

Complexing Ability of a New Type of Bis-amidato Ligand. Crystal Structure of *N,N'*-Bis(1-methyl-3-oxo-1-butenyl)oxamidato Copper(II) (CuL); Spectroscopic and Magnetic Properties and Redox Behaviour of CuL and the Related Nickel(II), Cobalt(II) and Cobalt(III) Complexes

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Abstract

Two original ligands (LH_2 and $L'H_2$) comprising amido groups adjacent to unsaturated fragments have been synthesized.

While reaction of metallic ions with $L'H_2$ results in breaking of the imine bonds, defined complexes of LH_2 [*N,N'*-bis(1-methyl-3-oxo-1-butenyl)oxamide] with copper(II), nickel(II), cobalt(II) and cobalt(III) may be isolated. The copper(II) complex (CuL) crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 8.862(2)$, $b = 16.014(2)$, $c = 9.105(1)$ Å, $\beta = 97.54(1)^\circ$. Intermolecular Cu...O interactions lead to the formation of pseudo dimers. From the micro-analytical spectroscopic and magnetic data, polynuclear structures may be attributed to the nickel(II) ($NiL \cdot MeOH$) and cobalt(II) ($CoL \cdot 3H_2O$) complexes whereas the cobalt(III) ($[CoL \cdot 2Py]ClO_4$) complex is likely a mononuclear species. The unexpected electrochemical behaviour of these complexes points to a significant electronic transfer from the metal to the ligand resulting from the presence of a large π -system.

Introduction

There is much current interest in ligands bearing an amido group because (i) they act as fundamental building blocks in many biomolecules; (ii) on complexation they shift the redox potentials of the metal centers toward more positive values [1] and, therefore, stabilize metal ions in their higher oxidation states [2–6]; (iii) when they are associated to form a dioxamido fragment [$-HN(O)C-C(O)NH-$], they lead to polymetallic systems with interesting magnetic properties [7–11].

In search of new polynucleating ligands, we have investigated the possibility of inserting an unsaturated

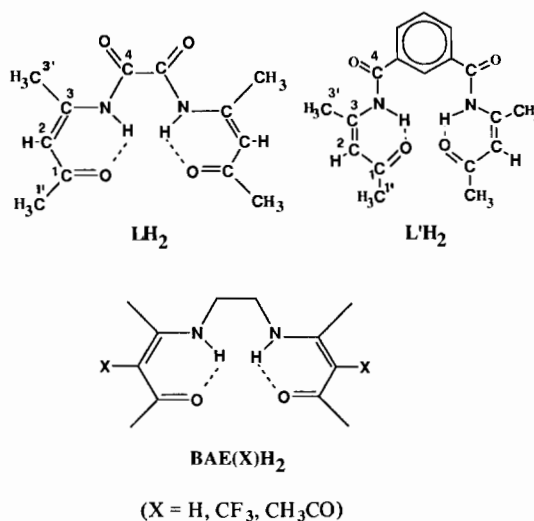


Fig. 1. Schematic representation of the ligands.

system, namely an acetylacetoniminato fragment, in the vicinity of an amido group. We succeeded in obtaining two such ligands. In the first one (LH_2 , Fig. 1), the two amido groups are adjacent while they are separated by a benzene ring in the second one ($L'H_2$). In spite of many attempts no complex involving the latter ligand can be isolated so that the present paper is mainly devoted to the mononuclear complexes of LH_2 , *N,N'*-bis(1-methyl-3-oxo-1-butenyl)oxamide. The properties of the related dinuclear complexes will be considered in a subsequent paper.

Experimental

Synthesis of the Ligands LH_2 and $L'H_2$

In a typical preparation of LH_2 , 5 g (0.05 mol) of 4-amino-3-pentene-2-one ($AcNH_2$) [12] and 5 g (0.05 mol) of triethylamine were dissolved in 150 ml of

