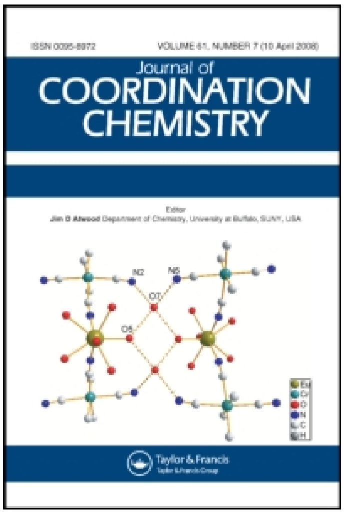

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Synthesis and characterization of TCNQ derivatives of Ni(II) and Cu(II) with pyrazole-based ligands

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Reactions between nickel(II) and copper(II) salts $[M(L)_n](ClO_4)_2$ [L: 2-(pyrazole-1-ylmethyl)-pyridine; $n=3$ for Ni(II) and $n=2$ for Ni(II) and Cu(II)] and LiTCNQ or mixture of LiTCNQ/TCNQ and $Et_3NH(TCNQ)_2$ yielded $[Ni(L)_3](TCNQ)_2 \cdot H_2O$, $[Ni(L)_2(TCNQ)_2]$, $[Ni(L)_3](TCNQ)_3$, $[Ni(L)_2(TCNQ)_3]$, and $[Cu(L)_2(TCNQ)_3] \cdot 3H_2O$. These complexes were characterized by infrared, electronic absorption, variable temperature magnetic moments and electron paramagnetic studies. Magnetic moments increase with increase in temperature attributed to contribution from TCNQ, which has also been examined by electron paramagnetic resonance.

Keywords: Pyrazole-based ligand; Nickel(II) and copper(II) complexes; 7,7′,8,8′-Tetracyanoquinodimethane; Variable temperature magnetic moments; Electron paramagnetic resonance studies

1. Introduction

Like polyazamacrocyclic ligands, pyrazole-based ligands form a variety of coordination complexes with metal ions. A review by Mukherjee describes the coordination chemistry of a number of pyrazole-based ligands [1]. Pyrazole is a poor π-acceptor with good π-donor ability; in combination with another heterocycle donor such as pyridine with an insulating linker, furnishes metal complexes with interesting properties [2]. With the vast array of coordination complexes of pyrazole-based ligands, there are few instances of donor acceptor complexes. In continuation of our ongoing interest [3–6] in the synthesis and investigation of charge transfer complexes, we thought that 7,7,8,8-tetracyanoquinodimethane (TCNQ), a good π-acceptor, could form derivatives with metal chelates of pyrazole-based ligands, capable of exhibiting interesting physical and chemical properties. Herein, we report the synthesis and characterization of TCNQ derivatives of nickel(II) and copper(II) chelates derived from 2-(pyrazole-1-ylmethyl) pyridine, (**L**).

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2. Experimental

2.1. *Reagents and physical measurements*

All reactions were carried out under a blanket of nitrogen and dry solvents were used. The starting materials, LiTCNQ and $Et_3NH(TCNQ)_2$, were prepared by following published methods [7] and their purity was checked by elemental analyses. ^1H NMR spectra were run on Bruker AC 200/300 MHz instruments using tetramethylsilane (TMS) as internal standard. Infrared spectra were recorded on a Shimadzu DR-8001 FT infrared spectrophotometer using KBr pellets. UV–Visible solution spectra were obtained on a Shimadzu 1601 PC spectrophotometer. Elemental analyses of the solid samples were performed on a Thermoelectron FLASH EA1112, CHNS analyzer. Variable temperature magnetic studies and electron paramagnetic resonance (X-band) studies were performed at Bhaba Atomic Research Centre (BARC), Bombay.

