Polyhedron Vol. 8, No. 10, pp. 1321–1328, 1989
Printed in Great Britain

0277–5387/89 $3.00+.00

THREE COORDINATED COPPER(I) COMPLEXES OF CHELATING LIGANDS DERIVED FROM 2,6-DIACETYLPYRIDINE AND PHENYLALANINE OR TYROSINE

W. L. KWIK* and ALICE W. N. TAY

Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511

(*Received* 7 *June* 1988; *accepted after revision* 18 *January* 1989)

Abstract—Copper(I) complexes of Schiff-base ligands, L_1 and L_2, derived from condensation of 2,6-diacetylpyridine with phenylalanine methyl ester or tyrosine ethyl ester have been prepared. On the basis of various spectroscopic data, it is proposed that these complexes in the solid-state have mononuclear structures in which the trimethine group acts as tridentate while retaining its planarity. In methanol, spectroscopic properties suggest at least partial dissociation of one-side arm leading to a two-coordinate copper(I) which then interacts with a free imino nitrogen of a second molecule of the copper(I) complex. This results in a more effective overlap of the copper(I) orbital with p_{π^*} of the ligand and hence an increase in absorption intensities.

Interesting examples of copper(I) Schiff-base complexes (Scheme 1) displaying reactivities towards dioxygen have recently been reported.[1–6] The Schiff-base ligands involved (Scheme 1) are those obtained from condensation of 2,6-diacetylpyridine and various amines, and span both the pentadentate types[1–5] (L^1, L^2) as well as those with only three nitrogen donors[6] (L^3, L^4, L^5). It has been noted[6] that some of the chemical behaviours of the five nitrogen and the three nitrogen Schiff bases are distinctly different.

We have previously reported[7] the synthesis and spectral properties of the copper(II) and zinc(II) complexes of the Schiff bases (Scheme 1) derived from condensation of 2,6-diacetylpyridine and phenylalanine methyl ester (L_1), or tyrosine ethyl ester (L_2) containing three nitrogen donor atoms as well as ester carboxylate groups in the side chain. In the following, the isolation and various chemical properties of the corresponding copper(I) complexes [**1** for $CuL_1(BF_4)$ and **2** for $CuL_2(BF_4)$] are presented.

* Author to whom correspondence should be addressed.

