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Structural effects of potentially hexadentate N$_4$O$_2$, N$_4$S$_2$ or N$_6$ ligands involving pyridine, amine and ether or thioether donors: crystal structure of copper(II) and zinc(II) complexes †

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The two new hexadentate ligands 1,12-bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane (pydado) and 1,12-bis-(2-pyridyl)-5,8-dithia-2,11-diazadodecane (pydadt), have been synthesized as their tetrahydrochloride salts and their protonation constants and the stability constants of the copper(II) and zinc(II) chelates determined by potentiometry. The formation of M(HL) and ML species was detected in all cases except for pydado which gives only ZnL species. The two central donor atoms (ether oxygen or thioether sulfur) of the ligands do not have a great influence on the protonation constants, but the stability constants of copper(II) complexes with pydadt are slightly greater than those of pydado. The solid copper(II) and zinc(II) complexes have been prepared as their perchlorate salts. The crystal structures of four complexes are reported. In all the zinc(II) complexes the metal center is encapsulated by the ligand in a distorted octahedral environment, whereas the copper(II) complex with pydado is a four-coordinated compound. The copper(II) complexes have been examined by ESR, electronic spectroscopy and cyclic voltammetry to show the effects of the two central donor atoms on the structure and properties.

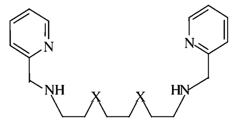
Introduction

The chemistry of metal complexes with chelate ligands containing nitrogen, sulfur or oxygen donors has extensively been studied in order to mimic reactions in: (i) the redox function of various metalloenzymes in living systems; (ii) the formation and reactivity of dioxygen in synthetic, industrial and biological processes. In enzymes metal ions have several functions: (i) redox as in superoxide dismutase-like activity,[1] (ii) structural and catalytic.[2,3] The complexation sites of these proteins are N, S or O donors coming from histidine, tyrosine, aspartic or glutamic acids and cysteine.[4–8]

For example, the crystal structures of poplar plastocyanin[5,6] and *Alcaligenes denitrificans* azurin[7,8] indicate that copper(II) ion is bound to a pair of aromatic nitrogen donors, a thiolate, a thioether sulfur donor and an oxygen donor. The presence of sulfur, a soft Lewis base, and oxygen, a hard one, in the various biological complexes plays an important role in the geometry and the redox activities of these compounds.[9] To mimic a small model of "blue" copper proteins, Lucas and co-workers[10] have studied copper(II) complexes where the ligands possess polythioethers bearing two pyridylmethyl groups and the metal ion is bound to two aromatic nitrogen atoms and two or three sulfur donors. Yamauchi *et al.*[11] have described the behavior in solution of analogous complexes where the ligands possess a disulfide bridge instead of thioether groups.

The zinc(II) ion is known to have a high affinity toward nitrogen and sulfur donor ligands.[12] In order to model the zinc environment in metalloenzymes such as carbonic anhydrase (3N donor set) or alcohol deshydrogenase (NS donor set), Vahrenkamp[13] and Mor-Oka and co-workers[14] have investigated zinc(II) complexes with tridentate 3N or N$_2$S ligands. To understand the reactivity of the pseudotetrahedral zinc center in proteins, Parkin and co-workers[15] recently investigated zinc(II) complexes with mixed N, O and S coordination.

In order to elucidate the role of metal ions in proteins, we report here a study of the coordination of copper(II) and zinc(II) ions with two novel potentially hexadentate ligands, 1,12-bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane (pydado) and 1,12-bis(2-pyridyl)-5,8-dithia-2,11-diazadodecane (pydadt) (Scheme 1), emphasizing the effects of the distinctive structural features of the ligands on the properties of the resulting complexes. The syntheses of the two ligands and their copper(II) and zinc(II) solid complexes, as well as the thermodynamic constants of the metal chelates formed by these ligands are described. Their structures, electronic and ESR spectra have been investigated and compared to those of pytrien complexes described earlier.[16,17] The results of an electrochemical study are also presented.



X = O (*pydado*)

X = S (*pydadt*)

X = NH (*pytrien*)

Scheme 1

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† Electronic supplementary information (ESI) available: potentiometric titration curves for L·4HCl, visible absorption spectra and cyclic voltammograms of complexes **1** and **2**. See http://www.rsc.org/suppdata/dt/b0/b010074i/

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Experimental

Chemicals and starting materials

All the solvents were purified by conventional procedures[18] and distilled prior to use. Chemicals commercially available (Aldrich) were used as supplied without further purification. The diamine 1,8-diamino-3,6-dithiaoctane was synthesized as described by Dwyer and Lions:[19] sodium ethylene-1,2-dithiolate was condensed with 2-bromoethylphthalimide in ethanol. The 1,8-diphthalimido-3,6-dithiaoctane obtained was reduced by hydrazine hydrate solution to give the diamine, a light yellow oil, which was used immediately to avoid absorption of carbon dioxide. The synthesis of 1,12-bis(2-pyridyl)-2,5,8,11-tetraazadodecane (pytrien) is reported in the literature.[16]

Synthesis of ligands

The two ligands were obtained as for pytrien reported by Arulsamy *et al.*,[16] after some modifications.

1,12-Bis(2-pyridyl)-5,8-dioxa-2,11-diazadodecane tetrahydrochloride hemihydrate (pydado·4HCl·0.5H$_2$O). 1,8-Diamino-3,6-dioxaoctane (1.48 g, 10 mmol) dissolved in 40 mL of ethanol was added dropwise with stirring to a solution of 2-pyridinecarbaldehyde (2.14 g, 20 mmol) in 50 mL of ethanol and the mixture refluxed for 2 h then allowed to cool at room temperature. Sodium tetrahydroborate (0.57 g, 15 mmol) was added in small portions and the mixture stirred overnight. It was neutralized with concentrated HCl (pH ≈ 7) and evaporated to dryness. The residue was taken up in an aqueous solution of 1 M NaOH, and extracted by dichloromethane (3 × 50 mL). The organic layer was dried over MgSO$_4$ and filtered. The filtrate was rotoevaporated to give a yellowish oil which was taken up in methanol (30 mL). The solution was acidified by concentrated HCl (pH ≈ 1.5) and stirred at room temperature for about 2 h. The yellowish crude crystalline product which precipitated was filtered off, washed with methanol and dried *in vacuo*. Yield *ca.* 70%; mp 220 °C. Found: C, 44.5; H, 6.1; Cl, 29.1; N, 11.5. $C_{18}H_{31}Cl_4N_4O_{2.5}$ requires C, 44.5; H, 6.4; Cl, 29.3; N, 11.6%. δ_H(250 MHz, D$_2$O) 8.80(d, 2H), 8.50(t, 2H), 8.10(d, 2H), 7.95(t, 2H), 4.65(s, 4H), 3.80(t, 4H), 3.65(s, 4H) and 3.40(t, 4H).

