

New macrocyclic dioxotetraamines bearing 2-methylfuran pendant(s): synthesis, properties and crystal structure of the copper(II) complexes

Xian He Bu,* Zhi Hui Zhang, Xi Chuan Cao, Shu Ying Ma and Yun Ti Chen

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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Abstract—A series of new macrocyclic dioxotetraamine ligands having 2-methylfuran pendant(s), 4-(2-methylfuran)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^1), 4,7-bis(2-methylfuran)-1,4,7,10-tetraazacyclotridecane-11,13-dione (H_2L^2), 1-(2-methylfuran)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (H_2L^3) and 1,11-bis(2-methylfuran)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (H_2L^4), have been synthesized and characterized. The solution behaviours of the copper(II) complexes of the four ligands have been studied with ESR, cyclic voltammetry (CV) and UV-vis techniques. A red-shift has been observed for the maximum absorption band of the electronic spectra of CuL^1 , CuL^3 and CuL^2 , CuL^4 in comparison to those of the corresponding unsubstituted copper(II) complexes CuL_{01} and CuL_{02} , respectively. Electrochemical studies suggest that the introduction of 2-methylfuran pendant(s) to the macrocyclic dioxotetraamines destabilizes the Cu^{III} ion comparing with the unsubstituted species for both of the two kinds of macrocycles (13-membered and 14-membered macrocycles). The copper(II) complex of H_2L^2 has been isolated as a single crystal and the crystal structure determined by X-ray diffraction analysis. It is interesting that the complex has an *N-meso* chiral nitrogen configuration. The Cu^{II} atom is in five coordination environment with four basal nitrogen atoms and one axial oxygen atom from H_2O , and it adopts a distorted square pyramidal configuration. © 1997 Elsevier Science Ltd

Keywords: macrocyclic dioxotetraamines; copper complex; properties; crystal structure; synthesis.

The introduction of additional functional groups into the macrocyclic dioxotetraamines causes a considerable change in the chemical properties and structures of their metal complexes [1–3]. For instance, macrocyclic dioxotetraamines can stabilize higher oxidation states of transition metal ions, but the macrocyclic dioxotetraamines attached some pendant groups show obvious destabilities for higher state of some transition metal ions [4,5], and these intramolecular pendants dramatically alter the properties of the macrocyclic dioxotetraamines [6]. In the previous papers, the syntheses, crystal structures and properties of nickel(II) complexes of macrocyclic dioxotetraamines bearing pendant groups have been reported [7–9]. In this paper, we report the syntheses, spectra and electrochemical properties of the copper(II) complexes of a series new macrocyclic

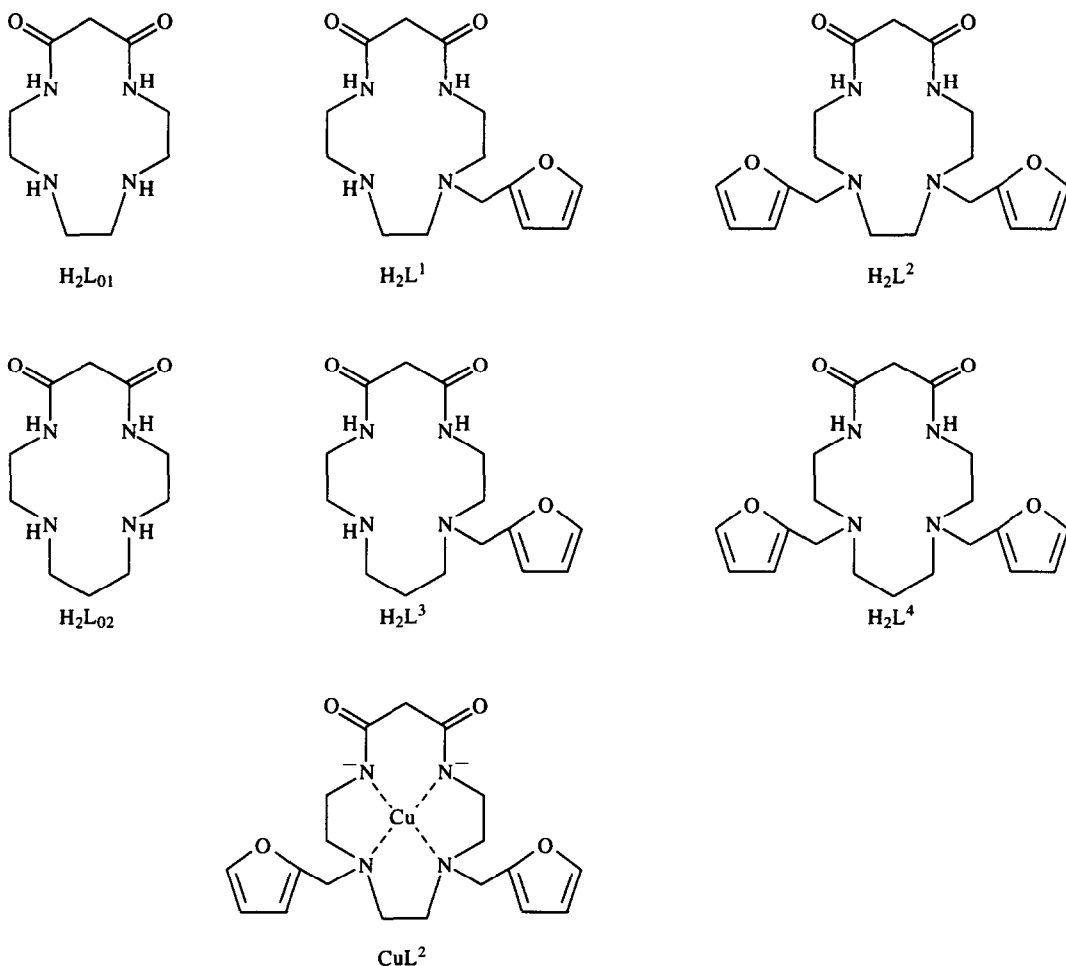
dioxo[13]ane N_4 and dioxocyclam ligands and the crystal structure of the copper(II) complex of 4,7-bis(2-methylfuran) - 1,4,7,10 - tetraazacyclotridecane - 11,13-dione (Scheme 1).

