

New macrocyclic dioxotetraamines bearing 2-pyridylmethyl as functional donor pendant(s): synthesis, properties and crystal structure of their copper(II) complexes†

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Two new macrocyclic dioxotetraamines 4-(pyridin-2-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^1) and 4,7-bis(pyridin-2-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^2) have been synthesized and characterized. The solution behaviors of their copper(II) complexes have been studied with ESR, UV/VIS and cyclic voltammetric techniques. Reaction of H_2L^2 with $Cu(O_2CMe)_2$ in methanol solution yielded a doubly deprotonated dioxotetraamine copper(II) complex, $[CuL^2] \cdot 6H_2O$, the structure of which has been determined by X-ray diffraction analysis. The Cu atom is five-co-ordinated by four basal nitrogens and one pendant pyridine nitrogen, forming a distorted square pyramid in which N(21) of the pendant pyridine nitrogen is at the apical site. The Cu–N(21) bond distance [2.203(7) Å] is longer than the basal average Cu–N bond length [1.985(4) Å] due to the Jahn–Teller effect.

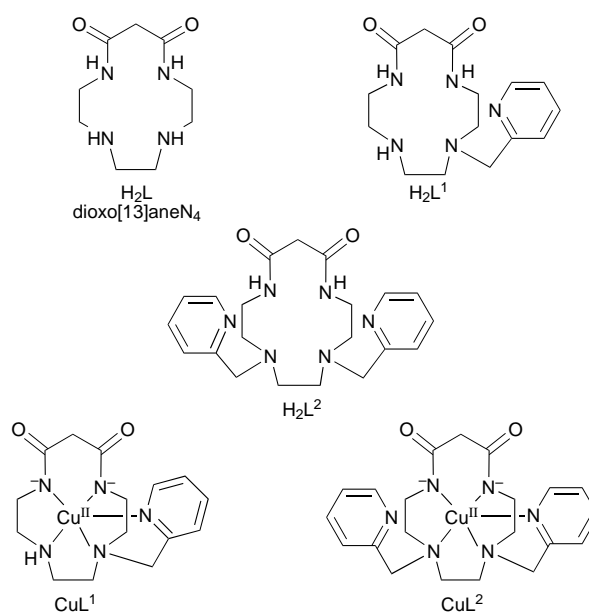
The chemistry of macrocyclic dioxotetraamines has received much attention and has been extensively studied in recent years.^{1–5} Macrocyclic dioxotetraamines are unique chelators for some transition-metal ions. They bear the dual structural features of macrocyclic tetraamines and oligopeptides and have many interesting properties and important functions. The strength of the ion binding is determined by the ion size, macrocyclic cavity size and ligand conformation. The two amide groups in macrocyclic dioxotetraamines are equivalent; when co-ordinated to a 3d metal ion they will be deprotonated simultaneously. They can stabilize the higher states of some transition metals^{1,2a,3,4,6} and have been developed as effective oxidants and biomimetic redox catalysts.⁷ Furthermore, some of these compounds have been used to construct supramolecules.⁸

So far, great effort has been devoted to the incorporation of functionalized pendant groups into a saturated macrocyclic tetraamine structure (e.g. 1,4,8,11-tetraazacyclotetradecane, cyclam) to modify its conformational properties and the redox properties of its metal complexes.⁹ However, up to now, only a few examples of such functionalized macrocyclic dioxotetraamines have been reported.^{2f,i,j,10,11} Herein, we report the synthesis and characterization of two novel macrocyclic dioxo[13]aneN₄ (1,4,7,10-tetraazacyclotridecane-11,13-dione) compounds bearing 2-pyridylmethyl as additional co-ordinating donor pendant(s), and their complexation properties with Cu^{II} as well as the crystal structure of one of their copper(II) complexes.

