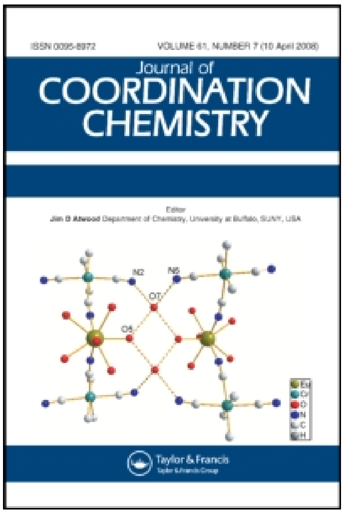

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Synthesis, crystal structure, and spectroscopic properties of CuL [H_2L=2,3-dioxo-5,6:13,14-dichlorobenzo-7,12-diphenyl-1,4,8,11-tetra-azacyclo-pentadeca-7,11-diene] and [(LCu)Cu(phen)(EtOH)]$(ClO_4)_2$ · EtOH · $0.25H_2O$: from mono- to dinuclear complex

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Synthesis, crystal structure, and spectroscopic properties of CuL [$H_2L = 2,3$-dioxo-5,6:13,14-dichlorobenzo-7,12-diphenyl-1,4,8,11-tetra-azacyclo-pentadeca-7,11-diene] and [(LCu)Cu(phen)(EtOH)]$(ClO_4)_2 \cdot EtOH \cdot 0.25H_2O$: from mono- to dinuclear complex

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Based on the complex ligand CuL ($H_2L = 2,3$-dioxo-5,6:13,14-dichlorobenzo-7,12-diphenyl-1,4,8,11-tetraazacyclo-pentadeca-7,11-diene) (**1**), a dinuclear complex [(LCu)Cu(phen)(EtOH)]$(ClO_4)_2 \cdot EtOH \cdot 0.25H_2O$ (**2**) was prepared. The crystal structures of **1** and **2** have been determined. IR, electronic and EPR spectra are discussed.

Keywords: Copper; Macrocycle; Complex ligand; Dinuclear complex; X-ray structure; EPR spectra

1. Introduction

Polynuclear complexes are currently of considerable interest in relation to magnetic exchange interactions between metal ions through bridging ligands, as building blocks to obtain new materials with novel properties and as models for the active sites of metallobiomolecules [1–7]. One of the best strategies to design and synthesize polynuclear species is the "complex as a ligand" approach, i.e., using mononuclear complex that contain potential donor groups for another metal ion [8–11]. It has been found that the oxamide group is an efficient bridging mediator of magnetic exchange between neighbouring metal ions, the type and magnitude of coupling depending on the metal ions used and their coordination environments. As a result, much work has been devoted to synthesising polynuclear complexes of macrocyclic ligands containing multiatomic bridges such as oxamide and oximate groups [12–15]. With these facts in our mind, we have synthesized a mononuclear copper(II) complex CuL (**1**)

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[H_2L = 2,3-dioxo-5,6:13,14-dichlorobenzo-7,12-diphenyl-1,4,8,11-tetra-azacyclo-pentadeca-7,11-diene]. Using it as precursor, we obtained a dinuclear copper(II) complex $[(LCu)Cu(phen)(EtOH)](ClO_4)_2 \cdot EtOH \cdot 0.25H_2O$ (**2**).

2. Experimental

All chemicals were of reagent grade and obtained commercially without further purification. The synthesis of the ligand L′ [L′ = 2,2′-(oxalyldiimino)bis(chlorobenzaldehyde)] was described previously [16]. IR spectra were recorded using KBr discs on a Shimadzu IR-408 spectrophotometer in the 4000–600 cm^{-1} region. Electronic spectra were measured on a JASCO V-570 spectrophotometer using dimethylformamide as solvent. X-band EPR spectra of a crystalline sample were recorded on a Bruker EMX-6/1 D-SPC spectrometer at room temperature.

