40. Models for Copper-Dioxygen Complexes: the Chemistry of Copper(II) with Some Planar Tridentate Nitrogen Ligands

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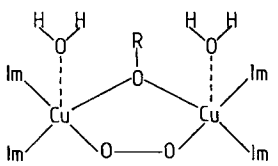
The solution chemistry of Cu(II) with a series of five planar tridentate nitrogen ligands, 2,6-bis(benzimidazol-2-yl)pyridine (bzimpy, **1**), 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy, **2**) 2,6-bis(benzothiazol-2-yl) pyridine (bzthpy, **3**), 2,6-bis(benzoxazol-2-yl)pyridine (bzoxpy, **4**), and 2,2′,6′,2″-terpyridyl (terpy, **5**) is reported. Electronic and EPR spectra are consistent with the complexes $[CuL]^{2+}$ having essentially tetragonal structure in solution, with the fourth coordination site in the plane of the ligand occupied by solvent. bzthpy and bzoxpy show smaller ligand-field splittings than bzimpy, mbzimpy, and terpy, and are easily decomplexed from the copper. Substitution of the coordinated solvent molecule in the plane of the ligand is observed with Cl^- and OH^- (provided that the ligand has no acidic protons) for all ligands except terpy. The reaction between $[Cu(mbzimpy)]^{2+}$ and imidazole has been studied by potentiometric titration in $MeCN/H_2O$ 1:1 and shows strong binding of the imidazole in the plane (log $K = 4.5$ at 25°), and also the formation of an imidazolate-bridged dinuclear species.

Introduction. – There is currently considerable interest in the chemistry of the oxygen transporting protein oxyhemocyanin [1] and related systems such as tyrosinase [2] and the laccases [3] which possess an active site of type III where the dioxygen moiety is thought to be bound to Cu(II) as in **I** below:



This structure has been proposed on the basis of the extended X-ray absorption fine structure (EXAFS) measurements [4], electronic [5], and resonance *Raman* [6] spectroscopy. However, some discrepancies between EXAFS results have led to the suggestion that three histidines may be bound to Cu(II) in the oxy form of hemocyanin [7], and a recent crystal-structure determination of deoxyhemocyanin shows the Cu(I) to be bound to three histidines in the deoxy form [8]. There is, however, general agreement as to the formulation of these complexes as μ-peroxodicopper(II) complexes, and a synthetic complex of this type has recently been characterised by X-ray crystallography [9].

In the search for possible precursors to stable copper-dioxygen complexes, our attention was attracted to planar tridentate nitrogen ligands, since such ligands show similari-

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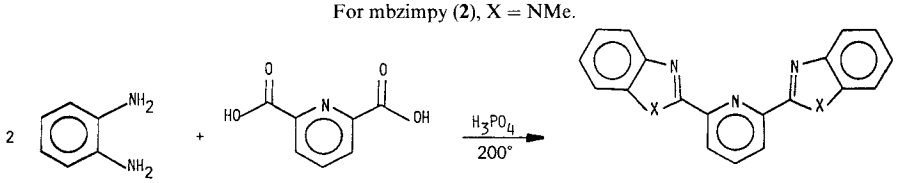
ties to the known natural systems, and, in view of the tendency of Cu(II) to display a distorted octahedral geometry with four short equatorial and two long axial bonds [10], Cu(II) complexed by a planar tridentate system is likely to show a strong affinity for ligands in the fourth equatorial binding site, and, under these conditions, the binding of O_2 in the form of peroxide at this site might be envisaged [11].

The following criteria were established for the choice of ligand: *i)* the ligand should be constrained to be planar; *ii)* the coordinating N-atoms should possess some unsaturated character in order to allow the stabilisation of Cu(I) [12]; *iii)* it should be possible to modify the ligands slightly in order to vary the ligand field strength, and thereby influence the copper redox potential. The ligands shown below, 2,6-bis(benzimidazol-2-yl)pyridine (bzimpy, **1**), 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy, **2**), 2,6-bis(benzothiazol-2-yl)pyridine (bzthpy, **3**), and 2,6-bis(benzoxazol-2-yl)pyridine (bzoxpy, **4**) satisfy these criteria and may readily be synthesised in high yield using the modified *Philips* reaction [13].

Scheme 1. *Synthesis of Ligands bzimpy* (**1**, X = NH), *bzoxpy* (**4**, X = O), *and bzthpy* (**3**, X = S). For mbzimpy (**2**), X = NMe.



A complex of bzimpy with Ni(II) [14] and a few complexes of bzthpy with Mn(II), Fe(II), Co(II), Ni(II) [15], and Cu(II) [16] have been reported in the literature, but no extensive studies have been made. During the preparation of this manuscript, however, we were informed of a very recent study reporting the preparation of some complexes of bzimpy and mbzimpy with Cu(II) and Zn(II), and the crystal structures of $[Cu(bzimpy)(MeCN)](ClO_4)_2$ and $[Cu(mbzimpy)_2(ClO_4)_2]\cdot H_2O$ [17], and a paper reporting the chemistry of bzimpy, mbzimpy, and bzthpy with Fe(II) and Fe(III) has also been published [18].

In this paper, we report on the solution chemistry of ligands **1**–**4** with Cu(II) and compare it with the well known tridentate N ligand 2,2′,6′,2″-terpyridyl (terpy, **5**) in order to: *i)* compare the bonding properties of the five ligands, *ii)* establish the coordination of the Cu(II) in solution, and *iii)* investigate to what extent these complexes do bind another ligand in the plane of the three N-atoms. We consider a thorough understanding of the properties of the $[CuL]^{2+}$ species to be essential for the assessment of the likely stability of a Cu(II)-peroxo complex. The chemistry of the most favorable of these ligands, mbzimpy, with Cu(I) will be reported later [19].

Experimental. – Unless otherwise stated, solvents and starting materials were purchased from *Fluka* (Switzerland) and used without further purification.

Preparation of Ligands. bzimpy (**1**) and bzthpy (**3**) were prepared according to the procedure described in [13], and this method was also applied to the synthesis of bzoxpy (**4**) obtained in good yield (51%). The yields are greatly increased, if mechanical stirring is applied during the reaction. All ligands were fully characterized by their IR, ^{1}H-NMR, and EI-MS (M^+: bzimpy, 311; bzthpy, 345; bzoxpy, 313). mbzimpy (**2**) was prepared under N_2 using *Schlenck* techniques. Tetramethylurea (TMU) and pentane were previously distilled from NaH under N_2. Compound **1** (4.0 g, 12.9 mmol) was dissolved in 30 ml of dry TMU. NaH (oil dispersion 58%; 1.62 g, 38.8 mmol) was washed with 5 × 10 ml of dry pentane and then suspended in 30 ml of dry TMU. This suspension was added to the

well-stirred soln. of **1** at 0°. The mixture was allowed to stand at r.t., then heated to 35° for 1 h. The mixture was cooled to 0°, 5.51 g (38.8 mmol) of MeI added, heated to 40° for 3 h, then hydrolysed with H_2O, the pH adjusted to 13 with 1M NaOH, and 3.86 g (11.4 mmol) of white **2** were separated by filtration and dried at 10^{-2} Torr/60° for 12 h (yield 89%). The product was characterized by its IR ($\tilde{\nu}$(NH) has disappeared and three new bands appear at 2910, 2840, and 1415 cm^{-1} characteristic for the Me groups), ^{1}H-NMR (in $CDCl_3$, a *singlet* at 4.25 ppm (CH_3)), and its EI-MS (339 (M^+)).