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TABLE 1. Analytical data

	Found (calc.) (%)					
	C	H	N	Cu	Ni	Co
L	57.20 (57.1)	6.3 (6.4)	11.2 (11.1)			
L'	65.7 (65.8)	6.2 (6.1)	8.3 (8.5)			
CuL	45.3 (45.9)	4.1 (4.5)	8.3 (8.9)	20.0 (20.2)		
NiL·CH ₃ OH	45.6 (45.8)	5.1 (5.3)	8.7 (8.2)		17.0 (17.2)	
Co ^{II} L·3H ₂ O	40.1 (39.7)	5.2 (5.5)	7.5 (7.7)			15.9 (16.2)
[Co ^{III} L·2py]ClO ₄	47.0 (46.6)	4.5 (4.3)	10.1 (9.9)			10.1 (10.4)

anhydrous diethyl ether. To the resulting solution kept at 0 °C, were added 4.5 g (0.035 mol) of oxalyl dichloride. The mixture was stirred at room temperature for 4 h. The amine chlorhydrate was removed by filtration and then the ether on a rotary evaporator. A pure sample of LH₂ was obtained by recrystallization from methanol (yield 60%). Similarly L'H₂ was obtained from the reaction of isophthaloyl dichloride with AcNH₂ (yield 65%). The purity of LH₂ and L'H₂ was checked by microanalyses* (Table 1) and by NMR spectroscopy (*vide infra*).

Synthesis of the Complexes of LH₂

For the copper and nickel complexes, a solution of 2 mmol of the perchlorate salt and 7 mmol of dimethoxypropane in 5 ml of methanol, was added dropwise to a solution of LH₂ (1 mmol) and triethylamine (2 mmol) in methanol (50 ml). The mixture was stirred for 4 h at room temperature and then evaporated. In both cases the resulting precipitate was washed with methanol and dried (yield 55%). A similar procedure was used for the cobalt(II) complex but all the manipulations were performed under an inert atmosphere and the reaction mixture was stirred at 60 °C for 1 h. The cobalt(III) complex was prepared according to Costa's procedure [13] as modified by Averill and Broman [14]. All attempts to prepare a methyl cobalt complex of LH₂ by Schrauzer's method [15] failed. In all cases the final product was identified (microanalytical data and ¹H NMR) as MeCoBAE(H)·H₂O**.

The microanalytical data characterizing the copper(II), nickel(II), cobalt(II) and cobalt(III) complexes are quoted in Table 1. They are consistent with the following formulations: CuL; NiL·MeOH; Co(II)L·3H₂O and [Co(III)L·2Py]ClO₄.

It should be underlined that we did not succeed in preparing any complex of the second ligand L'H₂. Reaction of L'H₂ with Cu²⁺, Ni²⁺, Co²⁺ and Co³⁺

ions under experimental conditions identical to those used in the case of LH₂ leads to the formation of the related complexes of 4-amino-3-penten-2-one M(AcNH)_n (n = 2 or 3).

Physical Measurements

¹H and ¹³C NMR spectra were run on a Bruker WH 90 spectrometer using SiMe₄ as internal reference. Infrared spectra of KBr discs were run on a Perkin-Elmer 984 spectrometer and visible spectra on a CARY 2300 instrument. Electrochemical measurements were performed as previously described [16]. A platinum auxiliary electrode and an Ag-AgCl (0.1 M KCl) reference electrode were used in conjunction with a dropping Hg electrode. ESR spectra were recorded at X-band frequency (9.4–9.5 GHz) with a Bruker 200 T spectrometer. Magnetic susceptibility data were collected on powdered samples with use of a Faraday-type magnetometer using memory tetra-(thiocyanato)cobaltate as standard (susceptibility at 20 °C, 16.4 × 10⁻⁶ cm³ mol⁻¹). Data were corrected for the diamagnetism of the ligand estimated from Pascal constants [17].

X-ray Crystal Structure Determination of CuL

Crystal data

C₁₂H₁₄CuO₄N₂, M = 313.8, monoclinic, space group P2₁/c, a = 8.862(2), b = 16.014(2), c = 9.105(1) Å, β = 97.54(1)°, V = 1281.0(5) Å³, Z = 4, D_c = 1.63 g cm⁻³, F(000) = 644, Mo Kα radiation, I = 71073 Å, μ = 17.18 cm⁻¹, 293 K.

Data collection

A single crystal was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell constants were determined from a least-squares refinement of the setting angles of 25 reflections (21 were in the range 18 < q < 23°). A unique data set (h, k, ±l; 0 < q < 30°) was recorded by the q-2q scan technique (scan width 0.85 + 0.35 tan q, scan speed 2–10° min⁻¹). The intensities of three standard reflections measured every hour showed no significant variation. A total of 3721 independent reflections was obtained and

*Microanalyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France.

**Me and Py stand for CH₃ and C₅H₅N, respectively while BAE(H) represents the dianionic form of N,N'-ethylene-bis(acetylacetonimine) (cf. Fig. 1).

corrected for Lorentz and polarization effects; 1951 reflections with $I > 3\sigma(I)$ were used for the structure determination. No absorption correction was applied.