1,12-Bis(2-pyridyl)-5,8-dithia-2,11-diazadodecane tetrahydrochloride dihydrate (pydadt·4HCl·2H$_2$O). The ligand pydadt was synthesized as described for pydado using 1,8-diamino-3,6-dithiaoctane (1.80 g, 10 mmol) as diamine. When the yellowish oil obtained was acidified the solvent was eliminated and the crude product taken up in methanol (30 mL) and allowed to stand at 5 °C for a night. Yield *ca.* 68%; mp 200 °C. Found: C, 39.5; H, 6.1; Cl, 25.8; N, 10.1. $C_9H_{17}Cl_2N_2OS$ requires C, 39.7; H, 6.3; Cl, 26.1; N, 10.3%. δ_H (250 MHz, D$_2$O) 8.80(d, 2H), 8.40(t, 2H), 8.00(d, 2H), 7.90(t, 2H), 4.65(s, 4H), 3.50(t, 4H), 3.00(s, 4H) and 3.90(t, 4H).

Synthesis of metal complexes

CAUTION: Although we have not experienced any problems while handling the substances described, readers are cautioned to handle these compounds as potentially explosive.

[Cu(pydado)][ClO$_4$]$_2$ 1 and [Cu(pydadt)][ClO$_4$]$_2$ 2. To an aqueous solution (30 mL) of pydado·4HCl (0.49 g, 1 mmol) or pydadt·4HCl (0.54 g, 1 mmol) and copper(II) perchlorate hexahydrate (0.37 g, 1 mmol) was added dropwise a solution of 0.5 M tetramethylammonium hydroxide to adjust the pH to around 8. Slow evaporation of the aqueous colored solutions obtained yielded [Cu(pydado)][ClO$_4$]$_2$ **1** as turquoise blue crystals in three months, suitable for X-ray diffraction studies. Yield *ca.* 75%; mp 236 °C. Found: C, 36.2; H, 4.1; Cu, 10.7; N, 9.3. $C_{18}H_{26}Cl_2CuN_4O_{10}$ requires C, 36.5; H, 4.4; Cu, 10.7; N, 9.5%. $\chi_m = 1860 \times 10^{-6}$ cgs units, $\mu_{eff} = 2.09$ μ_B. λ_{max}/nm (CH$_3$CN) 714 (ε/L mol^{-1} cm^{-1} 245); water 692 (195); (dmf) 701 (123). [Cu(pydadt)][ClO$_4$]$_2$ **2**, light blue powder. Yield *ca.* 75%; mp 204 °C. Found: C, 34.4; H, 4.0; Cu, 10.2; N, 8.8. $C_{18}H_{26}Cl_2CuN_4O_8S_2$ requires C, 34.6; H, 4.2; Cu, 10.2; N, 9.0%. $\chi_m = 1870 \times 10^{-6}$ cgs units, $\mu_{eff} = 2.09$ μ_B. λ_{max}/nm (CH$_3$CN, water or dmf) 668 (ε/L mol^{-1} cm^{-1} 86).

[Zn(pydado)][ClO$_4$]$_2$·H$_2$O 3, [Zn(pydadt)][ClO$_4$]$_2$ 4 and [Zn(pytrien)][ClO$_4$]$_2$·H$_2$O 5. A mixture of sodium acetate trihydrate (0.54 g, 4 mmol) and ligand tetrahydrochloride, pydado (0.49 g, 1 mmol), pydadt (0.54 g, 1 mmol) or pytrien (0.50 g, 1 mmol), in absolute ethanol (30 mL) was stirred, boiled for 10 min on a water bath, cooled and filtered. Zinc perchlorate hexahydrate (0.37 g, 1 mmol) in absolute ethanol (20 mL) was added dropwise to the filtrate and the solution stirred for 2 h at room temperature. The colorless powder formed was filtered off, washed with ethanol and dried *in vacuo*. [Zn(pydado)][ClO$_4$]$_2$·H$_2$O **3**: yield *ca.* 55%; mp 263 °C (Found: C, 35.4; H, 4.4; N, 9.2; Zn, 10.5. $C_{18}H_{28}Cl_2N_4O_{11}Zn$ requires C, 35.3; H, 4.6; N, 9.2; Zn, 10.7%). [Zn(pydadt)][ClO$_4$]$_2$ **4**: yield *ca.* 50%; mp 273 °C (Found: C, 34.3; H, 3.8; N, 8.7; Zn, 10.5. $C_{18}H_{26}Cl_2N_4O_8S_2Zn$ requires C, 34.5; H, 4.2; N, 8.9; Zn, 10.4%). [Zn(pytrien)][ClO$_4$]$_2$·H$_2$O **5**: yield *ca.* 60%; mp 209 °C (Found: C, 35.4; H, 4.8; N, 13.7; Zn, 10.7. $C_{18}H_{30}Cl_2N_6O_9Zn$ requires C, 35.4; H, 4.9; N, 13.8; Zn, 10.7%).

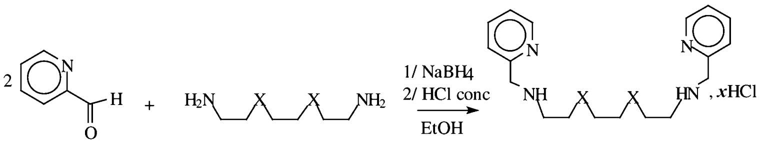
Measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer in our university. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus and chloride ions were determined potentiometrically using silver nitrate. Magnetic susceptibilities were determined at room temperature (20 °C) using HgCo(SCN)$_4$ as a calibrant; diamagnetic susceptibility corrections were calculated from Pascal's constants.[20]

Potentiometric. All chemicals used were of analytical grade. HNO$_3$ and KOH were purchased from Prolabo, KNO$_3$, Cu(NO$_3$)$_2$·3H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O from Fluka. All measurements were performed in a thermoregulated cell at 20.0 ± 0.1 °C, under N$_2$ to prevent absorption of CO$_2$. The measurement assembly included a microprocessor burette (Metrohm Dosimat 665) and a pH meter (Metrohm 713) equipped with a combined pH glass electrode (Metrohm AG 9101) linked to a PC. The complete automation of the titration was achieved with software developed in the GRECI laboratory. This enabled us in particular to choose different addition increment volumes and to fix a stability criterion for pH measurements, as well as the time interval during which this criterion must be respected. The electrode was calibrated by titrating a known amount of aqueous HNO$_3$ with a known concentration of KOH. A plot of mV (calculated) *vs.* pH gave a working slope and intercept so that the pH could be read as $-\log[H^+]$ directly. The pK_w used was 13.93.