2.2. *Synthesis*

2.2.1. Synthesis of 2-(pyrazole-1-ylmethyl) pyridine (L). A mixture of 2-(chloromethyl)pyridine hydrochloride (2.60 g, 0.016 mol), pyrazole (1.00 g, 0.018 mol), benzene (190 mL), 40% aqueous sodium hydroxide (24 mL) and 40% aqueous tetrabutylammonium hydrogen sulphate (15 drops) was refluxed for 6 h and then stirred at room temperature overnight. The organic layer was then separated, dried over Na_2SO_4 and evaporated under reduced pressure to yield an oil (Yield 90%). The structure of **L** [8] was checked by ^1H NMR spectrum recorded in $CDCl_3$, which showed signals at δ 5.46 (s, 2H, $-C\underline{H}_2-$), 6.32 (m, 1H, pyrazolyl C-4$\underline{H}$), 6.95 (d, 1H, Ar$\underline{H}$), 7.22 (m, 1H, Ar$\underline{H}$), 7.58 (m, 3H, Ar$\underline{H}$), 8.56 (m, 1H, Ar$\underline{H}$).

2.2.2. Synthesis of $[Ni(L)_3](ClO_4)_2$ [9] (1). $Ni(ClO_4)_2 \cdot 6H_2O$ (0.76 g, 0.002 mol) was added in portions to an ethanolic solution (25 mL) of **L** (1.0 g, 0.006 mol) with stirring. The mixture was stirred at room temperature for 2 h, whereupon a violet product separated; crystallization from acetonitrile furnished violet crystalline compound, which was filtered, washed with ethanol and dried under vacuum. Yield 75%. Calcd for $NiC_{27}H_{27}N_9Cl_2O_8$ (%): C, 44.09; H, 3.67; N, 17.15. Found: C, 43.90; H, 3.90; N, 16.83.

2.2.3. Synthesis of $[Ni(L)_2(ClO_4)_2] \cdot H_2O$ (2). A solution of **L** (1.0 g, 0.006 mol) in ethanol (5 mL) was added to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1.15 g, 0.003 mol) in ethanol (5 mL) with stirring. After some time, bluish grey product separated. The resulting product was recrystallized from acetonitrile, filtered, washed with ethanol and dried under vacuum. Yield: 75%. Calcd for $NiC_{18}H_{20}N_6Cl_2O_9$ (%): C, 36.38; H, 3.03; N, 14.1. Found: C, 35.72; H, 3.76; N, 13.93.

2.2.4. Synthesis of $[Cu(L)_2(ClO_4)_2]$ (3). A solution of ligand **L** (0.1 g, 0.6 mmol) in ethanol (5 mL) was added to the solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.12 g, 0.3 mmol) in ethanol (5 mL) with stirring. After some time, light blue product separated, was recrystallized from acetonitrile, filtered, washed with ethanol and dried under vacuum. Yield: 90%. Calcd for $CuC_{18}H_{18}N_6Cl_2O_8$ (%): C, 37.20; H, 3.10; N, 14.48. Found: C, 37.66; H, 3.24; N, 14.55.

2.2.5. Synthesis of [Ni(L)$_3$](TCNQ)$_2\cdot$H$_2$O (4). A solution of LiTCNQ (0.86 g, 0.004 mol) in dry methanol (10 mL) was added dropwise to a stirred solution of **1** (1.5 g, 0.002 mol) in acetonitrile (5 mL) under nitrogen. The reaction mixture was stirred for 2 h; dark blue solid precipitated, was filtered, washed with methanol and diethyl ether and dried under vacuum. Yield: 52%. Calcd for $NiC_{51}H_{37}N_{17}O$ (%): C, 63.63; H, 3.85; N, 24.76. Found: C, 62.85; H, 3.71; N, 24.17.

2.2.6. Synthesis of [Ni(L)$_3$](TCNQ)$_3$ (5). A solution of LiTCNQ (0.86 g, 0.004 mol) in methanol (10 mL) and neutral TCNQ (0.42 g, 0.002 mol) in acetonitrile (15 mL) was added dropwise to a stirred solution of **2** (1.5 g, 0.002 mol) in methanol (5 mL) under nitrogen. The reaction mixture was stirred at room temperature for about 1 h and the solvent concentrated under reduced pressure. Blackish blue solid was filtered, washed with methanol and diethyl ether, and dried under vacuum. Yield: 40%. Calcd for $NiC_{63}H_{39}N_{21}$ (%): C, 65.90; H, 3.40; N, 25.60. Found: C, 66.21; H, 3.45; N, 25.02.

