Complexes of manganese(III) oxochlorosulphate with some nitrogen bases

S A A Zaid*, Lutfullah & K S Siddiqi
Division of Inorganic Chemistry, Department of Chemistry, Aligarh Muslim University, Aligarh 202 002

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Manganese(III) oxochlorosulphate complexes of the type MnOSO$_3$ClL$_2$ and MnOSO$_3$ClL' 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$_3$v 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 oxochlorosulphate complexes of transition metals are scarce. In this note we are reporting the preparation and characterization of some Mn(III) oxochlorosulphate adducts with mono- and bi-dentate nitrogen containing bases.

Experimental

Manganese(III) oxochlorosulphate (MnOSO$_3$Cl) was prepared as described. 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. Manganese was analysed by EDTA titration. 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 Hg[CO(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 Cytronics conductivity bridge type 302 at 25 ± 0.1°C. All the manipulations were carried out in a dry box flushed with dry nitrogen.

A mixture of metal oxochlorosulphate (~20 mmol) and ligand (~44 mmol) was taken in anhydrous benzene and stirred for six hours at 35°C in dry nitrogen atmosphere. On cooling the contents to 10°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 MnOSO$_3$Cl. A positive shift in symmetric SO$_3$ stretching [v$_1$(A)] vibration (~30 to 35 cm$^{-1}$) and splitting of doubly degenerate modes [v$_2$(E), v$_3$(E) and v$_4$(E)] indicate that C$_3$v symmetry of chlorosulphate moiety has been lowered to C$_1$, although SO$_3$Cl$^-$ retains its tridentate nature. The lowering of chlorosulphate group symmetry is ascribed to the unsymmetrical coordination of oxygen atoms. A similar non-identical coordination of SO$_3$F$^-$ has also been reported for transition metal bisflouro sulphate. The vMn=O mode is slightly shifted to lower wave numbers (860-890 cm$^{-1}$) as compared to that in MnOSO$_3$Cl (910 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. 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.

Acetonitrile complex shows an increase in vC=N as a result of coordination through the nitrogen atom, while aniline and biphenyl amine complexes show a decrease in vN-H. 1,10-Phenanthroline and 2,2'-bipyridyl complexes show a positive shift in vC=N and vC=C. A new weak band at 1145 cm$^{-1}$ in the former and at 1380 cm$^{-1}$ in the latter has been ascribed to chelate formation with manganese ion. 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$^6$ configuration.

Six-coordinated manganese(III) ion generally exhibits two bands in the region 16000-21000
Table 1—Analytical, molar conductance, magnetic and spectral data of complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc. (Obs.), %</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
<th>( T_{2g} ) (em)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MnOSO}_3\text{Cl(An)}_2 )</td>
<td>38.67 (38.50)</td>
<td>4.78 (8.50)</td>
<td>20760 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(BPA)}_2 )</td>
<td>54.92 (54.83)</td>
<td>4.80 (5.98)</td>
<td>20710 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(ACet)}_2 )</td>
<td>17.88 (17.80)</td>
<td>4.76 (11.85)</td>
<td>20900 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(PY)}_2 )</td>
<td>34.84 (34.74)</td>
<td>4.78 (9.22)</td>
<td>20800 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(4-PY)}_2 )</td>
<td>36.51 (36.49)</td>
<td>4.75 (10.25)</td>
<td>20830 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(3,2-PY)}_2 )</td>
<td>27.06 (26.94)</td>
<td>4.75 (23.7)</td>
<td>20800 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(Acri)}_2 )</td>
<td>57.27 (57.20)</td>
<td>4.66 (6.44)</td>
<td>20790 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(BP)} )</td>
<td>35.03 (34.72)</td>
<td>4.80 (9.26)</td>
<td>20820 cm(^{-1})</td>
</tr>
<tr>
<td>( \text{MnOSO}_3\text{Cl(Phen)} )</td>
<td>39.30 (39.21)</td>
<td>4.77 (9.60)</td>
<td>20860 cm(^{-1})</td>
</tr>
</tbody>
</table>

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.

References


cm\(^{-1}\) which are assigned to spin-allowed transitions and a weak spin-forbidden transition around 10,000 cm\(^{-1}\) whose assignment is uncertain. The reflectance spectra of these complexes show a broad spin-allowed \( d-d \) transition at 20,630-20,900 cm\(^{-1}\) 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.