

## Complexes of manganese(III) oxychlorosulphate with some nitrogen bases

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Manganese(III) oxychlorosulphate complexes of the type  $\text{MnOSO}_3\text{Cl.L}_2$  and  $\text{MnOSO}_3\text{Cl.L}'$  with monodentate (aniline, biphenyl amine, acetonitrile, pyridine, 3-amino-2-chloropyridine, 4-cyanopyridine, acridine) and bidentate ligands (2,2-bipyridyl and 1,10-phenanthroline) have been characterized on the basis of their elemental analysis, molar conductance, magnetic susceptibility measurements, infrared and electronic spectral data. These studies, corroborate the tridentate nature and lowering of  $C_{3v}$  symmetry of the chlorosulphate group. The complexes are of high-spin octahedral type as evidenced by magnetic moment values and electronic spectral bands.

Investigations on oxychlorosulphate complexes of transition metals are scarce<sup>1,2</sup>. In this note we are reporting the preparation and characterization of some Mn(III) oxychlorosulphate adducts with mono- and bi-dentate nitrogen containing bases.

### Experimental

Manganese(III) oxychlorosulphate ( $\text{MnOSO}_3\text{Cl}$ ) was prepared as described<sup>3</sup>. Biphenylamine, acridine, 4-cyanopyridine, 3-amino-2-chloropyridine, 2,2'-dipyridyl and 1-10 phenanthroline (BDH, England) were used as such while aniline, pyridine and acetonitrile were dried and distilled before use.

Sulphur and chlorine were estimated gravimetrically<sup>4</sup>. Manganese was analysed by EDTA titration<sup>5</sup>. IR spectra of the complexes were obtained in mull using a Perkin-Elmer 621 spectrophotometer. Diffuse reflectance spectra were recovered on a Carl Zeiss VSU2P spectrophotometer using MgO as the standard. The magnetic susceptibilities were measured at 303 K by Gouy method using  $\text{Hg}[\text{CO}(\text{SCN})_4]$  as the calibrant. Diamagnetic corrections were applied using Pascal's constants. Electrical conductance values of  $10^{-3}$  M solutions of the complexes in anhydrous DMF were obtained using a Cystronics conductivity bridge type 302 at  $25 \pm 0.1^\circ\text{C}$ . All the manipulations were carried out in a dry box flushed with dry nitrogen.

A mixture of metal oxychlorosulphate ( $\sim 20$  mmol) and ligand ( $\sim 44$  mmol) was taken in anhydrous benzene and stirred for six hours at  $35^\circ\text{C}$  in dry nitrogen atmosphere. On cooling the contents to  $10^\circ\text{C}$ , solid compounds were obtained. They were vacuum-filtered and dried.

### Results and discussion

The infrared spectral assignments have been made by comparing the spectra of the complexes with those of the free ligands and  $\text{MnOSO}_3\text{Cl}$ . A positive shift in symmetric  $\text{SO}_3$  stretching [ $\nu_1(\text{A})$ ] vibration ( $\sim 30$  to  $35\text{ cm}^{-1}$ ) and splitting of doubly degenerate modes [ $\nu_6(\text{E})$ ,  $\nu_5(\text{E})$  and  $\nu_4(\text{E})$ ] indicate that  $C_{3v}$  symmetry of chlorosulphate moiety has been lowered to  $C_s$  although  $\text{SO}_3\text{Cl}^-$  retains its tridentate nature<sup>6</sup>. The lowering of chlorosulphate group symmetry is ascribed to the unsymmetrical coordination of oxygen atoms. A similar non-identical coordination of  $\text{SO}_3\text{F}^-$  has also been reported for transition metal bisfluorosulphate<sup>7</sup>. The  $\nu\text{Mn}=\text{O}$  mode is slightly shifted to lower wave numbers ( $860\text{--}890\text{ cm}^{-1}$ ) as compared to that in  $\text{MnOSO}_3\text{Cl}$  ( $910\text{ cm}^{-1}$ ) due to higher electron density at the metal ion. It has been established from infrared spectral data of pyridine derivatives like 4-cyanopyridine, 3-amino-2-chloropyridine, etc., and their complexes that coordination generally occurs only through pyridyl nitrogen even in the presence of other potential coordination sites<sup>8-12</sup>. A characteristic positive shift in out-of-plane ring vibration (16b) and in-plane ring deformation (6a and 8a) in pyridine derivatives and 2-2'-dipyridyl further support coordination through pyridyl nitrogen<sup>13</sup>.