2.2.7. Synthesis of [Ni(L)$_2$(TCNQ)$_2$] (6). A solution of LiTCNQ (0.85 g, 0.004 mol) in dry methanol (10 mL) was added dropwise to a stirred solution of **2** (1.2 g, 0.002 mol) in acetonitrile (5 mL) under nitrogen. The reaction mixture was stirred for 2 h. Blue solid was filtered, washed with methanol and diethyl ether, and dried under vacuum. Yield: 42%. Calcd for $NiC_{42}H_{26}N_{14}$ (%): C, 64.23; H, 3.31; N, 24.97. Found: C, 63.68; H, 4.1; N, 21.97.

2.2.8. Synthesis of [Ni(L$_1$)$_2$(TCNQ)$_3$ (7). A solution of $Et_3NH(TCNQ)_2$ (2.08 g, 0.004 mol) in dry acetonitrile (15 mL) was added dropwise to a stirred solution of **2** (1.2 g, 0.002 mol) in methanol (5 mL) under nitrogen. The reaction mixture was stirred for 2 h. The blackish blue solid which formed was filtered, washed with diethyl ether, and dried under vacuum. Yield: 44%. Calcd for $NiC_{54}H_{30}N_{18}$ (%): C, 65.54; H, 3.03; N, 25.48. Found: C, 65.07; H, 3.15; N, 25.38.

2.2.9. Synthesis of [Cu(L)$_2$(TCNQ)$_3$]$\cdot$3H$_2$O (8). A solution of LiTCNQ (0.87 g, 0.004 mol) in methanol (10 mL) and neutral TCNQ (0.42 g 0.002 mol) in acetonitrile (15 mL) was added dropwise to a stirred solution of **3** (1.2 g, 0.002 mol) in methanol (5 mL) under nitrogen. The reaction mixture was stirred at room temperature for about 1 h and the solvent concentrated under reduced pressure. The blackish blue solid which formed was filtered, washed with methanol and diethyl ether, and dried under vacuum. Yield: 40%. Calcd for $CuC_{54}H_{36}N_{18}O_3$ (%): C, 61.8; H, 3.40; N, 24.05. Found: C, 61.68; H, 3.45; N, 24.14.

Hazardous effects: Benzene is carcinogenic. Care must be taken.

3. Results and discussion

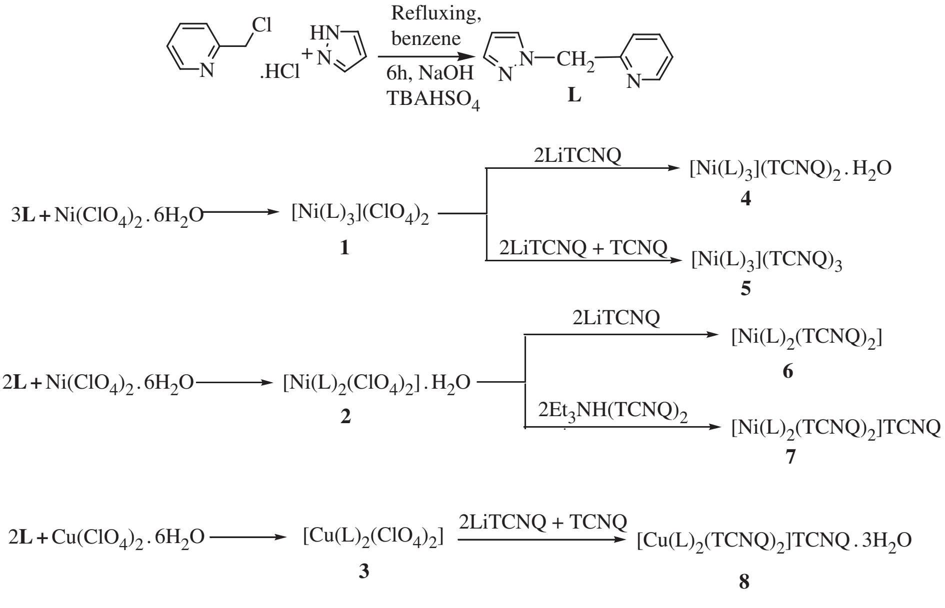
3.1. *Synthesis of the complexes*

The formation of the complexes is shown in scheme 1.