Structure Determination

The structure was solved by the heavy atom method using the SDP chain of program [18]. All calculations were performed on a VAX-11/780 DEC computer. The Cu atom was found by a Patterson map calculation. Subsequent full-matrix least-squares refinement and interpretation of Fourier and Fourier difference maps enabled all non-H atoms to be

TABLE 2. Positional parameters and their e.s.d.s for $C_{12}H_{14}CuO_4N_2$

Atom	x	y	z
Cu	0.22604(5)	0.05902(3)	-0.02968(5)
O(1)	0.0620(3)	0.0697(2)	-0.1893(3)
O(2)	0.2190(3)	0.1786(1)	-0.0245(3)
O(3)	0.3605(7)	-0.1674(2)	-0.1036(4)
O(4)	0.5603(3)	-0.0521(2)	0.2256(4)
N(1)	0.2226(4)	-0.0621(2)	-0.0290(4)
N(2)	0.3889(3)	0.0509(2)	0.1352(3)
C(1)	-0.0130(4)	0.0100(2)	-0.2516(4)
C(2)	0.0106(5)	-0.0749(3)	-0.2182(5)
C(3)	0.1218(4)	-0.1104(2)	-0.1164(5)
C(4)	-0.1366(5)	-0.0354(3)	-0.3739(5)
C(5)	0.1295(6)	-0.2043(3)	-0.1080(7)
C(6)	0.3369(4)	-0.0951(3)	0.0726(5)
C(7)	0.4413(5)	-0.0286(3)	0.1550(4)
C(8)	0.4504(4)	0.1176(3)	0.2176(4)
C(9)	0.4036(5)	0.1971(3)	0.1867(4)
C(10)	0.2919(5)	0.2249(2)	0.0714(4)
C(11)	0.5683(5)	0.1036(3)	0.3524(5)
C(12)	0.2533(6)	0.3158(3)	0.0616(5)

located. These were refined anisotropically. The H atoms were located on a Fourier-difference map and were refined isotropically. Unit weights were applied and gave satisfactory weight analysis. The final R was 0.033 ($R' = 0.035$). The error in an observation of unit weight was 1.1 electron. A last Fourier difference map showed no significant feature. Atomic coordinates are listed in Table 2.

Results and Discussion

The 1H NMR spectra show that, with respect to the reference compound BAE(H) H_2 (Fig. 1) [19], all the nuclei pertaining to LH_2 and $L'H_2$ are shifted downfield (Table 3). This effect which increases from *c.* 0.3 ppm (H_1') to *c.* 0.5 ppm (H_3') can be related to the influence of the amide groups. The splitting observed for the H_1' , H_2 and H_3 signals of LH_2 is likely attributable to the occurrence of a keto-enolic tautomeric equilibrium. In the spectrum of $L'H_2$, the H_3' signal only appears as a doublet, this may possibly result from an in-plane distortion of the molecular backbone.

In the ^{13}C spectra, the most significant indication of the presence of the amide group is the large chemical shifts of C_4 , i.e. 158.6 and 164.9 ppm for LH_2 and $L'H_2$, respectively.

One can anticipate that the most interesting feature of the IR spectra would occur in the 'double-bond' region. In the case of LH_2 , two well-defined bands are observed at 1710 and 1640 cm^{-1} . They are attributable beyond doubt to the amide-1 modes, $\nu(C=O)_2$ in-phase and out-of-phase [20]. The fact that the two $\nu(C=O)_2$ are IR active implies that the molecule has C_{2v} symmetry and therefore adopts a *cis*-configuration [20]. This is unusual since the

TABLE 3. 1H NMR and ^{13}C NMR shifts (ppm vs. TMS in $CDCl_3$)^a

	H_1'	H_2	H_3'	N-H...O	Phenyl	NCH_2-CH_2-N	
1H NMR							
BAE(H_2)	1.90(s)	4.98(s)	2.00(s)	11.4(m)		3.40(m)	
LH_2	2.17	5.51	2.42	13.1(m)			
	2.16	5.52	2.41				
$L'H_2$	2.52	5.5(s)	2.52	13.5(m)	7.5-8.8(m)		
	2.51		2.51				
$[Co^{III}L \cdot 2py]ClO_4$	2.20(s)	5.50	2.40(s)		7.3-9.0(m)		
	C_1	C_1'	C_2	C_3	C_3'	C_4	Phenyl
^{13}C NMR							
BAE(H_2)	195.3	28.6	95.9	162.7	181	43.3	
LH_2	199.5	30.5	108	151.6	20.9	158.6	
$L'H_2$	200.1	30.2	106.2	155.6	21.7	164.9	131.1; 129.4; 128.1

^am = multiplet; s = singlet; the numbering scheme is indicated in Fig. 1.