Preparation of Perchlorate Salts of the Complexes of Cu(II) with **1**–**4**. For **1** and **2**, 3.0 mmol of ligand were dissolved in 50 ml of EtOH at 50° and then a soln. of 1.11 g (3.0 mmol) of $[Cu(H_2O)_6](ClO_4)_2$ in the same solvent was added. The complex of **2** precipitated immediately and was recrystallized from DMF/EtOH to give 1.97 g (2.63 mmol) of deep green $[Cu(mbzimpy)](ClO_4)_2 \cdot 2$ DMF (**6**; yield 88%). The complex with **1** was crystallized by addition of dioxane. We obtained 1.51 g (2.40 mmol) of light green $[Cu(bzimpy)](ClO_4)_2 \cdot 3\ H_2O$ (**7**; yield 80%). The same procedure was applied for **3** and **4**, but their insolubility in almost all solvents required working with a two-phase system. A suspension of 1.6 mmol of ligand in MeCN at 50° was mixed with a stoichiometric quantity of $[Cu(H_2O)_6](ClO_4)_2$, and the mixture was stirred, until a clear deep green soln. was obtained. The complex was then crystallized by slow evaporation *in vacuo*. We obtained 0.66 g (0.98 mmol) of pale green $[Cu(bzoxpy)](ClO_4)_2 \cdot H_2O \cdot 2$ MeCN (**8**; yield 61%) and 0.68 g (1.09 mmol) of green $[Cu(bzthpy)](ClO_4)_2 \cdot H_2O$ (**9**; yield 68%). These four perchlorate salts were characterized by their IR and gave satisfactory elemental analysis (C, H, Cu, N).

Preparation of Chloro-Perchlorate Salts of the Cu(II) Complexes of **2**–**4**. For ligand **2**, 0.2 g (0.27 mmol) of **6** was dissolved in 8 ml of DMF, and 0.045 g (0.27 mmol) of Et_4NCl in a minimum of the same solvent was added. The product was precipitated by addition of 10 ml of Et_2O, separated by filtration, and washed with two portions of CH_2Cl_2 (to extract Et_4NClO_4). After recrystallization in DMF/Et_2O, we obtained 0.11 g (0.197 mmol) of light green $[Cu(mbzimpy)Cl](ClO_4) \cdot H_2O$ (**10**; yield 73%). $\tilde{\nu}$(Cu–Cl) = 320 cm^{-1}. For **3** and **4**, the same procedure was applied with MeCN instead of DMF, yielding products which crystallized directly from the mixture without addition of Et_2O. We obtained 73% of green $[Cu(bzoxpy)Cl](ClO_4)$ (**11**) and 75% of yellowish green $[Cu(bzthpy)Cl](ClO_4)$ (**12**). $\tilde{\nu}$(Cu–Cl) was observed at 330 and 315 cm^{-1} for **11** and **12**, respectively. These three Cu(II) chloro-perchlorate salts were characterized by IR and gave satisfactory elemental analyses.

Caution: perchlorate salts with org. ligands are potentially explosive and should be handled with the necessary precautions [20].

Preparation of Dichloro Salts of the Cu(II) Complexes of **1** *and* **2**. A soln. of 0.311 g (1 mmol) of **1** in EtOH (20 ml) was mixed with 0.17 g (1 mmol) of $CuCl_2 \cdot 2\ H_2O$ in the same solvent. The resulting precipitate was separated by filtration and recrystallized from 300 ml hot DMF. The formula $[Cu(bzimpy)]Cl_2$ DMF (**13**) was established by IR, elemental analysis, and an X-ray crystal-structure determination [21]. The light green complex $[Cu(mbzimpy)]Cl_2 \cdot H_2O$ (**14**) was obtained in the same way by using MeCN instead of EtOH and was recrystallized from MeCN/Et_2O (yield 83%). This complex was characterized by its IR ($\tilde{\nu}$(Cu-Cl) of 295 and 270 cm^{-1}) and gave a satisfactory elemental analysis.

We attempted to synthesize the Cu(II) dichloro complexes of **3** and **4**, but have not succeeded in obtaining reproducible compositions for the substances isolated (IR and elemental analysis differed from one batch to another).

Preparation of [Cu(mbzimpy)(imidazolate)Cu(mbzimpy)](ClO$_4$)$_3$ · H$_2$O (**15**). To a soln. of 0.3 g (0.4 mmol) of $[Cu(mbzimpy)](ClO_4)_2 \cdot 2$ DMF (**6**) in 18 ml of MeCN, 1 ml (0.2 mmol) of a 0.2M soln. of imidazole in MeCN and 1 ml (0.2 mmol) of a 0.2M soln. of Et_3N in MeCN were added slowly. The soln. rapidly turned turquoise; 30 ml of MeCN/EtOH 1:1 were added and, after standing at −25° for 3 h, the small turquoise crystals were separated by filtration. The filtrate was concentrated under vacuum, and further addition of MeCN/EtOH and refrigeration gave a second crop of crystals. After drying *in vacuo*, we obtained 0.185 g (0.156 mmol, 78%) of blue green crystals which gave a correct analysis for $[Cu(mbzimby)(imidazolate)Cu(mbzimpy)](ClO_4)_3 \cdot H_2O$ (**15**).

Physical Measurements. UV/VIS Spectra: in soln. with a *Perkin Elmer Lambda 5* spectrophotometer at 20° using quartz cells of 1, 0.1, and 0.01 cm path length. IR: KBr pellets, with a *Perkin Elmer IR 597* spectrophotometer. ^{1}H-NMR: on a *Varian EM360A* (60 MHz), a *Varian XL 200* (200 MHz), or a *Bruker WH360* (360 MHz) spectrometer. EI-MS (70 eV): *VG 7000 E* and *Finnigan 4000*. EPR: frozen solns. at 77 K, at 9 GHz on a *Bruker ER 200D-SRC*. Cyclic voltammograms were recorded using a *Tacussel PRGE-DEC* potentiostat connected to a function generator and a XY plotter. A 3-electrode system consisting of a stationary Pt disk working electrode, a Pt counter electrode, and a non-aqueous Ag/Ag^+ reference electrode was used. Bu_4NClO_4 (0.1M) or 0.1M Bu_4NPF_6 served as inert electrolytes. Propylene carbonate [22] and $MeNO_2$ [23] were purified according to the literature. MeCN was distilled from P_2O_5 and then passed through an *Alox* column (pH 9.5). All other solvents used were distilled under reduced pressure (10^{-2} Torr): DMSO from CaH_2, TMU from NaH and DMF from *Alox*. The reference potential (E° = +0.66 V *vs.* NHE) was standardized against the known complex $[Ru(bipy)_3](ClO_4)_2$ [24a].