EXPERIMENTAL

Materials and general methods

Most of the starting materials and solvents for syntheses were obtained commercially and purified by standard methods prior to use. The ligands, 1,4,7,10-tetraazacyclotridecane-11,13-dione (dioxo[13]ane N_4) and 1,4,8,11-tetraazacyclotetradecane-5,7-dione (dioxocyclam), were prepared according to the modified literature methods [10]. All the other reagents for syntheses and analyses were of analytical grade. FT-IR was taken on a 170SX (Nicolet) spectrometer. Elemental analysis was taken on a Perkin-Elmer 240

* Author to whom correspondence should be addressed.



Scheme 1.

analyzer. ^1H NMR was recorded on a Bruker AC-P200 spectrometer [200 MHz, 25°C , in DMSO (for H_2L^1 and H_2L^3) and in CDCl_3 (for H_2L^2 and H_2L^4)]. Chemical shifts (in ppm) are with reference to the residual protonic solvent peaks. Electronic absorption spectra were measured on a Shimadzu UV-240 spectrophotometer. EI-MS was carried out on a VGZAB-MS instrument.

Synthesis of 1-(2-methylfuran)-1,4,7,10-tetraazacyclo-tridecane-11,13-dione (H_2L^1) and 1,11-bis(2-methylfuran)-1,4,7,10-tetraazacyclo-tridecane-11,13-dione (H_2L^2)

A solution of 2-bromomethylfuran (2.4 g, 15 mmol) in 30 ml of diethyl ether was added into a solution of H_2L (3.2 g, 15 mmol) in 30 ml of dimethyl formamide (DMF) in the presence of an excess amount of fine and dried K_2CO_3 (deprotonating agent) at *ca* 60°C . The resulting mixture was heated at 60°C for *ca* 14 h under Ar. After filtration of the reaction mixture, the filtrate was dried and evaporated, and then the residue was purified by column chromatography on silica gel

by eluting with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (95:5 v/v). The product was finally recrystallized from methanol–diethyl ether as colorless crystals (yield 35% based on dioxo[13]ane N_4). ^1H NMR (DMSO): δ 2.49 (8H, s), 2.99 (4H, m), 3.20–3.32 (6H, m), 3.60 (2H, s), 6.98 (2H, m). IR (KBr pellet): 738, 1014, 1320, 1439, 1564, 1680(C=O), 2844, 3040, 3230 cm^{-1} . EI-MS: M^+ peak $m/e = 294$ ($\text{Mr} = 294.36$). Anal. calc. for $\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_3$: C, 57.12; H, 7.53; N, 19.03. Found: C, 57.23; H, 7.65; N, 19.10%.