All solutions were prepared at an ionic strength adjusted to 1 M with KNO$_3$. Solutions of the ligands pydado and pydadt in the concentration range 2.5 to 7.5 mM were titrated with 0.1 M KOH solution. The metal ion solutions were prepared (≈ 0.01 M) and standardized with Na$_2$H$_2$edta·2H$_2$O. The ratio of ligand to metal used was $1:1 < L:M < 4:1$ and metal concentrations were between 0.63 and 2.5 mM. A minimum of three titrations was performed for each ligand and each metal–ligand combination, each about 120 data points over the pH range 2–11.

The values of the acidity and stability constants were calculated and refined with the computer program PROTAF.[21] This program is based on a least-squares method which mini-



Scheme 2

mizes the weight sum of the residues of the experimental variables, namely the volume of KOH added and pH measured: $S = \Sigma_i[W_{V_i}R_{V_i}{}^2 + W_{pH_i}R_{pH_i}{}^2]$ where $R_{V_i} = V_{i\,exp} - V_{i\,refined}$, $R_{pH_i} = pH_{i\,exp} - pH_{i\,refined}$, W_{V_i} and W_{pH_i} are the weightings linked to the accuracy of the volumes and of the pH measurements.

As well as the acidity and stability constants, simultaneously it is possible to refine the other parameters of the titration, such as the ionic product of water and the concentrations of the studied solutions.

Spectroscopic. The UV–vis spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. Gaussian deconvolution was performed using an application developed under "QUATTRO PRO" by J. Rimbault in our laboratory. IR spectra were obtained as KBr pellets. The ESR spectra in acetonitrile were obtained at X band at 77 K and room temperature with a Varian E109 spectrophotometer. The *g* values were measured relative to the strong pitch. All NMR spectra were recorded in D_2O at room temperature with a Bruker AC 250 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual solvent.

Crystal structure determination. *Complex 1.* A blue block crystal was mounted on a glass fiber in a random orientation. Intensity data collection was carried out with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector, using monochromatized Mo-Kα radiation [$\lambda = 0.71073$ Å]. The structure was solved by the direct method and refined by full matrix least squares, based on F^2 using the SHELXTL software package.[22] An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.[23] All the hydrogen positions were initially located in the difference map and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms.

Zinc(II) complexes. The crystal data were collected on a Kappa CCD diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods. After refinement of the non-hydrogen atoms, Fourier difference maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were introduced as fixed contributors at calculated positions (C–H 0.95 Å, B(H) = 1.3 B_{eq}). Final difference maps revealed no significant maxima. All calculations were using the OPENMOLEN package.[24] Neutral atom scattering factors and anomalous dispersion coefficients were taken from a standard source.[25]

CCDC reference numbers 142187 and 155152–155154.

See http://www.rsc.org/suppdata/dt/b0/b010074i/ for crystallographic data in CIF or other electronic format.

Electrochemical. The cyclic voltammetry experiments were carried out with a conventional three-electrode cell using an EG&G PAR model 362 scanning potentiostat and a Kipp&Zonen BD91 X-Y recorder. A platinum disk (2 mm diameter) working electrode and a platinum wire auxiliary electrode were used. The reference was a Ag–AgCl–$LiCl_{saturated}$ electrode in acetonitrile (or in dmf) to which all potentials are referred. We have measured this to be 0.30 V positive of the SCE at 20 °C. Acetonitrile was purified by using standard methods while tetraethylammonium perchlorate was recrystallized from water before use. The copper(II) complex (10^{-3} M) was dissolved in deoxygenated acetonitrile (or dmf) containing tetraethylammonium perchlorate (0.1 M). All solutions were kept under nitrogen during electrochemical measurements.

Results and discussion

Synthesis

The two ligands, pydado and pydadt, were obtained from condensation of the triethylene dioxa- or dithia-diamine, and 2-pyridinecarbaldehyde in absolute ethanol, followed by reduction of the aldimino groups by $NaBH_4$. Potentiometric titration of the ligands by silver nitrate confirmed that these compounds were isolated as tetrahydrochloride salts; two aliphatic amino groups and the aromatic nitrogen of the two pyridyl groups are likely to be protonated (Scheme 2).

The blue copper(II) complexes of these two ligands were synthesized by reaction of an aqueous solution of the ligand hydrochloride salt with tetramethylammonium hydroxide and 1 equivalent of copper(II) perchlorate hexahydrate. The colorless zinc(II) compounds were obtained by treating an ethanolic suspension of the ligand hydrochloride salt and 4 equivalents of sodium acetate and zinc(II) perchlorate hexahydrate. The five complexes obtained were isolated as perchlorate salts, confirmed by the presence of a strong band at 1090 cm^{-1} in IR spectra. They were recrystallized from water by slow evaporation of the solvent at room temperature. Complexes **1**, **3**, **4** and **5** gave suitable crystals for structure determinations.

Solution equilibria

Ligand protonation constants. The ligand equilibrium constants (eqn. 1) of pydado and pydadt have been determined in

$$H_{(n-1)}L^{(n-1)+} + H^+ \rightleftharpoons H_nL^{n+} \qquad (1)$$

1 M KNO_3 in aqueous solution at 20.0 °C. The overall proton–ligand stepwise protonation constants, defined by $K^n_H = [H_nL^{n+}]/[H^+][H_{(n-1)}L^{(n-1)+}]$, were calculated from the titration curves and are listed in Table 1. Also listed for comparison are the protonation constants for closely related ligands: 1,4-bis(2-pyridylmethyl)-1,4-diazabutane (pyda),[26] 1,9-bis(2-pyridyl)-5-oxa-2,8-diazanonane (pydao),[27] 1,9-bis(2-pyridyl)-5-thia-2,8-diazanonane (pydat)[11,27] and 1,10-bis(2-pyridyl)-5,6-dithia-2,9-diazadecane (pydase).[11,27] The constants K^1_H and K^2_H correspond to those of protonation of aliphatic amine groups and

Table 1 Protonation constants (log K^n_H) of the pyridylmethyl ligands[a] (I = 1 M KNO_3 and 20 °C)

Ligand	log K^1_H	log K^2_H	log K^3_H	log K^4_H	Ref.
pyda[b]	8.23	5.45	1.81	1.62	26
pydao[b]	8.32	7.28	1.9	1.4	27
pydat[b]	7.98	6.96	1.9	0.9	11, 27
pydase[b]	7.88	7.02	1.87	0.9	11, 27
pydado	8.63(3)	7.76(4)	2.36(4)	1.5(6)	This work
pydadt	8.32(5)	7.58(4)	2.40(6)	1.6(5)	This work

[a] Values in parentheses represent 1σ standard deviation for the last significant digit. [b] Determined at 25 °C and I = 1 M (KNO_3).