The scan speed used was 0.2 V/s, and voltammograms were analyzed according to established procedures [24b]. Conductimetric results were obtained with a *Metrohm EA240* cell ($f = 0.61$ cm^{-1}) immerged in a thermostatted vessel at 25°. Conductivity measurements were made with a *Metrohm E527 Wheatstone* bridge; the conductivity was measured after each addition of the soln. of the anion from a syringe. The results were corrected for dilution. Potentiometric measurements were made in a closed cell thermostatted at 25 ± 0.1° using a *Metrohm* combined electrode and a *Metrohm E500* digital pH-meter. The conditions for a typical titration were as follows: to 25 ml of MeCN/H_2O 1:1 (*v/v*) were added 56.1 mg ($7.5 \cdot 10^{-5}$ mol) of **6**, 750 µl of *N*-methylimidazole (0.1M in MeCN/H_2O), and 750 µl of $HClO_4$ (0.1M in MeCN/H_2O), and the ionic strength was adjusted to 0.05M with KNO_3. This soln. was placed in the cell and the pH electrode introduced. The soln. was titrated with a soln. of 0.02M KOH in MeCN/H_2O whose ionic strength was adjusted to 0.05M with KNO_3. Acid and base solns. were standardized against *Merck* titrisol solns. The measured pH values (±0.02 units) were fitted to p*K* values using a non-linear least-squares program [25]. Elemental analyses (C, H, Cl, N) were performed by Dr. *H. Eder* of the Microchemical Laboratory of the University of Geneva. Cu was determined by atomic absorption *(Pye Unicam SP9)* after acidic oxidative mineralisation of the complex.

Results and Discussion. – 1. *Synthesis and Properties of Ligands.* We have followed the synthetic procedure developed by *Addison* and coworkers [13] to obtain bzimpy (**1**) and bzthpy (**3**), and we have extended it to the synthesis of bzoxpy (**4**). The double methylation of **1** was easily performed by deprotonation with 2 equiv. of NaH in dry TMU followed by alkylation with MeI to give mbzimpy (**2**) in 89% yield. The ligands **1** and **2** are sparingly soluble in EtOH, insoluble in H_2O, but very soluble in polar aprotic solvents like DMF or DMSO. Ligands **3** and **4** are very poorly soluble in all solvents except hot $CHCl_3$. The H-atoms of the benzo moiety of **1** give a symmetrical *AA'BB'*-spin system in the ^{1}H-NMR spectrum which becomes a very complicated *ABCD* system for the dimethyl-substituted derivative **2**. A first-order interpretation of the 360-MHz ^{1}H-NMR spectra ($CDCl_3$) of **3** and **4** is fully satisfactory with two *triplets* and two *doublets* for the benzo H-atoms between 7.5 and 8.0 ppm and a AB_2-spin system for the pyridine H-atoms 8.1–8.5 ppm *vs.* TMS. The UV spectra of these ligands in propylene carbonate solution consist of one broad envelope of $\pi \rightarrow \pi^*$ transitions centered around 31250 cm^{-1} with $\varepsilon_{max} = 30000$ M$^{-1} \cdot$cm^{-1}. The comparison with the spectrum of terpy (**5**) in the same solvent (36000 cm^{-1}, $\varepsilon_{max} = 20000$ M$^{-1} \cdot$cm^{-1}) shows a red-shift for our ligands of roughly 4700 cm^{-1}. This transition is assigned to $\pi_1 \rightarrow \pi^*$ according to *Nakamoto* [26].

2. *Properties of Isolated Complexes with* **1**–**4**. The proposed formulae of the Cu(II) complexes **6**–**14** were consistent with elemental analysis based on C, H, Cu, Cl, and N. In all cases, we isolated complexes with one ligand per Cu(II) and two anions. The IR spectra showed characteristic ligand vibrations (C=C, C=N stretching) in the 1620–1500-cm^{-1} range which are shifted toward high energy (about 15–25 cm^{-1}) upon complexation to Cu(II). The ClO_4^- anion showed two IR bands at 625 and 1095 cm^{-1} which are symmetric, when it was not coordinated. Only complex **11** shows a splitting of ClO_4^- vibrations compatible with coordination to Cu(II), which is confirmed by a new absorption at 375 cm^{-1} attributed to the Cu–$OClO_3$ stretching frequency. The stretching vibrations Cu–N(ligand) are rather weak and appear at *ca.* 305 cm^{-1} for **6** and **7**, and are displaced to lower energy for **8** (250 cm^{-1}) where benzoxazoles replace benzimidazoles. This is an indication of the weaker coordination of **4** to Cu(II) compared with **1** or **2**. A square-pyramidal structure for complex **13** was determined by X-ray diffraction [21], and the powder EPR spectrum at 298 K of the analogous complex with **2**, **14**, showed a $(d_{x^2-y^2})^1$ ground state with $g_\parallel = 2.22 > g_\perp = 2.10 > 2.0$ indicating a similar structure [10] [27].

3. *Chemistry of the Complexes in Aprotic Solution.* 3.1. *[Cu(L)](ClO$_4$)$_2$* (L = **1**–**4**). The complexes **6** and **7** are soluble in polar aprotic solvents like DMF, DMSO, propylene carbonate, MeCN, but **4** and **3** are decomplexed from Cu(II) in strong donor solvents (DMSO or DMF) resulting in precipitation of the poorly soluble free ligands which were isolated and characterized by IR. Complexes **8** and **9** have, therefore, only been studied in MeCN or propylene carbonate, and this last solvent was used for comparison of the different ligands.

The complexes **6**–**9** behave as 2:1 electrolytes in polar aprotic solution *(Table 1)* with molar conductivities corresponding to the highest values proposed by *Geary* [28] (220–340 in MeCN and 130–170 in DMF). However, our values are consistent with the results of *Nelson et al.* [29] for [Cu(L)$_2$](ClO$_4$)$_2$ in MeCN (250–270 $\Omega^{-1}\cdot mol^{-1}\cdot cm^2$, where L is a *Schiff* base derived from 2,6-diacetylpyridine whose greater size is presumably responsible for the lower value).

Table 1. *Conductivity Data at 25°*[a])

Complexes		Propylene carbonate	DMSO	Other solvents
[Cu(mbzimpy)](ClO$_4$)$_2$	(**6**)	83	103	196 (DMF)
[Cu(bzimpy)](ClO$_4$)$_2$	(**7**)	81	107	
[Cu(bzoxpy)](ClO$_4$)$_2$	(**8**)	80	–	360 (MeCN)
[Cu(bzthpy)](ClO$_4$)$_2$	(**9**)	77	–	340 (MeCN)
[Cu(mbzimpy)Cl](ClO$_4$)	(**10**)	27	53	
[Cu(bzoxpy)Cl](ClO$_4$)	(**11**)	32	–	
[Cu(bzthpy)Cl](ClO$_4$)	(**12**)	32	–	
Bu$_4$NClO$_4$		41	51	
Bu$_4$NCl		35	45	

[a]) Molar conductivities are given in $\Omega^{-1}\cdot mol^{-1}\cdot cm^2$ for 10^{-3} M soln. at 25°. Estimated experimental errors: ±5%.

