the atom labeling. Thermal ellipsoids are drawn at the 30% probability level. (b) A view of a fragment of the one-dimensional $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ chain running parallel to the c -axis.

performed on a VAX725 computer and molecular drawings were produced by the ORTEP¹⁷ program. The final atomic parameters and bond distances and angles are listed in Tables II and III, respectively. Complete crystal data, anisotropic thermal parameters, least-squares planes, and observed and calculated structure factors are given in Tables S1–S4.¹⁸

Results and Discussion

Description of the Structure. The structure of $[\text{Cu}_2\text{L}(\text{N}_3)_2]_n$ consists of neutral zigzag chains of copper(II) ions bridged by both mapox^{2-} and azido 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 and of a symmetry-related unit is depicted in Figure 1a. Inversion centers standing at the middle of the $\text{C}(1)–\text{C}(1)^{\text{ii}}$ bond and $\text{Cu}(1)–\text{Cu}(1)^{\text{i}}$ distance lead to one-dimensional chains of copper atoms running parallel to the c -axis as shown in Figure 1b.

Each copper atom is surrounded by four nitrogen atoms ($\text{N}(1)$, $\text{N}(2)$, $\text{N}(3)$, and $\text{N}(3)^{\text{i}}$) and one oxygen atom ($\text{O}(1)$) occupying the vertices of a distorted square-based pyramid. The basal plane is built by the carbonyl oxygen $\text{O}(1)$, amide nitrogen $\text{N}(1)$, and amine nitrogen $\text{N}(2)$ atoms of the oxamidate ligand and one azido-nitrogen $\text{N}(3)$ atom of the dissymmetrical azido bridge, the apical position being occupied by the symmetry-related azido nitrogen $\text{N}(3)^{\text{i}}$ atom of the other dissymmetrical azido bridge. The largest deviation from the least-squares plane through $\text{N}(1)\text{N}(2)\text{N}(3)\text{O}(1)$ is 0.039 Å at $\text{O}(1)$, and the metal atom is pulled out of this plane toward the apical site by 0.006 Å. The three equatorial copper(II) oxamidate distances (1.952 (7), 2.024 (9), and 1.980 (5) Å for $\text{Cu}(1)–\text{N}(1)$, $\text{Cu}(1)–\text{N}(2)$, and $\text{Cu}(1)–\text{O}(1)$, respectively) are close to those found in other oxamidate bridged copper(II) complexes.^{2d–g,6a,c,19–21} The significant shortening of

Table IV. Equilibrium Data^a for Basicity and Formation of $\text{Cu}(\text{II})$ Complexes with L^{2-} ($\text{L} = \text{mapox}$, dmapox) in Aqueous Solution (25 °C in 0.1 mol dm^{-3} NaNO_3)

reacn	log β	
	mapox	dmapox
(1) $2\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{H}_2\text{L}$	24.0 (2)	24.0 (2)
(2) $\text{H}^+ + \text{H}_2\text{L} \rightleftharpoons \text{H}_3\text{L}^+$	10.31 (1)	9.49 (1)
(3) $2\text{H}^+ + \text{H}_2\text{L} \rightleftharpoons \text{H}_4\text{L}^{2+}$	20.06 (1)	18.34 (1)
(4) $2\text{Cu}^{2+} + \text{H}_2\text{L} \rightleftharpoons [\text{Cu}_2(\text{H}_2\text{L})]^{4+}$	12.70 (2)	10.64 (9)
(5) $2\text{Cu}^{2+} + \text{H}_2\text{L} \rightleftharpoons [\text{Cu}_2(\text{HL})]^{3+} + \text{H}^+$	7.70 (8)	5.12 (50)
(6) $2\text{Cu}^{2+} + \text{H}_2\text{L} \rightleftharpoons [\text{Cu}_2\text{L}]^{2+} + 2\text{H}^+$	2.41 (1)	−0.76 (1)
(7) $3\text{Cu}^{2+} + 2\text{H}_2\text{L} \rightleftharpoons [\text{Cu}_3\text{L}_2]^{2+} + 4\text{H}^+$	−0.72 (1)	
(8) $4\text{Cu}^{2+} + 3\text{H}_2\text{L} \rightleftharpoons [\text{Cu}_4\text{L}_3]^{2+} + 6\text{H}^+$	−4.47 (1)	
(9) $\text{Cu}^{2+} + \text{H}_2\text{L} \rightleftharpoons [\text{CuL}] + 2\text{H}^+$	−6.91 (1)	
(10) $2\text{Cu}^{2+} + \text{H}_2\text{L} + \text{H}_2\text{O} \rightleftharpoons [\text{Cu}_2\text{L}(\text{OH})]^+ + 3\text{H}^+$		−9.34 (1)
(11) $2\text{Cu}^{2+} + \text{H}_2\text{L} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Cu}_2\text{L}(\text{OH})_2] + 4\text{H}^+$		−19.12 (1)