When 2:1 molar ratio of 2-bromomethylfuran and dioxo[13]ane N_4 was used in the above mentioned reaction, H_2L^2 was obtained as main product and it was recrystallized from methanol–diethyl ether, also as colourless needles (1.78 g, 40%). ^1H NMR (CDCl_3): δ 2.47–2.52 (8H), 3.24 (2H, s), 3.37–3.38 (4H, s), 3.65 (4H, s), 6.12–6.29 (4H, m), 7.24–7.33 (4H, m). IR (KBr pellet): 731, 913, 1018, 1265, 1328, 1470, 1533, 1568, 1635, 1680(C=O), 2837, 3087, 3250 (N-H) cm^{-1} . EI-MS: M^+ peak $m/e = 374$ ($\text{Mr} = 374.44$). Anal. Calc. for $\text{C}_{19}\text{H}_{26}\text{N}_4\text{O}_4$: C, 60.95; H, 7.00; N, 14.96. Found: C, 60.70; H, 6.82; N, 14.86%.

Synthesis of 1-(2-methylfuran)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (H_2L^3) and 1,11-bis(2-methylfuran)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (H_2L^4)

When 1 : 1 molar ratio of 2-bromomethylfuran (1.6 g, 10 mmol) and dioxocyclam (2.5 g, 10 mmol) was used in deoxygenated DMF and runned the same procedures as that of H_2L^1 , H_2L^3 was isolated as colorless needles. 1H NMR (in DMSO): δ 2.42–2.50 (4H, m), 3.06 (8H, m), 3.34–3.43 (4H, m), 3.69 (2H, s), 6.33 (4H, m), 7.81–7.61 (2H, m). IR (KBr pellet): 747, 1168, 1267, 1306, 1540, 1654, 1674(C=O), 2797, 2954, 3069, 3291, 3480 cm^{-1} . EI-MS: M^+ peak $m/e = 308$ ($Mr = 308.38$). Anal. Calc. for $C_{15}H_{24}N_4O_3$: C, 58.42; H, 7.84; N, 18.17. Found: C, 58.34; H, 7.95; N, 18.12%.

When 2 : 1 molar ratio of 2-bromomethylfuran and dioxocyclam was used, H_2L^4 ligand was obtained. 1H NMR (in $CDCl_3$): δ 1.6–1.8 (2H, m), 2.39–2.60 (8H, m), 3.2 (2H, s), 3.3 (4H, m), 3.59 (4H, s), 6.12–6.14 (2H, m), 6.26–6.30 (2H, m), 6.65 (2H, m), 7.35 (2H, s). IR (KBr pellet): 737, 1149, 1327, 1428, 1533, 1579, 1630, 1666(C=O), 2872, 2955, 3090, 3270, 3320 cm^{-1} . EI-MS: M^+ peak $m/e = 388$ ($Mr = 388.46$). Anal. Calc. for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.26; N, 14.42. Found: C, 61.91; H, 7.12; N, 14.53%.

Preparation of $[CuL^2 \cdot H_2O] \cdot H_2O$

The copper(II) complex of H_2L^2 , CuL^2 , was prepared by mixing a 1 : 1 molar ratio of $Cu(CH_3COO)_2$ and H_2L^2 in deoxygenated MeOH under reflux for *ca* 15 min. The blue reaction mixture was filtered and evaporated under Ar. The residue was then treated with CH_3CN . A crystal suitable for X-ray analysis was obtained from a CH_3CN -MeOH solution. Anal. Calc. for $C_{19}H_{30}N_4O_6Cu$: C, 48.76; H, 6.46; N, 11.97. Found: C, 48.83; H, 6.62; N, 11.82%.

ESR studies

ESR spectra were measured on a Bruker ER-200-DSRC10 spectrophotometer. Methanol solutions of the Cu^{II} complexes were prepared by mixing equimolar amounts of ligand and $Cu(NO_3)_2$ in methanol and adjusting pH to *ca* 8 (NaOH/MeOH). These solutions were then added into ESR tubes and the measurements were performed at room temperature and 110 K, respectively.

Electrochemical studies

Cyclic voltammetry (C.V.) measurements were performed with a PARC model 273 electrochemical apparatus in aqueous solution at $25 \pm 0.05^\circ C$ with 0.5 mol dm^{-3} of Na_2SO_4 as supporting electrolyte and the solution was bubbled with pure Ar gas before

measurements. The pH of the solution was adjusted with concentrated NaOH and H_2SO_4 aqueous solution. The cyclic voltammograms at the scan rate of 100 (for CuL^2 and CuL^4) or 200 (for CuL^1 and CuL^3) mV s^{-1} were evaluated graphically. A three electrode system was employed: glassy carbon as working electrode, saturated calomel electrode (SCE) as a reference and Pt coil as counter electrode.