Experimental

Materials and general methods

Most of the starting materials and solvents for syntheses were obtained commercially and purified prior to use. The compound dioxo[13]aneN₄ (H_2L) was prepared according to the literature method.¹² 2-Chloromethylpyridine hydrochloride from Aldrich Co. was used without further purification. All the other reagents for syntheses and analyses were of analytical grade. The Fourier-transform IR spectra were taken on a FT-IR



170SX (Nicolet) spectrometer, EI mass spectra on a VG ZAB-MS instrument. Elemental analyses were made on a P-E 240C analyzer. Proton NMR spectra were recorded on a Bruker AC-P 200 spectrometer (200 MHz) at 25 °C, in CDCl₃, with tetramethylsilane as the internal reference, electronic absorption spectra on a Shimadzu UV-240 spectrophotometer.

Syntheses

4-(Pyridin-2-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^1). A solution of 2-chloromethylpyridine hydrochloride (410 mg, 2.5 mmol) in deoxygenated dimethylformamide (dmf, 30 cm³) was added dropwise to a solution of dioxo[13]aneN₄ (2.16 g, 10 mmol) in deoxygenated dmf (80 cm³) in the presence of an excess amount of fine and dried K₂CO₃ at ca. 80 °C. The resulting mixture was heated and stirred at 80 °C for about 10 h under Ar. After filtration, the filtrate was evaporated to dryness and the residue dissolved in water and then extracted with CHCl₃. The combined CHCl₃

† Non-SI unit employed: G = 10⁻⁴ T.

solution was dried and evaporated, and then the residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2 -MeOH (100:1-10). The product was finally recrystallized from MeCN as colorless needles (270 mg, 35% yield based on 2-chloromethylpyridine hydrochloride). ^1H NMR (CDCl_3): δ 2.44-2.67 (8 H, m), 3.26 (2 H, s), 3.32 (2 H, quintet), 3.55 (2 H, quintet), 4.17 (2 H, s), 7.26-7.31 (2 H, m), 7.68-7.69 (1 H, m) and 8.52-8.55 (1 H, m). IR (KBr pellet): 611, 781, 837, 929, 1003, 1041, 1118, 1146, 1207, 1259, 1281, 1320, 1359, 1437, 1455, 1478, 1574, 1623, 1664 (ν_{CO}), 1690, 2812, 2839, 2895, 2942, 3084, 3273 and 3328 cm^{-1} . EI mass spectrum: $m/z = 305$ (M^+ , $M_r = 305.37$) (Found: C, 59.23; H, 7.36; N, 22.62. Calc. for $\text{C}_{15}\text{H}_{23}\text{N}_5\text{O}_2$: C, 59.00; H, 7.60; N, 22.93%).

4,7-Bis(pyridin-2-ylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^2). A solution of 2-chloromethylpyridine hydrochloride (1.64 g, 10 mmol) in deoxygenated dmf (50 cm^3) was added dropwise to a solution of dioxo[13]ane N_4 (0.72 g, 3.33 mmol) in deoxygenated dmf (50 cm^3) in the presence of an excess amount of fine and dried K_2CO_3 at ca. 80°C . The resulting mixture was heated and stirred at 80°C for about 10 h under Ar. After filtration, the filtrate was evaporated to dryness and the residue dissolved in water and then extracted with CHCl_3 . The combined CHCl_3 solution was dried and evaporated, and then the residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2 -MeOH (100:1-5). The product was finally recrystallized from MeCN as colorless needles (0.92 g, 70% yield based on dioxo[13]ane N_4). ^1H NMR (CDCl_3): δ 2.33-2.46 (8 H, m), 3.22 (2 H, s), 3.24-3.26 (4 H, m), 3.58 (4 H, s), 7.09-7.19 (4 H, m), 7.55-7.56 (2 H, m) and 8.41-8.49 (2 H, m). IR (KBr pellet): 529, 624, 752, 779, 991, 1050, 1124, 1149, 1252, 1298, 1322, 1368, 1437, 1477, 1517, 1566, 1593, 1670 (ν_{CO}), 2801, 2952, 3074, 3261 and 3347 cm^{-1} . EI mass spectrum: $m/z = 396$ (M^+ , $M_r = 396.49$) (Found: C, 63.35; H, 7.26; N, 21.43. Calc. for $\text{C}_{21}\text{H}_{28}\text{N}_6\text{O}_2$: C, 63.62; H, 7.07; N, 21.20%).