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

the $\text{Cu}(1)–\text{N}(1)$ bond length agrees with the stronger basicity of the deprotonated amide nitrogen atom (vide infra). The two copper–nitrogen (azido) bonds are markedly different from each other, the equatorial distance ($\text{Cu}(1)–\text{N}(3) = 1.976$ (8) Å) being shorter than the axial one ($\text{Cu}(1)–\text{N}(3)^{\text{i}} = 2.542$ (9) Å). This structural feature had been observed in other polynuclear copper(II) complexes containing asymmetrical end-on azido bridges.^{22–26} The $\text{N}(2)–\text{Cu}(1)–\text{O}(1)$ and $\text{N}(1)–\text{Cu}(1)–\text{N}(3)$ angles are 174.1 (4)° and 172.6 (3)°, respectively. Distortion of the metal environment is also evident from the values found for the $\text{N}(1)–\text{Cu}(1)–\text{O}(1)$ and $\text{N}(1)–\text{Cu}(1)–\text{N}(2)$ angles (83.6 (2)° and 95.7 (3)°, respectively).

The deprotonated mapox^{2-} ligand adopts the trans conformation forming one five- and one six-membered chelate ring on each metal ion. The three atoms around $\text{N}(1)$ lie in a plane with bond angles of 114.1 (5), 128.8 (6), and 116.8 (7)° for $\text{C}(1)^{\text{ii}}–\text{N}(1)–\text{Cu}(1)$, $\text{C}(2)–\text{N}(1)–\text{Cu}(1)$, and $\text{C}(1)^{\text{ii}}–\text{N}(1)–\text{C}(2)$, respectively. This fact together with the bond lengths and planarity of the oxamidato bridge indicate that $\text{N}(1)$ and its symmetry-related $\text{N}(1)^{\text{ii}}$ are sp^2 -hybridized and that the π -electrons of $\text{C}(1)^{\text{ii}}–\text{O}(1)^{\text{ii}}$ and of $\text{C}(1)–\text{O}(1)$ are delocalized to form a conjugated system. The least-squares plane through the four closest donor atoms of $\text{Cu}(1)$ ($\text{N}(1)$, $\text{N}(2)$, $\text{N}(3)$, $\text{O}(1)$) forms a dihedral angle of 3.8° with the oxamidato plane ($\text{N}(1)\text{C}(1)^{\text{ii}}\text{O}(1)^{\text{ii}}\text{O}(1)\text{C}(1)\text{N}(1)^{\text{ii}}$). The distance between the mean plane $\text{Cu}(1)\text{O}(1)\text{N}(1)\text{N}(2)\text{N}(3)$ and the symmetry-related one concerning the $\text{Cu}(1)^{\text{i}}$ atom is 2.602 Å. Mean planes $\text{Cu}(1)\text{O}(1)\text{N}(1)\text{N}(2)\text{N}(3)$ and $\text{Cu}(1)\text{N}(3)\text{Cu}(1)^{\text{i}}\text{N}(3)^{\text{i}}$ form a dihedral angle of 90.3°. The azido bridge is quasi-linear ($\text{N}(3)–\text{N}(4)–\text{N}(5) = 176.2$ (10)°, whereas the $\text{Cu}(1)–\text{N}(3)–\text{N}(4)$ linkage is bent (124.1 (7)°). The $\text{N}(3)–\text{N}(4)$ and $\text{N}(4)–\text{N}(5)$ bond lengths, equal 1.19(1) and 1.15(1) Å, respectively, differ by a significant amount as observed in other asymmetric end-on azido-bridged copper(II) complexes.^{22–26} In the cases where the azide anion acts as a terminal ligand, the two bond lengths concerned show a larger difference, the longer bond involving the nitrogen atom linked to the metal.^{22,24,25,27–29} This structural pattern of azido ligand essentially linear and asymmetric, the shorter $\text{N}–\text{N}$ bonds being more remote from the metal atoms, agrees with the general trend for coordinated azides.³⁰