Table 2. *Electronic Spectra in Propylene Carbonate Solution at 20°*[a])

Compound	Assignment		
	$\pi_1\rightarrow\pi^*$		d-d
bzimpy (**1**)	30400 (30000)		
1 + Zn^{2+}	28330 (25400)	32360 (25600)	
1 + Cu^{2+}	27780 (19500)	31850 (27000)	14470 (88)
mbzimpy (**2**)	31150 (29000)		
2 + Zn^{2+}	28330 (21500)	32570 (23500)	
2 + Cu^{2+}	27470 (16000)	31850 (23500)	14770 (98)
bzthpy (**3**)	30490 (28000)		
3 + Zn^{2+}	27550 (28800)	32360 (21200)	
3 + Cu^{2+}	27100 (21200)	31450 (14100)	13210 (77)
bzoxpy (**4**)	31450 (30000)		
4 + Zn^{2+}	28900 (21000)	33445 (20000)	
4 + Cu^{2+}	28090 (20000)	33110 (22000)	13120 (55)
terpy (**5**)	35970 (18800)		
5 + Zn^{2+}	30210 (17300)	35340 (15000)	
5 + Cu^{2+}	29326 (15000)	34970 (13500)	15080 (92)

[a]) Energies are given for the maximum of the band envelope in cm^{-1} and ε (in parentheses) in $M^{-1}\cdot cm^{-1}$. All values refer to 10^{-3} M propylene carbonate solution obtained either directly from the isolated complexes for Cu^{2+} or formed *in situ* (Zn^{2+}) by mixing stoichiometric quantities of ligand and [Zn(H$_2$O)$_6$](ClO$_4$)$_2$.

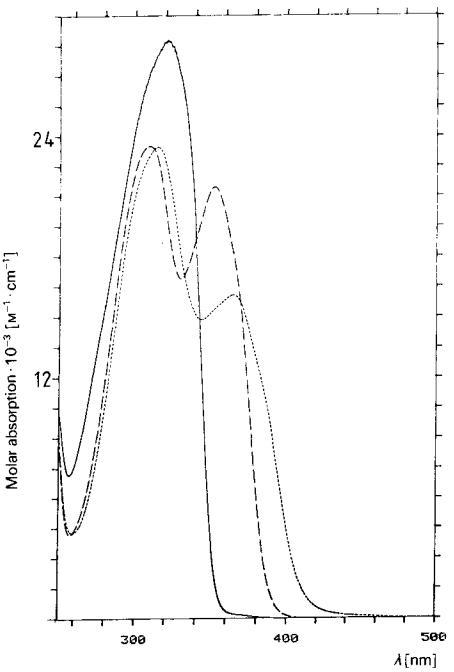
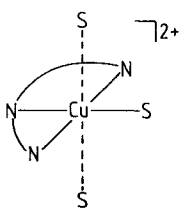


Fig. 1. *Electronic spectrum of the ligand mbzimpy* (**2**, full line), *[Zn(**2**)]*$^{2+}$ (dashed line), *and [Cu(**2**)]*$^{2+}$ (dotted line) *in* 10^{-3} M *propylene carbonate solution at 25°*

The electronic spectra of the complexes **6–9** in solution present two distinct absorption domains. Between 12500 and 15500 cm^{-1}, we find the envelopes of d-d transitions (ε = 50–100 $M^{-1} \cdot cm^{-1}$) and between 25000 and 37000 cm^{-1} the $\pi \rightarrow \pi^*$ transitions of the aromatic ligands (ε = 15000–25000 $M^{-1} \cdot cm^{-1}$). According to *Nakamoto* [26], terpy (**5**) shows two bands in the UV region attributed to two $\pi \rightarrow \pi^*$ transitions: $\pi_1 \rightarrow \pi^*$ at *ca.* 35700 cm^{-1} and $\pi_2 \rightarrow \pi^*$ at 41700 cm^{-1}. Upon complexation to Zn^{2+} or Ni^{2+} (or Mg^{2+} with 2,2-bipyridyl [30]), the $\pi_1 \rightarrow \pi^*$ is split into two components, with $\pi_1^b \rightarrow \pi^*$ at *ca.* 30300 cm^{-1} and $\pi_1^a \rightarrow \pi^*$ at 35300 cm^{-1} for [Zn(terpy)]Cl_2. These results are paralleled by the ligands **1–4** which show a similar splitting of the $\pi_1 \rightarrow \pi^*$ transition upon complexation with Zn^{2+} or Cu^{2+} in PC (*Table 2* and *Fig. 1*). We have found this splitting to be a useful confirmation of the complexation of ligands **1–4**.

Comparison of the d-d transition energies in propylene carbonates shows the benzimidazole ligands **1** and **2** to have comparable ligand-field strength to terpy, while **3** and **4** are appreciably weaker. Since the conductivity measurements suggest that the ClO_4^- anions are not coordinated, there are two axial and one equatorial binding sites free on the Cu(II) (*cf.* **II**), and solvent dependence of the spectra is expected and is, indeed, observed.



II

For $[Cu(\mathbf{2})]^{2+}$ the d-d maxima are 13720 (DMSO) < 14100 (DMF) < 14770 (propylene carbonate) < 15385 (MeCN) < 15870 cm^{-1} ($MeNO_2$). This order corresponds to increasing ligand-field strength in the spectrochemical series (f(MeCN) = 1.22, f(DMF) = 0.98, and f(DMSO) = 0.91 [31]), and decreasing donor character as established by *Gutmann* [32]. These results indicate strong interaction of the solvent with the vacant coordination sites. Similar solvent shifts on going from propylene carbonate to DMSO have been reported for Ni(II), Cr(III), and Cu(II) [22].

The EPR spectra of frozen propylene-carbonate solutions show pseudo-axial features with $g_{\parallel} > g_{\perp} > 2.0$ *(Table 3)* which are typical of a $(d_{x^2-y^2})^1$ ground state [10]. This implies that planarity of ligands is maintained in solution with the three coplanar heterocyclic

Table 3. *EPR Parameters* (in frozen propylene carbonate solution at 77 K) *and Electrochemical Reduction Potentials* (in propylene carbonate solution)[a])

Complexes	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$E_{p/2}$ [v]	$E_{pc} - E_{pa}$ [mV]
6	2.24	2.03	182	+0.38	–
7	2.26	2.04	172	+0.42	1000
8	2.29	2.06	151	+0.85	500
	2.35	2.06	149	+0.76	500
9	2.28	2.06	142	+0.73	600
				+0.63	700
6 + 1 equiv. Cl^-	2.23	2.03	–	+0.37	180/800
		2.06			
7 + 1 equiv. Cl^-	2.23	2.03	169	+0.27	380
		2.06			
8 + 1 equiv. Cl^-	2.25	2.05	153	+0.69	120/600
9 + 1 equiv. Cl^-	2.26	2.05	140	+0.58	140/700

[a]) EPR parameters: estimated errors of ±0.01 on $g_{\parallel}$, ±0.01 on $g_{\perp}$, and $\pm 3 \cdot 10^{-4}$ cm^{-1} for $A_{\parallel}$ which is given in 10^{-4} cm^{-1}. Electrochemical potentials for Cu(II)/Cu(I) are given *vs.* NHE for the half reduction peak at 20°. Estimated error on $E_{p/2}$ is ±0.01 V.

