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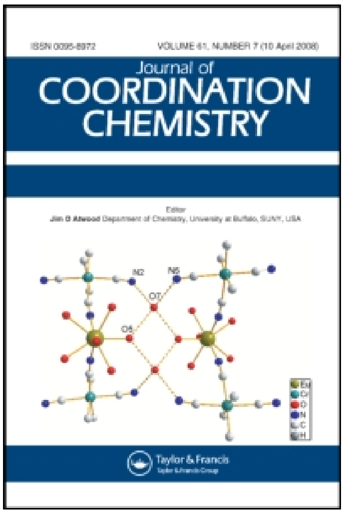

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Tetracyanoquinodimethane complexes of copper and a 17-membered N,O-donor macrocycle

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An axially elongated copper(II) complex, CuL^1Cl_2, has been obtained by reaction of copper(II) chloride with a 17-membered N,O-donor macrocyclic ligand (L^1). In an attempt to prepare the complex from copper(II) perchlorate, crystals of L^1 suitable for X-ray were obtained as its diperchlorate salt, $[H_2L^1][ClO_4]_2$. Further reaction of CuL^1Cl_2 with LiTCNQ and $Et_3NH(TCNQ)_2$ furnished the charge transfer copper(I) complexes $CuL^1(TCNQ)_2 \cdot 3H_2O$ and $CuL^1(TCNQ)_3$, with TCNQ carrying partially reduced charge. The presence of a diamagnetic metallic centre was confirmed by EPR and magnetic measurements.

Keywords: 7,7′,8,8′-Tetracyanoquinodimethane; Copper(II); X-ray structure; Charge transfer; Magnetic properties; EPR

1. Introduction

Macrocyclic ligands containing varying numbers of oxygen, nitrogen and sulfur donor atoms are of interest due to their metal ion selectivity and their ability to transport metal ions through biological and artificial membranes [1–4]. Of these, ligands containing mixed donor atoms have received relatively less attention. Planar metal chelates of such ligands combined with organic polynitrile ligands such as 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) gives compounds having interesting magnetic and electrical properties [5]. The nature of the donors and the molecular geometry are important in terms of these properties. In line with our interests [6–8] in the synthesis and properties of macrocyclic complexes, we report the synthesis of copper(II) chelates with a 17-membered N,O-donor macrocyclic ligand (L^1) and formation of charge transfer complexes with TCNQ and derivatives. Cu(II) has been reduced to Cu(I).

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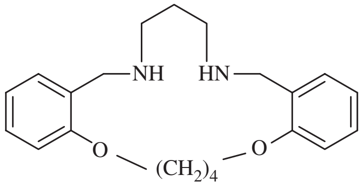

L^1

2. Experimental

Common chemicals were obtained commercially and used without further purification. All reactions were carried out under dry nitrogen and solvents were dried and degassed before use. LiTCNQ and $Et_3NH(TCNQ)_2$ were prepared by reported methods [9]. The ligand L^1 was prepared by a reported procedure and characterized spectroscopically [10–13]. IR spectra (KBr pellets) were recorded on a PYE UNICAM SP3-300 spectrophotometer and electronic spectra on a Shimadzu UV PC 1601 spectrophotometer. Variable temperature magnetic susceptibilities of complexes were recorded at BARC, Mumbai. Elemental analyses were performed using a Perkin-Elmer 2400 CHN instrument.

2.1. *Syntheses*

2.1.1. $Cu(L^1)Cl_2$ (1). To a warm solution of $CuCl_2 \cdot 2H_2O$ (0.11 g, 0.6 mmol) in dry methanol (5 cm^3) was added a solution of L^1 (0.1 g, 0.3 mmol) in dry methanol (5 cm^3) with constant stirring. The bluish green solid that formed was filtered off and washed with dry methanol and diethylether. Yield: 80%. Anal. Calcd for $Cu(C_{21}H_{28}N_2O_2)Cl_2$ (%): C, 53.16; H, 5.90; N, 5.90. Found: C, 52.54; H, 5.70; N, 6.26. This complex has been prepared previously by a high temperature, low yield procedure [14].