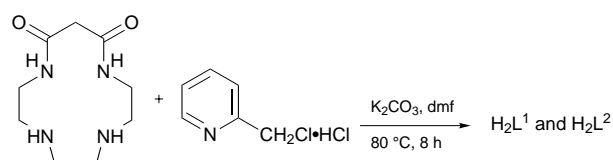
$[\text{CuL}^2]\cdot(6\text{H}_2\text{O})$ 1. A single crystal suitable for X-ray analysis was obtained by mixing a 1:1 molar ratio of $\text{Cu}(\text{O}_2\text{CMe})_2$ and H_2L^2 in deoxygenated MeOH under reflux for about 15 min, filtering the blue mixture and slow evaporation of the solvent. IR (KBr pellet): 625, 648, 730, 881, 1020, 1074, 1264, 1330, 1380, 1410, 1439, 1463, 1586 (ν_{CO}), 2947 and $3400\text{ (br)}\text{ cm}^{-1}$ (Found: C, 44.31; H, 6.88; N, 14.62. Calc. for $\text{C}_{21}\text{H}_{38}\text{CuN}_6\text{O}_8$: C, 44.56; H, 6.77; N, 14.85%).

ESR studies

The ESR spectra were measured on a Bruker ER-200-D-SRC10 spectrophotometer. Methanol solutions of copper(II) complexes were prepared by mixing equimolar amounts of ligand and $\text{Cu}(\text{NO}_3)_2$ in methanol solution, and the pH was adjusted to ≈ 8 by methanolic NaOH solution (in this pH region the amide groups will be doubly deprotonated).¹¹ The measurements were performed at room temperature and 112 K.

Electrochemical studies

Cyclic voltammetric (CV) measurement was performed with a PARC model 273 electrochemical apparatus in aqueous solution at 25°C with 0.50 mol dm^{-3} Na_2SO_4 as supporting electrolyte and the solution was bubbled with pure argon gas. The concentrations of CuL , CuL^1 and CuL^2 complexes were kept at $2 \times 10^{-3}\text{ mol dm}^{-3}$ [1.05:1 ligand and copper(II) sulfate aqueous solution]. The pH was adjusted with concentrated NaOH or H_2SO_4 solution. The cyclic voltammograms were evaluated graphically. A three-electrode system was employed: glassy carbon as working electrode, saturated calomel electrode (SCE) as reference and Pt as counter electrode.



Scheme 1

Crystallography

Crystal data for $[\text{CuL}^2]\cdot 6\text{H}_2\text{O}$ 1. $\text{C}_{21}\text{H}_{26}\text{CuN}_6\text{O}_2\cdot 6\text{H}_2\text{O}$, $M_r = 566.11$, monoclinic, space group C_2/c , $a = 24.452(5)$, $b = 14.543(3)$, $c = 18.205(4)$ Å, $\beta = 125.31(3)^\circ$, $U = 5283(2)$ Å³, $Z = 8$, $D_c = 1.424\text{ kg m}^{-3}$, $D_m = 1.43\text{ kg m}^{-3}$, $\mu = 8.80\text{ cm}^{-1}$, $T = 299\text{ K}$.