EXPERIMENTAL

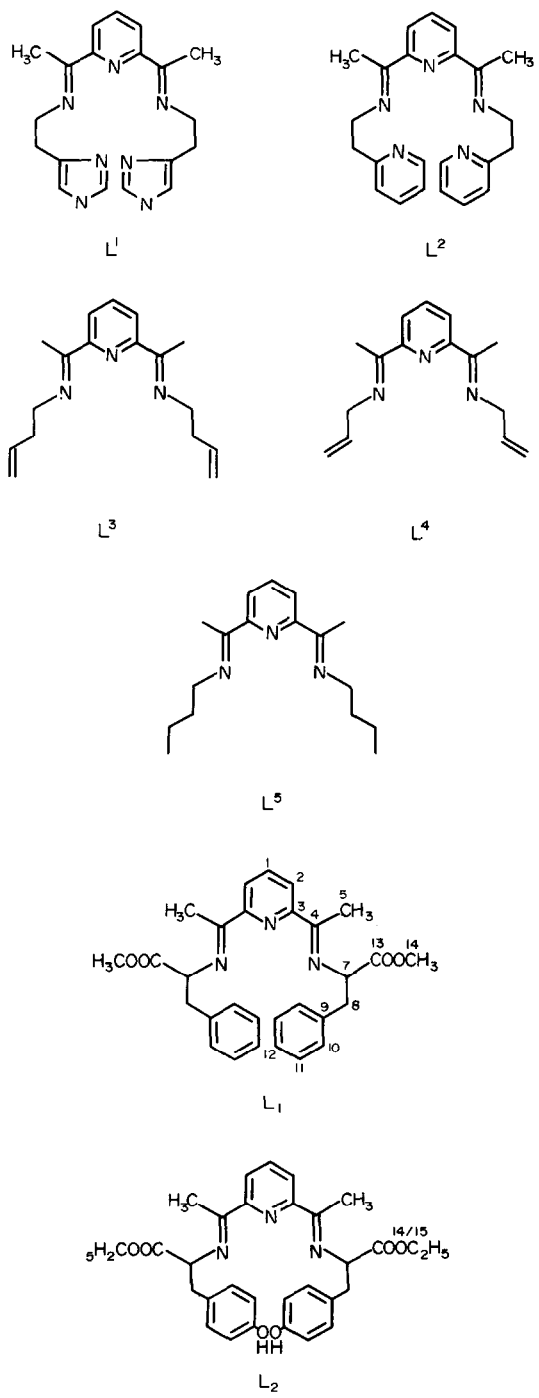
Synthesis

All solvents were deoxygenated and stored under nitrogen over molecular sieves (4 Å). Methanol, acetonitrile and dichloromethane were treated according to published procedures prior to use. Spectrochemical grade dimethyl sulphoxide (Aldrich, Gold Label) was used for electronic, electrochemical and conductivity measurements. Deuterated dimethyl sulphoxide (Aldrich, Gold Label) used for NMR spectral studies was stored under nitrogen in a dry-box.

2,6-Diacetylpyridine and 2-(2-aminoethyl)pyridine (Aldrich Chemical Company) were used as received. Phenylalanine methyl ester hydrochloride, tyrosine ethyl ester hydrochloride (Sigma Chemical Company) were treated to remove the hydrochloride by the method described by Casella *et al.*[5] Tetra(acetonitrile) copper(I) tetrafluoroborate was prepared by the method of Hemmerich and Sigwart. Electrochemical grade tetraethylammonium perchlorate (Eastman Chemicals) was used without further purification.

The ligand solution was prepared by refluxing 2,6-diacetylpyridine (2 mmol) and the base (4 mmol) (phenylalanine methyl ester/tyrosine ethyl ester) under nitrogen in dry, deoxygenated MeOH (100 cm^3) for about 20 h, whereupon an intense yellow colour developed.

Freshly prepared $[Cu(CH_3CN)_4]BF_4$ (2 mmol) was dissolved in deoxygenated CH_3CN (50 cm^3) and the solution filtered to remove trace amounts of blue copper(II) salt present. The colourless filtrate was warmed before being added to the hot ligand solution. The ensuing blood-red solution was then reduced to near dryness at 85°C by rotary evaporation, to yield a hygroscopic, dark red solid. This was recrystallized twice from deoxygenated MeOH in a dry-box. The final, dark red solid was dried *in vacuo* at 80°C for 6 h prior to elemental analysis.



Scheme 1.

Compound **1**. Found: C, 53.4; H, 4.9; N, 6.4; Cu, 9.6. Calc. for $C_{29}H_{33}N_3O_5CuBF_4$: C, 53.2; H, 5.0; N, 6.4; Cu, 9.6%. IR data (KBr, cm^{-1}): 1636 ($\nu_{C=N}$); 1740 ($\nu_{C=O}$); 1267 (ν_{C-OR}); 1636 ($\nu_{COO(as)}$); 1385 ($\nu_{COO(s)}$). Λ_M = 76 (MeOH); 37 (DMSO); 149 (CH_3CN) S cm^2 mol^{-1}.

Compound **2**. Found: C, 50.9; H, 5.0; N, 6.1; Cu. 8.6. Calc. for $C_{31}H_{39}N_3O_8CuBF_4$: C, 50.8; H, 5.3; N, 5.7; Cu, 8.7%. IR data (KBr, cm^{-1}): 1615 ($\nu_{C=N}$); 1734 ($\nu_{C=O}$); 1268 (ν_{C-OR}); 1615 ($\nu_{COO(as)}$); 1373 ($\nu_{COO(s)}$). Λ_M = 87 (MeOH); 36 (DMSO); 151 (CH_3CN) S cm^2 mol^{-1}.

Measurements

IR spectra in the 4000–400 cm^{-1} region were recorded on a Perkin–Elmer Model 1710 Fourier Transform IR spectrometer. Spectra extending into the far-IR region of 200 cm^{-1} were recorded on a Perkin–Elmer Model 567 spectrometer calibrated with polystyrene film. CsI and KBr pellets were employed throughout. Electronic spectra were recorded on a Perkin–Elmer Lambda 9 UV–vis–near-IR spectrophotometer. Conductivities of 10^{-3} M solutions of the complexes were measured at 30°C using a CM-115 conductivity meter (Kyoto Electronics). The ^1H and ^{13}C NMR spectra were obtained for samples in DMSO-d_6 solutions at 90 MHz using a Jeol Fx90 Q FT NMR spectrometer. Cyclic voltammograms were obtained in DMSO solutions at room temperature under a constant flow of N_2, using a Pine Instrument RDE 4 potentiostat. A three-electrode system was employed, with a glassy carbon ring-disc electrode (disc radius = 0.382 cm) serving as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All solutions were 0.1 mol dm^{-3} in tetraethylammonium perchlorate and 10^{-3} mol dm^{-3} in the complex.