The ligand **L** reacts with the $Ni(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ to yield **1**–**3**. The purity of these complexes was checked by different spectroscopic studies. These complexes were further reacted with TCNQ in different electronic states to yield **4**–**8**. All the complexes were characterized by spectroscopic techniques.

3.2. *Infrared spectral studies*

Complexes **1**–**3** have characteristic perchlorate bands. The broad intense band at 1022–1149 cm^{-1} in **1** shows no splitting indicating uncoordinated perchlorate, whereas the broad split bands in the range of 1068–1149 and 1076–1166 cm^{-1} for **2** and **3**, respectively, indicate coordinated perchlorate [10, 11]. The disappearance of these bands in **4**–**8** indicates replacement of perchlorate with TCNQ groups. Since coordination of three diamine ligands, $[M(L)_3]^{2+}$, gives a stable coordination environment to the metal center in **1**, the reaction of this complex with LiTCNQ takes place simply by replacement of the counterions. Therefore in the resulting complexes **4** and **5**, it has been proposed that TCNQ remains as uncoordinated dimer $(TCNQ)_2^{2-}$ and uncoordinated trimer $(TCNQ)_3^{2-}$, respectively. IR spectra have been used to derive information about the electronic states and the coordination of TCNQ in complexes [12]. The most characteristic bands of neutral TCNQ are $\nu(C{\equiv}N) = 2228$, $\nu(C{=}C) = 1545$ and $\delta(C\text{–}H) = 862\,cm^{-1}$. For the anionic $TCNQ^{-1}$, these vibrational modes are observed at 2194/2174, 1583/1503 and 828 cm^{-1}, respectively. In anionic $TCNQ^{-}$, the $\nu(C{\equiv}N)$ is split and shifted to lower frequency, which is attributable to the



Scheme 1. The formation of complexes **1**–**8**.

lowering of the symmetry in nitrile groups. In the IR spectrum of **4**, these bands appear at 2190/2154, 1573 and 825 cm^{-1}, respectively, indicating the presence of anionic TCNQ^{-1}. A different IR spectral pattern is obtained for **5**, with ν(C≡N), ν(C=C) and δ(C–H) at 2210/2169, 1573/1506 and 858/823 cm^{-1}, respectively, consistent with the presence of neutral as well as anionic TCNQ^{-1}.

In **2**, [Ni(L)$_2$(ClO$_4$)$_2$], the axial positions are occupied by perchlorate (inferred from the IR spectrum). In line with this, in the resulting TCNQ derivative **6** also, it is suggested that these positions are occupied by anionic TCNQ^{-1}. The presence of anionic TCNQ is further supported by the IR spectrum of **6**, which is similar to that of **4**. The ν(C≡N), ν(C=C) and δ(C–H) bands appear at the positions assigned to the anionic TCNQ^{-1}, 2187/2140, 1577/1502 and 825 cm^{-1}, respectively. The IR spectral pattern exhibited by **7** is different from **4**–**6**, especially in the region of δ(C–H), which shows a band at 840 cm^{-1} in addition to 827 cm^{-1}, indicating the presence of quasineutral TCNQ moieties [13]. The ν(C≡N) and ν(C=C) appear at 2189/2177/2160 and 1579/1502 cm^{-1}, respectively. The IR spectral pattern of **8** is almost identical to that of **5** with ν(C≡N), ν(C=C) and δ(C–H) bands at 2210/2169, 1542/1506 and 860/823 cm^{-1}, respectively, indicating the presence of neutral and anionic TCNQ^{-1}.

