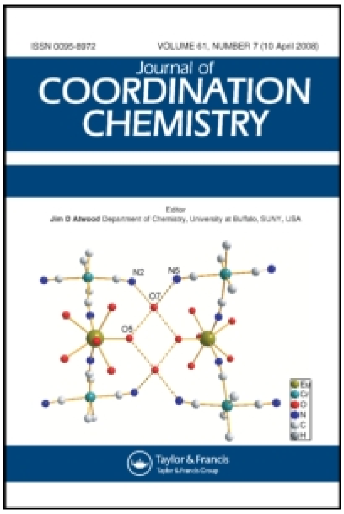

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Tetracyanoquinodimethane Derivatives of Pentagonal Bipyramidal Complexes of Manganese(II), Iron(II), Nickel(II) and Copper(II) with 2,6-diacetylpyridinebis(semicarbazone): Single Crystal Structure of dichloro[2,6-diacetylpyridinebis (semicarbazone)] Manganese(II)monohydrate

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TETRACYANOQUINODIMETHANE DERIVATIVES OF PENTAGONAL BIPYRAMIDAL COMPLEXES OF MANGANESE(II), IRON(II), NICKEL(II) AND COPPER(II) WITH 2,6-DIACETYLPYRIDINEBIS(SEMICARBAZONE): SINGLE CRYSTAL STRUCTURE OF DICHLORO[2,6-DIACETYLPYRIDINEBIS (SEMICARBAZONE)] MANGANESE(II)MONOHYDRATE

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By using the donor ligand 2,6-diacetylpyridinebis(semicarbazone) (DAPSC), pentagonal bipyramidal complexes of Mn(II), Fe(II), Ni(II) and Cu(II) have been obtained. The structure of $[MnCl_2(DAPSC)] \cdot H_2O$ has been determined by X-ray crystallography. Further reactions of these complexes with lithium salts of 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) yielded their corresponding adducts.

Keywords: Pentagonal bipyramidal; Semicarbazone; Tetracyanoquinodimethane; Diacetylpyridine; Charge transfer complex

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There has been considerable interest in the synthesis of 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) derivatives of transition metal chelates containing the ligand partner with different donor sets of N, O and S due to their interesting physical properties [1], *e.g.*, electrical conductivity and magnetism. Also, because the nature of the donor atoms in the ligand can optimise the metal redox potential of the chelates, reaction with TCNQ leads to the formation of charge transfer complexes having better electrical conductivities. The planarity of the metal chelates is a prerequisite for the favourable formation of these charge transfer complexes. In continuation of our interest [2] in the synthesis of charge transfer complexes, we report herein syntheses of pentagonal bipyramidal complexes of Mn(II), Fe(II), Ni(II) and Cu(II), using DAPSC as a macrocyclic donor system and as well as their respective TCNQ derivatives. To demonstrate some key structural features leading to anomalous epr behaviour during the syntheses [3] of metal chelates, suitable crystals of the complex dichloro[2,6-diacetylpyridinebis(semicarbazone)]manganese(II)monohydrate, $MnCl_2(DAPSC)] \cdot H_2O$ were obtained and its structure determined. A diagram of the structure, as determined by X-ray diffraction [4] methods is shown in Figure 1 and the coordination geometry is most conveniently described as pentagonal bipyramidal. The five equatorial sites of a planar pentagon are occupied by the three nitrogen and two oxygen atoms from the planar DAPSC ligand and the two chlorine atoms lead to pentagonal bipyramidal stereochemistry about the central metal atom.