N,N'-dialkyl (or diaryl) oxamides are known to exist in the *trans*-configuration. Assignment of the other bands characteristic of the amide group is not straightforward. The amide(II) bands are expected at *c.* 1520 and 1550 cm^{-1} so that they likely overlap with $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ of the $-\text{N}-\text{C}(\text{CH}_3)-\text{CH}-\text{C}(\text{CH}_3)-\text{CO}$ fragment [21, 22]. In fact, a broad ill-resolved absorption centered at *c.* 1580 cm^{-1} is observed. In the case of $\text{L}'\text{H}_2$, the amide-1 band is located at 1640 cm^{-1} .

The complexes CuL , $\text{NiL}\cdot\text{MeOH}$, $\text{Co}^{\text{II}}\text{L}\cdot 3\text{H}_2\text{O}$ and $[\text{Co}^{\text{III}}\text{L}\cdot 2\text{Py}]\text{ClO}_4$ were prepared by well-established methods (cf. 'Experimental') which do not deserve any particular comment. However it may be noted that Schrauzer's method fails to give the methyl cobalt complex of LH_2 . The product of the reaction, identified as MeCoBAE(H) , shows that the reduction step involved in the method is not restricted to the metal center but also affects the ligand.

As for $\text{L}'\text{H}_2$, its reaction with metal ions leads to the isolation of products identified (microanalyses, NMR and IR spectroscopies [23, 24] as complexes of 4-amino-3-penten-2-one, $\text{M}(\text{AcNH})_n$ with $\text{M} = \text{Cu}^{2+}$, Ni^{2+} and Co^{3+} . Breaking of the $\text{C}=\text{N}$ bonds is likely due to steric constraints.

Returning to the complexes of LH_2 , the characterization and study of $\text{NiL}\cdot\text{MeOH}$ and $\text{Co}^{\text{II}}\text{L}\cdot 3\text{H}_2\text{O}$ are severely hampered by the very low solubility of these two complexes and the lack of crystal suitable for structural determination. This is unfortunate more especially as the IR data point to striking differences between, on the one hand, CuL and $[\text{Co}^{\text{III}}\text{L}\cdot 2\text{Py}]\text{ClO}_4$ and, on the other hand, $\text{NiL}\cdot\text{MeOH}$ and $\text{Co}^{\text{II}}\text{L}\cdot 3\text{H}_2\text{O}$.

Focusing our interest on the amide-1 band, it appears as a strong and well-defined absorption at 1700 cm^{-1} in the spectra of the two former complexes. On the contrary the spectra of the two latter complexes are devoid of any signal in the 1750–1659 cm^{-1} range but show broad bands at 1610 and 1580 cm^{-1} . The 1610 cm^{-1} band may be attributed to the amide-1 since it has been found at 1620 cm^{-1} in the case of $[\text{CuLCuB}]^{2+}$ [25] (B being terpyridine). According to available structural data, the main difference between CuL and $[\text{CuLCuB}]^{2+}$ originates in the coordinating behaviour of the oxamide fragment which acts as a chelating ligand via its NH groups in CuL (*vide infra*) and as a bridging ligand through its NH and $\text{C}=\text{O}$ groups in $[\text{CuLCuB}]^{2+}$ [25]. Therefore we are inclined to think that the 1700 cm^{-1} value would correspond to essentially mononuclear structures in which the amide $\text{C}=\text{O}$ groups are free or eventually involved in weak intermolecular associations whereas the 1620 cm^{-1} value would characterize polynuclear structures with bridging oxamide fragments. A dinuclear structure, similar to that found for $[\text{CuLCuB}]^{2+}$, cannot be retained for the nickel and cobalt(II) complexes which contain

one molecule of ligand per metal ion. Polynuclear structures are also consistent with the very low solubility of these two species. Such a structure is precluded for the cobalt(III) complex which is coordinatively saturated by one molecule of ligand LH_2 and two molecules of pyridine.

