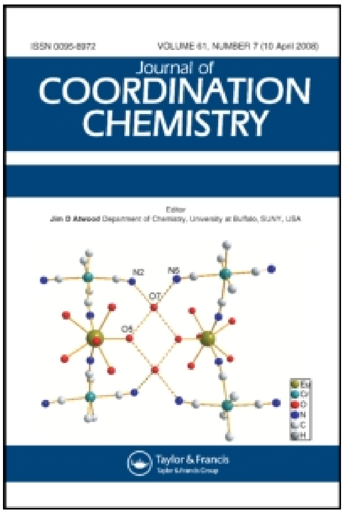

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SHORT COMMUNICATION

Neutral Four-coordinate Tetrahedral Manganese(II) Species Involving Coordinated Chloro- and Thiocyanato-Groups

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INTRODUCTION

Although high-spin and some low-spin octahedrally coordinated anionic and neutral complexes of manganese(II) are common, tetrahedral coordination in manganese(II) is mainly exhibited[1] in anionic species $[MnX_4]^{2-}$, X = Cl, Br, CN, NCO, NCS or NCSe. Whereas manganese(II) bromide is known to form neutral four-coordinated structures[1] MnL_2Br_2, L = Me_3NO, C_5H_5NO, Ph_3PO or Ph_3AsO, four-coordinated tetrahedral manganese(II) complexes as neutral species involving coordinated chloro- and thiocyanato-groups, MnL_2X_2 (L = a monodentate ligand, and X = Cl or NCS) are rather unknown. We report the isolation of 1 : 2 manganese(II) chloride and thiocyanate complexes with 4-cyanopyridine N-oxide (4-CPO) which are shown from room temperature magnetic moments, electronic spectral, ligand field parameters and i.r. spectral studies down to 200 cm^{-1} as neutral species exhibiting four-coordinated high-spin, monomeric tetrahedral environments around manganese(II) containing coordinated chloro- and thiocyanato- groups in the solid state.

EXPERIMENTAL

The 1 : 2 manganese(II) chloride and thiocyanate complexes with 4-CPO were obtained by mixing together the ligand and the respective manganese(II) salt solutions in ethanol. The complexes which crystallized out were suction-filtered, washed with ethanol and dried at ~150°C.

$Mn(4\text{-}CPO)_2Cl_2$ Found: Mn, 15.1; Cl, 19.3 Calc.: Mn, 15.0; Cl, 19.4%.

$Mn(4\text{-}CPO)_2(NCS)_2$ Found: Mn, 13.5; NCS, 28.0 Calc.: Mn, 13.4; NCS, 28.2%.

Conductivity measurements were made on freshly prepared $\sim 10^{-3}$ M solutions in purified DMF with a Philips conductivity bridge Model PR 9500. Electronic spectra of the complexes were recorded as nujol mulls in the range 33000–6000 cm^{-1} on a Cary 14 recording spectrophotometer. I.r. spectra of the uncoordinated 4-CPO and of the manganese(II) complexes were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics. Magnetic susceptibilities were measured at room temperature by the Faraday's method with a Cahn R.G. Electrobalance Model 7550 using $HgCo(NCS)_4$ as the magnetic susceptibility standard. Pascals' constants were used for diamagnetic corrections and the magnetic moments were calculated using the equation

$$\mu_{eff} = 2.84\sqrt{\chi_M \, corr_T}.$$

RESULTS AND DISCUSSION

The 1 : 2 manganese(II) chloride and thiocyanate complexes with 4-CPO isolated in the present study are mustard-yellow in colour and are soluble in ethanol and DMF in which they behave as electrolytes. No absorption bands were observed which could be attributed to water or ethanol in any of the spectra thus establishing these complexes to be anhydrous and free from coordinated or lattice water/ethanol. The rock salt region i.r. spectra of the manganese(II) complexes indicate clearly that νCN at 2260 cm^{-1} in uncoordinated 4-CPO remains almost unchanged suggesting thereby that the cyano group of 4-CPO does not participate in coordination. However, the strong absorption band at 1280 cm^{-1} assigned to νNO in the i.r. spectrum of uncoordinated[2] 4-CPO suffers a significant negative shift in the manganese(II) chloride and thiocyanate complexes. This decrease in the frequency of νNO is attributed to a change in the nature of nitrogen–oxygen bond as a result of oxygen-to-metal coordination which thereby brings about a decrease of the NO double bond character thus resulting in lowering of the νNO frequency.[3] The δNO appearing as a strong band at 850 cm^{-1} in the i.r. spectrum of uncoordinated 4-CPO is observed with almost the same intensity but shifted slightly to lower energies (848 cm^{-1} in $Mn(4\text{-}CPO)_2Cl_2$ and 845 cm^{-1} in $Mn(4\text{-}CPO)_2(NCS)_2$). These observations agree well with the results for pyridine N-oxide complexes with metal(II) salts.[3] It is thus clear that 4-CPO is present exclusively as terminally N-oxide oxygen bonded monodentate ligand in both the complexes and that the N-oxide oxygen is more basic than the nitrile group.