- (17) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.
 (18) Supplementary material.
 (19) Bencini, A.; Benelli, C.; Fabretti, A. C.; Franchini, G.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 1063.
 (20) Bencini, A.; Di Vaira, M.; Fabretti, A. C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 1620.
 (21) Yoshino, A.; Nowacki, W. Z. *Krystallogr.* **1974**, *139*, 337.

- (22) Chaudhuri, P.; Oder, K.; Wiegart, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2818.
 (23) Bkouche-Waksman, I.; Boillot, M. L.; Kahn, O.; Sikorav, S. *Inorg. Chem.* **1984**, *23*, 4454.
 (24) Bkouche-Waksman, I.; Sikorav, S.; Kahn, O. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 303.
 (25) Commarmond, J.; Plumere, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.
 (26) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 444.
 (27) Goher, M. A. S.; Mak, T. C. W. *Inorg. Chim. Acta* **1984**, *85*, 117.
 (28) Buchnell, G. W.; Kahn, M. A. *Can. J. Chem.* **1974**, *52*, 3125.
 (29) Agrell, I. *Acta Chem. Scand.* **1969**, *23*, 1667, and **1966**, *20*, 1281.

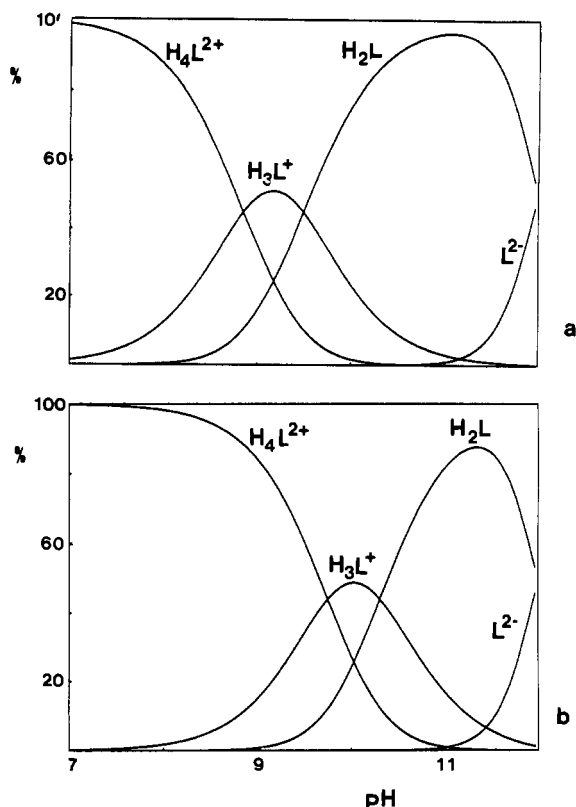


Figure 2. Distribution diagram for the system H^+/L^{2-} , $L = \text{mapox}^{2-}$ (a) and dmapox^{2-} (b).