3.3. *Electron absorption spectral data*

The electronic absorption spectra of these systems in solution are less informative because in solution the metal-TCNQ interaction is diminished resulting in independent absorptions due to isolated cationic metal complex and the TCNQ groups, but it does decipher the electronic status of TCNQ. The anionic TCNQ^{-1} shows two locally excited levels at 842 and 395 nm, and the neutral TCNQ shows single absorption at 395 nm. From the intensity ratio $\varepsilon(395)/\varepsilon(842)$ (≤ 0.5), the presence of anion species can be discerned, whereas from the intensity ratio greater than 0.5, presence of neutral TCNQ can be inferred [14]. In **4** and **6** the ratio equal to 0.5 indicates the presence of anionic TCNQ^{-1} whereas the intensity ratio, 1.1, in **5**, **7** and **8** indicates the presence of neutral TCNQ. These electronic absorption studies support the observations made on the basis of IR spectral studies.

3.4. *Magnetic and electron paramagnetic resonance studies*

The magnetic data for the complexes were recorded in the range of 5–300 K. The magnetic moments calculated by employing the relation, $\mu_{\text{eff}} = 2.83C^{1/2}$, correspond to the presence of nickel(II) in octahedral and copper(II) in distorted octahedral environment with two and one unpaired electrons, respectively. However, the magnetic moments increase with increase in temperature, especially beyond 100 K, indicating that the anionic TCNQ^{-1} is contributing to the total paramagnetism at higher temperature due to the population of the excited triplet state [15] (figure 1). For the copper complex at 0–10 K, the magnetic moment is less (1.43 BM) than the value expected for one unpaired electron. This decrease is due to the antiferromagnetic interaction (table 1, figure 1). The EPR spectrum of the precursor complex **3**, [Cu(L)$_2$(ClO$_4$)$_2$], is characteristic of the axially elongated octahedral with hyperfine splitting with $g_{11} = 2.27$, $g_{\perp} = 2.02$, $A_{11} = 180$ G (figure 2) [16]. No hyperfine splitting is

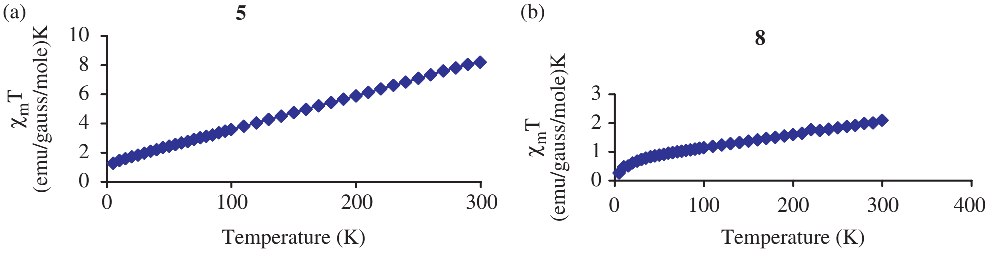


Figure 1. Variation of $\chi_m T$ of **5** and **8** with temperature.

Table 1. Magnetic moment data for the TCNQ complexes.

Complex	Temperature (K)	$\mu_{eff} = 2.83C^{1/2}$ (BM)
$[Ni(L)_3](TCNQ)_2 \cdot H_2O$ (**4**)	5	3.16
	300	4.48
$[Ni(L)_3](TCNQ)_3$ (**5**)	5	2.9
	300	5.09
$[Ni(L)_2(TCNQ)_2]$ (**6**)	5	3.18
	300	**5.11**
$[Ni(L)_2(TCNQ)_3]$ (**7**)	5	2.81
	300	4.56
$[Cu(L)_2(TCNQ)_3] \cdot 3H_2O$ (**8**)	5	1.45
	300	4.04