A blue crystal (approximately $0.2 \times 0.3 \times 0.3\text{ mm}$) of the complex was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal monochromator situated in the incident beam for data collection. The unit cell determination and data collection were performed with Mo-K α radiation ($\lambda = 0.71073$ Å). Unit-cell dimensions were obtained by least-squares refinements using 25 reflections in the range $7.89 \leq \theta \leq 11.79^\circ$. The intensities of reflections were measured at the ω - 2θ scan mode in the range $2 \leq \theta \leq 23^\circ$ at room temperature. A total of 3515 ($R_{\text{int}} 0.082$) independent reflections was collected, of which 2158 with $I > 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. An empirical absorption correction was made. The structure was solved using SHELXS 86.^{13a} The Cu atom was located from an E map. The other non-hydrogen atoms were determined by successive Fourier-difference syntheses. The final refinement (based on F^2) was performed by full-matrix least squares using SHELXL 93^{13b} with anisotropic thermal parameters for non-hydrogen atoms and converged with unweighted and weighted (unit weights for all observed reflections) agreement factors of 0.060 and 0.060. The highest peak of the final Fourier-difference map had a height of 0.58 e Å^{-3} . The hydrogen atoms were treated as riding on their attached atoms, refined isotropically and placed at calculated positions.

CCDC reference number 186/802.

Results and Discussion

Syntheses of the macrocycles

The starting macrocyclic compound dioxo[13]ane N_4 (H_2L) was synthesized following the method reported by Tabushi *et al.*¹⁴ The new compounds were prepared according to Scheme 1. For the preparation of H_2L^1 , an excess amount of dioxo[13]ane N_4 was used to obtain the monoalkylated product. The main product H_2L^1 was purified by silica gel column chromatography and recrystallized from CH_2Cl_2 -MeCN as colourless needles in 35% yield. The doubly substituted compound H_2L^2 was also obtained as a by-product and can be isolated by column chromatography from the monoalkylated product. For the preparation of H_2L^2 , an excess amount of 2-chloromethylpyridine hydrochloride was used. The yield of this reaction was quite satisfactory (over 70%). All the analytical and spectral data are in good agreement with the proposed compositions.

The new compound H_2L^2 when treated with 1 equivalent of $\text{Cu}(\text{O}_2\text{CMe})_2$ in deoxygenated MeOH under reflux gave the 1:1 copper(II) complex $[\text{CuL}^2]\cdot 6\text{H}_2\text{O}$ as deep blue crystals. This complex is air-stable in the solid state. The elemental analysis (C, H, N) and IR data showing only one C=O absorption band at 1586 cm^{-1} for the two deprotonated amides are consistent with the proposed formula.

Crystal structure

The molecular structure of complex 1 is shown in Fig. 1. Important bond lengths and angles are listed in Table 1. From

Table 1 Selected bond lengths (Å) and angles (°) for complex **1** with estimated standard deviations in parentheses

Cu–N(1)	2.085(5)	N(1)–C(11)	1.496(11)
Cu–N(2)	2.038(6)	N(2)–C(2)	1.508(7)
Cu–N(3)	1.921(6)	N(2)–C(3)	1.494(12)
Cu–N(4)	1.915(6)	N(3)–C(4)	1.427(12)
Cu–N(21)	2.203(7)	N(3)–C(5)	1.296(7)
O(1)–C(5)	1.268(9)	N(4)–C(7)	1.300(7)
O(2)–C(7)	1.279(9)	N(4)–C(8)	1.460(9)
N(1)–C(1)	1.498(11)	C(11)–C(12)	1.519(8)
N(1)–C(9)	1.479(9)		
N(1)–Cu–N(2)	87.0(2)	Cu–N(1)–C(11)	114.2(4)
N(1)–Cu–N(3)	147.3(3)	C(1)–N(1)–C(11)	113.8(5)
N(2)–Cu–N(3)	84.7(3)	C(9)–N(1)–C(11)	112.7(7)
N(1)–Cu–N(4)	86.1(2)	Cu–N(2)–C(3)	103.3(4)
N(2)–Cu–N(4)	165.9(3)	Cu–N(2)–C(2)	107.4(5)
N(3)–Cu–N(4)	94.5(3)	C(4)–N(3)–C(5)	118.7(6)
N(1)–Cu–N(21)	100.6(2)	Cu–N(3)–C(5)	125.1(6)
N(2)–Cu–N(21)	80.4(3)	Cu–N(3)–C(4)	115.7(4)
N(3)–Cu–N(21)	109.1(2)	C(7)–N(4)–C(8)	120.4(6)
N(4)–Cu–N(21)	112.9(3)	Cu–N(4)–C(7)	124.8(5)
Cu–N(1)–C(1)	101.3(4)	Cu–N(4)–C(8)	113.2(4)
Cu–N(1)–C(9)	101.0(3)		