The copper...copper separations through mapox^{2-} and azido bridges are 5.247 (2) and 3.360 (2) Å for $\text{Cu}(1)\cdots\text{Cu}(1)^{\text{ii}}$ and $\text{Cu}(1)\cdots\text{Cu}(1)^{\text{i}}$, respectively. The shortest interchain metal-metal separation is 6.667 Å for $\text{Cu}(1)\cdots\text{Cu}(1)^{\text{iii}}$ or $\text{Cu}(1)\cdots\text{Cu}(1)^{\text{iv}}$ where iii and iv denote the symmetry operations $x - 1/2, 3/2 - y, z - 1/2$ and $x + 1/2, 3/2 - y, z + 1/2$, respectively.

Acidity Constants of $H_4\text{mapox}^{2+}$ and $H_4\text{dmapox}^{2+}$. Aqueous solutions of $H_2\text{mapox}$ or $H_2\text{dmapox}$ of variable concentration ($c_L = (1-8) \times 10^{-3} \text{ mol dm}^{-3}$) previously acidified 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 ranges 8.0–11.6 ($H_2\text{mapox}$) and 7.5–11.6 ($H_2\text{dmapox}$) allowed us to determine their deprotonation constants. They are listed in Table IV (eqs 1–3) under the form of protonation constants. These values show that L^{2-} behaves as a relatively strong base in the two first protonation steps (eq 1) and its basicity decreases slightly in the two last protonation steps (eqs 2 and 3). 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. Taking into account that the value of $\log \beta_3$ for eqs 2 (10.12 (1)) and 3 (19.57 (1)) in the case of $L = \text{apox}$,^{6c} the proton affinity of the pendant amine groups follows the usual trend ($H_2\text{mapox} > H_2\text{apox} > H_2\text{dmapox}$) observed for N-alkyl-substituted amines. 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.³¹ The distribution diagrams for H^+/mapox^{2-} and H^+/dmapox^{2-} are depicted in parts a and b of Figure 2, respectively. The only existing species at lower pH values is H_4L^{2+} in both cases. H_3L^+ is the major species in a very narrow pH range around 10 for mapox and 9.4 for dmapox , whereas the neutral H_2L one predominates at $\text{pH} > 10.5$ (mapox) or $\text{pH} > 9.7$ (dmapox). At $\text{pH} > 11$, the deprotonation of H_2L occurs to yield the fully deprotonated L^{2-} species. We have treated potentiometrically data up to $\text{pH} = 11.6$ where less than 20% of L^{2-} is present. The high value of the overall protonation constant