Acetonitrile complex shows an increase in  $\nu\text{C}=\text{N}$  as a result of coordination through the nitrogen atom<sup>13,14</sup>, while aniline and biphenyl amine complexes show a decrease in  $\nu\text{N}-\text{H}$ <sup>15,16</sup>.

1,10-Phenanthroline and 2,2'-bipyridyl complexes show a positive shift in  $\nu\text{C}=\text{N}$  and  $\nu\text{C}=\text{C}$ . A new weak band at  $1145\text{ cm}^{-1}$  in the former and at  $1380\text{ cm}^{-1}$  in the latter has been ascribed to chelate formation with manganese ion<sup>17,18</sup>. It is obvious that 1:2 complexes with monodentate ligands and 1:1 complexes with bidentate ligands would be *trans*- and *cis*-octahedral respectively. The magnetic moments of the complexes fall in the range 4.75-4.80 BM corresponding to the high-spin  $d^4$  configuration.

Six-coordinated manganese(III) ion generally exhibits<sup>19,20</sup> two bands in the region 16000-21000

Table 1—Analytical, molar conductance, magnetic and spectral data of complexes

Compound	Calc. (Obs.), %						$\mu_{\text{eff.}}$ (B.M.)	$\left( {}^5E_g \xrightarrow{\lambda_{\text{max}}} {}^5T_{2g} \right)$
	C	H	N	M	S	Cl		
MnOSO <sub>3</sub> Cl(An) <sub>2</sub>	38.67 (38.50)	3.76 (3.70)	7.52 (7.40)	14.74 (14.58)	8.59 (8.50)	9.53 (9.43)	4.78	20760 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(BPA) <sub>2</sub>	54.92 (54.83)	4.19 (4.10)	5.34 (5.24)	10.47 (10.38)	6.10 (5.98)	6.77 (6.70)	4.80	20710 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(ACet) <sub>2</sub>	17.88 (17.80)	2.24 (2.21)	10.43 (10.37)	20.45 (20.38)	11.92 (11.85)	13.23 (13.18)	4.76	20900 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(PY) <sub>2</sub>	34.84 (34.74)	2.90 (2.85)	8.13 (8.09)	15.94 (15.84)	9.29 (9.22)	10.31 (10.25)	4.78	20800 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(4-PY) <sub>2</sub>	36.51 (36.49)	2.03 (2.00)	14.19 (14.11)	13.92 (13.80)	8.11 (8.01)	9.00 (8.90)	4.75	20630 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(3,2-PY) <sub>2</sub>	27.06 (26.94)	2.26 (2.23)	12.63 (12.58)	12.38 (12.30)	7.22 (7.17)	24.01 (23.7)	4.75	20800 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(Acri) <sub>2</sub>	57.27 (57.20)	3.30 (3.24)	5.14 (5.04)	10.08 (9.98)	5.87 (6.44)	6.52 (6.40)	4.66	20790 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(BP)	35.03 (34.72)	2.34 (2.31)	8.17 (8.10)	16.02 (15.94)	9.34 (9.26)	10.36 (10.28)	4.80	20820 cm <sup>-1</sup>
MnOSO <sub>3</sub> Cl(Phen)	39.30 (39.21)	2.18 (2.13)	7.64 (7.56)	14.98 (14.87)	8.73 (8.65)	9.69 (9.60)	4.77	20860 cm <sup>-1</sup>

An = aniline, BPA = biphenyl amine, Acet = acetonitrile, Py = pyridine, 4-Py = 4-cyanopyridine, 3-2-Py = 3-amino-2-chloropyridine, BP = 2,2'-dipyridyl, Phen = phenanthroline, Acri = acridine.

cm<sup>-1</sup> which are assigned to spin-allowed transitions and a weak spin-forbidden transition around 10,000 cm<sup>-1</sup> whose assignment is uncertain. The reflectance spectra of these complexes show a broad spin-allowed *d-d* transition at 20,630-20,900 cm<sup>-1</sup> which may be assigned to  ${}^5E_g \rightarrow {}^5T_{2g}$  transition. The other low energy band could not be observed in these complexes. These evidences suggest that the manganese(III) complexes are spin-free octahedral.

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