Torsion angles

C(1)–N(1)–C(9)–C(8)	–155.5 (7)
C(8)–N(4)–C(7)–C(6)	–178.9 (7)
C(4)–N(3)–C(5)–C(6)	–177.4 (7)
C(3)–N(2)–C(2)–C(1)	–83.6 (9)
N(1)–C(1)–N(2)–C(2)	–54.4 (9)
N(2)–C(3)–C(4)–N(3)	–41.4 (9)
C(7)–C(6)–C(5)–N(3)	–40.5 (11)
C(9)–N(1)–C(1)–C(2)	156.3 (7)
C(7)–N(4)–C(8)–C(9)	140.6 (8)
C(5)–N(3)–C(4)–C(3)	–171.8 (7)
C(2)–N(2)–C(3)–C(4)	163.0 (7)
N(4)–C(7)–C(6)–C(5)	51.4 (11)
N(1)–C(9)–C(8)–C(4)	49.2 (10)

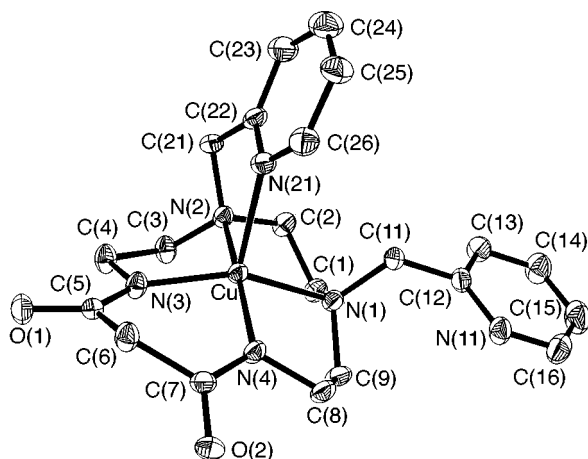
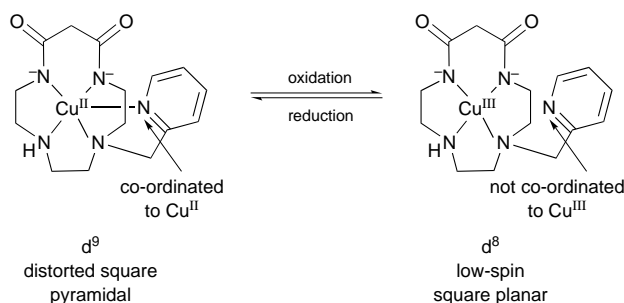
**Fig. 1** An ORTEP drawing of complex $[\text{CuL}^2]$ with 35% probability thermal ellipsoids

Fig. 1 it is seen that the Cu atom is five-co-ordinated [to N(1), N(2), N(3), N(4) and N(21)] and forms a distorted square-pyramidal configuration. The two deprotonated amide nitrogens [N(3), N(4)] have stronger bonds (Cu–N[–] average 1.92 Å) than those of the secondary amines [N(1) and N(2) 2.04–2.09 Å]. The four equatorial basal nitrogens [N(1), N(2), N(3) and N(4)] are nearly coplanar. The Cu^{II} deviates from the least-square plane of the four basal nitrogens towards the pendant nitrogen N(21) by *ca.* 0.4 Å to accept axial co-ordination. The Cu–N distances of the four basal nitrogens fall in the range 1.92–2.09 Å, being normal co-ordination bonds.¹¹ The Cu–N(21) distance of 2.203(7) Å is longer than those of the