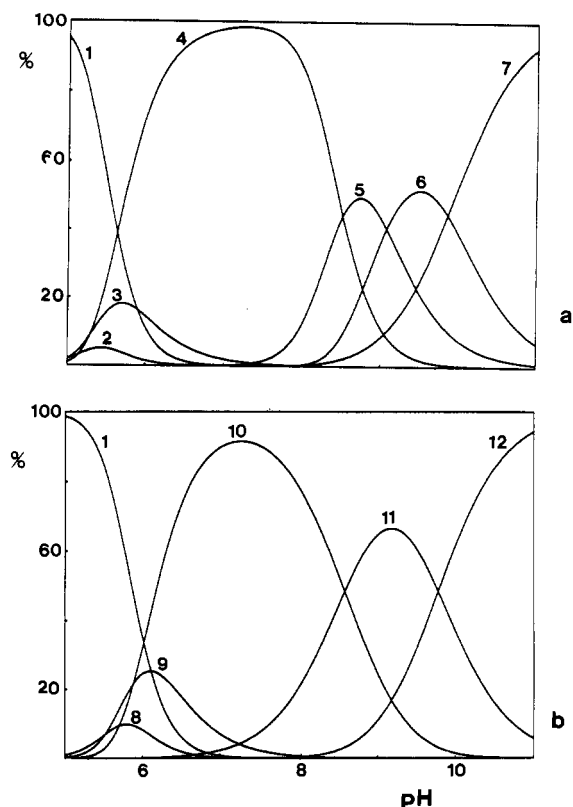


Figure 3. Distribution diagram for the systems $\text{Cu}^{2+}/\text{mapox}^{2-}/H^+$ (a) and $\text{Cu}^{2+}/\text{dmapox}^{2-}/H^+$ (b) as a function of pH ($c_M = c_L = 5 \times 10^{-3} \text{ mol dm}^{-3}$). 1, 2, 3, 4, 5, 6, and 7 in (a) refer to $[\text{Cu}^{2+}]$, $[\text{Cu}_2(\text{H}_2\text{mapox})]^{4+}$, $[\text{Cu}_2(\text{Hmapox})]^{3+}$, $[\text{Cu}_2(\text{mapox})]^{2+}$, $[\text{Cu}_3(\text{mapox})_2]^{2+}$, $[\text{Cu}_4(\text{mapox})_3]^{2+}$, and $[\text{Cu}(\text{mapox})]$, respectively. 1, 8, 9, 10, 11, and 12 in (b) correspond to $[\text{Cu}^{2+}]$, $[\text{Cu}_2(\text{H}_2\text{dmapox})]^{4+}$, $[\text{Cu}_2(\text{Hdmapox})]^{3+}$, $[\text{Cu}_2(\text{dmapox})]^{2+}$, $[\text{Cu}_2(\text{dmapox})(\text{OH})]^+$, and $[\text{Cu}_2(\text{dmapox})(\text{OH})_2]$, respectively.

of the oxamidato group that we have determined illustrates the great basicity of this entity and accounts for the difficulty associated to its potentiometric determination in aqueous solution. In spite of the lack of accuracy in the determination of this constant, we have observed that the deprotonation of the amide groups of oxamide is not influenced by the nature of its N,N'-substituents. In fact, a value close to 24 for $\log \beta_2$ is obtained for other oxamidate ligands.⁶