2.1. *Synthesis of the mononuclear copper(II) complex 1*

Complex **1** was prepared by refluxing L′ (1.53 g, 2.96 mmol), 1,2-diaminopropane (0.440 g, 5.92 mmol) and $Cu(Ac)_2 \cdot H_2O$ (0.59 g, 2.96 mmol) for 10 h in 50 cm^3 of MeOH, in the presence of 2.80 cm^3 of 2 M NaOH. After the mixture was cooled and filtered, complex **1** precipitated as a red polycrystalline powder and was washed with water and dried under vacuum. The deep red filtrate was kept at room temperature for several days and gave red crystals suitable for X-ray analysis.

2.2. *Synthesis of the dinuclear copper(II) complex 2*

To a stirred solution of complex **1** (0.308 g, 0.5 mmol) in 50 cm^3 of EtOH, $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 0.5 mmol) was added; 10 min later 1,10-phenanthroline (phen) (0.0991 g, 0.58 mmol) was added. The mixture was then refluxed for 10 h and filtered. By slow evaporation of the filtrate, grey crystals suitable for X-ray investigation were obtained after 1 month.

2.3. *Crystallographic studies*

Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature on a Bruker Smart 1000 CCD area detector equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Diffaction data were collected using ω-2θ scans. LP corrections were applied to the data. The structures were solved by direct methods using SHELXS-97 and refinement on F^2 was performed using SHELXL-97 by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms [17, 18]. All hydrogen atom positions were located in calculation positions and refined isotropically. Crystal data and refinement details are summarized in table 1.

Table 1. Crystal data and details of structure determination of CuL (**1**) and $[(LCu)Cu(phen)(EtOH)](ClO_4)_2 \cdot EtOH \cdot 0.25H_2O$ (**2**).

Complex	**1**	**2**
Empirical formula	$C_{31}H_{22}Cl_2CuN_4O_2$	$C_{47}H_{42.50}Cl_4Cu_2N_6O_{12.25}$
Formula weight	616.97	1156.25
Temperature (K)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.7330(17)	10.805(3)
b (Å)	14.891(2)	18.091(4)
c (Å)	16.229(2)	25.971(7)
β (°)	106.501(2)	90.996(5)
V (Å^3)	2718.6(7)	5076(2)
Z, Calculated density (Mg m^{-3})	4, 1.507	4, 1.513
Absorption coefficient (mm^{-1})	1.037	1.115
F (000)	1260	2362
Crystal size (mm^3)	$0.30 \times 0.26 \times 0.20$	$0.22 \times 0.20 \times 0.18$
θ range for data collection (°)	1.89–26.37	1.37–25.00°
Limiting indices	$-14 \le h \le 13$, $-18 \le k \le 13$, $-20 \le l \le 20$	$-12 \le h \le 12$, $-21 \le k \le 20$, $-14 \le l \le 30$
Reflections collected/unique	14830/5548 [R(int) = 0.0364]	25402/8940 [R(int) = 0.0879]
Completeness to $\theta = 26.37$ (%)	99.5	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.683	1.000 and 0.671
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5548/0/362	8940/166/713
Goodness-of-fit on F^2	1.052	1.027
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0423$, $wR_2 = 0.1106$	$R_1 = 0.0738$, $wR_2 = 0.1794$
R indices (all data)	$R_1 = 0.0821$, $wR_2 = 0.1375$	$R_1 = 0.1552$, $wR_2 = 0.2330$
Largest diff. peak and hole (e Å^{-3})	0.548 and −0.484	0.792 and −0.605

3. Results and discussion

3.1. *Crystal structure of complex 1*

The structure of complex **1** consists of the copper(II) complex of the N_4 macrocyclic oxamide dianion. A perspective view of complex **1** with the atom numbering scheme is depicted in figure 1 and selected bond lengths and angles are listed in table 2. The macrocyclic ligand coordinates to the copper atom via two deprotonated oxamide nitrogens and two imine nitrogens. The copper atom resides in the mean plane of the four donor atoms, and deviations from the mean plane are 0.3149 Å for N1, 0.1649 Å for N2, 0.0827 Å for N3 and −0.1699 Å for N4. Cu–N bond lengths 1.869 (N1, N2) 1.884 (N3) and 1.879 Å (N4), respectively.