Table 2 Stability constants (log β)[a] and deprotonation constants (log K) for Cu^{2+} and Zn^{2+} complexes of pydado and pydadt ($I = 1$ M KNO_3 and 20 °C)

	pydao[b]		pydat[b]		pydado		pydadt	
Complex	log β	log K	log β	log K	log β	log K	log β	log K
CuL(OH)	—	—	—	—	—	—	5.17(8)	—
CuL	15.38	—	18.10	—	15.88(4)	1.52	16.65(2)	2.73
Cu(HL)	—				17.4(1)		19.38(4)	
ZnL	9.52	—	10.64	1.53	9.77(2)	—	8.94(1)	4.43
Zn(HL)	—		13.52		—		13.37(4)	

[a] Values in parentheses represent 1σ standard deviation for the last significant digit. [b] Ref. 27.

K^3_H and K^4_H to protonation of nitrogen atoms in the pyridyl moiety, considering that nitrogen atoms on pyridyl groups are less basic than those of aliphatic amines because the former is more s-characteristic than the latter.[28] Each stepwise protonation constant for pydado is similar to that for pydadt. So the donor atoms, O or S (hard or soft respectively), in the aliphatic chain do not influence the protonation of these two ligands. This is contrary to an early study of N-substituted iminodiacetic acids by Schwarzenbach *et al.*[29] who showed that the influence of a sulfur ether group, in reducing the basicity of the basic amino group, was considerably greater than that of an oxygen ether group. By comparison of the acidities of these ligands (pydado and pydadt) with that of the parent (see Table 1), we note that the log K^2_H values (protonation of the second amino group) increase with the length of the aliphatic amine chain. Lacoste and Martell[26] explained this trend in terms of the inductive effect of the two pyridyl groups.

Metal chelate formation constants. Complexation of Cu^{2+} with these two ligands occurs below pH 3 and under more acidic conditions than for Zn^{2+} which forms the weaker complexes. Cu^{2+} forms Cu(HL) and CuL complexes with both ligands, whereas the protonated metal chelate M(HL) with Zn^{2+} ion and pydado was not formed in sufficient concentration to be determined potentiometrically. Further complex (Cu^{2+}–pydadt) deprotonation occurs beyond pH 9, which indicates the existence of some hydroxo species.

The stability constants $\beta = [M(HL)^{3+}]/[M^{2+}][L][H^+]$ for equilibrium (2) for copper(II) and zinc(II) complexes of pydado and

$$M^{2+} + L + H^+ \rightleftharpoons M(HL)^{3+} \qquad (2)$$

pydadt appear in Table 2. In addition, corresponding values of pydao and pydat are given for comparison.[25] For each metal complex the stability constant with pydado is smaller than that with pydadt and close to that with pydao. The stability constants for metal chelates with pyridyl ligands which possess a thioether donor in the aliphatic chain form more stable complexes than that of those with an ether donor. However, it is generally recognized that the ether sulfur coordinates more strongly than ether oxygen to divalent transition metals, an effect that is not reflected by the relative basicities of the ligands. The preference of these metals to bind to the softer thioether may be also explained by the larger size of the sulfur atom, allowing it more closely to approach the metal ion with less contraction of the ligand backbone.[26]

The chelate protonation constants for equilibrium (3) defined

$$ML^{2+} + H^+ \rightleftharpoons M(HL)^{3+} \qquad (3)$$

as $K = [M(HL)^{3+}]/[ML^{2+}][H^+]$ also appear in Table 2. The protonation constant of Cu^{2+}–pydado is close to K^4_H for the corresponding protonation of one pyridyl group in the "free" ligand. This is well explained by considering the protonated complex $[Cu(Hpydado)]^{3+}$, where one pyridyl nitrogen is protonated. The K value for M^{2+}–pydadt ($M = Cu^{2+}$ or Zn^{2+}) is higher than the ligand protonation constant K^3_H; this implies protonation of one aliphatic amine.[26,30]

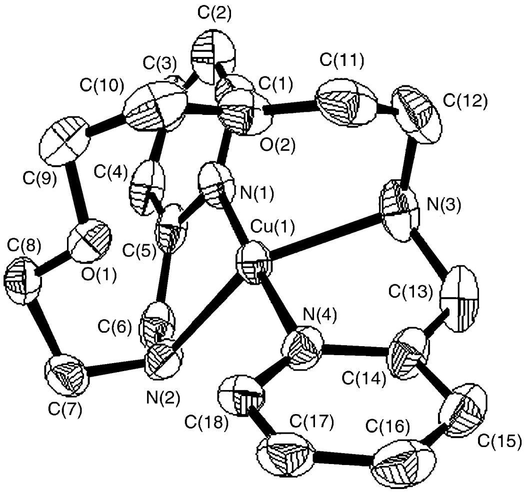


Fig. 1 An ORTEP[31] drawing of the cation $[Cu(pydado)]^{2+}$ showing 30% probability ellipsoids and the atom labelling scheme. Hydrogen atoms are omitted for clarity.

X-Ray diffraction studies

The crystal structures of complexes $[Cu(pydado)][ClO_4]_2$ **1**, $[Zn(pydado)][ClO_4]_2 \cdot H_2O$ **3**, $[Zn(pydadt)][ClO_4]_2$ **4** and $[Zn(pytrien)][ClO_4]_2 \cdot H_2O$ **5** were determined by single crystal X-ray diffraction. Pertinent crystallographic and refinement details are reported in Table 3.

$[Cu(pydado)][ClO_4]_2$ 1. The crystal structure determination revealed that blue crystals of $[Cu(pydado)][ClO_4]_2$ consist of $[Cu(pydado)]^{2+}$ cations which are well separated from perchlorate anions. A view of the cation with the labelling scheme is shown in Fig. 1. Principal bond distances and angles are listed in Table 4.