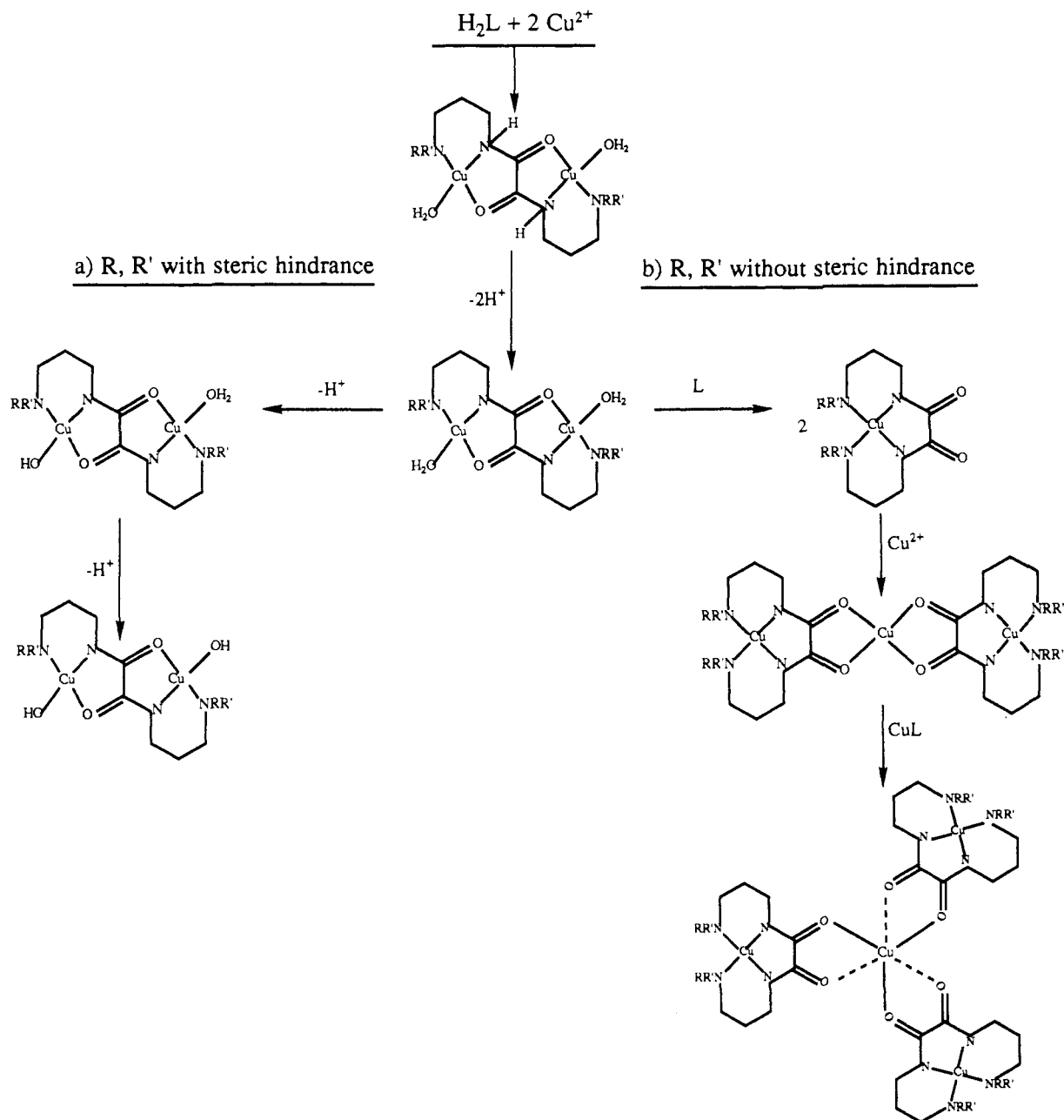
Stability Constants of the Complexes $\text{Cu}^{\text{II}}-\text{H}_2\text{mapox}$ and $\text{Cu}^{\text{II}}-\text{H}_2\text{dmapox}$. Aqueous solutions of copper(II) nitrate and H_2L ($c_L/c_M = 0.5-1.5$; $c_M = (1-5) \times 10^{-3} \text{ mol dm}^{-3}$ ($L = \text{mapox}$) and $c_M = (2-4) \times 10^{-3} \text{ mol dm}^{-3}$ ($L = \text{dmapox}$)), previously acidified, were titrated with KOH (0.1 mol dm^{-3}). Data processing by the programs SUPERQUAD and BEST of 164 ($\text{Cu}^{\text{II}}-\text{H}_2\text{mapox}$) and 122 ($\text{Cu}^{\text{II}}-\text{H}_2\text{dmapox}$) experimental points from different experiments in the pH range 5.2–10.1 allowed us to characterize thermodynamically the equilibria involved in the formation of mono-, di-, tri-, and tetranuclear complexes whose stoichiometries and stability constants are listed in Table IV (eqs 4–11).

The distribution diagrams of the systems $\text{Cu}^{\text{II}}-\text{H}_2\text{mapox}$ and $\text{Cu}^{\text{II}}-\text{H}_2\text{dmapox}$ are depicted in parts a and b of Figure 3, respectively. As shown in Figure 3a, the dinuclear complexes $[\text{Cu}_2(\text{H}_2\text{mapox})]^{4+}$ and $[\text{Cu}_2(\text{Hmapox})]^{3+}$ are formed in low percentages at lower pH values. $[\text{Cu}_2(\text{mapox})]^{2+}$ is the main species in neutral conditions, whereas the formation of the trinuclear and tetranuclear complexes occurs at $\text{pH} \geq 8$. The mononuclear complex $[\text{Cu}(\text{mapox})]$ is the predominant species at $\text{pH} > 10$ for a 1:1 $\text{Cu}^{\text{II}}/\text{H}_2\text{mapox}$ molar ratio. This distribution diagram is very close to the previously reported one for the parent $\text{Cu}^{\text{II}}-\text{H}_2\text{apox}$ system.^{6c} In contrast, only the dinuclear species $[\text{Cu}_2(\text{H}_2\text{dmapox})]^{4+}$, $[\text{Cu}_2(\text{Hdmapox})]^{3+}$, $[\text{Cu}_2(\text{dmapox})]^{2+}$, $[\text{Cu}_2(\text{dmapox})(\text{OH})]^+$, and $[\text{Cu}_2(\text{dmapox})(\text{OH})_2]$ are formed in the $\text{Cu}^{\text{II}}-\text{H}_2\text{dmapox}$ system. As in the preceding system, the