Structure of the CuL Complex

A view of the complex unit with the atom numbering scheme is given in Fig. 2. Relevant atomic distances and angles are quoted in Table 4. There are four such molecules per unit cell. The copper atom is surrounded by two nitrogen and two oxygen atoms to give an almost planar CuN_2O_2 chromophore. Indeed the planes defined by $\text{CuN}(1)\text{O}(1)$ and $\text{CuN}(2)\text{O}(2)$ make an angle of 3.6° . However the molecule as a whole is distinctly bent since the two mean planes of the six-membered rings make an angle of 10.9° (Fig. 3(b)). It should be noted that in the related anhydrous complex CuBAE(H) [26] a larger value of 15.5° is observed. Developing the comparison between CuL and CuBAE(H) , we may remark that although the structures of these two complexes offer formal similitudes, a closer examination points to some significant differences. The most important are located near the $\text{C}(6)-\text{C}(7)$ bridge as expected. Whereas two significantly different $\text{C}-\text{N}$ distances are observed in CuBAE(H) , viz. $\text{C}(6,7)-\text{N}(1,2) \sim 1.43$ Å and $\text{N}(1,2)-\text{C}(3,8) \sim 1.30$ Å, the four $\text{C}-\text{N}$ bonds in CuL have almost identical lengths, from *c.* 1.36 to *c.* 1.38 Å. Similarly, the angles $\text{N}(1)\text{C}(6)\text{C}(7)$ and $\text{C}(6)\text{C}(7)\text{N}(2)$ are slightly larger in the present complex with a mean value of 113.9° than in CuBAE(H) (mean value 110.0°). These differences are likely related to the fact that the carbon atoms $\text{C}(6)$ and $\text{C}(7)$ display different hybridizations in the two complexes.

Interestingly, the $\text{C}(2,9)-\text{C}(1,10)$ and $\text{C}(1,10)-\text{O}(1,2)$ bond lengths display very similar values in CuL and CuBAE(H) and these values are consistent

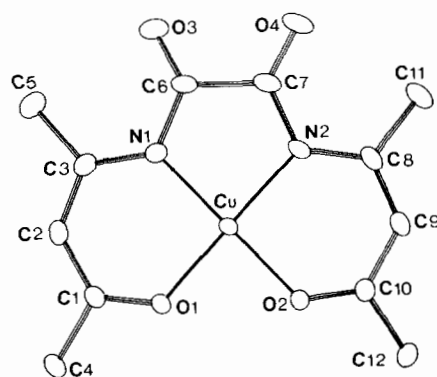


Fig. 2. View of the molecule $[\text{N,N}'\text{-bis}(1\text{-methyl-3-oxo-1-butenyl})\text{oxamidato copper(II)}$ showing the atom numbering scheme (the thermal ellipsoids are drawn at the 20% probability level).

TABLE 4. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Cu environment			
Cu–N(1)	1.940(3)	N(1)–Cu–N(2)	86.6(1)
Cu–N(2)	1.946(3)	N(1)–Cu–O(1)	94.6(1)
Cu–O(1)	1.923(3)	O(1)–Cu–O(2)	84.6(1)
Cu–O(2)	1.916(3)	O(2)–Cu–N(2)	94.1(1)
Cu...O(4)	2.769(4)		
Ligand environment			
O(1)–C(1)	1.256(5)	O(2)–C(10)	1.258(5)
C(1)–C(2)	1.403(6)	C(10)–C(9)	1.417(6)
C(2)–C(3)	1.383(6)	C(9)–C(8)	1.357(6)
C(1)–C(4)	1.512(5)	C(10)–C(12)	1.495(6)
C(3)–C(5)	1.507(6)	C(8)–C(11)	1.520(6)
C(3)–N(1)	1.357(5)	C(8)–N(2)	1.376(5)
N(1)–C(6)	1.385(5)	N(2)–C(7)	1.359(5)
C(6)–O(3)	1.203(5)	C(7)–O(4)	1.220(5)
Cu–O(1)–C(1)	125.5(2)	Cu–O(2)–C(10)	126.2(3)
O(1)–C(1)–C(2)	125.8(3)	O(2)–C(10)–C(9)	125.1(4)
O(1)–C(1)–C(4)	114.7(4)	O(2)–C(10)–C(12)	116.1(3)
C(4)–C(1)–C(2)	119.5(4)	C(12)–C(10)–C(9)	118.8(4)
C(1)–C(2)–C(3)	128.0(4)	C(10)–C(9)–C(8)	127.8(4)
C(2)–C(3)–N(1)	121.1(4)	C(9)–C(8)–N(2)	121.8(3)
C(2)–C(3)–C(5)	117.9(4)	C(9)–C(8)–C(11)	117.7(4)
C(5)–C(3)–N(1)	121.1(4)	C(11)–C(8)–N(2)	120.4(4)
C(3)–N(1)–Cu	125.3(3)	C(8)–N(2)–Cu	124.7(3)
C(3)–N(1)–C(6)	122.8(3)	C(8)–N(2)–C(7)	123.4(3)
Cu–N(1)–C(6)	112.0(3)	Cu–N(2)–C(7)	111.8(2)
N(1)–C(6)–C(7)	113.6(3)	N(2)–C(7)–C(6)	114.3(3)
N(1)–C(6)–O(3)	127.9(4)	N(2)–C(7)–O(4)	128.0(4)
O(3)–C(6)–C(7)	118.5(4)	O(4)–C(7)–C(6)	117.7(4)