The structure shows the presence of two independent molecules. In each the copper(II) ion has a coordination number of four and can be described as distorted octahedral with two *cis*-open sites, the two pyridyl nitrogen atoms and two secondary amine nitrogen atoms each being mutually *trans*. The bond angles N(1)–Cu–N(4) and N(2)–Cu–N(3) are 177.7(2) and 145.6(2)° respectively. The average bond distances of Cu–$N_{pyridyl}$ and Cu–N_{amine} are 1.999 and 2.108 Å respectively. These distances are comparable with those of copper(II) compounds having the same geometry with CuN_4 chromophore.[32,33] Neither of the ether oxygen atoms coordinates to the copper center. A six membered chelate ring containing two coordinated ether oxygen atoms may be unsuitable for copper(II) ion. However, two oxygen atoms O(1) and O(2) sit on two *cis* sites for Cu with an average distance of 2.452 Å. This value suggests that weak interaction occurs between Cu and O. This kind of interaction is comparable to that in similar structures such as

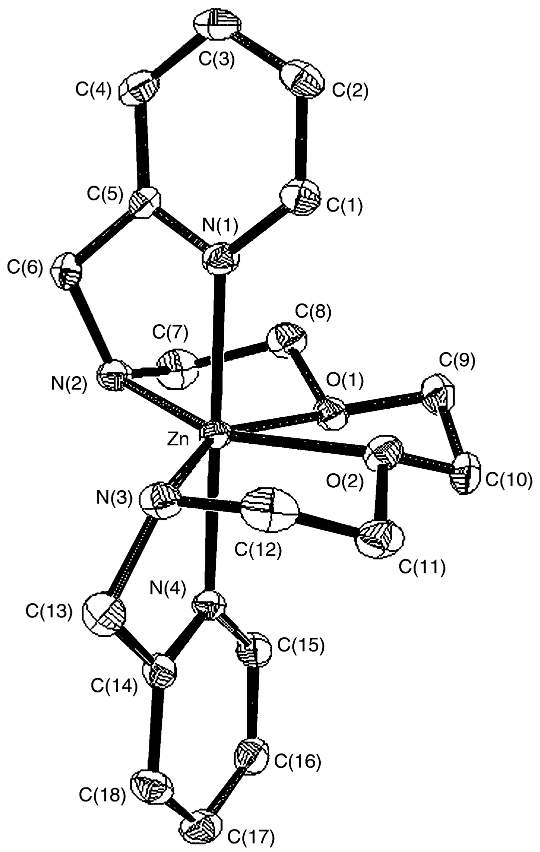


Fig. 2 ORTEP drawing of the cation $[Zn(pydado)]^{2+}$. Details as in Fig. 1.

that formed by 1,5-bis[2-(pyridine-2-carboxamido)phenyl]-1,5-dithiapentane.[33]

The two ClO_4^- anions are both ordered and well behaved, with Cl–O bond lengths and the O–Cl–O angles consistent with those reported earlier.[17]

$[Zn(pydado)][ClO_4]_2 \cdot H_2O$ 3. The molecular structure of complex **3** consists of $[Zn(pydado)]^{2+}$ cations and ClO_4^- anions. The perchlorate anions are ordered and well behaved. A perspective drawing of the cation is shown in Fig. 2. The zinc(II) center is coordinated by two aromatic nitrogens [N(1) and N(4)], two secondary amine nitrogens [(N2) and N(3)] and two ether oxygens [O(1) and O(2)]. With this hexadentate ligand it is expected that the disposition of the two pyridyl groups around the zinc could be either *cis* or *trans*. However, the crystal structure reveals a *trans* geometry.

The bond angles N(1)–Zn–N(4), N(2)–Zn–O(2) and N(3)–Zn–O(1) are 179.4(2), 152.0(2) and 152.8(2)° respectively. The bond distances of $Zn–N_{amine}$ (average, 2.103 Å) are slightly shorter than those of $Zn–N_{pyridyl}$ (average, 2.133 Å); both are shorter than those of $Zn–O_{ether}$ (average, 2.187 Å). This $Zn–O_{ether}$ bond length lies in the middle of values for $Zn–O_{alcoholate}$ (2.135 Å) and $Zn–O_{carboxylate}$ (average, 2.210 Å).[34,35] Related six-coordinate zinc complexes like those of 1,4,7-triazacyclononane[36] do not display angular distortions, but they do show similar average Zn–N and Zn–O bond lengths.

Thus, the coordination geometry around zinc is described as an equatorially distorted octahedron occupied by N(2), O(1), O(2) and N(3) on the equatorial sites and N(1) and N(4) on the axial sites.

$[Zn(pydadt)][ClO_4]_2$ 4. The coordination sphere in complex **4** is pseudo-octahedral with the zinc atom coordinated by two aromatic nitrogen atoms [N(1) and N(4)], two secondary amine nitrogen atoms [(N2) and N(3)] and two thioether sulfur atoms [S(1) and S(2)] of this hexadentate ligand. The $[Zn(pydadt)]^{2+}$ cation, shown in Fig. 3, has a 2-fold axis passing through zinc and the midpoint of C(9) and C(10). The largest angular distortion around zinc (Table 4) involves the aromatic nitrogen; thus, N(1)–Zn–N(3) 103.4(2), N(2)–Zn–N(4) 102.5(2), N(1)–Zn–S(1) 159.8(1) and N(4)–Zn–S(2) 159.9(1)°. The $Zn–N_{pyridyl}$ (average, 2.128 Å) and $Zn–N_{amine}$ (average, 2.153 Å) bond lengths are comparable to those in related compounds.[37] However, the Zn–S (average, 2.617 Å) bond distances seem rather long. Such long bond distances are particularly observed in octahedral zinc(II) complexes with chelating N, S ligands[38] in which the Zn–S distances range from 2.47 to 2.63 Å. Brand and Vahrenkamp[39] explained this trend by the fact that octahedral zinc compounds with Zn–S coordination are rare and that Zn–S bonding may be weak in such complexes.

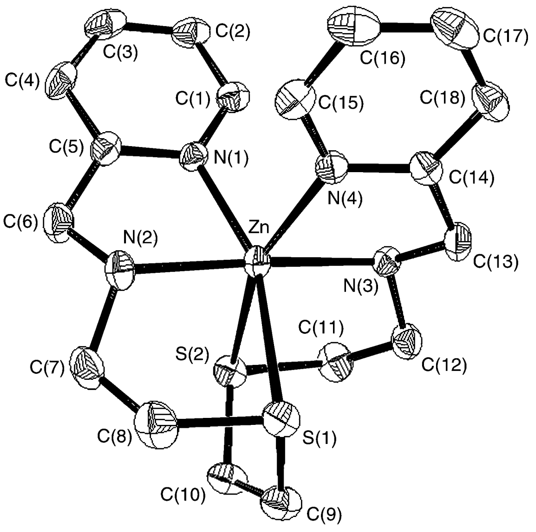


Fig. 3 ORTEP drawing of the cation $[Zn(pydadt)]^{2+}$. Details as in Fig. 1.