RESULTS AND DISCUSSION

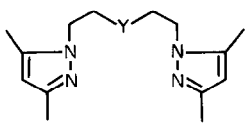
IR spectral study

The IR spectra of **1** and **2** are similar in important aspects to those of the free ligands, though there

Table 1. Chemical shifts (ppm) of ^{1}H NMR signals

Compound/complex	Protons H(1)	H(2)	H(7)	H(10)	H(11)	H(12)	H(14)	H(8)
2,6-diacetylpyridine	8.16	2.73	—	—	—	—	—	—
Phenylalanine methyl ester		—	3.58	7.21	7.21	7.21	3.58	3.58
Tyrosine ethyl ester		—	3.40	6.65	6.95	—	4.00	2.68 2.74
L_1	8.15	2.73	3.70	7.25	7.25	7.25	3.60	3.10
L_2	8.15	2.71	3.50	6.70	7.00	—	4.00	3.00
1	8.14	2.75	4.20	7.30	7.30	7.30	3.60	3.15
2	8.14	2.72	4.20	6.74	7.04	—	4.10	3.00

are distinct shifts of the characteristic bands. Both display strong IR absorptions at: (i) 1740, 1286 and 1240 cm^{-1} of the ester carbonyl (COOR),[8-10] (ii) 1636 cm^{-1} for **1** and 1625 cm^{-1} for **2** of the imino $\nu_{C=N}$[11] and (iii) 1050 cm^{-1} for the BF_4^- ion. As there is no significant difference in the IR absorption characteristics of the two copper(I) complexes, it is tentatively concluded that there is no significant structural difference between the two complexes. The presence of only one distinct absorption band due to the imino stretching ($\nu_{C=N}$) in the 1600–1660 cm^{-1} region, suggests that both complexes assume a structure in which the two imino (C=N) groups are equivalent. It appears that a dinuclear structure in which the two imino (C=N) nitrogen atoms are bonded to different copper centres can be excluded for these two copper(I) complexes.[6] It would seem reasonable to assume that the trimethine group functions as a tridentate chelating group to a single copper(I) ion, thus retaining planarity upon complexation. Moreover, a comparison of the IR spectra of these complexes shows that they closely resemble those of other metal complexes where trimethine group planarity has been proven by X-ray analysis.[5] These considerations lead us to propose that in **1** and **2**, the copper(I) ions are mononuclear and three-coordinate. This is consistent with the presence of uncoordinated ester groups as suggested from the IR absorption characteristics.[8-10] The most probable disposition of the donor atoms in L_1 and L_2 is such that the metal ion has a T-shaped geometry. Such a geometry, though unusual, has been observed in the ligand systems,[6] bis[2-(3′,5′-dimethylpyrazol-1-yl)ethyl]ether (Y = O) and the corresponding sulphide (Y = S) and amine (Y = NH), see Structure 1.



Structure 1.

^{1}H *NMR spectral study*

Both the copper(I) complexes display broad ^{1}H NMR signals at 25°C, most likely due to the presence of trace amounts of copper(II) ions. As the temperature is raised to 100 and 150°C, the spectra became better resolved.

A comparison of the spectra of the free ligands versus those of the complexes and those reported by Nelson,[6] reveals that the effect of complexation on the chemical shift is most significant for H(7) yielding a change in δ_H values of *ca* 0.5–0.7 ppm (Table 1). This is consistent with the proximity of H(7) to the imino nitrogen and similar changes in δ_H values have been observed for the zinc(II) analogues.[7,12] It is also of interest to note that the protons of the carboxylate group of the amino acid components are only marginally affected by condensation and complexation. This observation further points to the absence of any interaction between the carboxylate oxygen and the copper(I) ion in these complexes, in contrast to the case of the analogous zinc(II) complexes.[7,12]

^{13}C *NMR spectral study*

The ^{13}C NMR spectra of **1** and **2**, as well as those of the ligands L_1 and L_2, are generally of well-resolved peaks (Table 2). Assignments were made with the aid of the "off-resonance" technique, whereby the number of protons bound to each unique carbon atom could be determined without loss of the nuclear overhauser enhancement.[13,14] Reference was also made to values of ^{13}C chemical shifts reported for similar complexes.[6]