Table 2 Electrochemical and UV/VIS spectral data for the copper complexes

	[CuL]	[CuL ¹]	[CuL ²]
CV ^a			
Scan rate/mV s ^{–1}	100	200	50
pH	≈5.5	≈6	≈7
E _{pa} /V	0.54	0.69	0.81
E _{pc} /V	0.62	0.79	0.89
E ₁ /mV	80	100	80
E ₂ /V	0.58	0.75	0.85
UV/VIS ^b			
λ _{max} /nm	516	576	620
ε/dm ³ mol ^{–1} cm ^{–1}	100	140	160

^a In water at 25 °C, in V vs. SCE. The concentrations of all the complexes were kept at 2 × 10^{–3} mol dm^{–3}. ^b At 25 °C, solvent MeOH; the solution was preneutralized with NaOH.

**Scheme 2**

basal Cu–N distances, indicating weak co-ordination of the pendant nitrogen, due to the Jahn–Teller effect. The distances C(5)–N(3) [1.296(7)] and C(7)–N(4) [1.300(7) Å] are obviously shorter than that of a normal C–N distance (1.47 Å), and show partial double-bond character which arises from the conjugation between O(1)–C(5)–N(3) and O(2)–C(7)–N(4). The conjugation was also confirmed by the IR spectrum (the C=O vibration band for [CuL²] is 84 cm^{–1} lower than that of H₂L²). The dihedral angle between the co-ordinated pyridyl plane and the basal least-squares plane is 68.7°. Only one of the two pendants takes part in the co-ordination to the central Cu^{II}, the other remains in a *cis* position. In the unit cell eight different neutral molecules are linked by water molecules through hydrogen bonds, and the structure may thus be stabilized.

Electrochemical studies

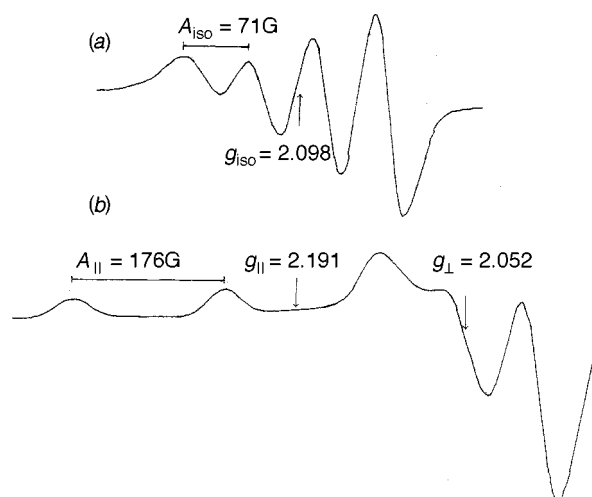
The cyclic voltammograms of the copper(II) complexes of H₂L, H₂L¹ and H₂L² were examined in aqueous solution (0.5 mol dm^{–3} Na₂SO₄, at 25 °C) and the electrochemical data are summarized in Table 2. The cyclic voltammograms showed that a redox wave for complex **1** was observed at E₁ = 0.85 V vs. SCE with redox peak separation ΔE_p = 80 mV (pH ≈ 7), indicating a quasi-reversible redox process for Cu^{II} → Cu^{III}. The complexes [CuL] and [CuL¹] also display a quasi-reversible redox process. The Cu^{III/II} potential of [CuL¹], +0.75 V vs. SCE, is 0.17 V more positive than that for [CuL] under similar conditions (E₁ = 0.58 V vs. SCE),^{1a} implying that the ligand L appended with a 2-methylpyridyl pendant destabilizes the copper(III) state compared with the unsubstituted L.

