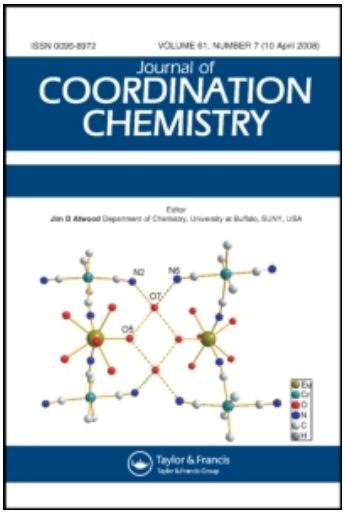

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SYNTHESIS, CHARACTERIZATION AND STRUCTURE OF $(N_2H_5)_3MnX_5$ (X = Cl and Br)

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Two new hydrazinium complexes of manganese, $(N_2H_5)_3MnX_5$ (X = Cl and Br), have been prepared and characterized by analysis, infrared and visible spectra. The single crystal X-ray structure of the chloride complex has been determined. Only one of the three $N_2H_5^+$ cations is coordinated to the metal. In the anion, $[Mn(N_2H_5)Cl_5]^{2-}$, the coordination polyhedron around the manganese atom is a slightly distorted octahedron.

Keywords: Hydrazinium cation, manganese complex, X-ray structure.

INTRODUCTION

The present work represents part of our investigation of a series of hydrazinium metal sulphate,[1] oxalate,[2-4] hydrazinecarboxylate,[5] chloride,[6,7] and thiocyanate[8] complexes. Presently, the preparation of $(N_2H_5)_3MnX_5$, where X = Cl and Br, and the single-crystal X-ray structure of $(N_2H_5)_3MnCl_5$ is reported.

EXPERIMENTAL

The chloride complex was prepared by mixing saturated aqueous solutions of $MnCl_2.2H_2O$ and $N_2H_4.HCl$ in a 1:3 mole ratio. The resulting solution was kept in a desiccator over P_2O_5. Light, pink crystals were formed in a week. These were removed from the solution, dried by pressing between filter paper and stored in an air-tight bottle. Alternatively, the complex can be prepared by decomposing the solid hydrazinecarboxylate complex, $Mn(N_2H_3COO)_2.(H_2O)_2$[9] in dilute HCl. Anal: calcd. for $(N_2H_5)_3MnCl_5$: Mn, 16.6; N_2H_4, 29.9; Cl, 53.5%. Found: Mn, 16.7; N_2H_4, 29.4; Cl, 53.1%.

The bromide complex was prepared by reaction of solid $Mn(N_2H_3COO)_2.(H_2O)_2$ with dilute HBr. Anal: calcd. for $(N_2H_5)_3MnBr_5$: Mn, 9.9; N_2H_4, 17.9; Br, 72.2%. Found: Mn, 9.4; N_2H_4, 18.1; Br, 71.1%.

The compositions of the complexes were found by chemical analysis.[10] Metal contents were determined by titrating with EDTA, hydrazine by titrating with standard KIO_3 under Andrews conditions, chloride and bromide by Volhard's method.

Infrared spectra of the complexes in the region 4000–600 cm^{-1} were recorded on a Perkin-Elmer 781 spectrophotometer in nujol mulls. The reflectance spectrum of the

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chloride complex was recorded on a Shimadzu UV-240 double beam spectrophotometer in a nujol mull using $BaSO_4$ as standard.

For X-ray measurements, a crystal of the chloride complex of dimensions 0.50 × 0.20 × 0.10 mm was used. Since the compound is deliquescent, the crystal was mounted in a Lindemann capillary. Cell dimensions and space group were determined using a Weissenberg camera and subsequently refined on the diffractometer. Intensity data were collected on a CAD-4 diffractometer in the usual manner.

Structure solution and refinement

The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares procedures (SHELX-76),[11] with anisotropic temperataure factors for all non-hydrogen atoms. Hydrogen atoms were not located. Scattering factors and anomalous dispersion corrections for manganese were taken from reference 12. The ORTEP II programme[13] was used. All details regarding data collection and structure solution are listed in Table I. Full lists of anisotropic thermal parameters and observed and calculated structure factors are available from KCP.