Crystallographic studies

A crystal of CuL^2 was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator for data collection. The determination of unit cell parameters and the data collection were carried out with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell dimensions were obtained by least-squares refinement of one setting angle of 25 reflections in the range 9.64 – 12.26° . The correction for LP factors was applied to the data, and the structure was solved by direct methods (MULTAN 82 [11]). The Cu atom was located from an E-map. The other non-hydrogen atoms were determined with successive difference Fourier synthesis. Final refinement by full-matrix least-squares methods was carried out with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were treated as riding on their attached atoms and placed at the calculated positions. All the calculations were performed on a PDP 11/44 and IBM-486 computers, using the SDP-PLUS program package [12].

RESULTS AND DISCUSSION

Syntheses

The ligands were prepared as follows: 2-bromomethylfuran was prepared in dried DMF by mixing newly evaporated 2-methylhydroxide furan and equimolar amounts of PBr_3 , for *ca* 14 h in 76% yield.

For the preparation of H_2L^1 or H_2L^3 , 2-bromomethylfuran and an excess amount of dioxo[13]ane N_4 or dioxocyclam were used to prepare the mono-substituted products. The main product H_2L^1 or H_2L^3 was purified by silica-gel column chromatography and recrystallized from $C_2H_5OC_2H_5$ - C_2H_5OH as colourless needles in 35–40% yield. The disubstituted product H_2L^2 or H_2L^4 was also obtained as the minor product which was eluted more rapidly than H_2L^1 or H_2L^3 . When dioxo[13]ane N_4 or dioxocyclam and 2 equiv. of 2-bromomethylfuran were used with similar procedures, the main product was H_2L^2 or H_2L^4 . All the analytical and spectral data are in good agreement with the theoretical requirements of the four new ligands.

Spectroscopic studies

The absorption maxima data of CuL^1 , CuL^3 , CuL^2 and CuL^4 in MeOH solution at $25^\circ C$ are 534 nm

Table 1. Physical properties of copper complexes

Complexes	CuL ₀₁	CuL ₀₂	CuL ¹	CuL ³	CuL ²	CuL ⁴
C. V. pH	5.0	5.5	4.6	5.0	4.3	5.5
$E_{1/2}$ vs SCE	0.60	0.69	0.71	0.81	0.85	0.93
UV-vis λ_{\max} (nm)	517	505	534	525	558	546
(ϵ , mol ⁻¹ dm ³ cm ⁻¹)	(90)	(100)	(130)	(100)	(150)	(110)

($\epsilon = 130 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), 525 nm ($\epsilon = 100 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), 558 nm ($\epsilon = 150 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and 546 nm ($\epsilon = 110 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), respectively (Table 1). It is obvious that the $d-d$ transition bands of CuL¹ and CuL² give the remarkable red-shifts observed in comparison with those of the unsubstituted complexes CuL₀₁, respectively. CuL² gives the remarkable red-shifts also in contrast with the monosubstituted species CuL¹, indicating weakened in-plane bonding in CuL¹ and CuL² compared with that of CuL₀₁ due to the increase of the number of *N*-substituted 2-methylfuran pendants in these complexes.

There are the same tendency as 13-membered ring complexes for the 14-membered ring complexes. Furthermore, the maxima absorption bands of the copper(II) complexes of the 13-membered ring ligands have slightly red-shifts in comparison with those of the copper(II) complexes of the 14-membered ring ligands. The reason is that the cavity of the 14-membered ring fits Cu^{II} ion quite well and the copper(II) ion just inserts into the cavity, while the cavity of the 13-membered ring is very tight for Cu^{II} and the copper(II) ion is raised out the macrocyclic plane. Therefore, H₂L³ and H₂L⁴ have more stronger coordination abilities with Cu^{II} atom than those of H₂L¹ and H₂L².