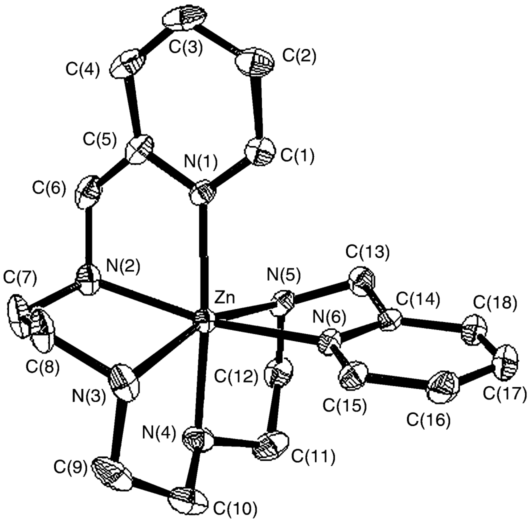


Fig. 4 ORTEP drawing of the cation $[Zn(pytrien)]^{2+}$. Details as in Fig. 1.

One of the two perchlorate ions is disordered in two sets of positions around a pseudo-5-fold axis along Cl(2)–O(5); this kind of perchlorate disorder has been observed in several other structures.[17,40]

$[Zn(pytrien)][ClO_4]_2 \cdot H_2O$ 5. The crystal structure of complex **5** consists of $[Zn(pytrien)]^{2+}$ cations well separated from ClO_4^- anions. As in **1** and **3**, the perchlorate ions are ordered and well behaved. A view of the cation is shown in Fig. 4. The zinc atom is bound to a pytrien ligand through the six nitrogen atoms, giving an octahedral coordination geometry. Though several isomers can be isolated with the hexadentate ligand, the

Table 3 X-Ray experimental data for compounds **1**, **3**–**5**

	1	**3**	**4**	**5**
Formula	$C_{18}H_{26}Cl_2CuN_4O_{10}$	$C_{18}H_{28}Cl_2N_4O_{11}Zn$	$C_{18}H_{26}Cl_2N_4O_8S_2Zn$	$C_{18}H_{30}Cl_2N_6O_9Zn$
M	592.87	612.72	626.83	610.75
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	9.5178(2)	9.3266(5)	13.5168(9)	10.5701(5)
b/Å	13.9439(2)	11.6770(5)	9.8812(3)	15.8048(9)
c/Å	18.3494(2)	12.2295(5)	19.824(1)	15.2231(6)
α/°		94.039(5)		
β/°	93.1180(10)	99.520(5)	109.594(5)	98.749(5)
γ/°		107.008(5)		
U/Å^3	2431.64(7)	1246.1(2)	2494.5(5)	2513.6(4)
T/K	296	173	194	173
Z	2	2	4	4
μ(Mo-Kα)/mm^{-1}	1.178	1.264	1.418	1.250
Reflections measured	16933	8342	10397	10613
Unique reflections collected	9516	5674	5945	5974
$wR(F^2)$	0.0939	0.080	0.064	0.066
$R1(I > 2\sigma(I))$	0.0388	0.055	0.036	0.045
R_{int}	0.024	0.040	0.040	0.040

Table 4 Selected bond lengths (Å) and angles (°) for complexes **1**, **3**, **4** and **5**

Complex **1**			
Cu–N(1)	1.987(4)	Cu–N(3)	2.117(4)
Cu–N(2)	2.098(3)	Cu–N(4)	2.012(4)
N(1)–Cu–N(4)	177.7(2)	N(2)–Cu–N(3)	145.6(2)
N(1)–Cu–N(2)	82.5(2)	N(4)–Cu–N(3)	81.0(2)
N(1)–Cu–N(3)	96.8(2)	N(4)–Cu–N(2)	99.6(2)
Complex **3**			
Zn–N(1)	2.133(4)	Zn–N(4)	2.140(4)
Zn–N(2)	2.107(4)	Zn–O(1)	2.188(3)
Zn–N(3)	2.098(4)	Zn–O(2)	2.186(4)
N(1)–Zn–N(2)	79.6(2)	N(2)–Zn–O(2)	152.0(2)
N(1)–Zn–N(3)	100.4(2)	N(3)–Zn–N(4)	79.8(2)
N(1)–Zn–N(4)	179.4(2)	N(3)–Zn–O(1)	152.8(2)
N(1)–Zn–O(1)	80.4(2)	N(3)–Zn–O(2)	81.2(2)
N(1)–Zn–O(2)	152.0(2)	N(4)–Zn–O(1)	89.3(2)
N(2)–Zn–N(3)	125.9(2)	N(4)–Zn–O(2)	81.2(2)
N(2)–Zn–N(4)	99.9(2)	O(1)–Zn–O(2)	74.1(1)
N(2)–Zn–O(1)	80.4(2)		
Complex **4**			
Zn–N(1)	2.114(5)	Zn–N(4)	2.142(5)
Zn–N(2)	2.149(5)	Zn–S(1)	2.623(2)
Zn–N(3)	2.157(5)	Zn–S(2)	2.611(2)
N(1)–Zn–N(2)	79.5(2)	N(2)–Zn–S(2)	97.3(1)
N(1)–Zn–N(3)	103.4(2)	N(3)–Zn–S(1)	96.0(1)
N(1)–Zn–N(4)	91.8(2)	N(3)–Zn–S(2)	81.6(1)
N(1)–Zn–S(1)	159.8(1)	N(3)–Zn–N(4)	78.4(2)
N(1)–Zn–S(2)	95.5(1)	S(1)–Zn–S(2)	82.2(6)
N(2)–Zn–N(3)	176.9(2)	N(4)–Zn–S(1)	97.1(1)
N(2)–Zn–N(4)	102.5(2)	N(4)–Zn–S(2)	159.9(1)
N(2)–Zn–S(1)	80.9(2)		
Complex **5**			
Zn–N(1)	2.142(3)	Zn–N(4)	2.164(3)
Zn–N(2)	2.189(3)	Zn–N(5)	2.182(3)
Zn–N(3)	2.158(3)	Zn–N(6)	2.188(3)
N(1)–Zn–N(2)	78.7(1)	N(2)–Zn–N(6)	170.2(1)
N(1)–Zn–N(3)	100.8(1)	N(3)–Zn–N(4)	80.9(1)
N(1)–Zn–N(4)	174.3(1)	N(3)–Zn–N(5)	161.2(1)
N(1)–Zn–N(5)	97.5(1)	N(3)–Zn–N(6)	99.0(1)
N(1)–Zn–N(6)	91.6(1)	N(4)–Zn–N(5)	81.1(1)
N(2)–Zn–N(3)	83.0(1)	N(4)–Zn–N(6)	93.6(1)
N(2)–Zn–N(4)	96.2(1)	N(5)–Zn–N(6)	78.1(1)
N(2)–Zn–N(5)	102.9(1)		

only one obtained with pytrien and the first transition metal series [Fe^{II} and Ni^{II},[16] Co^{III} and Cu^{II}[17]] has the pyridine nitrogen atom in the *cis* position.