TABLE I
Details of X-ray analysis for $(N_2H_5)_3MnCl_5$.

formula	$(N_2H_5)_3MnCl_5$	d_m	1.98 g cm^{-3}
M_r	331.2	d_c	1.998 g cm^{-3}
crystal system	monoclinic	scan mode	$\omega/2\theta$
radiation	0.71069 Å	2θ range	60°
T	293 K	reflections measured.	$\pm h, k, l$
space group	$P2_1/n$	no. of measured reflections.	3820
a	8.988(3) Å	no. of unique data	3375
b	10.974(2) Å	no. of data used	2835
c	11.788(4) Å	cut-off criterion	$F > 3.0\sigma(F)$
β	94.33(3)	abs. coeff. (μ_{Mo})	22.5 cm^{-1}
V	1159.3 Å^3	R_{int}	0.038
z	4	weights*	A = 0.01672
		R	0.059
		R_w	0.072

* Weighting scheme; $w = 1/[\sigma^2(F_o) + A|F_o|^2]$.

RESULTS AND DISCUSSION

The complexes $(N_2H_5)_3MnX_5$ (X = Cl and Br) can be prepared from solid $Mn(N_2H_3COO)_2(H_2O)_2$ and the corresponding dilute acid. The reaction is exothermic. The chloride complex can also be prepared from $MnCl_2.4H_2O$ and $N_2H_4.HCl$. It has been observed that irrespective of the reactant mole ratios, the product obtained was of the same composition. Both complexes are very hygroscopic.

Infrared spectra of both complexes show two sharp bands at 995 and 985 cm^{-1}, corresponding to the ν(N–N) stretch of the $N_2H_5^+$ ions. The values indicate the presence of both coordinated and non-coordinated $N_2H_5^+$ ions in the complexes.[14]

Reflectance spectral data for the chloride complex are given in Table II, the assignments being made on the basis of earlier studies.[15] These values correspond to an octahedral Mn(II) ion.

TABLE II
Electronic spectral data for $(N_2H_5)_3MnCl_5$.

frequency (cm^{-1})	assignment
18900	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
22625	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
23865	$^6A_{1g} \rightarrow {}^4E_g(G)$
25910	$^6A_{1g} \rightarrow {}^4A_{1g}(G)$
26880	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$
28010	$^6A_{1g} \rightarrow {}^4E_g(D)$

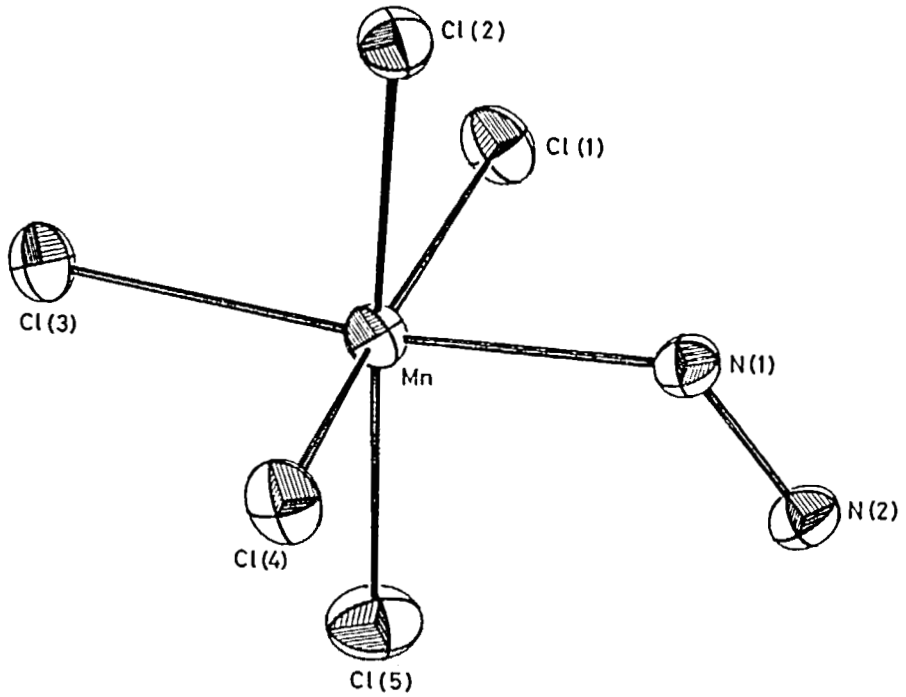

FIGURE 1. ORTEP[13] diagram of the anion $[Mn(N_2H_5)Cl_5]^{2-}$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The structure of $(N_2H_5)_3MnCl_5$ consists of complex $[Mn(N_2H_5)Cl_5]^{2-}$ anions and $N_2H_5^+$ ions. The manganese atom is surrounded by five chlorine atoms and one nitrogen atom of an $N_2H_5^+$ ion. The coordinated atoms are arranged at the apices of a slightly distorted octahedron, as illustrated in Figure 1. Fractional atomic coordinates and interatomic distances and angles observed in the complex are listed in Tables III and IV respectively.

