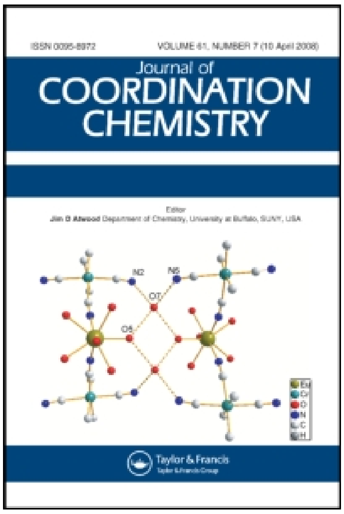

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Tetracyanoquinodimethane complexes of nickel(II) with an *N*,*O*-donor macrocycle

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A nickel(II) chelate, NiL^1Cl_2, has been obtained by reaction of nickel(II) chloride with a 15-membered *N*,*O*-donor macrocyclic ligand. Single-crystal X-ray studies reveal an octahedral environment around nickel(II). 7,7′,8,8′-Tetracyanoquinodimethane (tcnq) derivatives of the nickel(II) chelate were prepared by reaction with Litcnq and $Et_3N(tcnq)_2$. Spectroscopic measurements show the presence of only anionic tcnq in $[NiL_1(tcnq)_2]\cdot 4H_2O$ and a mixture of non-coordinating anionic and neutral tcnq species in $[NiL_1](tcnq)_4\cdot H_2O$.

Keywords: *N*,*O*-Donor macrocycle; 7,7′,8,8′-Tetracyanoquinodimethane; Nickel(II);
X-ray structure; Magnetism

1. Introduction

The chemistry of macrocyclic ligands can be divided into two major categories. The first involves polyether ‘crown’ compounds incorporating varying numbers of oxygen donor atoms and which have affinity for alkali and alkaline earth ions [1,2]. The second involves the incorporation of nitrogen, sulfur or phosphorus donors and displays affinity for transition metal ions [3,4]. Of these, ligands containing nitrogen donors have been extensively studied. In contrast, ligands containing mixed donor atoms have attracted relatively less but still very significant attention. The macrocyclic ligands often yield planar metal complexes which may act as donors in electron transfer reactions with 7,7′,8,8′-tetracyanoquinodimethane (tcnq) and other related compounds. The nature of the donor atoms as well as the molecular geometry and planarity of the metal chelates are important parameters with respect to electrical properties and magnetism of corresponding tcnq derivatives. In continuation of our studies [5,6] involving the chemistry of mixed heteroatom crowns, we have synthesized a nickel(II) chloride

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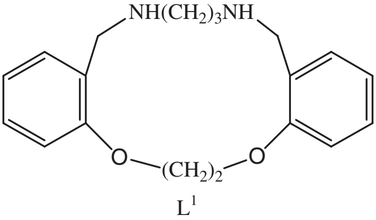
complex of an *N*,*O*-donor macrocycle, L^1. Herein we report its synthesis and structural characterization and some tcnq derivatives of the cationic complex.



L^1

2. Experimental

All reactions were carried out under dry nitrogen and solvents were dried and degassed before use. IR spectra were recorded using KBr pellets on a Pye Unicam SP3-300 spectrophotometer. Electronic spectra were recorded on a Shimadzu Graphicord 240 spectrophotometer. Variable temperature magnetic susceptibilities were recorded at BARC, Mumbai. The ligand L^1, Litcnq and $Et_3NH(tcnq)_2$ were prepared using reported methods [7,8].

2.1. *Syntheses*

2.1.1. [NiL^{1}Cl$_2$] (1). A warm methanol solution of L^1 (0.1 g, 0.32 mmol) was added to a warm solution of $NiCl_2 \cdot 6H_2O$ (1.52 g, 0.64 mmol) in methanol (5 cm^3). The mixture was stirred and heated for 30 min, during which time a green product precipitated. This was filtered off, washed with methanol and dried *in vacuo* (yield 77%). Anal. Calc. for $NiC_{19}H_{24}N_2O_2Cl_2$ (%): C, 51.70; H, 5.44; N, 6.35. Found: C, 51.68; H, 5.50; N, 6.34.