2.1.2. $CuL^1(TCNQ)_2 \cdot 3H_2O$ (2). To a solution of **1** (0.1 g, 0.136 mmol) in ethanol–water mixture (1 : 1 v/v, 10 cm^3) was added a solution of LiTCNQ (0.058 g, 0.27 mmol) in dry methanol (10 cm^3). The mixture was stirred at room temperature under nitrogen for 1 h. The dark green solid that formed was filtered off, washed with dry methanol and diethylether and dried in vacuum. Yield: 60%. Anal. Calcd for $CuC_{45}H_{42}N_{10}O_5$ (%): C, 62.39; H, 4.8; N, 16.17. Found: C, 62.84; H, 5.16; N, 15.76.

2.1.3. $CuL^1(TCNQ)_3$ (3). To a solution of **1** (0.1 g, 0.136 mmol) in ethanol–water mixture (1 : 1 v/v, 10 cm^3) was added a solution of $Et_3NH(TCNQ)_2$ (0.39 g, 0.27 mmol) in dry acetonitrile. The mixture was stirred for 1 h at room temperature. The dark green solid that formed was filtered off, washed with dry methanol and diethylether and dried in vacuum. Yield: 64%. Elemental analyses, Anal. Calcd for $CuC_{57}H_{40}N_{14}O_2$ (%): C, 67.36; H, 3.9; N, 19.3. Found: C, 66.16; H, 3.81; N, 19.3.

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2.2. *X-ray crystallography*

Crystals of the ligand, L^1, were obtained as a diperchlorate salt, $[H_2L^1](ClO_4)_2$, during an attempt to prepare the complex with copper(II) perchlorate in dry methanol. Crystal data: $C_{22}H_{29}Cl_2N_2O_{10}$, M = formula weight 540.36, monoclinic, space group $P2/c$, $a = 16.707(2)$, $b = 10.190(1)$, $c = 16.747(1)$ Å, $\beta = 118.21(1)^\circ$, $\gamma = 90^\circ$, $V = 2512.4(4)$ Å^3, $Z = 4$, $D_c = 1.429\ \mathrm{Mg\,m^{-3}}$, range of data collection (θ) 2.43 to 27.50°, range of indices measured $h = 0$ to 13, $k = 0$ to 13, $l = -12$ to 19, independent reflections 2268, unique reflections 2365, refinement by full-matrix least squares on F^2 (SHELXL 93), data/restraints/parameters 2268/0/159, goodness-of-fit on F^2 1.078, final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0502$, $wR_2 = 0.1294$, R indices (all data): $R_1 = 0.0735$, $wR_2 = 0.1449$, largest difference peak and hole 0.357 and -0.302 e Å^{-3}.

3. Results and discussion

Crystals of L^1 suitable for X-ray analysis were expeditiously obtained as $[H_2L^1][ClO_4]_2$ from the reaction of L^1 with copper(II) perchlorate [15]. Figure 1 shows the structure of the salt. Both the amine nitrogen atoms are protonated. The macrocycle in the solid state possesses a two-fold rotation axis that passes through C_9 and bisects the C_{11}–C_{11A} bond. All bond lengths and angles are normal (tables 1 and 2). The phenyl ring is planar and the two symmetry-related rings make a dihedral angle of 42°. The perchlorate ions are held in the lattice by strong N–H ⋯ O and N–H ⋯ Cl interactions to form a three-dimensional network. Besides these, weak C–H ⋯ O interactions are present and the fourth oxygen of the perchlorate ion is H-bonded to phenylene C4 and methylene C11 atoms.

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Reaction of **1** with LiTCNQ and $Et_3NH(TCNQ)_2$ yielded $CuL^1(TCNQ)_2 \cdot 3H_2O$ (**2**), and $CuL^1(TCNQ)_3$ (**3**). All complexes are air-stable. IR spectra of **1** show characteristic