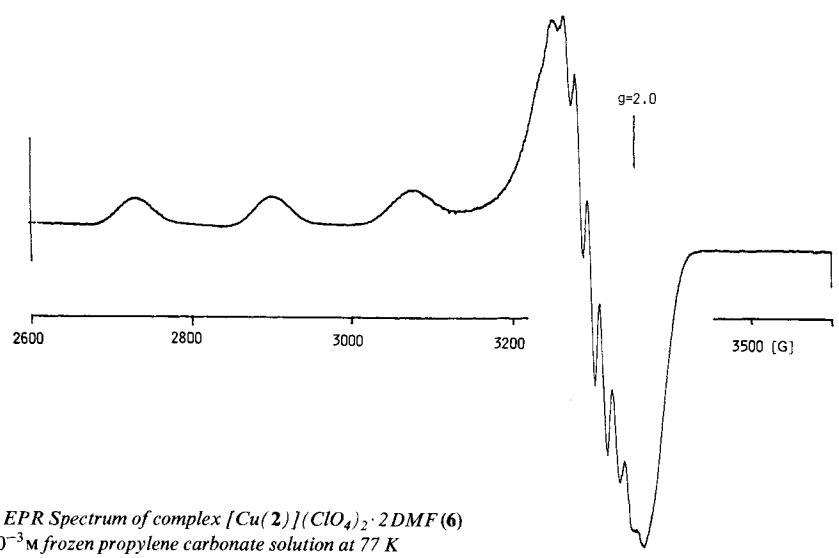


Fig. 2. *EPR Spectrum of complex* $[Cu(\mathbf{2})](ClO_4)_2 \cdot 2DMF$ (**6**) *in* $5 \cdot 10^{-3}$ M *frozen propylene carbonate solution at 77 K*

N-atoms bound to Cu(II) destabilising the $d_{x^2-y^2}$ orbital. It has been shown that, for any given Cu(II) coordination compound, its position on a plot of $g_\parallel$ against $A_\parallel$ is governed by *a)* the nature of the donor atoms in the tetragonal plane, with increasing $g_\parallel$ values S < N < O, *b)* the formal charge carried by the four donor atoms plus the metal, and *c)* the dihedral angle [33]. The values for the four complexes **6–9** lie near to a N_4 donor set on the plot and are fully compatible with a $[Cu(N_3)(solvent)]^{2+}$ unit in pseudo-tetragonal plane. The existence of such a unit is confirmed by the isolation of $[Cu(\mathbf{1})(MeCN)](ClO_4)_2$ from EtOH/MeCN [17]. Hyperfine structure is visible for **6** in the $g_\perp$ domain due to N superhyperfine coupling ($A \approx 14.10^{-4}$ cm^{-1}), confirming the coordination of three N-atoms to Cu(II) *(Fig. 2)*. Complex **8** (with the ligand bzoxpy (**4**)) shows two axial species, one with $g_\parallel = 2.35$ and the other with $g_\parallel = 2.29$ which have been tentatively assigned to two differently solvated pseudo-axial species as proposed by *Reed et al.* [34] in a similar case, and complex **9** (ligand bzthpy (**3**)) shows a similar effect in MeCN solution. There is a slight solvent dependence of the EPR parameters.

Cyclic voltammetry studies of complexes **6–9** show highly irreversible Cu(II)/Cu(I) redox waves, and *Table 3* reports the half-peak reduction potentials $E_{p/2}$ in propylene carbonate solution. The apparent ease of reduction of the bzoxpy (**4**) and bzthpy (**3**) complexes **8** and **9**, respectively, is probably not significant, since we have evidence that **4** and **3** dissociate from Cu(I) [19], and, in propylene carbonate solution, the $Cu^{2+}_{solv.}/Cu^{+}_{solv.}$ couple is even more positive ($E_{p/2} = +1.03$ V); furthermore, **8** and **9** show two reduction peaks. For complexes **6** and **7**, the reduction peaks are strongly solvent dependent: for **6** the potentials (*vs.* NHE) vary in the order +0.25 (DMSO) < +0.29 (DMF) < +0.38 (PC) < +0.60 V ($MeNO_2$). This order correlates with decreasing solvent donor strength [32]. If *Addison*'s formula [12] for E° is applied for Cu(II) with three heterocyclic N donors, the predicted value is +0.33 V, in reasonable agreement with our results given that the donor number for H_2O (18) is intermediate between DMF (26.6) and propylene carbonate (15.1).

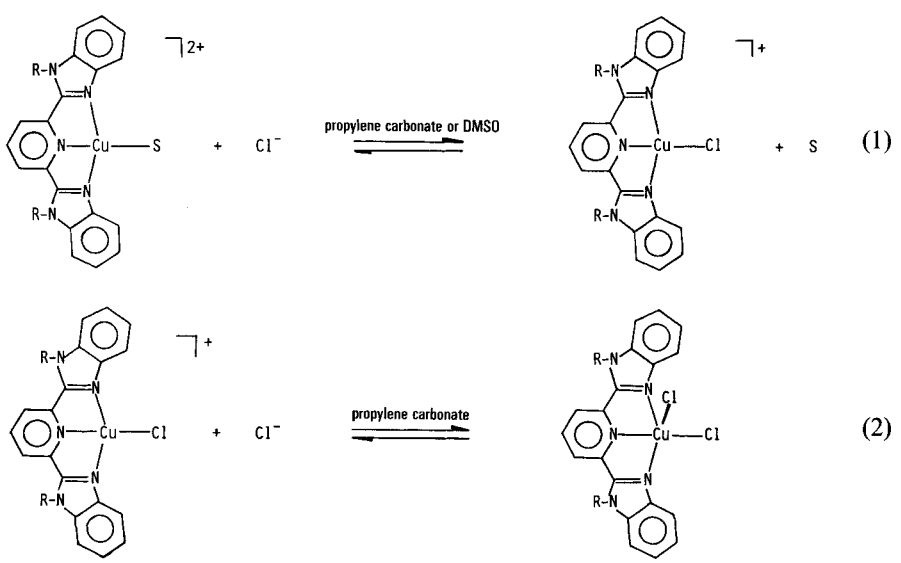
3.2. *Reactivity of [Cu(L)](ClO$_4$)$_2$ (**6–9**) with Chloride.* To determine whether the strong binding at the fourth equatorial site noted in the crystal structure [21] of $[Cu(\mathbf{1})]Cl_2$ is also observed in solution, we have investigated the reactivity of the complexes $[Cu(L)]^{2+}$ (L = **1–4**) with Cl^- and OH^- ions in 10^{-3} M solution, following the reactions by conductivity and UV/VIS spectroscopy. Conductimetric titrations have previously been used to show that $[Cu(terpy)(OH_2)]^{2+}$ binds two Cl^- in $MeNO_2$ solution [35]. The results for OH^- are discussed in the following section.

On titration with Bu_4NCl, solutions of **6–9** in propylene carbonate show a change in conductivity with a more or less well resolved end point at 1 equiv. of Cl^- per Cu. The conductivity of the solution is consistent with that of an equimolar mixture of Bu_4NClO_4 and another 1:1 electrolyte; similar results are obtained for **6** and **7** in DMSO. The electronic spectra also show end points at 1 equiv. per Cu. The d-d band is red-shifted by 300–900 cm^{-1} *(Table 4)*, and there is a rise in absorption around 38400 cm^{-1} which we associate with $Cl^- \rightarrow Cu(II)$ charge transfer (an analogous band has been observed at 36500 cm^{-1} for $CuCl^+$ in propylene carbonate [22]). The complexes $[Cu(L)Cl]^+$ have been isolated as ClO_4^- salts for ligands **2–4**, and their spectra and conductivities are identical with those determined by titration. The spectra of the monochloro complexes are less sensitive to change in solvent than the diperchlorato salts, the variation for $[Cu(mbzimpy)Cl]^+$ (**10**) being 13550 (DMSO) < 13717 (DMF) < 14085 cm^{-1} (propylene car-

bonate), a range of 535 cm^{-1}, while, in the absence of coordinated Cl^-, the variation was 1050 cm^{-1}. EPR spectra of the monochloro complexes show a $(d_{x^2-y^2})^1$ ground state, but for [Cu(bzimpy)Cl]$^+$ and [Cu(mbzimpy)Cl]$^+$ the $g_\perp$ signal is slightly split into two components g_{xx} and g_{yy} as described by *Siddiqui* and *Shepherd* [36] for tetragonal complexes such as [Cu(cyclam)]$^{2+}$. The values of $g_\parallel$ decrease upon Cl^- coordination, presumably as a result of 'core-charge' diminution [27] [33], but $A_\parallel$ is virtually unchanged. The addition of the Cl^- lowers the reduction potential by 50–150 mV *(Table 3)*, probably as a result of the decrease in the charge of the complex [37], the systems remaining irreversible.