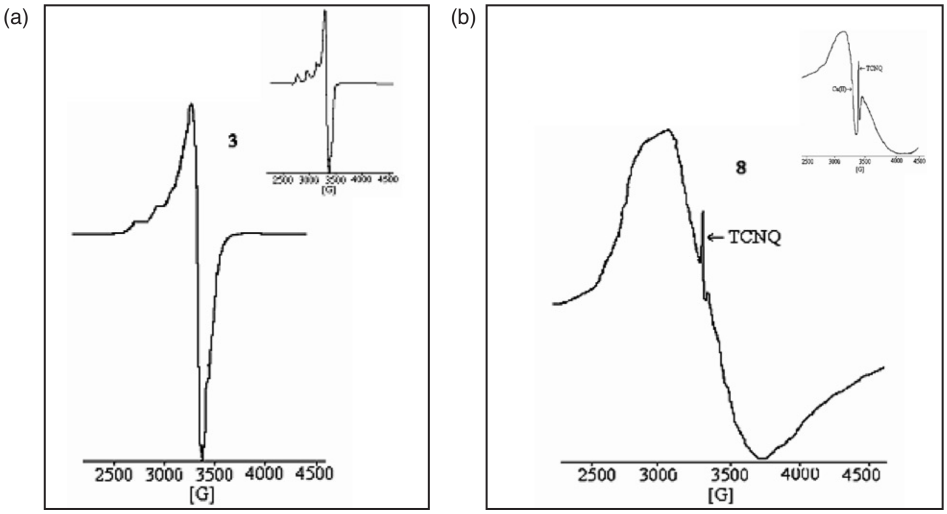


Figure 2. EPR spectra of **3**(a) and **8**(b) in solid state at room temperature. Inset: **3** and **8** in DMSO at 77 K.

observed in the spectrum of the TCNQ complex **8**, $[Cu(L)_2(TCNQ)_3] \cdot 3H_2O$, which shows a signal at $g = 2.03$ attributed to copper(II) accompanied by a very narrow band ($\Delta H = 2$–4 G) at $g = 2.0$ attributed to anionic TCNQ [15] (figure 2). This is in good agreement to that of the magnetic moment results.

4. Conclusions

The TCNQ derivatives of the nickel(II) and copper(II) complexes with pyrazole-based ligands have been prepared as saturated and unsaturated coordination environments. The electronic status of TCNQ is found to be anionic, neutral/anionic and quasineutral. From the variable temperature magnetic studies, it is evident that TCNQ contributes to the total magnetism of the complexes at high temperature, attributable to the population of its excited triplet state. The EPR spectrum of the copper(II) complex shows the peak attributed to anionic TCNQ in addition to the copper(II) band.

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References

[1] R. Mukherjee. *Coord. Chem. Rev.*, **203**, 151 (2000).
[2] E.C. Constable, P.J. Steel. *Coord. Chem. Rev.*, **93**, 205 (1989).
[3] P. Kaur, W.T. Robinson, K. Singh. *J. Coord. Chem.*, **55**, 281 (2002).
[4] P. Kaur, A. Sarangal, E. McInnes, W.T. Robinson. *J. Coord. Chem.*, **57**, 797 (2004).
[5] P. Kaur, A. Sarangal, G. Hundal, T.V. Chandrasekhar Rao. *J. Coord. Chem.*, **56**, 495 (2005).
[6] P. Kaur, A. Sarangal, E. McInnes, G. Hundal. *J. Coord. Chem.*, **59**, 821 (2006).
[7] L.R. Melby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson, W.E. Mochel. *J. Am. Chem. Soc.*, **84**, 3374 (1962).
[8] P.J. House, P.J. Steel, A.A. Watson. *Aust. J. Chem.*, **39**, 1525 (1986).
[9] T.K. Lal, R. Mukherjee. *Polyhedron*, **16**, 3577 (1997).
[10] X.Y. Xu, Q.H. Luo, M.C. Shen, X.Y. Huang, Q.J. Wu. *Polyhedron*, **16**, 915 (1997).
[11] H. Keypour, S. Salehzadeh, R.G. Pritchard, R.U. Parish. *Polyhedron*, **19**, 1633 (2000).
[12] R. Bozio, A. Girbano, C. Pecile. *J. Chem. Soc., Faraday Trans.*, **71**, 1237 (1975).
[13] E. Ghezzal, A. Brau, J.P. Farges, P. Dupis. *Mol. Cryst. Liq. Cryst.*, **211**, 327 (1992).
[14] M. Schwartz, E. Hatfield. *Inorg. Chem.*, **26**, 2823 (1987).
[15] L. Ballesher, A.M. Gil, A. Gutierrez, M.F. Perpinam, M.T. Azcondo, A.E. Sanchez, C. Marzin, G. Tarrago, C. Bellito. *Chem. Eur. J.*, **8**, 2539 (2002).
[16] B.J. Hathaway, D.E. Billing. *Coord. Chem. Rev.*, **5**, 143 (1970).