Comparison of the chemical shifts of L_1 and L_2 and those of the corresponding copper(I) complexes showed that the largest change is observed for the imino carbon, C(4). The shift of C(4) from 198.5 to 166.8–175 ppm upon condensation and complexation is not only supported by reported values

Table 2. Chemical shifts (ppm) of ^{13}C NMR signals

Compound/complex	C(1)	C(2)	C(3)	C(4)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)
2,6-diacetylpyridine	138.8	124.4	152.1	198.5	—								
Phenylalanine methyl ester					41.0	55.9	137.7	128.6	129.5	126.8	175.5	51.7	
Tyrosine ethyl ester					40.0	55.8	127.5	115.0	130.0	155.6	174.9	59.8	14.0
1	138.5	126.6	152.2	170.0	54.6	55.5	138.5	128.1	128.8	127.9	170	52.1	
2	139.1	124.0	152.2	170.4	53.9	55.1	128.0	115.5	130.3	156	170	65.1	14.0

but also consistent with the lower electronegativity of nitrogen in comparison to that of oxygen.

The proximity of C(7) to the imino nitrogen is expected to induce significant changes in the chemical shifts upon condensation and complexation. Indeed, changes of 13.6–13.9 ppm have been observed for both copper(I) complexes. The larger changes of these three nitrogen systems, in comparison to the five nitrogen complexes (Table 2), would seem to indicate stronger imino nitrogen–metal interactions in the former.

Cyclic voltammetric studies

1 and **2** display a small cathodic wave at 0–40 mV and a larger wave at −450 to −500 mV, but there is only one anodic wave at +300 to +460 mV. The range of values into which these waves fall indicate that they are most likely attributable to the electrode processes of $Cu^{2+} \rightarrow Cu^{+}$ and $Cu^{+} \rightarrow Cu^{0}$ for the cathodic wave, and of $Cu^{+} \rightarrow Cu^{2+}$ for the anodic wave. Moreover, the larger ΔE_p for the first process means that the electron transfer is irreversible in each case.

That the $Cu^{2+} \rightarrow Cu^{+}$ process was detected as a small but distinct wave is not unexpected in view of the ease with which **1** and **2** undergo oxidation. That the anodic process of $Cu^{0} \rightarrow Cu^{+}$ is not detected is probably a manifestation of a coupled chemical reaction which occurs after the electrode reduction steps in the forward cathodic scan.

Electronic spectral study: nature of the complexes in solution

At room temperature, as well as at 80 K, solution and solid-state (KBr/Nujol mull) electronic spectra measured over the range 30,000–10,000 cm^{-1} (Table 3) are found to be solvent dependent. Whereas absorption maxima at ~ 35,700 cm^{-1}, attributable to the ligands $\pi \rightarrow \pi^*$ transition, are observed in MeOH, DMSO and CH_3CN and intense well-defined bands at ~ 22,730 and ~ 22,220 cm^{-1} for **1** and **2**, respectively (Fig. 1), are displayed only in MeOH and DMSO. In CH_3CN, a shoulder of much lower intensity appeared at 25,000 cm^{-1}. The high molar absorptivities of these lower energy bands in MeOH and DMSO (Table 3) clearly indicate that these are due to the charge-transfer transitions (CT) from filled *d*-orbitals of the copper(I) to the vacant π^* orbital of the trimethine group.[11] These bands are further characterized by a steady increase in intensity over a time period of ~ 30 and 60 min in carefully deoxygenated MeOH and DMSO, respectively.

Similar increases in absorbances with time were observed over a five-fold concentration range, 2×10^{-4}–1×10^{-3} M [Fig. 2(a)]. The apparent "ε"s

Table 3. Electronic spectral absorptions

Solvents	$10^{-3}/cm^{-1}$ (ε/$dm^3\ mol^{-1}\ cm^{-1}$) **1**	**2**
KBr pellet	20.8, 35.7	21.0, 35.7
Nujol mull	20.8	21.0
MeOH	22.2(2500), 35.7(16,000)	22.7(2500), 35.7(1500)
5:1 MeOH–ETG[a] (298 K)	22.2(2500), 35.7(16,000)	22.7(2500), 35.7(15,000)
5:1 MeOH–ETG[a] (80 K)	22.2(3800), 33.3(24,000)	22.7(3900), 35.7(23,000)
DMSO	22.7(3000), 35.7(15,000)	22.7(3000), 35.7(15,000)
CH_3CN	25.6(sh), 35.7(16,000)	25.6(sh), 35.7(15,000)

[a] ETG = ethyleneglycol.