3.2. *Crystal structure of complex 2*

The structure of complex **2** consists of the dinuclear $[(LCu)Cu(phen)(EtOH)]^{2+}$ cation, two perchlorate ions, one ethanol molecule and 0.25 H_2O molecules. A perspective view of the complex is shown in figure 2, and selected bond lengths and angles are listed in table 3. Oxamide groups bridge the two copper(II) ions in the dinuclear cation. The Cu–Cu bond distance is 5.102 Å. For Cu1, the copper(II) ion lies in a slightly distorted

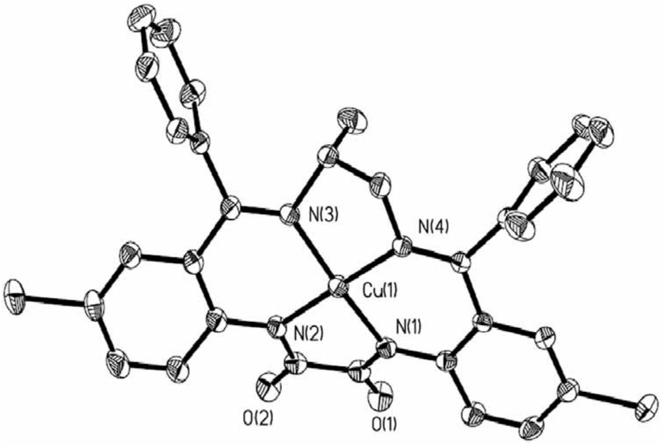

Figure 1. Perspective view of CuL with its atom labelling scheme.

Table 2. Selected bond lengths (Å) and angles (°) for CuL (**1**).

Cu(1)–N(2)	1.869(3)	N(1)–C(1)	1.375(4)
Cu(1)–N(1)	1.869(3)	N(1)–C(31)	1.396(4)
Cu(1)–N(4)	1.878(3)	N(2)–C(2)	1.359(4)
Cu(1)–N(3)	1.884(3)	N(2)–C(3)	1.385(4)
Cl(1)–C(28)	1.741(4)	N(3)–C(9)	1.297(4)
Cl(2)–C(6)	1.749(4)	N(3)–C(16)	1.495(4)
O(1)–C(1)	1.218	N(4)–C(19)	1.298(4)
O(2)–C(2)	1.219(4)	N(4)–C(18)	1.497(4)
N(2)–Cu(1)–N(1)	86.58(12)	C(3)–N(2)–Cu(1)	126.2(2)
N(2)–Cu(1)–N(4)	176.65(13)	C(9)–N(3)–C(16)	120.4(3)
N(1)–Cu(1)–N(4)	93.92(11)	C(9)–N(3)–Cu(1)	129.7(2)
N(2)–Cu(1)–N(3)	92.70(12)	C(16)–N(3)–Cu(1)	109.7(2)
N(1)–Cu(1)–N(3)	171.01(12)	C(19)–N(4)–C(18)	119.2(3)
N(4)–Cu(1)–N(3)	87.32(11)	C(19)–N(4)–Cu(1)	130.1(2)
C(1)–N(1)–C(31)	120.6(3)	C(18)–N(4)–Cu(1)	110.7(2)
C(1)–N(1)–Cu(1)	110.8(2)	O(1)–C(1)–N(1)	127.8(3)
C(31)–N(1)–Cu(1)	127.8(2)	O(1)–C(1)–C(2)	119.6(3)
C(2)–N(2)–C(3)	121.0(3)	N(1)–C(1)–C(2)	112.6(3)
C(2)–N(2)–Cu(1)	112.8(2)	O(2)–C(2)–N(2)	128.6(3)
O(2)–C(2)–C(1)	119.4(3)	N(2)–C(3)–C(4)	121.1(3)
N(2)–C(2)–C(1)	112.0(3)	N(2)–C(3)–C(8)	121.2(3)