The room temperature magnetic moments of both these complexes (Table I) are consistent with high-spin manganese(II). Because of the additional stability of the half-filled d-shell manganese(II) generally forms high-spin complexes. Since the high spin manganese(II) complexes have an orbitally degenerate ^6S ground state term the spin-only magnetic moment of ~5.92 B.M. will be independent of the temperature and of the stereochemistry. The frequencies of the observed bands in the electronic spectra (Table I) and the mustard-yellow colour of both these complexes strongly suggest tetrahedrally coordinated manganese(II)[4,5] as the octahedral manganese(II) complexes are generally pale-pink or almost white and exhibit[4] a strong absorption band at ~25000 cm^{-1}. The Orgel diagrams for manganese(II), a d^5 configuration, for octahedral and tetrahedral environments are identical except

TABLE I
Magnetic moments (B.M.), characteristic i.r. and electronic bands and ligand field parameters (cm^{-1})

$Mn(4\text{-}CPO)_2Cl_2$	$Mn(4\text{-}CPO)_2(NCS)_2$	Assignment
5.91	5.73	μ_{eff}
1240	1214	νNO
848	845	δNO
20410	19800	ν_1
28570	23800	ν_2
34840	30770	ν_3
4207	2890	10 Dq
680	825	B
0.71	0.86	β
290		νMn—Cl
320	320	νMn—O (4-CPO)
	2090, 2060	νCN
	820	νCS
	470, 455	δNCS
	296	νMn—NCS

that the value of 10 Dq for tetrahedral complexes is much smaller than for the octahedral ones.[4] The calculated values of 10 Dq for the two complexes studied are in agreement with tetrahedral environments[4,5] around manganese(II). 10 Dq value for octahedrally coordinated manganese(II) complexes is fairly high,[5,6] ~7900–12300 cm^{-1}.

The 650–200 cm^{-1} region i.r. spectrum of the 1 : 2 manganese(II) chloride-4-CPO complex shows absorption bands at 320 and 290 cm^{-1}. The former band is assigned as νMn-O (4-CPO) and its frequency is consistent with similar mode in several complexes of metal(II) halides with pyridine N-oxide and its derivatives.[3] The band at 290 cm^{-1} is identified as νMn—Cl consistent with monomeric tetrahedral environments around the metal(II) ions.[7] Thus the colour, magnetic moment value, absorption bands in the electronic spectrum, ligand field parameters, terminally N-oxide oxygen bonded 4-CPO molecules and frequency of νMn—Cl strongly suggested that the 1 : 2 manganese(II) chloride complex with 4-CPO is a monomeric, four-coordinated neutral species with a high-spin tetrahedral environment of two oxygen atoms (from two 4-CPO molecules) and two terminally bonded chlorides around manganese(II) and rule out the chlorine-bridged or N-oxide oxygen-bridged polymeric octahedral structure for the complex in the solid state.

In addition to the ligand bands i.r. spectrum of the 1 : 2 manganese(II) thiocyanate-4-CPO complex shows absorption bands at 2090, 2060, 830, 470, 455, 320 and 296 cm^{-1}. These additional bands are identified as νCN (2090, 2060 cm^{-1}), νCS (820 cm^{-1}), βNCS (470, 455 cm^{-1}) and νMn—NCS (296 cm^{-1}) consistent[8] with terminally N-bonded NCS groups. (The band at 320 cm^{-1} is assigned as νMn—O (4-CPO) mode.) It is suggested that the 1 : 2 manganese(II) thiocyanate complex with 4-CPO is a monomeric four-coordinated neutral species with a high-spin tetrahedral environment of two oxygen atoms (from two 4-CPO molecules) and two nitrogen atoms (from two terminal N-bonded NCS groups) around manganese(II) in the solid state.

Neutral species involving coordinated chloro- and thiocyanato-groups with tetrahedral environments MnL_2X_2, L = a monodentate ligand and X = Cl or NCS, are rather unknown for manganese(II) and the present complexes seem to be the first examples. However, unambiguous characterization of these compounds be based on complete crystal structure determinations.

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