The bond lengths involving pyridine nitrogen atoms (Zn–$N_{pyridyl}$ average, 2.165 Å) are not significantly different from those involving amine nitrogen atoms (Zn–N_{amine} average, 2.173 Å). All metal–nitrogen bond lengths in this complex are longer than those in complexes of Fe^{II}, Ni^{II}, Co^{III} or Cu^{II}, reflecting the larger radius of Zn^{2+}.

The structure of the $[Zn(pytrien)]^{2+}$ cation is very similar to that of $[Co(pytrien)]^{2+}$ described earlier,[17] however the octahedral polyhedron around the zinc is more distorted than that around the cobalt: the five chelate bond angles of 78.1–83.0° (average 80.4°) subtended by the ligand at the zinc are each smaller than their analogues of 83.6–87.1° (average 85.2°) in the cobalt complex.

The structures of the three octahedral zinc(II) complexes described here reveal an interesting change not only in their configuration (*cis* or *trans*) but also in their metal bond distances which depend on the nature of the two central donors atoms of the chelate; thus, Zn–O (average, 2.187), Zn–S (average, 2.617), Zn–N_{amine} (average, 2.161) and Zn–$N_{pyridyl}$ (average, 2.140 Å). One aspect that is observed with the octahedral zinc(II) compound with pydadt is the relatively low affinity displayed by Zn for thioether sulfur coordination which is manifested in long Zn–S bonds.

Mixed nitrogen–ether oxygen or nitrogen–thioether sulfur coordination to Zn is found in structural sites such as "zinc finger" proteins which are now recognized as having a much wider role with an enzymatic function as well.[34] Comparison between Zn–donor atom bond lengths found in these complexes and various metalloproteins reveals the expected similarities with few exceptions. The average Zn–O bond length for compound **3** of 2.187 Å is shorter than Zn–O_{Glu} or Zn–O_{Tyr} bond distances (2.5 and 3.0 Å respectively) reported for bacillolysin[41] and protease enzymes.[42] The Zn–S bond distances (average, 2.617 Å) for complex **4** are longer than those reported for zinc proteins such as cobalamin with Zn–S bond distances of 2.32 Å.[43] Thus the two ligands (pydado and pydadt) reported here seem good platforms with which to model the structure or "reactivity" of zinc metalloproteins.

Spectroscopic studies

Absorption spectra. The peak positions and molar absorption coefficients for complexes **1** and **2** in various solvents are presented in the Experimental section. The spectra for the two

Table 5 Summary of ESR and electrochemical data for complexes **1** and **2**

	ESR						
Complex	g_{iso}	$g_{\parallel}$	$g_{\perp}$	$10^4\ A_{iso}/cm^{-1}$	$10^4\ A_{\parallel}/cm^{-1}$	$10^4\ A_{\perp}/cm^{-1}$	$g_{\parallel}A_{\parallel}^{-1}/cm$
1	2.148	2.248	2.098	62.6	173	7.5	130
2	2.080	2.213	2.014	—	130	—	170
	E_{pa}/V	E_{pc}/V	$\Delta E_p/mV$	$E_{1/2}/V$[a]			
1	0.615			—			
2	0.165	0.005	160	0.085			

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ with E_{pc} = cathodic potential and E_{pa} = anodic potential.

compounds exhibit essentially similar patterns in the 250–500 nm region, with two strong bands due to intraligand and charge transfer transitions. In the visible region a d–d band is obtained in each case. The most significant differences are the red shift (*ca.* 45 nm) of the λ_{max} value with a relatively high ε value (245 L mol^{-1} cm^{-1}) and a broad band with a shoulder on the low energy side observed for **1**. This absorption envelope could clearly be resolved into just two Gaussian components, obtained by Yokoi and Addison[43] for pseudotetrahedral CuN_4 chromophores. The enhanced intensity in the case of **1** is suggestive of a four-coordinated compound, apparently caused by the non-coordination of the two oxygen donor atoms of the ligand. Also, complex **1** exhibits a blue shift of the visible band maximum as the solvent is changed from water to dmf and from dmf to acetonitrile, indicative of axial coordination by solvent molecules. Belford *et al.*[45] explain this trend by the basicity of the axial ligand. The crystal structure confirmed the four-coordination of Cu^{2+} ion.

It is interesting that the visible absorption spectrum of complex **2** resembles that reported earlier[17] for [Cu(pytrien)][ClO$_4$]$_2$ (CuN_6 chromophore), with a more symmetrical band. Gaussian deconvolution of this band shows only one component. The fact that **2** does not exhibit a shift of the visible band as the solvent is changed and the relatively low intensity of this d–d band (86 L mol^{-1} cm^{-1}) leads us to suppose that compound **2** may have a CuN_4S_2 chromophore.

ESR spectra. To extract complementary information on the degree of distortion in complex **1** and the nature of coordination in **2**, ESR studies were performed. The X-band room-temperature ESR spectra in acetonitrile solution of complex **1**, together with the frozen solution at 77 K, are shown in Fig. 5, and data are given in Table 5. It can be seen that the spectrum is split into four equally spaced absorptions. When the solution is frozen at 100 K a spectrum characteristic of axial symmetry is observed. From the parameters graphically evaluated, the value of the quotient $g_{\parallel}/A_{\parallel}$, which is a convenient empirical index[46] of four-coordination, is 130 cm. This result is similar to those obtained for other complexes with CuN_4 chromophores described by Mukherjee and co-workers.[32]

Complex **2** exhibits only a broad near isotropic spectrum at room temperature, indicating that it is more symmetric than **1**. At 77 K the spectrum obtained (Fig. 6 bottom) indicates a $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp}$, $g_{min} > 2.03$)[47] and thus suggests a dominantly tetragonal component in solution. The values are comparable to those obtained by Wood and co-workers[48] for a tetragonal CuN_6 chromophore. The solution $d_{x^2-y^2}$ ground state thus leads to a tentative assignment of the d–d band as $d_{x^2-y^2} \longrightarrow d_{z^2}$.