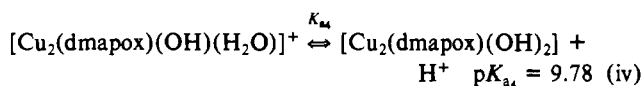
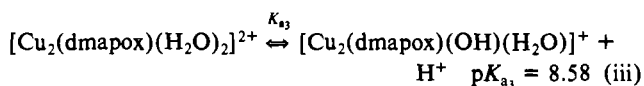
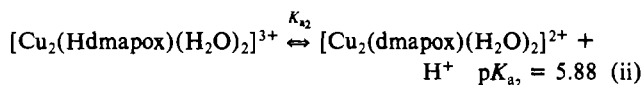
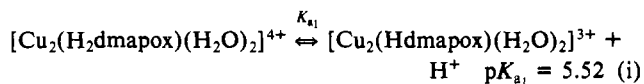
(30) Dori, Z.; Ziolo, R. F. *Chem. Rev.* 1973, 73, 247.

(31) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1974, 1975, 1976, 1977, 1982, 1989; Vols. 1–6.

Scheme I



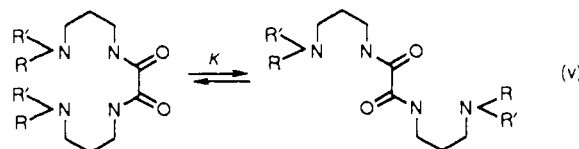
dinuclear $[\text{Cu}_2(\text{dmapox})]^{2+}$ complex is the main species in neutral conditions, $[\text{Cu}_2(\text{H}_2\text{dmapox})]^{4+}$ and $[\text{Cu}_2(\text{Hdmapox})]^{3+}$ being formed in low percentages at lower pH values. At high pH values, the deprotonation of coordinated water molecules occurs leading to the formation of hydroxo complexes. The acid-base equilibria involving these species are given in eqs i-iv. The first two $\text{p}K_a$



values (eqs i and ii) are very close and more than 2 orders of

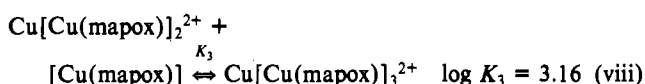
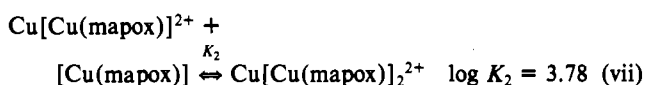
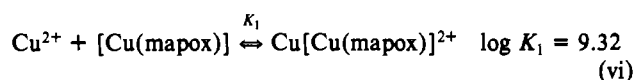
magnitude greater than the two later ones (eqs iii and iv). The first pair would correspond to the deprotonation of coordinated amido groups, whereas the second pair would concern the deprotonation of coordinated water molecules. The acidity of the coordinated water in $[\text{Cu}_2(\text{dmapox})(\text{H}_2\text{O})_2]^{2+}$ (eq iii) is close to those reported for the copper(II) complexes $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$ ($\text{p}K_a = 9.17$)^{32a} and $[\text{Cu}(\text{terpy})(\text{H}_2\text{O})]^{2+}$ ($\text{p}K_a = 8.11$),^{32b} dien and terpy being diethylenetriamine and 2,2':6',2''-terpyridine.