ESR studies

Figure 1 represents the ESR spectra of CuL² in MeOH solution at room temperature and 110 K. It can be seen that the spectrum of CuL² is split into four equally spaced absorption by the interaction with the Cu^{II} nucleus ($I = 3/2$) at room temperature. The isotropic ESR parameters are $g_{\text{iso}} = 2.093$ and $A_{\text{iso}} = 85 \text{ G}$ ($8.30 \times 10^{-3} \text{ cm}^{-1}$) (Table 2). When the solution is frozen at 110 K, an ESR spectrum characteristic of nearly axial symmetry is observed, which is very similar to that of the CuL₀₁ complex. The approximate ESR parameters of CuL² are graphically evaluated as $g_{\parallel} = 2.186$, $g_{\perp} = 2.047$, $A_{\parallel} = 189 \text{ G}$ ($1.93 \times 10^{-2} \text{ cm}^{-1}$), and $A_{\perp} = 33 \text{ G}$ ($3.15 \times 10^{-2} \text{ cm}^{-1}$), where $g_{\perp} = (3g_{\text{iso}} - g_{\parallel})/2$ and $A_{\perp} = (3A_{\text{iso}} - A_{\parallel})/2$ [13]. All the parameters for other complexes are also listed in Table 2. It is obvious that the observed A values decrease and g_{\parallel} values increase for the copper(II) complexes from CuL₀₁ to CuL¹ to CuL² and from CuL₀₂ to CuL³ to CuL⁴. The tendency for A_{\perp} to decrease and for g_{\parallel} to increase can be taken as a measure of the lowering of the strength of in-plane ligand fields under the tetragonal basal square arrangement of copper(II) complexes [14]. Therefore,

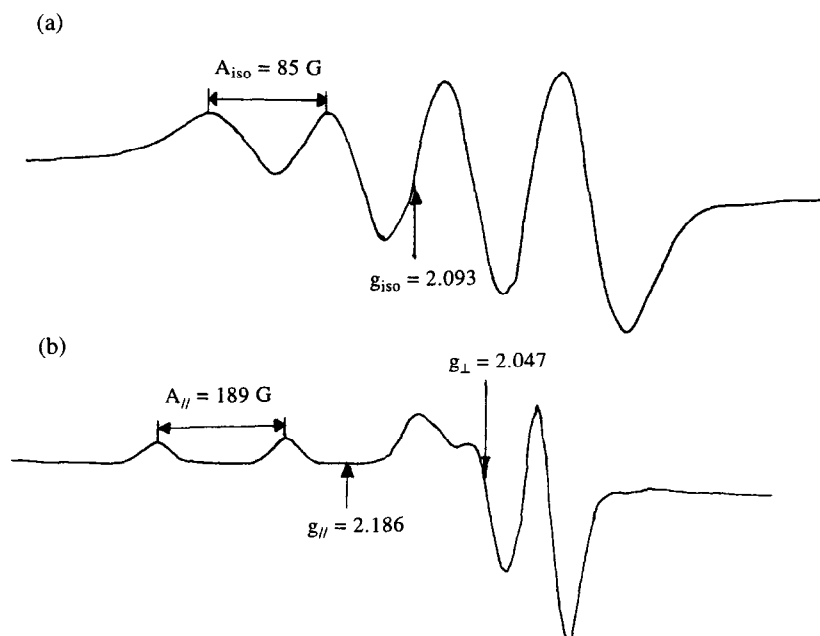


Fig. 1. The x-band ESR spectra of CuL² in methanol: (a) 298 K; (b) 110 K.

Table 2. ESR parameters of the copper(II) complexes in methanol solution at 298 K and 110 K^a

Complex	298 K			110 K		
	g_{iso}	$A_{\text{iso}}, \text{G}(10^3 \text{ cm}^{-1})$	g_{\parallel}	g_{\perp}	$A_{\parallel}, \text{G}(10^3 \text{ cm}^{-1})$	$A_{\perp}, \text{G}(10^2 \text{ cm}^{-1})$
CuL ₀₁	2.083	91(8.84)	2.173	2.018	201(2.04)	36(3.42)
CuL ₀₂	2.085	97(9.44)	2.173	2.042	206(2.09)	43 4.10
CuL ¹	2.088	89(8.67)	2.179	2.043	195(1.98)	36(3.43)
CuL ³	2.088	90(8.77)	2.172	2.046	201(2.04)	35(3.35)
CuL ²	2.093	85(8.30)	2.186	2.047	189(1.93)	33(3.15)
CuL ⁴	2.090	86(8.38)	2.175	2.048	187(1.90)	36(3.44)

^a A_{\perp} was calculated according to formula: $3A_{\text{iso}} = A_{\parallel} + 2A_{\perp}$ and g_{\perp} according to formula: $3g_{\text{iso}} = g_{\parallel} + 2g_{\perp}$.

ESR spectra also show the weakened in-plane bonding in CuL² and CuL⁴ compared with those of CuL₀₁, CuL₀₂ and CuL¹, CuL³. This is consistent with the results of UV-vis measurements. The ESR parameters for CuL¹, CuL², CuL³ and CuL⁴ also indicate a d_{xy}^2 ground state of Cu^{II} in these complexes. But A_{\parallel} values of the copper(II) complexes of dioxocyclam are higher than those of the copper(II) complexes of dioxo[13]aneN₄ indicating the stronger coordinating bonds of dioxocyclam copper(II) complexes than those of dioxo[13]aneN₄ copper(II) complexes.