with a significant degree of electronic delocalization along the two C(3, 8)–C(2, 9)–C(1, 10)–O(1, 2) moieties. The quasi identity of the four C–N bond lengths in CuL suggests an enlargement of the π -system toward the amide groups.

Molecules related through inversion centers at (0, 0, 0) and $(\frac{1}{2}, 0, 0)$ stack along the *a* axis and widely overlap. The overlapping scheme is shown on Fig. 3(a). The distances between molecule mean planes are 3.26 Å through (0, 0, 0) and 3.31 Å through $(\frac{1}{2}, 0, 0)$. These distances are markedly shorter than twice the van der Waals thickness of aromatic cycles [27], i.e. $2 \times 1.85 = 3.70$ Å.

A side view of the stack repeat unit (Fig. 3(b)) shows the double copper–oxygen bridge due to Cu...O(4) separations of 2.769(4) Å between molecules related through $(\frac{1}{2}, 0, 0)$. This dimerization gives the copper a 4 + 1 square pyramidal coordination geometry.

Magnetic Properties

$[\text{Co}^{\text{III}}\text{L}\cdot 2\text{Py}]\text{ClO}_4$ is diamagnetic and therefore can be characterized by NMR spectroscopy. Its ^1H spectrum (cf. Table 3) is practically identical to that of the free ligand except that the N–H signal is

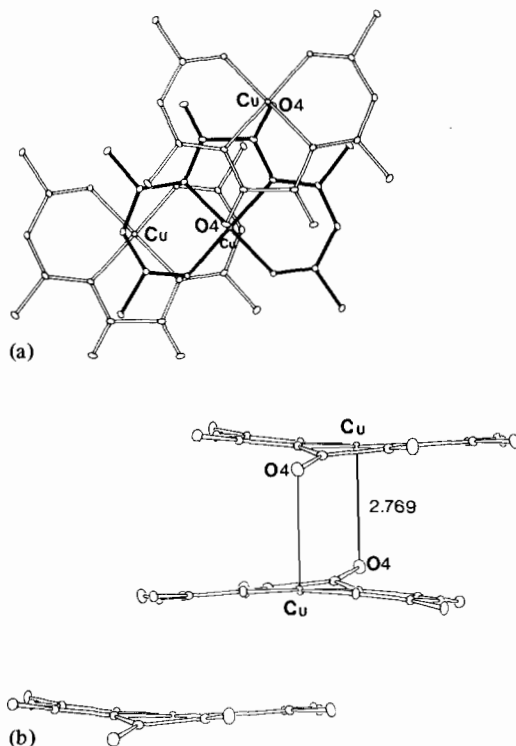


Fig. 3. View of three neighbouring stacked molecules: (a) projection onto the plane defined by the atoms O(1), O(2) and N(2) showing the overlap; (b) a side view showing the molecule bent geometry and the double intermolecular copper–oxygen contact.

no longer observed. Room temperature measurements show that $\text{NiL}\cdot\text{MeOH}$ and $\text{Co}^{\text{II}}\text{L}\cdot 3\text{H}_2\text{O}$ are paramagnetic with moments of 2.6 and 4.5 BM, respectively.

In the 5–300 K range, the magnetic susceptibility of CuL obeys a Curie–Weiss law with $C = 0.388$ and $\theta = 0.24$. The Curie constant is as expected for a copper(II) ion characterized by a *g* value of 2.03. The small but positive θ value is indicative of a weak antiferromagnetic interaction which is consistent with the intermolecular association pointed out by structural data.

At room temperature a powdered sample of CuL gives an almost axial ESR spectrum with $g_{\parallel} = 2.19_7$ and $g_{\perp} = 2.04_6$. Axial spectra are also observed for frozen solutions (methylene chloride, toluene) with well-resolved hyperfine and superhyperfine structures on the parallel component. The following parameters are deduced

$$g_{\parallel} = 2.19_5, \quad A_{\parallel}(\text{Cu}) = 201.3 \times 10^{-4} \text{ cm}^{-1},$$

$$A_{\parallel}(\text{N})^* = 13.4 \times 10^{-4} \text{ cm}^{-1}$$

*In accordance with the presence of two nitrogen atoms in the coordination sphere, five superhyperfine lines are observed.