It is known that oxamidate ligands can adopt either cis or trans conformations (eq v). In a previous work,^{6c} we demonstrated that



(32) (a) Castro, I.; Faus, J.; Julve, M.; Lloret, F.; Verdaguer, M.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Vaisserman, J. *J. Chem. Soc., Dalton Trans.* 1990, 2207. (b) Castro, I.; Faus, J.; Julve, M.; Philoche-Levisalles, M. *Transition Met. Chem. (Weinheim, Ger.)*, in press.

this conformational change does not involve a significant potential barrier at room temperature and an ab initio calculation showed the trans conformation to be more stable than the cis one ($\log K = 1.6$ in eq v) in the lack of steric hindrance. The cis conformation would lead to mononuclear complexes which can act as ligands yielding di-, tri-, and tetranuclear entities (see Scheme I). The formation of these species has been observed in the complexes with mapox and apox ligands. The formation of the monomeric species involving the cis conformation of dmapox must be prohibited due to the steric hindrance between the four methyl substituents on the amine nitrogen atoms in contrast to what is observed for mapox, where the replacement of two methyl groups by two H atoms makes possible both conformations. At this respect, it seems interesting to compare the values of the logarithms of the stepwise stability constants given in eqs vi–viii. Too large



a difference can be observed between the values of $\log K_1$ and $\log K_2$. This apparent anomaly can be explained by taking into account the cis–trans conformational change of mapox which is involved in eqs vi and vii. In reaction vi, mapox goes from the cis conformation ($[\text{Cu}(\text{mapox})]$) to trans ($[\text{Cu}_2(\text{mapox})]^{2+}$), whereas in (vii) it moves from trans (dinuclear species) to cis (trinuclear species) (see Scheme I). No conformational change

occurs in reaction viii. The higher stability of the trans conformer with regard to the cis one provides an additional stabilization of the dimeric species (eq vi) and, consequently, a decrease in the stability of the trimer (eq vii). Taking into account the energetic cost of the cis–trans conformational change ($\log K = 1.6$ in eq v) we can obtain the values of $9.32 - 1.6 = 7.72$ and $3.78 + 1.6 = 5.38$ for $\log K_1$ and $\log K_2$ (eqs vi and vii), respectively. The trend of the corrected values for the stepwise stability constants is in a better agreement with the expected result from a statistical viewpoint.

The monohydroxo complex $[\text{Cu}_2(\text{dmapox})(\text{OH})]^+$ is a very interesting precursor of copper(II) chains with alternating oxamidato and hydroxo bridges. In this respect, we have isolated a compound of formula $\text{Cu}_2(\text{dmapox})(\text{OH})(\text{NO}_3) \cdot 3\text{H}_2\text{O}$ whose IR spectrum and magnetic behavior reveal the presence of both oxamidato and hydroxo bridges. Unfortunately, we have not yet succeeded in growing crystals of this interesting complex. The replacement of the coordinated water molecules by other related polyatomic ligands such as cyanate and thiocyanate allowed us to obtain single crystals of one-dimensional copper(II) chains with alternating oxamidato and pseudohalogen bridges which are similar to that reported herein.

Acknowledgment. Financial support from the Comisión Interministerial de Ciencia y Tecnología (Project PB88-0490) and the Programa de Acciones Integradas Hispano-Francesas is gratefully acknowledged. R. Ruiz thanks the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana for a doctoral fellowship.

Supplementary Material Available: Listings of crystallographic data (Table S1), anisotropic thermal parameters (Table S2), and least-squares planes (Table S3) and IR data on $[\text{Cu}_2(\text{mapox})(\text{N}_3)_2]_n$ (4 pages); a listing of calculated and observed structure factors (Table S4) (4 pages). Ordering information is given on any current masthead page.