The behaviour on adding more than 1 equiv. of Cl^- is extremely varied. In propylene carbonate solution the bzimpy (**1**) and mbzimpy (**2**) complexes **6** and **7**, respectively, show a second conductimetric end-point after the addition of 2 equiv. per Cu, and [Cu(L)]Cl_2 precipitates, but in DMSO the spectra are unchanged by the addition of excess Cl^-, suggesting that no further complexation occurs. This is confirmed by the observation that [Cu(**2**)]$Cl_2 \cdot H_2O$ (**14**) dissolves in DMSO to give a 1:1 electrolyte (conductivity 53 $\Omega^{-1} \cdot mol^{-1} \cdot cm^{-1}$) expected for [Cu(**2**)Cl]$^+ + Cl^-$. The solutions of the complexes with bzoxpy (**4**) and bzthpy (**3**) in propylene carbonate change from green to yellow on addition of a second equiv. of Cl^-: the d-d band falls to 11 560 cm^{-1}, a new band appears at 21 280 cm^{-1} (ε = 340 $M^{-1} \cdot cm^{-1}$), and the $\pi_1^{a,b} \rightarrow \pi^*$ bands coalesce to the single broad band observed for the free ligand. When 4 equiv. of Cl^- are added, the 21 280-cm^{-1} band shifts to 24 630 cm^{-1}; these values are typical for the $Cl^- \rightarrow$Cu(II) charge transfer of $CuCl_2$ and $CuCl_4^{2-}$, respectively [22]. If the complexes with **4** and **3** are titrated with Bu_4NBr, then the solutions become violet, and the characteristic [38] $Br^- \rightarrow$Cu(II) charge-transfer bands of $[CuBr_3]^-$ and $[CuBr_4]^{2-}$ are observed at 18 870 cm^{-1} and 15 385 cm^{-1}, respectively, confirming the formation of halide complexes, and the displacement of the heterocyclic ligand. These observations presumably explain our failure to isolate [Cu(L)Cl_2] (L = **3**, **4**) *(Scheme 2)*.

Scheme 2. *Reactivity of* $[CuL]^{2+}$ *with* Cl^- *in Aprotic* (propylene carbonate or DMSO) *Solution*



(1)

(2)

For L = **3**, **4**, *Reaction 2* in *Scheme 2* is replaced by

$$[CuLCl]^+ + Cl^- \rightarrow L + CuCl_2 \quad (3)$$

To compare ligands **1**–**4** with terpy (**5**), we have carried out similar experiments with this ligand. The behaviour of **5**, however, is surprisingly complex. It has been known for a long time that **5** is very rapidly exchanged in Cu(II) complexes [39]. *Harris* and *Lockyer* [35] have reported that green $[Cu(\mathbf{5})_2]^{2+}$ is stable in presence of halide ions in aqueous solution, but instantaneous rearrangement to the mono complex $[Cu(terpy)]X_2$ occurs in $MeNO_2$. In propylene carbonate, we have established by spectrophotometric titrations of **5** with $Cu(H_2O)_6(ClO_4)_2$ that two species, $[Cu(terpy)]^{2+}$ and $[Cu(terpy)_2]^{2+}$, are present in solution. The complex with Cu/ligand ratio 1:2 possesses a weak characteristic band at 21370 cm^{-1} ($\varepsilon = 155$ $M^{-1} \cdot cm^{-1}$) absent in the 1:1 complex. Titrations with NBu_4X ($X = Cl^-$ or Br^-) of $[Cu(terpy)]^{2+}$ formed *in situ* in propylene carbonate solution show the sudden appearance of the 21370-cm^{-1} band (with an intensity corresponding to half of the Cu(II) present) for 1.0 or more X^- per Cu(II). In a donor solvent such as DMSO, the characteristic band of the 2:1 complex is always present indicating that 1:1 complex is not formed under these conditions. Thus, we propose that terpy (**5**) is rapidly exchanged in the presence of good donors (DMSO, Cl^-, Br^-, OH^-).

$$[Cu(II)(\mathbf{5})(S)]^{2+} + X^- \rightarrow [Cu(II)(\mathbf{5})X]^+ + S \quad (4)$$

$$[Cu(II)(\mathbf{5})(X)]^+ \rightarrow 1/2[Cu(II)(\mathbf{5})_2]^{2+} + 1/2\ CuX_2 \quad (5)$$

This behaviour is similar to that of $[Mn(\mathbf{5})X_2]$ which dissociates rapidly in aqueous solution to give $[Mn(\mathbf{5})_2]^{2+}$ [39]. Despite the close similarity of the crystal structures of $[Cu(\mathbf{1})Cl_2]$ [21] and $[Cu(\mathbf{5})Cl_2]$ [40], **5** behaves very differently in solution, from the ligands **1**–**4**.

3.3. *Reactivity of [Cu(L)](ClO$_4$)$_2$* (**6**–**9**) *with OH$^-$*. We have used the same methods to investigate the reactivity of the basic nucleophile OH^- toward complexes **6**–**9**. Conductimetric titrations in propylene carbonate (and in DMSO for **6**, **7**) with NBu_4OH (0.1M in i-PrOH/MeOH) give two end-points after 1 and 2 OH^- per Cu(II); the conductivities after addition of 1 equiv. of OH^- suggest the formation of a 1:1 electrolyte. Complexes **6**, **8**, and **9** show essentially similar behaviour, the electronic spectra showing a slight shift on coordination of 1 OH^- (*Table 4*); if more than 1 equiv. of OH^- is added, the splitting of the ligand $\pi^{a,b} \rightarrow \pi^*$ band disappears, and, on standing, precipitation of free ligand and poorly soluble $Cu(OH)_2$ species is observed. For **9**, the precipitation of the free ligand was confirmed by IR spectroscopy. These precipitates are not soluble in excess hydroxide. EPR spectra of frozen propylene carbonate solutions of **6** and **8** with 1 equiv. of OH^-

Table 4. *d-d Maximum Energies for Complexes Formed in Propylene Carbonate Solution at 20°*[a])

Complexes	1 equiv. Cl^-	1 equiv. OH^-
6	14085 (97)	14600 (81)
7	13890 (95)	16180 (88)
8	12820 (84)	14025 (55)
9	12300 (103)	13850 (60)

[a]) Energies are given in cm^{-1} and ε (in parentheses) in $M^{-1} \cdot cm^{-1}$ for 10^{-3} M solutions.