IR spectra of complexes $Mn(DAPSC)(TCNQ)_2$ (1), $Fe(DAPSC)(TCNQ)_2$ (2), $Ni(DAPSC)(TCNQ)_2$ (3) and $Cu(DAPSC)(TCNQ)_2$ (4) show a strong $\nu(C{\equiv}N)$ band in the range $2130-2190\,cm^{-1}$ characteristic of $TCNQ^{-1}$. By examining the IR spectra in the regions $1500-1550\,cm^{-1}$ and $800-850\,cm^{-1}$, it is possible to determine the charge distribution on TCNQ, *i.e.*, whether it exists as $TCNQ^{2-}$, $TCNQ^{-1}$, $TCNQ^{\delta-}$ or TCNQ as the b_{1u} mode of TCNQ is sensitive to the charge distribution on TCNQ. A stretch appears [7, 8] at $1545\,cm^{-1}$ for the neutral molecule and at $1508\,cm^{-1}$ for singly charged TCNQ. Further, these complexes show only a single absorption in the range $800-850\,cm^{-1}$ attributed to δ(C—H), a clear indication of the presence of $TCNQ^{-1}$. The Ag activated modes in the range $1580-320\,cm^{-1}$ indicate the presence of the anionic TCNQ as the dimer $(TCNQ)_2^{2-}$ in the solid state. The electronic absorption spectrum of coordinated $TCNQ^{-1}$ has been shown to be similar to that of the free anion [9, 10]. Further, spectra in solution show mainly two transitions corresponding to locally excited levels LE_1 and LE_2 at *ca* 11900 and $25400\,cm^{-1}$ and the absorption ratio of these two transitions can also be used to deduce

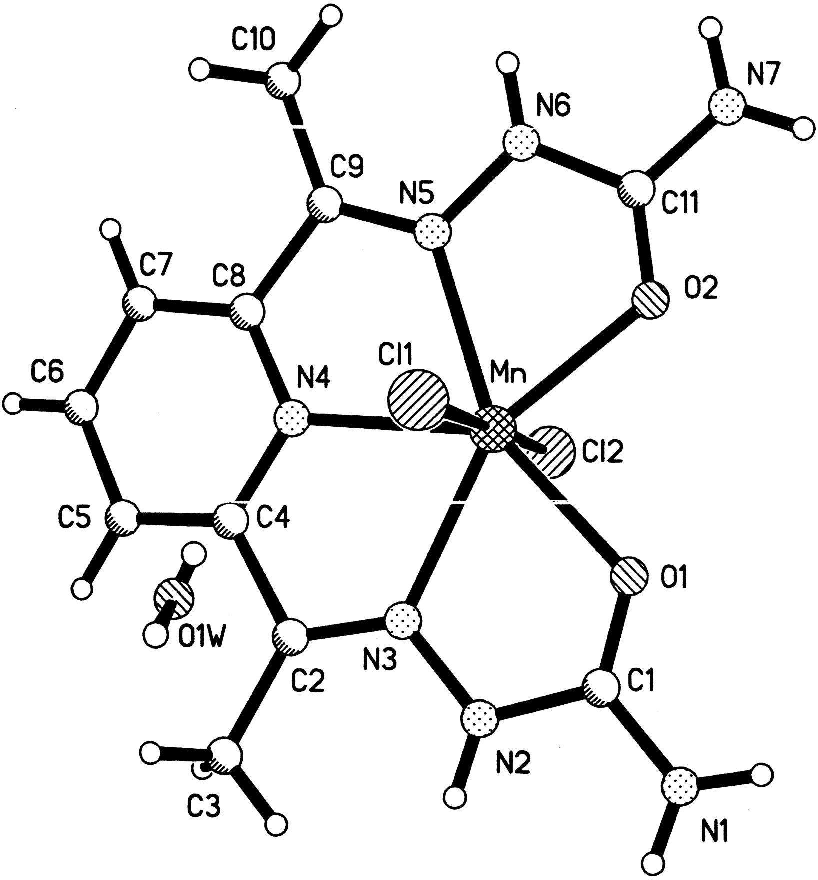

FIGURE 1 Molecular structure of $[MnCl_2(DAPSC)] \cdot H_2O$.

information about the nature of TCNQ (neutral or anionic). In the complexes (1–4), the intensity ratio $\varepsilon(25400)/\varepsilon(11900)$ is less than 0.5, which clearly indicates that only $TCNQ^{-1}$ is present in solution.

Ligand to metal charge transfer bands have been observed in the range 32258–29490 cm^{-1} in all the complexes. The d–d transitions could be identified in case of (2) and (4) as strong and weak bands at 20533 and 20000 cm^{-1}, respectively. However, the solid state reflectance spectra of the complexes show a broad band in the range 16666–14258 cm^{-1} indicating that the $TCNQ^-$ is present as $(TCNQ)_2^{2-}$, further supported by the magnetic moment values of the complexes which show no contribution from $TCNQ^{-1}$.