This behavior can be interpreted as follows: the change from Cu^{II} (d⁹) to Cu^{III} (d⁸, low spin) involves a drastic reduction of the metal-ion radius and a change of electronic configuration (Scheme 2).^{3b} In the two new complexes the pyridine pendants co-ordinate to the central Cu^{II} from the apical site, and the Cu^{II} resides above the mean plane of the four basal nitrogens. The co-ordination of one pyridine pendant to Cu^{II} stabilizes the latter ion. However, when Cu^{II} is oxidized to Cu^{III}, like Ni^{II} (d⁸, low spin), Cu^{III} tends to adopt a square-planar co-ordination

Table 3 The ESR parameters of the copper(II) complexes in methanol solution at room temperature and 112 K*

Ligand	298 K		112 K			
	g_{iso}	A_{iso}/G (cm^{-1})	g_{\parallel}	g_{\perp}	A_{\parallel}/G (cm^{-1})	A_{\perp}/G (cm^{-1})
L	2.083	91 (8.85×10^{-3})	2.173	2.038	201 (2.04×10^{-2})	36 (3.43×10^{-3})
L ¹	2.094	81 (7.92×10^{-3})	2.185	2.048	185 (1.89×10^{-2})	29 (2.77×10^{-3})
L ²	2.098	71 (6.95×10^{-3})	2.191	2.052	176 (1.80×10^{-2})	19 (1.82×10^{-3})

* A_{\perp} was calculated according to the formula $3A_{\text{iso}} = A_{\parallel} + 2A_{\perp}$ and g_{\perp} according to $3g_{\text{iso}} = g_{\parallel} + 2g_{\perp}$. The pH value was adjusted to ≈ 7 .

**Fig. 2** X-Band ESR spectra of the complex [CuL²] in MeOH at (a) 298 K and (b) 112 K

rather than a five-co-ordinated one, which means the pyridine pendant will not co-ordinate to Cu^{III}. Since the N-substitution by the pyridine pendant(s) increases the steric constraint of the macrocycle ring and lowers its co-ordinative ability, the Cu^{III} is not stabilized to the same extent as with unsubstituted dioxo-[13]aneN₄. The results are similar to those for the copper(II) complex of dioxocyclam appended with 8-methylquinoline.^{11,16}

Spectroscopic studies

The absorption maxima for [CuL], [CuL¹] and [CuL²] in MeOH solution are listed in Table 2. The d-d transition band of complexes [CuL¹] and [CuL²] is significantly shifted to higher wavelengths compared with that for [CuL] (516 nm). Since this band gives an empirical measure of the in-plane Cu^{II}-N interactions,¹⁷ the remarkable red-shift observed for **1** indicates weakened in-plane bonding in these complexes.

ESR Studies

Table 3 presents the ESR spectral data for [CuL], [CuL¹] and [CuL²] in MeOH solution at room temperature and 112 K at the pH region in which the doubly deprotonated copper(II) complexes are formed. For complex [CuL²] it can be seen that the spectrum is split into four equally spaced absorptions by the interaction with the copper(II) nucleus ($I = \frac{3}{2}$) (Fig. 2) at room temperature. When the solution is frozen at 112 K, an ESR spectrum characteristic of nearly axial symmetry is observed, very similar to that of the [CuL] complex. The approximate ESR parameters of [CuL²] were graphically evaluated as $g_{\parallel} = 2.191$, $g_{\perp} = 2.052$, $A_{\parallel} = 176$ G (1.80×10^{-2} cm⁻¹) and $A_{\perp} = 19$ G (1.82×10^{-3} cm⁻¹), where $g_{\perp} = (3g_{\text{iso}} - g_{\parallel})/2$ and $A_{\perp} = (3A_{\text{iso}} - A_{\parallel})/2$.¹⁸ The ESR spectrum of complex [CuL¹] is quite similar to those of [CuL²] and [CuL]. The observed A_{\parallel} values decrease and g_{\parallel} values increase from [CuL] to [CuL¹] to [CuL²]. These tendencies have been employed to measure the lowering of the strength of in-plane ligand fields in the tetragonal basal square arrangement of copper(II) complexes.¹⁹

Therefore, the ESR spectra also support the weakened in-plane bonding in the complexes [CuL¹] and [CuL²] compared with that in [CuL]. This is consistent with CV and UV/VIS measurements. The ESR parameters of [CuL¹] and [CuL²] also indicate a $d^1_{x^2-y^2}$ ground state for Cu^{II} in the complexes.

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