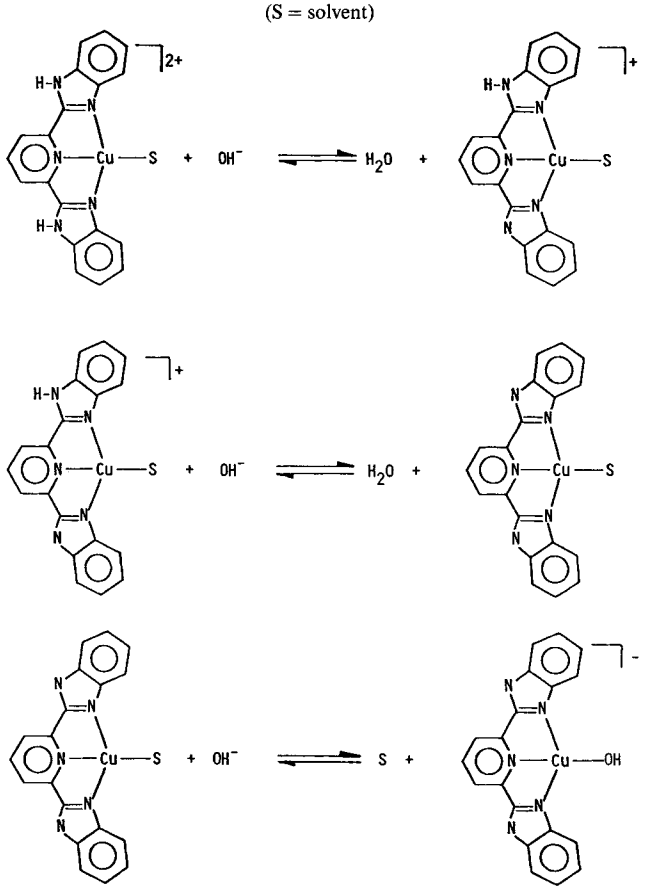
show monomeric species with $(d_{x^2-y^2})^1$ ground state similar to the monochloro complexes ($g_{\|} = 2.23$ for **6**, 2.25 for **8**). Cyclic voltammograms of the 1:1 complexes show irreversible Cu(II)/Cu(I) couples with the reduction potentials slightly lowered as observed for the monochloro complexes. We conclude that a monohydroxo complex similar to the chloro complex is formed initially, and then that the ligands **2**, **4**, and **3** are displaced by excess OH^-.

$$[CuL(S)]^{2+} + HO^- \rightarrow [CuLOH]^{2+} + S \quad (6)$$

$$[CuLOH]^{+} + HO^- \rightarrow L + Cu(OH)_2 \quad (7)$$

The behaviour of **7**, with the ligand **1**, is, however, quite different: although the conductivity measurements suggest formation of a 1:1 electrolyte after addition of 1 equiv. of OH^-, and precipitation occurs on adding more than 1 equiv., the precipitate redissolves completely when 3 equiv. of OH^- per Cu(II) have been added. The spectra also show a significant rise in the d-d transition energy (by 1710 cm^{-1} to 16180 cm^{-1} after addition of 1 OH^-, to 16475 cm^{-1} after addition of 3 OH^-), whereas the complex with the

Scheme 3. *Reactivity of [Cu(bzimpy)]$^{2+}$* (**7**) *with OH$^-$ in Aprotic* (propylene carbonate or DMSO) *Solution* (S = solvent)



similar ligand **2** shows no such sharp rise. We explain this difference by the presence of the two weakly acidic protons of the benzimidazoles, which may be removed by base: this would be expected to increase the donor power of the ligand, and raise the d-d transition energy. To confirm this hypothesis, we have titrated solutions of **6** and **7** in DMF solution with the weak, sterically hindered base Et_3N. Complex **6** shows no change in spectrum, showing that Et_3N does not coordinate to the Cu(II), but with **7** the spectrum obtained after addition of 1 equiv. of Et_3N is identical to that found after addition of 1 equiv. of OH^-, as would be expected, if the first reaction is indeed deprotonation of the ligand. We propose, therefore, that the reaction of $[Cu(\mathbf{1})]^{2+}$ with OH^- involves two deprotonations of the ligand **1** to give an insoluble neutral complex of H_2 bzimpy, followed by redissolution of an anionic complex $[Cu(H_2bzimpy)(OH)]^-$. Deprotonation of **1** coordinated to Fe(II) and Fe(III) has previously been observed [17] [41]. It is worth noting that OH^- does not displace the deprotonated form of **1** from the Cu(II).

With terpy (**5**) in propylene carbonate solution, the electronic spectrum after the addition of 1 equiv. of OH^- shows the formation of $[Cu(\mathbf{5})_2]^{2+}$ with the formation of a fine precipitate, suggesting that reactions similar to *Eqns. 4* and *5* are also observed for OH^-.

4. *Equilibrium Studies of Binding to [Cu(mbzimpy)]*$^{2+}$. To obtain a quantitative estimate of the strength with which additional ligands may be bound to the Cu(II) in these complexes, we have carried out a number of potentiometric titrations of solutions of $[Cu(mbzimpy)]^{2+}$ (hereafter referred to as CuL) in 1:1 $MeCN/H_2O$. This solvent was chosen for reasons of solubility. The solutions (at 25° and with an ionic strength of 0.05M) were titrated with KOH, and the resulting pH/(volume of base) curves analyzed by a non-linear least-squares program [25] to obtain apparent pK_a values (determined as the pH value at half neutralisation). Each system investigated was studied at several concentrations of CuL, and the quoted constants are the averages obtained from several titrations.

For solutions of CuL alone, we observe the titration of two protons, the first in the pH range 5.5 to 10, and the second between pH 10 and 12. The completion of the second deprotonation is accompanied by precipitation of $Cu(OH)_2$ and free ligand. The titration curve in the range where no precipitation is observed is fitted within experimental error by two constants corresponding to the reactions

$$[CuLOH_2]^{2+} \rightleftharpoons [CuLOH]^+ + H^+, \; pK_8 = 7.80(5) \tag{8}$$

$$[CuLOH]^+ + H_2O \rightleftharpoons Cu(OH)_2\downarrow + L\downarrow + H^+, \; pK_9 = 13.3(1) \tag{9}$$

As expected, the apparent pK_a for *Reaction 8* is independent of the total Cu(II) concentration (and excludes the formation of a hydroxo-bridged dimer), whereas that of *Reaction 9* increases with the initial concentration of CuL. The dependence of the apparent pK_a values upon total CuL concentration has been used as confirmation of the stoichiometry of all the reactions studied. The observed pK_a of H_2O coordinated to $[CuL]^{2+}$ is in the range observed for $Cu^{2+}_{aq.}$ (7.3–8.0) [42] and slightly below the values found for $[Cu(terpy)(OH_2)]^{2+}$ (8.3 [43]) and $[Cu(pip)(OH_2)]^{2+}$ (8.4 [44], pip = 2-{[2-(2-pyridyl)ethylimino]-methyl}pyridine).