The solid state room temperature epr spectrum of complex (4) shows a single isotropic line with $g = 2.01$ consistent with the distorted geometry around Cu(II). Epr spectra of (2) and (3) are not very informative due to large zero field splitting. Epr spectrum of (1) is much more interesting, since the magnetic moment of the complex is 6.47 BM, indicating that it is a high spin Mn(II) complex with spin value 5/2, and consequently, should give five peaks in the epr spectrum; however, the complex shows only one broad peak at $g = 2.4$. This may be attributed to the large ligand field splitting as a result of which, in the presence of a magnetic field, epr transitions are observed only between $Ms = \pm 1/2$ spin states. If Mn(II) were in the pure $^6S_{5/2}$ state with no crystal field splitting, its g value would be 2.0023, whereas the observed g value is greater than this. The positive contribution to the g value can be due to covalent bonding [11] which results from the mixing of low lying ligand states with the manganese d states (which has already been indicated by the appearance of a ligand to metal charge transfer band at $32258\,cm^{-1}$). This complex is thus one of the rare examples among the Mn(II) complexes which exhibit a one line epr spectrum while in spin $\pm 5/2$ states [12]. No signal for $TCNQ^-$ was observed in the complexes reported herein, further supporting the presence of dimerised $(TCNQ)_2^{2-}$ as against our earlier observation [2a] in the case of a Cu(II) complex, when a sharp band attributable to $TCNQ^-$ was observed. Conductivity measurements in dimethylformamide at room temperature, 46.0×10^{-6}, 42.0×10^{-6}, 86.0×10^{-6} and $16.50 \times 10^{-6}\,S\,cm^{-1}$ for the complexes (1–4), respectively, indicate that all are only weakly conducting.

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[3] Synthesis: to a suspension of DAPSC (0.370 g, 1.19 mmol) in ethanol and water ($25\,cm^3$), was added $MnCl_2 \cdot 4H_2O$ (0.2 g, 1.17 mmol) with stirring. The mixture was heated at 70–80°C for about 3–4 hours. A yellow solid was isolated, washed with ethanol and water in succession, and dried *in vacuo*. The complex $[Mn(DAPSC)Cl_2] \cdot H_2O$ was further treated

with LiTCNQ[13] under nitrogen to obtain its TCNQ adduct. Other complexes were similarly prepared. Microanalytical data were consistent with predicted stoichiometries.

[4] Three-dimensional X-ray data were collected at -105°C to a maximum two theta value of 54° using a Siemens SMART CCD area detector and 0.3° ϕ scans and MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods (SHELXL 93) [5]. Complex scattering factors were taken from Ref. [6] and from SHELXL 93. Empirical formula = $C_{11}H_{17}MnN_7O_3$, Formula weight (M) = 421.16, Temperature = 158(2) K, Crystal system = monoclinic, Space group = $P2_1/c$, unit cell dimensions: $a = 7.106$ (4), $b = 12.892$ (8), $c = 18.780$ (11) Å, $\beta =$ 102.904 (6); volume (U) = 1677 (18) Å^3, $Z = 4$, density calculated (D_c) = 1.668 Mg m^{-3}, absorption coefficient (μ) = 1.132 mm^{-1}, $F(000) = 860$, crystal size = 0.6 × 0.08 × 0.08 mm, θ range for data collection = 3.16 to 26.43°, index ranges = $-7 \le h \le 2$, $-11 \le k \le 16$, $-22 \le 1 \le 23$, reflections collected = 4908, independent reflections = 2805, $R(int) =$ 0.0489, completeness of data 92%, refinement method = full-matrix least-squares on F^2. data/restrains/parameters = 2805/0/229, Goodness-of-fit on $F^2 = 0.925$, final R indices $[I > 2\sigma(I)] = R1 = 0.067$; $wR2 = 0.160$, R indices (all data) = $R1 = 0.095$; $wR2 = 0.179$, Largest difference peak and hole (e Å^3) = 0.852 and -1.443. Crystallographic data are available from the authors on request.

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