At room temperature these solutions display usual isotropic spectra with

$$g_{\text{iso}} = 2.094, \quad A_{\text{iso}}(\text{Cu}) = 88.0 \times 10^{-4} \text{ cm}^{-1},$$

$$A_{\text{iso}}(\text{N}) = 12.7 \times 10^{-4} \text{ cm}^{-1}$$

An analysis of these ESR parameters can be performed according to the conventional perturbation approach developed in different papers [28, 29].

We assume that the symmetry of the metal environment may be approximated as $C_{2v}(x)$, the molecular plane being chosen as the x, y - plane and the x -axis bisecting the $\text{N}(1)\text{--Cu--N}(2)$ angle (cf. Fig. 2).

With this choice, the ground state molecular orbital is the antibonding combination of the d_{xy} orbital on the metal and the ligand σ orbital transforming as B_2 in $C_{2v}(x)$, i.e. [28–33]

$$\Psi_{B_2} = \alpha|x y\rangle - \alpha'/2|B_2\rangle$$

Similar expressions are written for the other relevant orbitals; they are reported in ref. 31. The coefficients of $d_{x^2-y^2}$, d_{yz} and d_{xz} in the appropriate molecular orbitals are β , γ and γ' , respectively. Overlap is included only for the Ψ_{B_2} state, α and α' being related by $\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1$ [29]. In keeping with the axial symmetry of the ESR spectrum, we will assume that the molecular orbitals Ψ_{B_1} and Ψ_{A_2} are virtually degenerated and $\gamma = \gamma'$.

In principle the coefficients α , α' , β and γ are easily deduced from the EPR parameters via a set of relations [28, 32, 33]. However, the energy differences $\Delta(E_{x^2-y^2} - E_{xy})$ and $\Delta'(E_{xz, yz} - E_{xy})$ are also involved in these relations and the difficulty arises from the fact that their values are often uncertain.

Fortunately in the case of axially symmetric ESR spectra, α can be approximated via a simplified expression which only involves ESR parameters (A_{\parallel} , A_i , g_{\parallel} and g_{\perp}) [31]. Another independent determination of α' and, via the normalization condition, of α is possible when the ^{14}N superhyperfine structure is observed [34]. Nevertheless the difficulty in evaluating Δ and Δ' remains when one tries to evaluate β and γ .

This is exemplified by the data reported for $\text{CuBAE}(\text{H})$. Examination of Table 5 shows that Δ has been taken equal to 18 000 [35], 18 500 [36]

and 27 000 [37] cm^{-1} . In the latter instance, a Δ' value of 18 000 has been retained to evaluate γ . Furthermore these attributions differ from the one suggested by Hitchman [38], i.e. $\Delta = 16 400 \text{ cm}^{-1}$, an absorption located at $18 400 \text{ cm}^{-1}$ being attributed to $A_1(d_{z^2}) \rightarrow B_2(d_{xy})$.

As for CuL , the spectrum related to a solution in an inert solvent (CHCl_3) consists of a broad absorption at $18 700 \text{ cm}^{-1}$ and a shoulder which is observed at $c. 21 700 \text{ cm}^{-1}$ on the low energy side of an intense absorption centred at $24 700 \text{ cm}^{-1}$. In keeping with its intensity the latter absorption which does not appear in the spectrum of the free ligand is likely a charge-transfer band. As for the two other absorptions, we are inclined to attribute the lower energy band to the $A_1(d_{x^2-y^2}), A_1(d_{z^2}) \rightarrow B_2(d_{xy})$ transitions and the higher energy one to the $B_1(d_{xz}), A_2(d_{yz}) \rightarrow B_2(d_{xy})$ transitions. The related sequence $d_{xy} \gg d_{z^2} > d_{x^2-y^2} \sim d_{xz}$, with a possible inversion of d_{z^2} and $d_{x^2-y^2}$, is the most generally retained for square-based copper(II) complexes but can only be considered tentative. Therefore we have also considered the other possible attributions. The resulting data are quoted in Table 5. The various constants involved in the analysis have their usual values [30, 35].