square planar environment, and is situated 0.1597 Å out of the mean plane of the four nitrogen donors of the macrocycle; the average deviation of the nitrogen atoms from the plane is 0.0377 Å. The average Cu–N distance is 1.924 Å. For Cu2, the copper(II) ion is pentacoordinate and has a distorted square pyramidal coordination environment. The donors atoms of the oxamide (O1, O2) and the phen ligand (N5, N6) form the basal plane and an oxygen atom of an ethanol molecule occupies the apical position. The related bond lengths are Cu2–N5 = 1.958, Cu2–N6 = 1.984, Cu2–O1 = 1.955, Cu2–O2 = 1.923 and Cu2–O3 = 2.412 Å. Deviations of the four donor atoms from the N_2O_2 mean plane are 0.0463 (N5), −0.0458 (N6), −0.0467 (O1), 0.0462 Å (O2) and the copper(II) ion lies 0.0463 Å out of the plane.

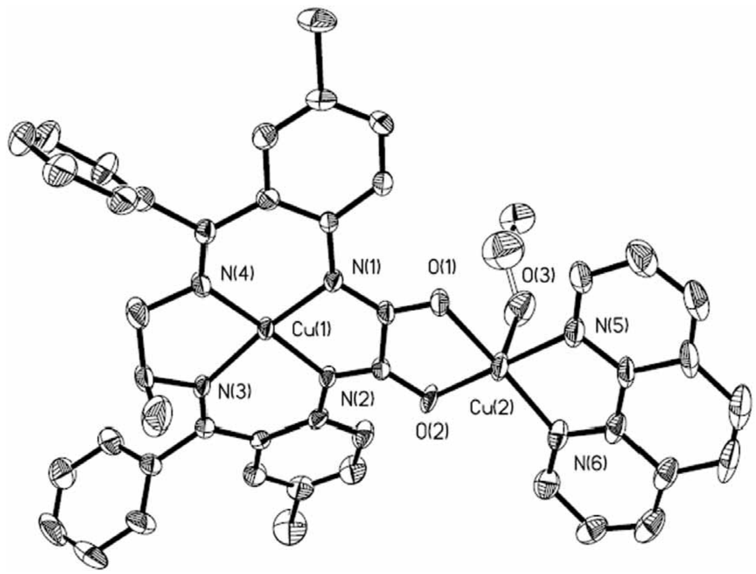

Figure 2. Perspective view of $[(LCu)Cu(phen)(EtOH)]^{2+}$ with its atom labelling scheme.

Table 3. Selected bond lengths (Å) and angles (°) for $[(LCu)Cu(phen)(EtOH)](ClO_4)_2 \cdot EtOH \cdot 0.25H_2O$ (**2**).

Cu(1)–N(1)	1.915(6)	Cu(2)–O(1)	1.955(5)
Cu(1)–N(3)	1.924(6)	Cu(2)–N(5)	1.958(7)
Cu(1)–N(4)	1.927(6)	Cu(2)–N(6)	1.984(7)
Cu(1)–N(2)	1.928(5)	Cu(2)–O(3)	2.412(7)
Cu(2)–O(2)	1.923(5)		
N(1)–Cu(1)–N(3)	168.2(3)	C(3)–N(2)–Cu(1)	126.6(5)
C(9)–N(3)–Cu(1)	128.2(5)	C(1)–N(1)–Cu(1)	109.8(5)
N(1)–Cu(1)–N(4)	92.9(3)	C(10)–N(3)–Cu(1)	109.6(5)
N(3)–Cu(1)–N(4)	87.0(2)	N(1)–Cu(1)–N(2)	86.4(2)
C(12)–N(4)–Cu(1)	129.1(5)	C(18)–N(1)–Cu(1)	126.4(5)
N(3)–Cu(1)–N(2)	92.2(2)	C(11)–N(4)–Cu(1)	109.6(5)
N(4)–Cu(1)–N(2)	172.7(3)	O(2)–Cu(2)–O(1)	84.3(2)
C(32)–N(5)–Cu(2)	129.6(6)	N(6)–Cu(2)–O(3)	94.7(3)
O(2)–Cu(2)–N(5)	178.8(3)	C(43)–N(5)–Cu(2)	111.6(6)
O(1)–Cu(2)–N(5)	95.1(3)	N(5)–Cu(2)–O(3)	93.6(3)
O(2)–Cu(2)–N(6)	96.8(3)	C(41)–N(6)–Cu(2)	129.0(6)
O(1)–Cu(2)–N(6)	173.5(3)	C(42)–N(6)–Cu(2)	110.8(6)
N(5)–Cu(2)–N(6)	83.6(3)	C(1)–O(1)–Cu(2)	111.4(5)
O(2)–Cu(2)–O(3)	87.5(3)	C(2)–O(2)–Cu(2)	113.0(5)
O(1)–Cu(2)–O(3)	91.8(3)		