TABLE III

Fractional atomic coordinates and equivalent isotropic temperature factors* ($Å^2$) for $(N_2H_5)_3MnCl_5$, with esd's in parentheses.

atom	x/a	y/b	z/c	U_{eq}
Mn	0.02155(5)	0.25212(4)	0.21958(4)	0.0223(2)
Cl(1)	0.02958(9)	0.48656(7)	0.20554(7)	0.0298(2)
Cl(2)	0.05540(9)	0.27792(8)	0.43332(7)	0.0307(2)
Cl(3)	−0.26096(9)	0.25376(7)	0.22597(7)	0.0303(3)
Cl(4)	0.04008(9)	0.02358(7)	0.25218(8)	0.0327(3)
Cl(5)	0.0019(1)	0.2311(1)	0.00854(8)	0.0391(3)
N(1)	0.2858(3)	0.2576(2)	0.2384(2)	0.0248(7)
N(2)	0.3755(3)	0.2484(2)	0.1425(2)	0.0251(8)
N(3)	0.7069(4)	0.5679(3)	0.0353(3)	0.039(1)
N(4)	0.7656(4)	0.4529(3)	0.0062(3)	0.042(1)
N(5)	0.2660(4)	0.0290(3)	1.0246(3)	0.044(1)
N(6)	0.2649(5)	0.0177(4)	0.9043(4)	0.052(1)

* Temperature factor is of the form: $U_{eq} = \frac{1}{3} \sum \sum U_{ij} a^*_i a^*_j a^-_i . a^-_j$.

TABLE IV

Observed bond lengths(Å) and angles(°) in $(N_2H_5)_3MnCl_5$.

Mn–Cl(1)	2.579(1)	Mn–N(1)	2.369(3)
Mn–Cl(2)	2.531(1)	N(1)–N(2)	1.441(4)
Mn–Cl(3)	2.546(1)	N(3)–N(4)	1.419(5)
Mn–Cl(4)	2.541(1)	N(5)–N(6)	1.424(6)
Mn–Cl(5)	2.491(1)		
Cl(1)–Mn–Cl(2)	87.16(3)	Cl(3)–Mn–Cl(5)	91.98(3)
Cl(1)–Mn–Cl(3)	91.58(3)	Cl(4)–Mn–Cl(5)	93.35(3)
Cl(1)–Mn–Cl(4)	172.93(3)	Mn–N(1)–N(2)	122.8(2)
Cl(1)–Mn–Cl(5)	91.64(3)	N(1)–Mn–Cl(1)	87.01(7)
Cl(2)–Mn–Cl(3)	90.86(3)	N(1)–Mn–Cl(2)	81.93(7)
Cl(2)–Mn–Cl(4)	87.61(3)	N(1)–Mn–Cl(3)	172.71(7)
Cl(2)–Mn–Cl(5)	176.95(4)	N(1)–Mn–Cl(4)	87.55(7)
Cl(3)–Mn–Cl(4)	93.25(3)	N(1)–Mn–Cl(5)	95.21(7)

The metal chlorine distances in the complex anion vary from 2.491(2) to 2.579(1) Å, with an average distance of 2.537 Å. These distances are comparable to those found in $[MnCl_5(H_2O)]^{3-}$, in which the average Mn–Cl distance is 2.545 Å.[16] The $[MnCl_5(N_2H_5)]^{2-}$ anion has an essentially octahedral geometry, the *cis* angles differing by only 3° from the ideal values. The Mn–N bondlength of 2.369(3) Å is longer than usual Mn–N distances, *e.g.*, 2.19(2) and 2.21(2) Å found in $Mn(N_2H_3COO)_2(H_2O)$,[9] and indicates a weak Mn–N interaction.

The N–N bondlength in the coordinated $N_2H^+_5$ cation is 1.441(4) Å, similar to that found in iron[6] and platinum[7] complexes. N–N bondlengths in the uncoordinated $N_2H^+_5$ ions are 1.419(5) and 1.424(6) Å. The Mn–N(1)–N(2) angle in the complex is

122.7(4)°, a value comparable to those found in the iron and platinum complexes. The bromide complex is expected to have the same structure.

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