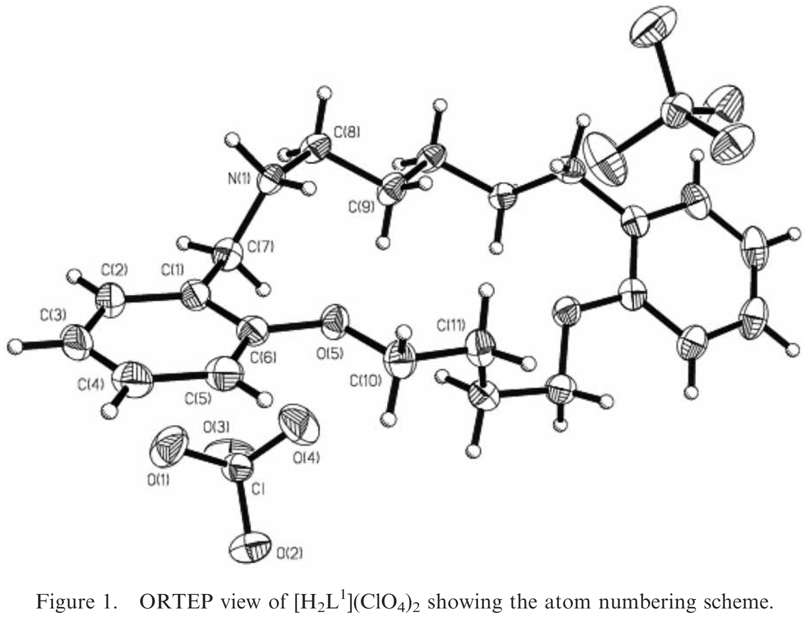

Figure 1. ORTEP view of $[H_2L^1](ClO_4)_2$ showing the atom numbering scheme.

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Table 1. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å} \times 10^3$] for $[H_2L^1](ClO_4)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl	6592(1)	1121(1)	5551(1)	50(1)
O(1)	7485(2)	92(3)	6199(2)	94(1)
O(2)	6603(2)	2413(2)	5200(2)	67(1)
O(3)	6248(2)	212(3)	4823(2)	88(1)
O(4)	6040(3)	1106(4)	5972(2)	107(1)
O(5)	6569(1)	1521(2)	8291(1)	48(1)
N(1)	6669(2)	−1364(2)	8481(1)	40(1)
C(1)	7756(2)	201(3)	8392(2)	47(1)
C(2)	8664(2)	1(4)	8665(2)	59(1)
C(3)	9299(3)	979(4)	9110(2)	67(1)
C(4)	9025(3)	2149(4)	9294(2)	66(1)
C(5)	8114(2)	2378(3)	9035(2)	55(1)
C(6)	7479(2)	1407(3)	8580(2)	45(1)
C(7)	7053(2)	−831(3)	7898(2)	48(1)
C(8)	5839(2)	−2195(3)	7993(2)	46(1)
C(9)	5000	−1340(4)	7500	52(1)
C(10)	6249(2)	2748(3)	8461(2)	53(1)
C(11)	5232(2)	2688(3)	8014(2)	55(1)

Table 2. Bond lengths [Å] and bond angles [°] for $[H_2L^1](ClO_4)_2$.

Cl–O(4)	1.401(3)	O(4)–Cl–O(1)	108.6(2)
Cl–O(1)	1.409(3)	O(4)–Cl–O(3)	109.3(2)
Cl–O(3)	1.419(2)	O(1)–Cl–O(3)	111.0(2)
Cl–O(2)	1.446(2)	O(4)–Cl–O(2)	110.7(2)
O(5)–C(6)	1.364(4)	O(1)–Cl–O(2)	108.52(17)
O(5)–C(10)	1.440(4)	O(3)–Cl–O(2)	108.83(14)
N(1)–C(7)	1.500(4)	C(6)–O(5)–C(10)	117.3(2)
N(1)–C(8)	1.495(4)	C(7)–N(1)–C(8)	114.9(2)
C(1)–C(2)	1.376(5)	C(2)–C(1)–C(6)	119.0(3)
C(1)–C(6)	1.400(4)	C(2)–C(1)–C(7)	122.1(3)
C(1)–C(7)	1.500(4)	C(6)–C(1)–C(7)	118.9(3)
C(2)–C(3)	1.388(5)	C(1)–C(2)–C(3)	121.0(4)
C(3)–C(4)	1.363(6)	C(4)–C(3)–C(2)	119.7(4)
C(4)–C(5)	1.392(5)	C(3)–C(4)–C(5)	120.7(3)
C(5)–C(6)	1.386(4)	C(6)–C(5)–C(4)	119.5(3)
C(8)–C(9)	1.521(4)	O(5)–C(6)–C(5)	124.7(3)
C(9)–C(8)#1	1.521(4)	O(5)–C(6)–C(1)	115.2(3)
C(10)–C(11)	1.499(5)	C(5)–C(6)–C(1)	120.1(3)
C(11)–C(11)#1	1.517(6)	N(1)–C(7)–C(1)	111.0(2)
		N(1)–C(8)–C(9)	110.5(2)
		C(8)#1–C(9)–C(8)	110.1(3)
		O(5)–C(10)–C(11)	107.8(2)
		C(10)–C(11)–C(11)#1	114.7(4)