Electrochemical properties

The cyclic voltammograms of the complexes of Cu^{II} with ligands dioxo[13]aneN₄, H₂L¹, H₂L² and dioxocyclam, H₂L³, H₂L⁴ were examined in aqueous solution (0.5 mol dm⁻³, Na₂SO₄, at 25°C), and the data are summarized in Table 3. All the cyclic voltammograms show that there are one quasi-reversible redox wave in these complexes, and they are all pH sensitive and could be obtained only in a very narrow pH range. The Cu^{III}/Cu^I potential for CuL¹ $E_{1,2} = +0.71 \text{ V vs}$

Table 3. Crystal data and data collection summary for CuL²

Formula	C ₁₀ H ₂₈ CuN ₄ O ₆
<i>Mr</i>	472.00
Crystal colour	blue
Crystal system	orthorhombic
Space group	Pna2 ₁
Cell dimensions	
<i>a</i> (Å)	7.375 (2)
<i>b</i> (Å)	22.126 (4)
<i>c</i> (Å)	12.689 (4)
<i>V</i> (Å ³)	2070 (1)
<i>Z</i>	4
Density (calc.) (g cm ⁻³)	1.514
μ (cm ⁻¹)	10.98
<i>F</i> (000)	988
Crystal dimension (mm)	0.2 × 0.3 × 0.4
Radiation	MoK α
Scan mode	$\omega/2\theta$
λ (Å)	0.71073
2θ (max) (°)	46
Scan speed (° min ⁻¹)	0.92–5.49
Index range: <i>h, k, l</i>	–13 to 13, –8 to 0, 0 to 24
No. measured reflections	3212
No. independent reflections	2672 ($R_{\text{int}} = 0.031$)
No. unique reflections	1885 [$I > 3\sigma(I)$]
Absorption correction	empirical absorption corrections
No. parameters refined	271
<i>R</i>	0.045
<i>R_w</i>	0.053
Weighting scheme	$w = 1/(\sigma^2(F) + 0.0001 F^2)$
Goodness of fit	0.87
Max. residual peak (e Å ⁻³)	0.41

SCE is 0.11 V more positive than that for CuL_{01} ($E_{1/2} = +0.60$ V), while the $\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$ potential for CuL^2 , $E_{1/2} = +0.85$ V vs SCE is 0.25 V more positive than that for CuL_{01} under the same conditions, implying that H_2L^1 and H_2L^2 appended with one or two 2-methylfuran pendants destabilize the copper(III) state compared with the unsubstituted dioxo[13]ane N_4 .

This behaviour can be interpreted in terms of less favourable fitting of the d^8 Cu^{III} ion in a square-pyramidal cavity. The change from the Cu^{II} to Cu^{III} state (d^8 , low spin) involves drastic reduction of the ion radius [15]. For a square-planar complex of Cu^{III} with a deprotonated tripeptide, a $\text{Cu}^{\text{III}}-\text{N}^-$ (deprotonated amide) distance of 1.80 Å and a $\text{Cu}^{\text{III}}-\text{N}_{\text{amine}}$ distance of 1.90 Å have been found [10]. Such distances fit quite well with the 13-membered macrocyclic cavity. For CuL^1 and CuL^2 complexes, when Cu^{II} is oxidized to Cu^{III} , the ion would insert completely into the cavity rather than reside above the least-squares plane of the four basal nitrogen atoms. Therefore, the coordination of 2-methylfuran pendant to the central Cu^{III} ion would become very difficult or impossible due to steric constraints [1]. Since *N*-substitution increases the steric constraint of the dioxo[13]ane N_4 ring, Cu^{III} ions in the two complexes are not stabilized to the same extent as in the unsubstituted complex CuL_{01} . The $\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$ potentials for CuL^1 and CuL^2 are thus more positive than of CuL_{01} .

For the complexes CuL_{02} , CuL^3 and CuL^4 , there is a same tendency in the cyclic voltammograms as that

of complexes CuL_{01} , CuL^1 and CuL^2 . But the $E_{1/2}$ value of each copper(II) complex of dioxo[13]ane N_4 is more positive than that of the corresponding to copper(II) complex of dioxocyclam. The reasons are the same as the explanations in UV-vis and ESR sections.