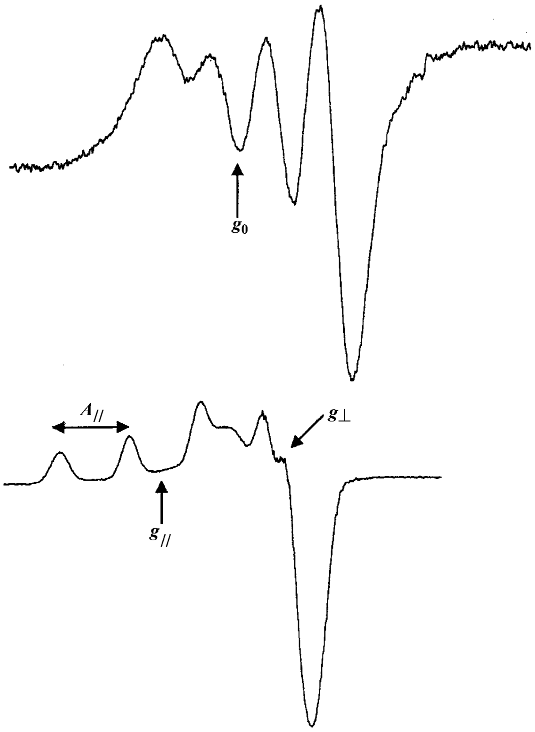


Fig. 5 X-Band ESR spectra of complex **1** in acetonitrile (concentration 10^{-3} mol L^{-1}) at room temperature (top) and 77 K.

Redox studies

In order to characterize the differences in the coordination environment among the copper(II) complexes **1** and **2**, their redox potentials, *vs.* Ag–AgCl–LiCl, were determined by cyclic voltammetry in acetonitrile and dmf. The two complexes exhibit different electrochemical behaviors. The data collected in Table 5 reveal a substantial shift of the potentials and different redox processes between **1** and **2**. The suggestion that the redox processes are metal centered is based on the CV of the "free" ligands which shows no wave in the experimental potential range. At more negative potentials the two ligands were reduced, so the possible reduction of Cu^{II} to Cu^{I} cannot be observed.

Complex **1** shows an irreversible process in both solvents used (the peak potential is a function of the scan rate used in the range 20–500 mV s^{-1}), and this irreversibility is more important in dmf, whereas **2** gives, in all cases, a reversible redox process. It is of interest to explain the differences in redox potentials and electron transfer processes exhibited by the two complex cations.

As expected, the probably more electron rich six-coordinated complex **2** is reversibly oxidized at a lower potential, the four-coordinated **1** at more positive potential. The very positive value observed is consistent with the low ligand field associated with pydado; however, we note in this case the potential measured includes kinetic contributions since the wave is irreversible.

Comparison of the electrochemistry of complex **2** with that of [Cu(pytrien)][ClO$_4$]$_2$[17] which has a CuN_6 chromophore

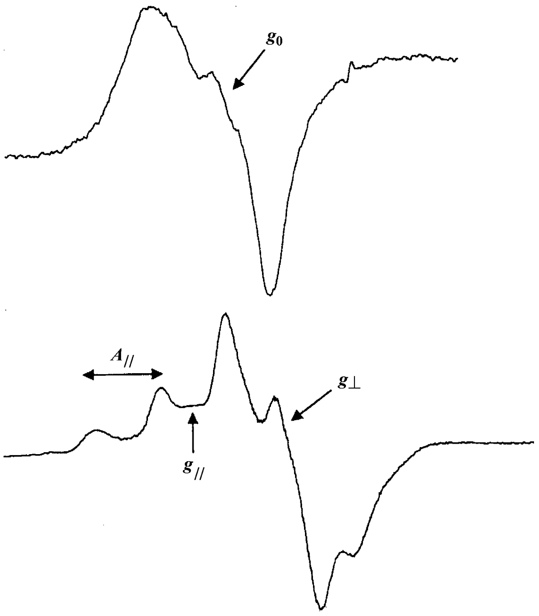


Fig. 6 X-Band ESR spectra of complex **2** in acetonitrile. Details as in Fig. 5.

shows that replacing the two thioether sulfur atoms by nitrogen donor atoms causes a change in oxidation potential from +0.20 to +0.50 V (+300 mV) which is consistent with the influence of thioether sulfur reported.[49] With the two ligands, which have the same aliphatic chain length but differ by the two central heteroatoms (N_6 and N_4S_2), we can note that when the oxidation potential increases the reversibility of the Cu^{III}–Cu^{II} system decreases, and $E(CuN_6) > E(CuN_4S_2)$.

Conclusion

Solid state and solution structures of the complexes described reveal that the nature of the two central heteroatoms of the ligands modifies the geometry around the metal ion and induces different electronic effects in the ESR spectra as well as the redox properties of the copper(II) complexes.

X-Ray crystallographic studies show that the three zinc(II) complexes are all octahedral with significant variation in their configurations; the two pyridyl groups are *trans* when the central heteroatoms are O, whereas they are *cis* in the case of N or S donor atoms. It is of interest that in complex **4** the Zn–S bond lengths are significantly weaker than $Cu–N_{pyridyl}$ or $Cu–N_{amine}$, and this is typical of octahedral zinc(II) complexes involving thioether sulfur donor atoms.[38,39]

The crystal structure and spectroscopic results are consistent with the difference between the two copper(II) compounds; **1** is four-coordinated, whereas **2** seems to be octahedral. This difference of behavior has been also observed in the electrochemical studies; the electron transfer process for the oxidation of copper(II) to copper(III) is irreversible with **1** and quasi-reversible with **2**. The main factor that determines the geometry around Cu^{2+} ion and the relative stability of Cu^{III} in these complexes is the nature of the central heteroatoms of the ligands. Contrary to N or O donor atoms which are hard, the thioether sulfur atom is soft, and this lowers the value of the oxidation potential.

It seems to us worthwhile to extend this work by synthesizing the same kind of ligands which possess carbamoyl groups to get a more complete picture of the factors influencing the stereochemical and redox behavior. It would contribute to the synthesis of model compounds and help our understanding of the function of metalloproteins. Further work along this line is in progress.

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