Symmetry transformation used to generate equivalent atoms at #1 is $-x+1$, y, $-z+3/2$.

absorptions of the macrocyclic ligand with ν(N–H) modes at 2947, 2929 and 2869 cm^{-1}. Electronic spectra show a single, broad d–d band at 662 nm. The EPR spectrum is characteristic of copper(II) in an axially elongated environment with $g_{||} = 2.14$ and $g_{\perp} = 2.05$. The parallel peak is a quartet, indicating hyperfine coupling with copper(II) ($I = 3/2$) with A_{11} 80 G. Infrared studies have been used in the past to obtain information about charge and coordination status of TCNQ species [16, 17]. TCNQ^0 and TCNQ$^-$ exhibit CH out-of-plane bending at 863 and 828 cm^{-1}, respectively.

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A band attributable to this mode is observed at 834 cm^{-1} in complex **2**. The ν(CN) vibrational modes ($TCNQ^0$ ν(CN) 2225 cm^{-1}; $TCNQ^-$ ν(CN) 2180 cm^{-1}) appear at 2200 cm^{-1} and 2136 cm^{-1} and indicate that charge on $TCNQ^-$ has been partially reduced. Since complex **3** is formed by reaction of CuL^1Cl_2 with $Et_3NH(TCNQ)_2$, containing a combination of anionic and neutral TCNQ, its IR spectrum shows bands characteristic of both (with partially reduced charge) TCNQ species [18, 19]. CH out-of-plane bending and ν(CN) modes appear at 860, 824 and 2221–2150 cm^{-1}, respectively. In solution the copper(II) macrocycle and the TCNQ entities exist as independent species; anionic TCNQ exists as $(TCNQ)_2^{2-}$. Thus the solution electronic spectrum shows characteristic transitions of TCNQ species [20]. Two transitions due to locally excited levels (LE_1 and LE_2) appear at 842 and 394 nm, respectively. The intensity ratio of these two bands indicates the oxidation state of the TCNQ species. A ratio $\varepsilon(394/842)$ less than 0.5 indicates the presence of only anionic TCNQ, whereas a higher value indicates the presence of neutral TCNQ in solution [21]. In **2**, the ratio is 0.53, indicating that anionic TCNQ with a slightly reduced charge is present. The electronic spectrum of **3** gives the ratio $\varepsilon(394/842) = 4$. This suggests the presence of neutral TCNQ in solution in large amount. Since $Et_3NH(TCNQ)_2$ itself contains one anionic and one neutral TCNQ, the presence of neutral TCNQ in solution is expected. The higher ratio than for other reported complexes with $Et_3NH(TCNQ)_2$ may be attributed to partial reduction of charge on anionic TCNQ resulting in the formation of $(TCNQ)_3^-$ and $TCNQ^0$.

The EPR spectrum of complex **2** at room temperature exhibits a symmetric signal centred at $g = 2.003$ with a line width of 9.7 G. The observed g value corresponds to the value of 2.003 for $TCNQ^-$ alone [22] and the pattern is different from that observed for **1**. A similar EPR pattern is observed for **3**. It shows a very narrow signal at 2.004 with a line width 2 G, which points to the presence of small amounts of anionic TCNQ. In CH_3CN solution at room temperature, no significant change is observed. Magnetic moments of complexes **2** and **3** also confirm the presence of diamagnetic metal centres. Thus **2** and **3** are best formulated as copper(I) complexes in which each TCNQ carries an equal fractional charge in accord with the stoichiometries obtained from analysis. Solid state conductivities of **2** and **3** at room temperature are of the order of 10^{-10} S cm^{-1}, indicating that the complexes are weak conductors. This may be attributed to structural arrangements of TCNQ species in the complexes [23].

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 256498. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336-033; E-mail:deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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