Crystal structure of $[\text{CuL}^2 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$

The crystallographic data and data collection details for CuL^2 are summarized in Table 3. The molecular structure of CuL^2 is shown in Fig. 2, and the important bond lengths and bond angles are listed in Table 4.

From Fig. 2, it can be seen that in complex CuL^2 , the copper atom is five coordinate with the four macrocycle nitrogen atoms [N(1), N(2), N(3), N(4)] and one axial oxygen atom [O(5)] from H_2O , and adopts a distorted square-pyramidal configuration. The four nitrogen atoms [N(1), N(2), N(3), and N(4)] are nearly co-planar. The Cu^{II} atom deviates from the least-squares plane of these atoms towards the axial oxygen [O(5)] by *ca* 0.4 Å. This is probably due to the very tight cavity of the 13-membered ring for Cu^{II} . As anticipated, the two deprotonated amide nitrogen atoms [N(3) and N(4)] have stronger coordination bonds [Cu—N bond average is equal to 1.922 (7) Å] than those of tertiary amines N(1) [2.044 (7) Å] and

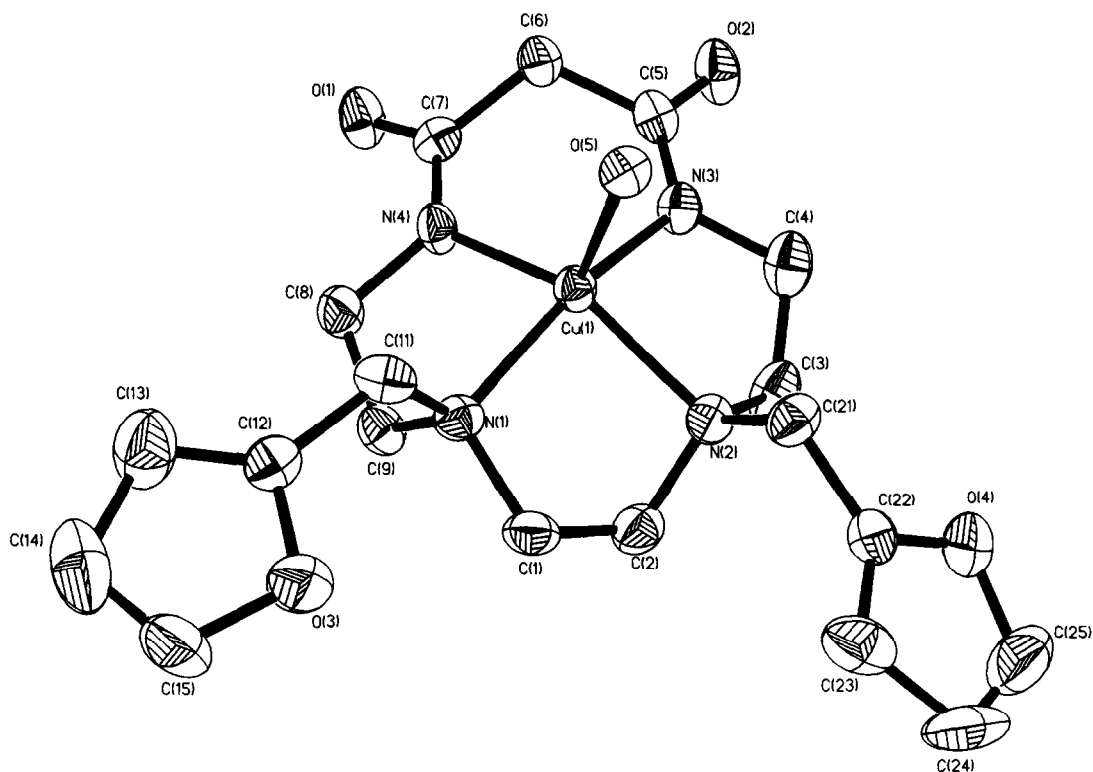


Fig. 2. ORTEP view of CuL^2 complex.