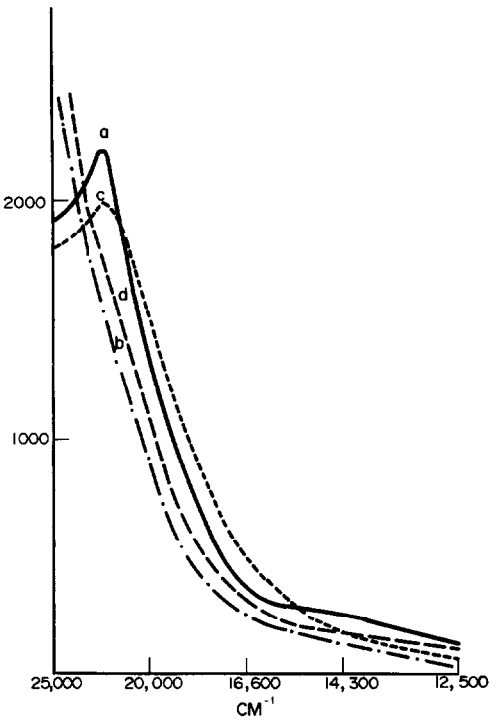


Fig. 1. Electronic spectra of **1** (a ——) in deoxygenated DMSO; (b — · —) solution a after oxygenation for *ca* 1 h; (c -----) solution b after degassing—gentle heating under N_2 for *ca* 1 h; (d – – – –) solution c after oxygenation for *ca* 30 min.

calculated for these absorption maxima are seen to be fairly constant, within some inherent experimental error, due to oxidation/decomposition of the complexes in solution.

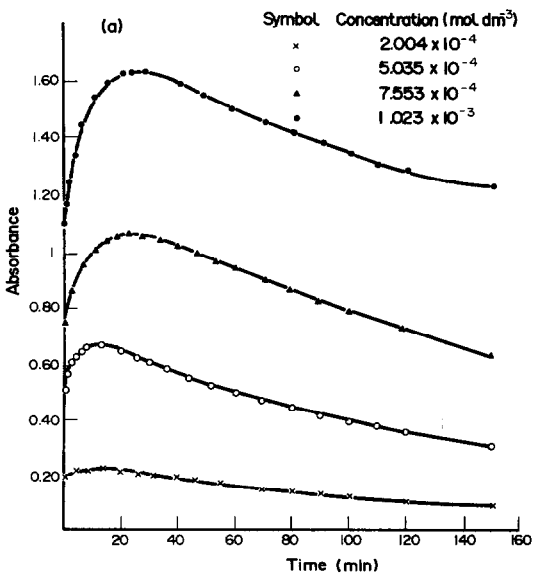


Fig. 2(a). Plot of absorbance of **1** vs *t* (min) at different concentrations in MeOH.

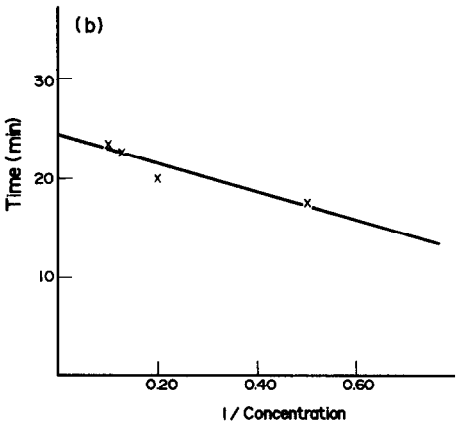


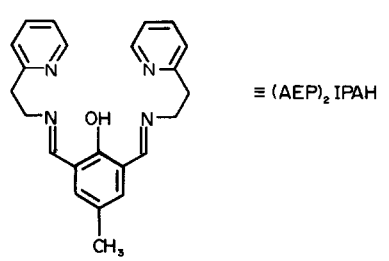
Fig. 2(b). Plot of $1/C$ vs *t* (min).