3.3. *Spectroscopic properties*

IR spectra of these two complexes are very similar, both displaying an oxamide carbonyl stretch at 1660 cm^{-1}. Absorption between 3200–3400 cm^{-1} may be assigned to the O–H stretches of H_2O and EtOH [19]. Moreover, bands at 1610 and 1595 cm^{-1} for CuL and 1620 and 1590 cm^{-1} for **2** may be assigned to C=N absorptions [20–22]. Electronic spectra of **1** and **2** in DMF both display a strong absorption band in the

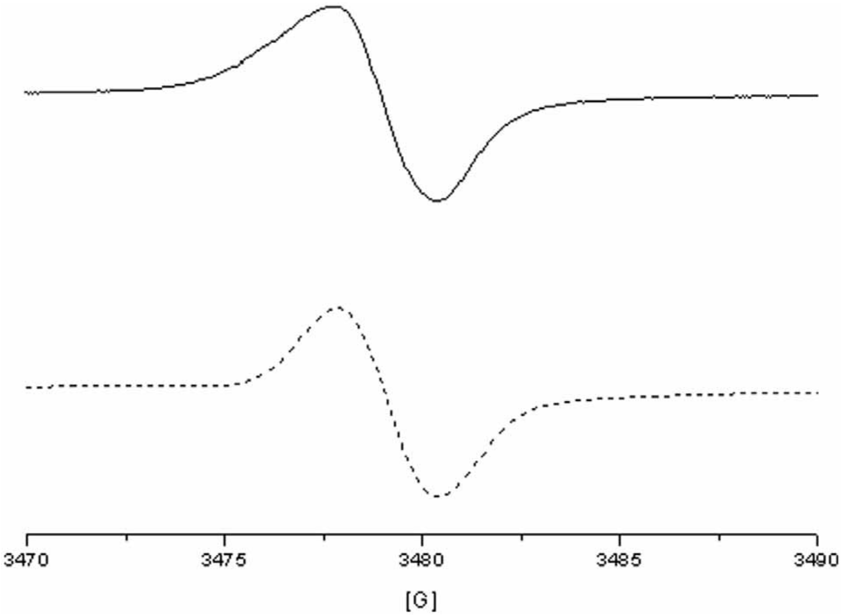

Figure 3. Experimental (solid line) and simulated (dashed line) X-band EPR spectrum of complex **2**.

420–260 nm region, attributed to charge transfer and/or ligand transitions. A broad and much less intense band for **1** was observed at 538 nm, assignable to envelope of the d–d transitions of copper(II) in an environment close to square planar. Compared with complex **1**, the d–d transition of **2** was observed at 520 nm.

EPR spectra of **2** measured on a polycrystalline power at room temperature showed an intense, almost isotropic, signal. EPR data were simulated by the WINEPR program to give $g_x = 2.0025$, $g_y = 2.0021$ and $g_z = 2.2550$. As shown in figure 3, the simulated curve reproduces very well the experimental data over the whole magnetic field range investigated.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 277417 and 277418.

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