2.1.2. [NiL^1(tcnq)$_2$] · 4H$_2$O (2). A solution of Litcnq (0.095 g, 0.45 mmol) in methanol (10 cm^3) was added dropwise to a stirred solution of [NiL^{1}Cl$_2$] (0.10 g, 0.22 mmol) in ethanol : water (1 : 1, 10 cm^3). The mixture was stirred at room temperature for 6 h and the volume reduced at low pressure. The dark green product that formed was filtered off, washed with dry methanol and diethylether (anhydrous), and dried *in vacuo* (yield 74%). Anal. Calc. for $NiC_{43}H_{40}N_{10}O_6$ (%): C, 60.00; H, 4.70; N, 16.40. Found: C, 59.00; H, 4.0; N, 15.6.

2.1.3. [NiL^1(tcnq)$_4$] · H$_2$O (3). A solution of $Et_3NH(tcnq)_2$ (0.23 g, 0.45 mmol) in acetonitrile (20 cm^3) was added dropwise to a stirred solution of [NiL^{1}Cl$_2$] (0.10 g, 0.22 mmol) in ethanol : water (1 : 1, 10 cm^3). The mixture was stirred at room temperature for 6 h and the volume reduced at low pressure. The blackish green product that formed was isolated as above (yield 84%). Anal. Calc. for $NiC_{67}H_{42}N_{18}O_3$ (%): C, 66.70; H, 3.48; N, 20.9. Found: C, 65.96; H, 3.41; N, 19.00.

2.2. *Crystallography*

Crystals of the complex [NiL^{1}Cl$_2$] were grown by slow evaporation of a solution in chloroform. Crystal data: $C_{19}H_{24}N_2O_2Cl_2$, green plates, M_r 442.01, monoclinic, $a = 12.529(2)$, $b = 10.886(1)$, $c = 14.472(2)$ Å, $\beta = 92.94(1)^\circ$, $V = 1971.2(5)$ Å^3, $Z = 4$,

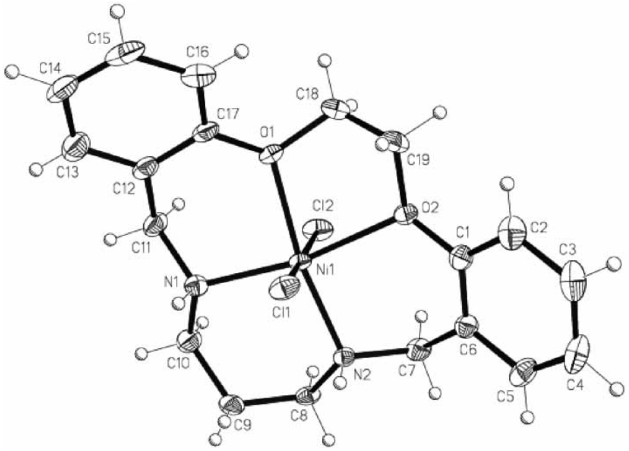


Figure 1. ORTEP view of [NiL^1Cl_2] showing the atom numbering scheme.

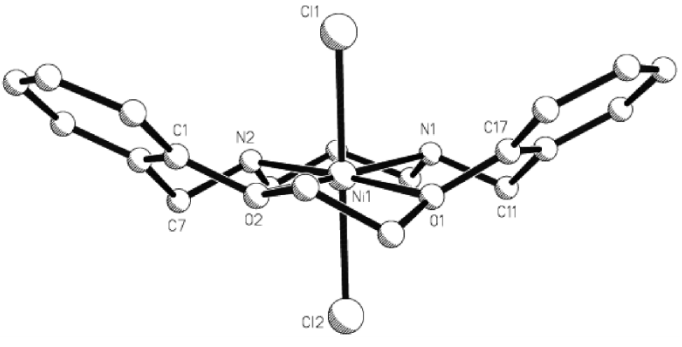


Figure 2. Perspective view of the molecule perpendicular to the Cl–Ni–Cl axis.