The plot of $1/C$ (with C being the concentration of the respective complex) vs *t* (the time taken to reach maximum absorbance at each concentration) [Fig. 2(b)], was found to be linear for both complexes in MeOH over the concentration range, 2×10^{-4}–1×10^{-3} M. This is an interesting observation, although no further conclusions could be drawn at this stage because of the complexities of possible decompositions due to the ease of oxidation of these complexes in solution. Moreover, the remarkably similar behaviour of **1** and **2** suggests that the process does not involve the phenolic OH in the tyrosine component to any significant extent.

In the following, an attempt will be made to account for: (i) the markedly different absorption spectra at 25,000–20,000 cm^{-1} in CH_3CN and in MeOH/DMSO; (ii) the remarkable increases in intensities of the absorption maxima at 22,700/22,200 cm^{-1} for **1** and **2**, respectively, in MeOH, as well as in DMSO.

Proposed mechanism for (i)

It must be mentioned that such markedly different absorption behaviour in CH_3CN and MeOH–DMSO are not unique for **1** and **2**. Urbach and coworkers[15,16] reported similar solvent dependence of electronic absorptions for a mononuclear copper(I) complex with the ligand shown in Structure 2.



Structure 2.

Thus the copper(I) complex of $(AEP)_2IPAH$ displays only one band at 22,600 cm^{-1} in MeOH and DMSO, but two bands at 22,400 and 28,300 cm^{-1} in MeCN, with the first band being reduced in intensity relative to that in MeOH. This behaviour was interpreted as a competition between the ligand and acetonitrile for coordination of the copper(I) according to the equilibrium:

$$[Cu(AEP)_2IPAH]^+ + CH_3CN\,(excess) \longrightarrow (AEP)_2IPAH + [Cu(CH_3CN)_n]^+.$$

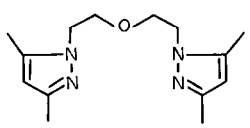
This equilibrium is reasonable in light of the known affinity of copper(I) for acetonitrile.[16] It was also found in this case, that addition of excess $[Cu(CH_3CN)_4]BF_4$ to an acetonitrile solution of the $[Cu(AEP)_2IPAH]^+$ produces a dramatic increase in intensity for the 22,400 cm^{-1} band which was associated with the complex, while the 28,300 cm^{-1} band, due to the free ligand, disappeared.

For **1** and **2** it was found that addition of excess $[Cu(CH_3CN)_4]BF_4$ to a methanolic solution containing 10% CH_3CN brought about a significant increase in absorbances at 22,200–22,700 cm^{-1}. Such behaviour suggests the relatively weaker binding of L_1 and L_2 as compared to $(AEP)_2IPAH$. This is not surprising in view of the binding of copper(I) by two more pyridine rings in the latter.[16]

Proposed mechanism for (ii)

The electronic absorption spectra of the copper(I) complexes of L^3 and similar Schiff-base bands reported by Nelson *et al.*,[6] comprise absorptions at 22,200–22,700 cm^{-1} appearing only as a shoulder of relatively weak intensity. On the other hand, the five-coordinated copper(I) complexes of Schiff-base ligands L^1 and L^2 due to Wilson *et al.*,[4] display well-defined absorptions similar to those of **1** and **2**.

The weaker CT band as observed for complexes of L^4 and L^5, can be rationalized by consideration of the coordination geometry of the copper(I) complexes due to the disposition of donor atoms in these complexes. It was found that the metal ion would in fact have a T-shaped geometry. Such an unusual geometry has been observed in a few copper(I) complexes[17–19] with ligands such as bis[2-(3′,4′-dimethylpyrazol-1-yl)ethyl]ether (pze) (Structure 3).

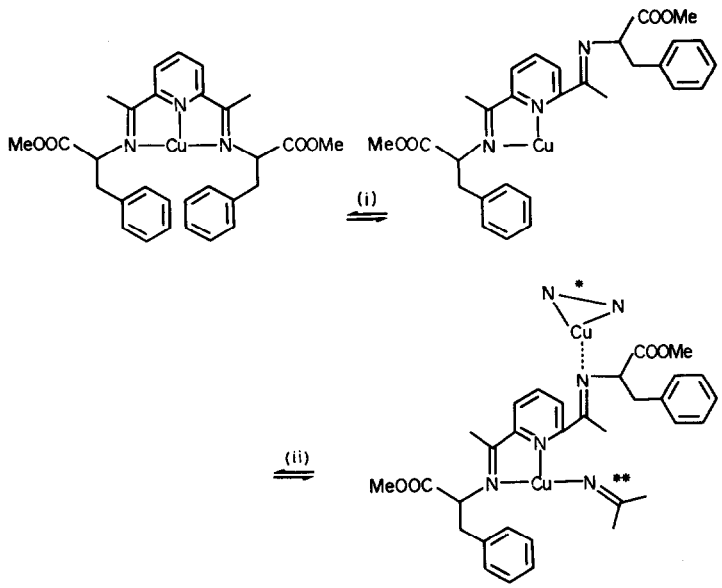


Structure 3.