Table 4. Selected bond lengths (Å) and bond angles (°) for CuL² with e.s.d.s. in parentheses

Cu(1)—O(5)	2.241(6)	Cu(1)—N(1)	2.044(7)
Cu(1)—N(2)	2.089(8)	Cu(1)—N(3)	1.913(7)
C(7)—O(1)	1.247(11)	C(5)—O(2)	1.254(10)
N(4)—C(7)	1.318(12)	N(4)—C(8)	1.470(12)
N(3)—C(5)	1.304(12)	N(3)—C(4)	1.444(12)
N(1)—C(9)	1.493(12)	N(1)—C(11)	1.478(13)
N(1)—C(1)	1.495(11)	N(2)—C(3)	1.472(13)
N(2)—C(21)	1.485(12)	N(2)—C(2)	1.472(12)
C(6)—C(7)	1.516(12)	C(5)—C(6)	1.524(12)
C(8)—C(9)	1.497(15)	C(1)—C(2)	1.519(14)
C(3)—C(4)	1.510(15)	C(11)—C(12)	1.482(13)
C(21)—C(22)	1.488(13)		
O(5)—Cu(1)—N(1)	102.1(2)	O(5)—Cu(1)—N(2)	98.2(3)
N(1)—Cu(1)—N(2)	86.8(3)	O(5)—Cu(1)—N(4)	111.2(3)
Cu(1)—N(2)—C(3)	102.8(6)	Cu(1)—N(3)—C(4)	113.7(5)
Cu(1)—N(4)—C(7)	124.8(6)	Cu(1)—N(3)—C(5)	126.0(6)
Cu(1)—N(4)—C(8)	113.9(6)	N(1)—Cu(1)—N(4)	83.9(3)
N(2)—Cu(1)—N(4)	150.4(3)	N(3)—Cu(1)—N(4)	95.0(3)
Cu(1)—N(1)—C(11)	113.0(6)	Cu(1)—N(2)—C(21)	115.8(6)
Cu(1)—N(1)—C(9)	100.7(5)	Cu(1)—N(2)—C(2)	100.7(6)

N(2) [2.089 (8) Å]. The Cu—N distances, 1.913–2.09 Å, can be considered as normal coordination Cu—N bonds [16]. The distance of N(4)—C(7) [1.318 (1) Å] and N(3)—C(5) [1.304 (12) Å] are shorter than the normal single C—N bond, showing their partial double bond character which arises from the conjugation in the O(1)—C(7)—N(4) and O(2)—C(5)—N(3) systems, respectively. Figure 3 shows a perspective drawing of the molecular stacking of CuL² in the unit cell. It is obvious that a H₂O molecule links with the macrocycle of CuL² at O(2) through hydrogen bonding.

The two 2-methylfuran pendants are uncoordinated to copper(II), and they are on the same side of the macrocycle plane. The macrocycle takes a *cis* configuration. The complex has an *N-meso* chiral nitrogen configuration [(*R*) N(1), (*S*) N(2)]. It is interesting to note that we have recently reported the crystal structure of a copper(II) complex of a dioxo[13]aneN₄ ligand functionalized by two 8-methylquinoline pendants [1]. This complex, in contrast to CuL², the two additional quinoline pendants are coordinated to the metal ion, and is obtained as the *N-racemic* compound. It could be that furan has a weaker coordination ability than quinoline due to the less electronic density on the furan ring and the metal ion incorporation is "guided" to degree by the coordinating side arms.

Supplementary material

Full details of the crystal data and collections, thermal parameters, bond distances and angles, torsion angles, mean plane and dihedral angles between the

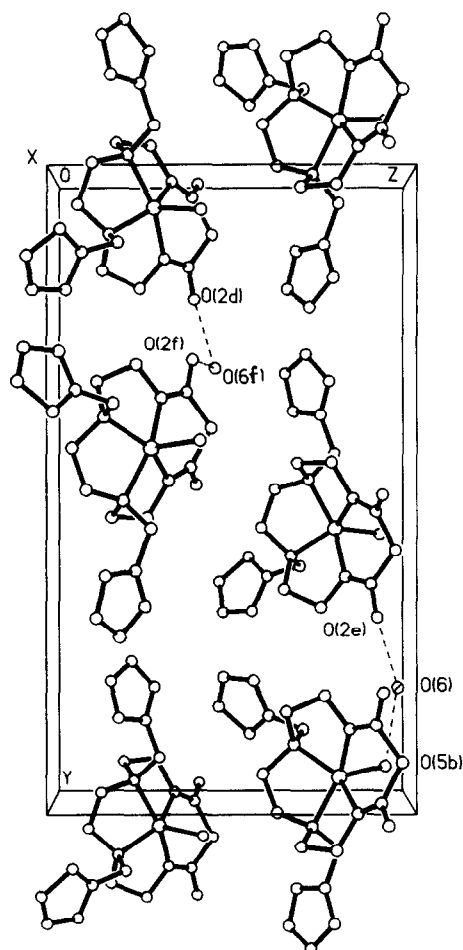


Fig. 3. Perspective drawing of the molecular stacking of CuL² in the unit cell.

planes, and listings of observed and calculated structural factors for complex CuL^2 are available from the authors.

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