$D_c = 1.489\,\mathrm{g\,cm^{-3}}$; range for data collection (θ) 2.10–25.0°, range of indices measured $h = 0$ to 2, $k = 0$ to 12, $l = -17$ to 17, independent reflections 3397, unique reflections 3228, refinement by full-matrix least-squares on F^2 (SHELXL 93); data/restraints/parameters 3226/0/235, goodness of fit on F^2 1.061, final R indices [$I = 2\sigma(I)$] $R_1 = 0.0632$, $wR_2 = 0.1395$, R indices (all data) $R_1 = 0.1259$, $wR_2 = 0.1739$. Largest difference peak and hole 0.518 and $-0.445\,\mathrm{e\,\AA^{-3}}$.

3. Results and discussion

An ORTEP drawing of [NiL^1Cl_2] is shown in figure 1. Nickel(II) lies at the centre of the macrocyclic cavity and is coordinated by the both nitrogen and oxygen atoms of the macrocycle in equatorial positions and two chloride ions in axial positions leading to slightly distorted octahedral geometry. The conformation of the complex is akin to that of an open book (figure 2). Data concerning bond lengths, bond angles and atomic coordinates are given in tables 1 and 2. Corresponding tcnq derivatives of the complex were prepared by reacting it with Litcnq and $Et_3NH(tcnq)_2$. The complexes

Table 1. Bond lengths (Å) and angles (°) for the complex [NiL^1Cl_2].

Ni–N(1)	2.020(5)	Ni–N(2)	2.055(6)
Ni–O(2)	2.104(5)	Ni–O(1)	2.211(5)
Ni–Cl(1)	2.393 (2)	Ni–Cl(2)	2.410(2)
O(1)–C(1)	1.393(9)	O(1)–C(19)	1.462(8)
O(2)–C(17)	1.389(9)	O(2)–C(18)	1.467(9)
N(1)–C(7)	1.481(9)	N(1)–C(8)	1.493(8)
N(2)–C(11)	1.480(9)	N(2)–C(10)	1.489(9)
C(1)–C(6)	1.387(10)	C(1)–C(2)	1.396(11)
C(2)–C(3)	1.378(12)	C(3)–C(4)	1.385(13)
C(4)–C(5)	1.357(12)	C(5)–C(6)	1.386(10)
C(6)–C(7)	1.509(10)	C(8)–C(9)	1.523(10)
C(9)–C(10)	1.529(10)	C(11)–C(12)	1.526(11)
C(12)–C(13)	1.379(11)	C(12)–C(17)	1.398(11)
C(13)–C(14)	1.379(12)	C(14)–C(15)	1.366(13)
C(15) –C(16)	1.368(12)	C(16)–C(17)	1.372(11)
C(18)–C(19)	1.476(12)		
N(1)–Ni–N(2)	100.2(2)	O(1)–Ni–Cl(2)	86.7(2)
N(2)–Ni–O(2)	98.4(2)	C(1)–O(1)–C(19)	116.3(6)
N(2)–Ni–O(2)	167.9(2)	C(19)–O(1)–Ni	108.2(4)
N(1)–Ni–Cl(1)	92.9(2)	C(17)–O(2)–Ni	122.5(4)
O(2)–Ni–Cl(1)	85.8(2)	C(7)–N(1)–C(8)	110.2(5)
N(1)–Ni–Cl(2)	90.7(2)	C(8)–N(1)–Ni	114.0(4)
O(2)–Ni–Cl(2)	90.0(2)	C(11)–N(2)–Ni	112.8(5)
Cl(1)–Ni–Cl(2)	174.6(1)	C(6)–C(1)–O(1)	116.3(7)
C(1)–O(1)–Ni	118.7(4)	O(1)–C(1)–C(2)	122.5(7)
C(17)–O(2)–C(18)	122.2(6)	C(4)–C(3)–C(2)	120.1(9)
C(18)–O(2)–Ni	109.8(4)	C(4)–C(5)–C(6)	123.2(8)
C(7)–N(1)–Ni	111.2(4)	C(1)–C(6)–C(7)	123.2(7)
C(11)–N(2)–C(10)	110.4(6)	N(1)–C(7)–C(6)	111.9(6)
C(10)–N(2)–Ni	113.5(5)	C(8)–C(9)–C(10)	115.4(6)
C(6)–C(1)–C(2)	121.2(8)	N(2)–C(11)–C(12)	112.1(6)
C(3)–C(2)–C(1)	119.3(8)	C(13)–C(12)–C(17)	117.8(8)
C(5)–C(4)–C(3)	119.2(9)	C(17)–C(12)–C(11)	121.6(7)
C(1)–C(6)–C(5)	116.9(7)	C(15)–C(14)–C(13)	119.4(9)
C(5)–C(6)–C(7)	119.9(7)	C(15)–C(16)–C(17)	118.8(9)
N(1)–C(8)–C(9)	111.2(6)	C(16)–C(17)–C(12)	121.5(8)
N(2)–C(10)–C(9)	113.3(6)	O(2)–C(18)–C(19)	110.5(6)
N(1)–Ni–O(2)	170.4(2)	C(13)–C(12)–C(11)	120.5(8)
N(1)–Ni–O(1)	91.3(2)	C(14)–C(13)–C(12)	121.0(9)
O(2)–Ni–O(1)	79.2(2)	C(14)–C(15)–C(16)	121.5(9)
N(2)–Ni–Cl(1)	93.8(2)	C(16)–C(17)–O(2)	123.9(8)
O(1)–Ni–Cl(1)	89.2(2)	O(2)–C(17)–C(12)	114.6(7)
N(2)–Ni–Cl(2)	89.6(2)	O(1)–C(19)–C(18)	106.8(7)