The X-ray structure of the Cu^I–pze complex shows that the copper(I) is essentially two-coordinate with a weak interaction by the oxygen atom. Thus it is expected that the T-shaped disposition in copper(I) complexes of L^4 and L^5 ensues in poor overlap of the pyridine *p*-orbital with the filled *d*-orbital of copper(I). This, in turn, leads to CT bands of relatively lower intensity. The stronger CT band in the five-coordinated copper(I) complexes reported by Wilson *et al.*[4] is probably due to stronger binding brought about by the two imidazyl/pyridyl nitrogen donors (in addition to the DAP pyridine nitrogen) in these ligands. In fact as shown recently,[4] the trimethine group assumes a highly distorted, non-T-shaped disposition, the bond angle between the two imino to copper(I) bonds being 148° and significantly different from the 180° expected of the T-shaped geometry. Such distortion from T-shaped geometry in turn allows for better overlap between the pyridyl (trimethine) nitrogen *p*-orbital and the filled *d*-orbital of copper(I) and thus the observed intense CT band.

A consideration of electronic spectral behaviour in relation to the structures of the two series of copper(I) complexes mentioned above, leads to a possible explanation of the observed increase in intensities of the CT bands for **1** and **2** with time in MeOH–DMSO. It appears that such an increase must be related to a change in geometry around copper(I), so that more efficient overlap of the respective orbitals of the ligand L_1/L_2 and of copper(I) can be brought about. Taking all experimental data available into consideration, the equilibrium indicated in Scheme 2 appears most favourable.

In the above equilibrium it is proposed that one of the imino nitrogen swings open leaving a two-coordinated copper(I); the driving force for step (i) probably arises from the strong hydrogen bonding ability, particularly of MeOH, with which the free imino nitrogen can form hydrogen bonds, as first suggested by Urbach.[12] Step (ii) is proposed on the basis that the rate of increase in absorbance is inversely proportional to the concentration of the complex. It would seem reasonable that at least two copper(I) centres must be involved. These copper(I) centres may attain four-coordination through bonding with a MeOH molecule; alternatively it may remain three-coordinate but with more efficient overlap of the filled *d*-orbital on copper(I) with pyridyl nitrogen *p*-orbital. Furthermore, as step (ii) is statistically unfavourable, there is a slow increase over a time period of 30–60 min. It should



Scheme 2. * N | N only the part of the trimethine group that binds to the two-coordinate copper(I) is shown: ** N< only the bound N donor of the trimethine group is shown.

be emphasized that these time periods are only approximate upper limits, as the processes suggested in steps (i)/(ii) are competing against decomposition of the complexes produced by slow oxidation. Finally, the involvement of hydrogen bonding in step (i) is consistent with the order of observed increases in absorbances at 22,700–22,200 cm^{-1} for MeOH > DMSO > acetone; in the last case the increase lasted for only 7 min.

The proposed equilibrium is also consistent with the observed ^{1}H and ^{13}C NMR spectra described above. Thus the peak due to the methyl protons, C(5), was found to be extremely broadened, probably the result of an average of the two sets of imino methyl protons. Likewise, the imino C(5) appears as a broad peak in the ^{13}C NMR spectra of **1** and **2**. The fact that no separate signals were observed for the protons and carbons associated with the two imino nitrogens could be due to rapid exchange of the bound and unbound imino groups.

In addition, such a change in coordination geometry, brought about by opening up of one of the side arms in solution, is also consistent with the observed differences in spectra of samples dispersed in KBr/Nujol mull and of methanol/DMSO solutions. In KBr/Nujol mull, the absorption at 22,700 cm^{-1} appears only as a broad shoulder (Table 3). In glassed solution the bands at 22,200–22,700 cm^{-1} become better defined. This is in no way contradictory to the proposed equilibrium, as some of the copper(I) is already in the geometry type resulting from step (ii) of the above equilibrium in such a glassed solution.