For CuL , a striking and, perhaps, somewhat fortuitous agreement occurs between the two evaluations of α (and α') whereas a small discrepancy is observed in the case of $\text{CuBAE}(\text{H})$. Considering the values deduced from the ^{14}N shf, α^2 is slightly smaller for CuL than for $\text{CuBAE}(\text{H})$. However in both cases, the σ -bonding displays a significant covalent character. A more significant difference between the two complexes is established by β^2 . Whatever choice of Δ values is retained, larger values characterize CuL pointing to a decrease of the covalent character of the 'in-plane π -bonding'. Finally, it may be noted that the γ^2 value obtained for CuL (0.645 or more probably 0.745) supports the occurrence of fairly strong out-of-plane π -bonding which would be consistent with the structural data.

Electrochemical Study

The experimental data related to the one-electron reversible or quasi-reversible processes $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ and $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$ are collected in Table 6. Due to their

TABLE 5. Molecular orbital coefficients

	CuL	CuBAE		
α^2	0.76(0) ^{a, b}	0.76(0) ^{a, c}	0.77(2) ^{b, d}	0.81(0) ^{a, b, e}
α'^2	0.32(5) ^{a, b}	0.32(5) ^{a, c}	0.34(0) ^{b, d}	0.27(2) ^{a, b, e}
β^2	0.79(5) ^f , 0.91(0) ^g	0.72(5) ^c , 0.66(0) ^h	0.66(5) ^f	0.69(2) ^e
γ^2	0.64(5) ^f , 0.74(7) ^g	—	—	0.66(0) ^e

^aFrom Cu h.f.s. ^bFrom N s.h.f.s. ^cRef. 35. ^dRef. 36. ^eRef. 37. ^f Δ or $\Delta' = 18 700 \text{ cm}^{-1}$. ^g Δ or $\Delta' = 21 700 \text{ cm}^{-1}$.

^hValues calculated $\alpha^2 = 0.76(2)$, $\Delta = 16 400 \text{ cm}^{-1}$. ⁱValues calculated $\alpha^2 = 0.772$, $\Delta = 16 400 \text{ cm}^{-1}$.

TABLE 6. Electrochemical data at ambient temperature

Complex	Polarography		Cyclic voltammetry $E_{1/2}^c$ ($E_{pc} + E_{pa}$) (V)	No. exchanged
	$E_{1/2}^c$	Slope (V)		
CuL ^a	-0.89(0)	75	-0.88(7)	1
[Co ^{III} L·2py]ClO ₄ ^b	-0.22(9)	73	-0.22(7)	1

^aComplex 10⁻³ M in pyridin-Bu₄NClO₄ (0.1 M).^bComplex 10⁻³ M in DMF-Bu₄NClO₄ (0.1 M).^cvs. Ag-Ag⁺.

very low solubilities and the uncertainty regarding their structures, the nickel(II) and cobalt(II) complexes are not considered.

In order to stress the abnormal behaviour of the present complexes, they may be compared to their homologues derived from BAE(H) which display the following potentials: -1.50 V for CuBAE(H) [39] and -0.59 V for [CoBAE(H)·2Py]ClO₄ [40].

Obviously, replacing the dimethylene fragment of BAE(H) by a dioxamide group causes the half-wave potentials to shift significantly toward much less negative values. Qualitatively this influence of the dioxamide group is unexpected since several literature reports [2, 5] state that, in complexes, the presence of amide groups increases the electron donor ability of the corresponding ligands and causes the redox potentials of the metal centers to move toward more cationic values. The quantitative importance of the shifts observed is also surprising. Indeed to obtain rather similar values of the potentials in the series [Co^{III}BAE(X)·2Py]ClO₄ it is necessary to substitute strong electron-withdrawing groups for the methine protons: $E_{1/2} = -0.57$ V (X = H) [40], -0.41 V (X = Cl) [40], -0.27 V (X = CF₃) [41] and -0.24 V (X = CH₃CO) [42].

According to a generally accepted assumption, the half-wave potential gives a measure of the electron density on the metal as a composite of σ and π contributions. Therefore two factors are important in ascertaining the influence of a ligand: the nature of the bonding atoms, i.e. electronegativity and π -withdrawal properties, and the possibility of π -delocalization of the metal electron density over the ligand.

In keeping with the other data reported in this paper, the seemingly abnormal redox behaviour of CuL and [Co^{III}L·2Py]ClO₄ is attributable to the third factor. Substituting a dioxamide group for the dimethylene fragment in the structure of BAE(H) would cause an extension of the π -system over the whole ligand. This would allow more extensive delocalization of the d electrons and hence facilitate the reduction process.

An alternative view would be to consider structural factors. The structural data militate against

this possibility since the N₂O₂ chromophore deviates less from planarity in CuL than in CuBAE(H).

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