formed have stoichiometries [$NiL^1(tcnq)_2$] $\cdot$ $4H_2O$ and [NiL^1]$(tcnq)_4 \cdot H_2O$, respectively. [$NiL^1(tcnq)_2$] $\cdot$ $4H_2O$ contains only anionic tcnq and shows bands characteristic of the anion radical in its IR spectrum [$\nu(CN) = 2196$, $2177\,cm^{-1}$; $\nu(CC) = 1577$, $1504\,cm^{-1}$; $\delta(CH) = 820$–$834\,cm^{-1}$]. IR spectra of [NiL^1]$(tcnq)_4 \cdot H_2O$ are very broad in the range 1700–4000 cm^{-1}, indicating electron delocalization [$\nu(CN)$ appears as a broad band at $2154\,cm^{-1}$, $\nu(CC)$ at 1500–1549 cm^{-1} and $\delta(CH)$ at 833 and $865\,cm^{-1}$]. The band at $865\,cm^{-1}$ is due to neutral tcnq [9,10]. Solution electronic spectra of anionic tcnq show two peaks at 842 and $395\,cm^{-1}$ with intensity ratio $\varepsilon(395/842)$ equal to 0.5, whereas neutral tcnq shows only one peak at $395\,cm^{-1}$. An intensity ratio greater than 0.5 shows the presence of both anionic and neutral tcnq. In [$NiL^1(tcnq)_2$] $\cdot$ $4H_2O$ the intensity ratio of 0.5 indicates the presence of only anionic tcnq, but in [NiL^1]$(tcnq)_4 \cdot H_2O$, the ratio 1.9 indicates the presence of neutral as well as anionic