Finally solvation by MeOH/DMSO to give rise to four-/five-coordinated copper(I), as well as participation of the phenyl ring of the tyrosine/phenylalanine residue in L_1/L_2 have been considered. However, mechanisms involving these processes could not fully account for the observed experimental findings.

Reactions with dioxygen

Both **1** and **2** have reasonable air stabilities over periods of days in the solid-state. The solutions in the presence of air, however, develop green or green–brown colours at rates dependent on the nature of the complex and of the solvent.

As the intensely red coloration was retained in DMSO over a significantly longer time than in MeOH, this was selected to be the solvent used for studying the oxygenation. Upon exposure to dioxygen (1 atm), the red coloration of a solution of **1** and **2** in deoxygenated dry DMSO at room temperature disappears, yielding a green–yellow solution. The change is complete in about 1.5 h and can be partially reversed by gentle heating of the oxygenated solution under a stream of dry nitrogen (Fig. 1). The degree of reversibility of the reaction determined spectrophotometrically is about 70%

and the oxy–deoxy cycle process can be repeated 2–3 times until the solution became brown and did not show any further colour change upon further exposure to dioxygen.

The change of colour of a methanolic solution of **1** or **2** upon exosure to dioxygen was found to be completely irreversible. A similar finding has previously been reported by Ibers and co-workers.[5]

Reactions with carbon monoxide

In view of the similarity in structure of the ligands L_1 and L_2 to those reported by Nelson *et al.*,[6] **1** and **2** are expected to interact with CO. Upon introduction of 1 atm of CO to a degassed DMSO solution of **1** or **2**, the solution changed from a red to yellow–brown colour. The spectral changes were found to be only partially reversible. Similar spectral changes have been reported by Nelson *et al.*[6] in a study of the carbonylation reaction of the copper(I) complex of the Schiff-base ligands, L^3–L^5. However, further investigation of the carbonylation of **1** and **2** was rendered difficult due to the strong IR absorption of DMSO in the region of interest.

REFERENCES

1. M. G. Simmons and L. J. Wilson, *J. Chem. Soc., Chem. Commun.* 1978, 634.
2. M. G. Simmons, C. L. Merrill, L. J. Wilson, L. A. Bottomley and K. M. Kadish, *J. Chem. Soc., Dalton Trans.* 1980, 1827.
3. C. L. Merrill, L. J. Wilson, T. J. Thamann, T. N. Loehr, N. S. Ferres and W. H. Woodruff, *J. Chem. Soc., Dalton Trans.* 1984, 2207.
4. J. A. Goodwin, D. M. Stanbury, L. A. Wilson, C. W. Eigenbrot and W. R. Scheidt, *J. Am. Chem. Soc.* 1987, **109**, 279.
5. L. Casella, M. E. Silver and J. A. Ibers, *Inorg. Chem.* 1984, **23**, 1409.
6. S. M. Nelson, A. Lavery and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.* 1986, 911.
7. W. L. Kwik, K. P. Ang and A. W. N. Tay, *Polyhedron* 1988, **7**, 695.
8. A. D. Cross and R. A. Jones, *An Introduction to Practical Infrared Spectroscopy*. Butterworth, London (1969).
9. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*. Chapman and Hall, London (1975).
10. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley, New York (1987).
11. L. Casella and M. Gullotti, *Inorg. Chem.* 1981, **20**, 1306.
12. R. H. Bible, *Interpretation of NMR Spectra*. Plenum Press, New York (1966).
13. D. H. Busch, D. J. Olzanski, J. C. Stevens, W. P. Schammel, N. Kojima, N. Herron, L. Zimmer, K. A. Holter and J. Mocak, *J. Am. Chem. Soc.* 1981, **103**, 1472.
14. R. J. Abraham and P. Loftus, *Proton and C-13 NMR Spectroscopy*. Heyden, London (1978).
15. J. J. Grzybowski and F. L. Urbach, *Inorg. Chem.* 1980, **19**, 2604.
16. S. E. Manahan and R. T. Iwamoto, *J. Electroanal. Chem.* 1967, **14**, 213.
17. T. N. Sorrell and M. R. Malachowski, *Inorg. Chem.* 1983, **22**, 1883.
18. T. N. Sorrell, C. Shen, C. J. O. O'Connor and C. J. O'Connor, *Inorg. Chem.* 1987, **26**, 1755.
19. M. J. Schilstra, P. J. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem.* 1987, **21**, 2637.