Titration of CuL in the presence of 1 equiv. of 1-methylimidazolium ($Hmim^+$) shows three deprotonations corresponding successively to *Reactions 10, 11,* and *9*:

$$[CuL(OH_2)]^{2+} + Hmim^+ \rightleftharpoons [CuL(mim)]^{2+} + H_3O^+, pK_{10} = 2.1(2) \quad (10)$$

$$[CuL(mim)]^{2+} + 2\,H_2O \rightleftharpoons [CuLOH]^+ + mim + H_3O^+, pK_{11} = 12.1(2) \quad (11)$$

These assignments were confirmed by the dependence of apparent pK_a upon total Cu(II) concentration. Using the pK_a value of 6.57(2) determined for $Hmim^+$ under our conditions, we obtain for *Reaction 12*

$$[CuL(OH_2)]^{2+} + mim \rightleftharpoons [LCu(mim)]^{2+} + H_2O \log K_{12} = 4.5(2) \quad (12)$$

significantly greater than that found for $[Cu(mim)(pip)]^{2+}$ ($\log K = 3.3(1)$ [44]). If imidazole (Him) is used instead of mim, the first deprotonation corresponds to formation of the complex $[CuL(Him)]^{2+}$ and gives a stability constant $\log K = 4.5(1)$ identical to that of mim; no difference between mim and Him was found for [Cu(pip)] [44].

The possibility of forming imidazolate-bridged dimers on further titration of imidazole complexes is now well-established [44] [45] and, on titrating a 2:1 mixture of $[CuL]^{2+}$ and H_2im^+, a second deprotonation corresponding to

$$[CuL(Him)]^{2+} + [CuL(OH_2)]^{2+} \rightleftharpoons [CuL(im)CuL]^{3+} + H_3O^+, pK_{13} = 4.1(2) \quad (13)$$

is observed *(Fig. 3, a)*. The observed pK_a is identical to that observed for the formation of the glycylglycine complex [(glygly)Cu(im)Cu(glygly)]$^-$ (4.1 [45]). Formation of the dimer is confirmed by the correct negative dependence of the apparent pK_a on the total Cu(II) concentration, and by the isolation of $[LCu(im)CuL](ClO_4)_3 \cdot H_2O$ (**15**). The IR spectrum of this compound shows an absorption due to H_2O of crystallisation at 3450 cm^{-1}, but no $\tilde{\nu}$(N–H) in the region of 3100–3300 cm^{-1}. The EPR spectrum of the powder at room temperature shows a broad rhombic signal in the $g = 2$ region and a signal corresponding to the $\Delta m_s = \pm 2$ transition at $g = 4.2$, confirming the presence of a bridged dimer [44].

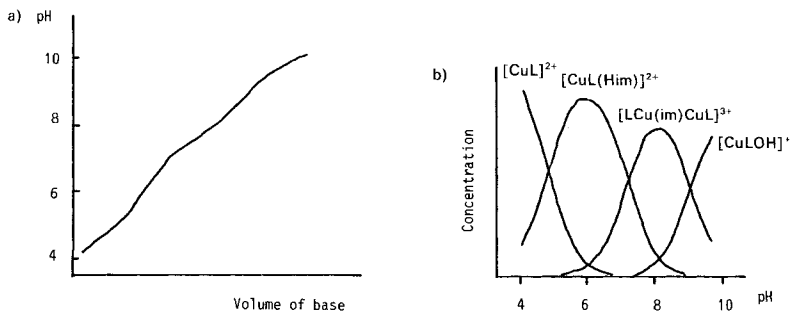


Fig. 3. a) *Typical titration curve of a 2:1 mixture of* $[Cu(\mathbf{2})]^{2+}$ *and* H_2im^+. b) *Calculated species distribution as a function of pH for the titration curve in* (a). The assignment of $[Cu(\mathbf{2})OH]^+$ is tentative (see text).

Solutions of **15** in MeCN at 25° give a molar conductivity of 123 ± 5 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ which is consistent with a 3:1 electrolyte *(Table 1)*. Using the constant determined above, we may determine

$$[CuL(imH)]^{2+} + [CuLOH]^+ \rightleftharpoons [LCu(im)CuL]^{3+} + H_2O, \log K_{14} = 3.7(2) \quad (14)$$

If the titration is continued after the formation of the dimer, further deprotonation is observed, leading eventually to precipitation of $Cu(OH)_2$ and free L. The UV/VIS spectra

of the solutions after the addition of a 3rd equiv. of base suggest the major species in solution to be $[CuLOH]^+$

$$[LCu(im)CuL]^{3+} + 3\ H_2O \rightleftharpoons 2\ [CuLOH]^+ + Him + H_3O^+ \qquad (15)$$

as was observed with the system $[Cu(pip)]^{2+}$ [44]. The dependence of the observed pK_a on total Cu(II) concentration does not, however, agree with this, and we cannot exclude the presence of $[CuL(im)]^+$ as seen with the glycylglycine complex [45]. Study of this reaction is hindered by precipitation, but the observed titration curves show that the dimer $[LCu(im)CuL]^{3+}$ is stable in the pH range of 7–9 *(Fig. 3, b)*. Titration of 1:1 mixtures of $[CuL]^{2+}$ and H_2im^+ show initial formation of $[CuL(Him)]^{2+}$ followed by a deprotonation which is consistent with formation of the dimer; further titration leads to precipitation as for the 2:1 mixtures.

Conclusions. – On the basis of the d-d band maxima for $[CuL]^{2+}$, $[CuLCl]^+$, and $[CuLOH]^+$, the ligands bzimpy (**1**) and mbzimpy (**2**) are only slightly weaker donors than terpy (**5**), whereas bzthpy (**3**) and bzoxpy (**4**) are significantly weaker. This agrees with the *Mössbauer* results for the complexes $[FeL_2]^{2+}$, where the complexes with **1** and **2** are low-spin and with **3** and **4** are high-spin at room temperature [41]. In solution, the EPR and UV/VIS spectra of $[CuL]^{2+}$ are consistent with expected tetragonal structure, and the change in the magnitude of the solvent effect on the electronic spectrum on going from $[CuL]^{2+}$ to $[LCuCl]^+$ shows that the *Lewis* acidity is indeed concentrated in the fourth equatorial site. From a purely structural point of view, therefore, all five ligands studied here seem to satisfy our initial requirements. A closer examination of their solution chemistry reveals, however, that bzthpy (**3**) and bzoxpy (**4**) are too easily decomplexed by donor solvents or other ligands to be of much use. More surprising, but equally limiting for model studies, is the observation of the ease with which $[Cu(terpy)]^{2+}$ complexes disproportionate to give $[Cu(terpy)_2]^{2+}$ and CuX_2 *(Eqn. 5)*. Of the two remaining ligands, bzimpy (**1**) suffers from the weak acidity of the benzimidazole protons which are likely to interfere with any basic peroxo complex. The most promising precursor for a copper-dioxygen complex is, therefore, the complex $[Cu(mbzimpy)]^{2+}$; this complex shows good thermodynamic stability, being decomplexed only by an excess of OH^- at fairly high pH. The potentiometric measurements show that imidazole and 1-methylimidazole are quite strongly bound to the fourth coordination site ($\log K = 4.5$), an order of magnitude greater than $[Cu(pip)]^{2+}$. The formation of an imidazolate-bridged dimer, although of more direct interest for modelling the active site of superoxide dismutase [44] [45], shows that dimerisation of $[Cu(mbzimpy)]^{2+}$ units is not impossible sterically, and that the formation of a peroxo-bridged dimer may be envisaged.

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