Table 2. Final atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å $\times 10^3$] for **1**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Ni	3639(1)	2166(1)	5923(1)	26(1)
Cl(1)	3871(2)	4257(2)	6401(2)	43(1)
Cl(2)	3331(2)	26(2)	5579(1)	37(1)
O(1)	4103(4)	1573(5)	7348(3)	34(1)
O(2)	2158(4)	2262(5)	6543(3)	37(1)
N(1)	5163(4)	2021(5)	5544(4)	26(1)
N(2)	2888(5)	2626(5)	4675(4)	30(2)
C(1)	4970(6)	781(7)	7486(5)	34(2)
C(2)	4956(7)	−219(8)	8090(6)	49(2)
C(3)	5859(8)	−931(9)	8223(7)	56(3)
C(4)	6751(8)	−696(9)	7725(7)	58(3)
C(5)	6741(6)	279(8)	7140(6)	44(2)
C(6)	5865(6)	1046(7)	6697(5)	33(2)
C(7)	5928(6)	2132(7)	6354(5)	36(2)
C(8)	5446(6)	2904(7)	4806(5)	32(2)
C(9)	4675(6)	2799(8)	3961(5)	38(2)
C(10)	3570(6)	3360(8)	4068(6)	44(2)
C(11)	1849(6)	3245(8)	4778(6)	40(2)
C(12)	1034(6)	2399(7)	5200(6)	37(2)
C(13)	83(7)	2126(9)	4722(6)	51(2)
C(14)	−669(7)	1384(9)	5106(7)	56(3)
C(15)	−452(7)	879(9)	5959(8)	54(3)
C(16)	480(7)	1127(8)	6457(6)	48(2)
C(17)	1207(6)	1903(7)	6087(5)	36(2)
C(18)	3236(7)	2186(9)	7552(5)	51(2)
C(19)	3132(6)	1241(9)	7808(5)	49(2)

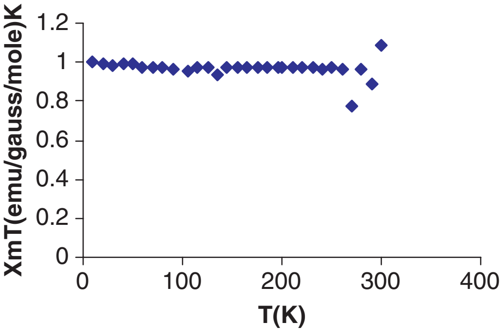


Figure 3. XmT as a function of temperature for [NiL$_1$(tcnq)$_2$].

tcnq [11–13]. Magnetic susceptibilities of the complexes have been measured over the temperature range 2–300 K. [NiL^1](tcnq)$_4 \cdot H_2O$ obeys the Curie Weiss law (figure 3); the Curie constant is 1.12 emu/gauss K mole^{-1}. The effective magnetic moment obtained using the relation $\mu_{\text{eff}} = 2.83\,C^{1/2}$ is 2.99 μ_B, which corresponds to octahedral nickel(II). There is no contribution from tcnq, which suggests that anionic tcnq is present as an antiferromagnetically coupled (tcnq)$_2^{-2}$ dimer [13,14]. [NiL^1](tcnq)$_4 \cdot H_2O$ is weakly paramagnetic, indicating square planar geometry. The weak paramagnetism may be due to the presence of small amounts of anionic tcnq impurities, as evidenced by the very low *C* value 5.6×10^{-4} emu/gauss K mole^{-1} (figure 4) [15].

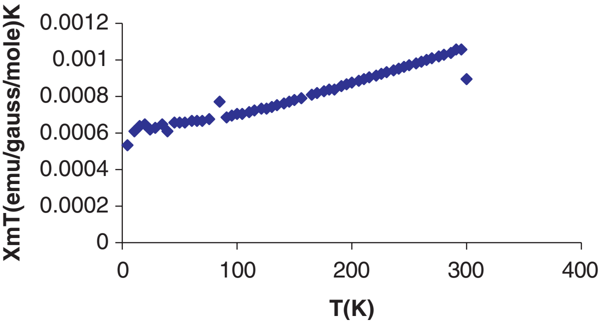


Figure 4. XmT as a function of temperature for $[NiL_1](tcnq)_4$.

Supplementary data

Crystallographic data (excluding structure factors) for the structure of **1** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication CCDC 256499. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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