MANGANESE(III) COMPLEXES OF DITHIOCARBAMATES DERIVED FROM SOME HETEROCYCLIC SECONDARY AMINES

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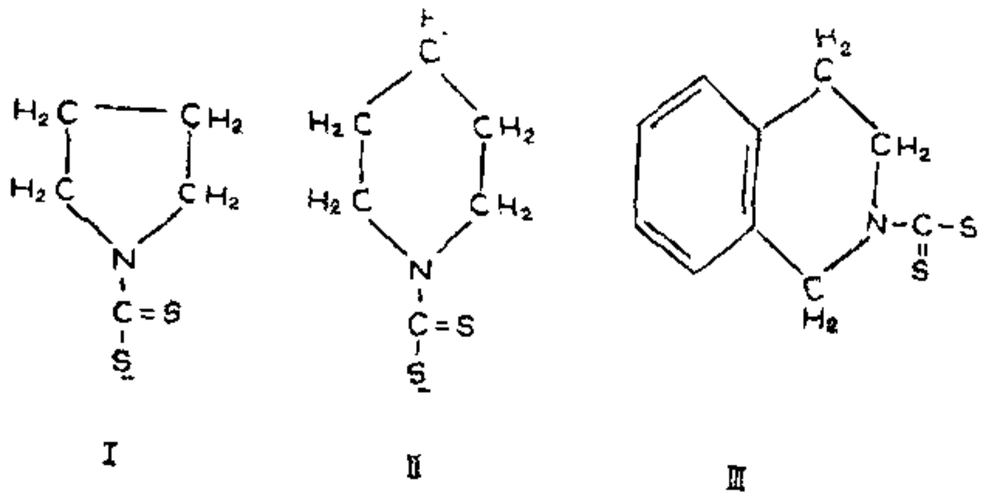
ABSTRACT

Manganese(III) complexes of dithiocarbamates derived from heterocyclic secondary amines, pyrrolidine, piperidine and tetrahydroisoquinoline have been prepared. They are of the general formula, MnL_3 where L is a ligand. The complexes are non-electrolytes in nitrobenzene and acetonitrile. Magnetic moment data show that they are of the spin–free type. Infrared spectra reveal the bidentate nature of the ligands. The electronic spectra suggest a lowering of symmetry from O_h.

DIALKYL dithiocarbamate complexes have been the subject of numerous investigations[1-4]. Comparatively, very little work has been done on the complexes of the dithiocarbamates derived from heterocyclic secondary amines. The results of our studies on the complexes of manganese(III) with pyrrolydyl-N-carbodithioate(I), piperidyl-N-carbodithioate(II) and tetrahydroisoquinoline-N-carbodithioate(III) are reported.



I II III

Sodium salts of the N-carbodithioates were prepared by the following method. An aqueous solution (200 ml. 5N) of sodium hydroxide and 0·5 mole of the appropriate amine were introduced into a three necked flask, cooled in a freezing mixture of ice and salt. Carbon disulphide (32 ml) was added dropwise from the separating funnel and the mixture was stirred for about 2 hr. The solid that separated out was washed several times with petroleum ether and recrystallised from water.

The complexes were prepared by mixing methanolic solutions of stoichiometric amounts (metal : ligand as 1 : 3) of manganese(III) acetate dihydrate and respective sodium-N-carbodithioates with stirring, when brown crystals of the complexes separated. The crystals were filtered, washed with methanol and dried in vacuum.

All the complexes are brown in colour and were found to be non-hygroscopic. They are soluble in benzene, CCl_4 and acetonitrile but are insoluble or only sparingly soluble in water and methanol.

Manganese in the complexes was estimated as pyrophosphate. Sulphur was estimated as $BaSO_4$ after bromine oxidation of the complexes.

The analytical data given in Table I show that the complexes have the general formula MnL_3 where L is a ligand with a uninegative charge. Conductivity measurements were made on a Philips GM 4249 conductivity bridge. The conductance data show the non-electrolytic nature of the complexes both in acetonitrile and nitrobenzene. The magnetic measurements were made at room temperature using the Gouy method. The effective magnetic moment values (Table I) show that the complexes are of the spin-free type. These further indicate that manganese in the complexes are in the trivalent state with four unpaired electrons. The complexes do not show any magnetic interaction.

Usually, dithiocarbamates behave as monovalent bidentate ligands. Unidentate behaviour has been reported in the case of ruthenium(III) complex[5] where a number of additional bands at 970–980, 1060–1065, 1260–1265, 1410 and 1460–1470 cm^{-1} are observed. The infrared spectra of the complexes under investigation resemble those of the bidentate dithiocarbamates. A strong band observed around 1500 cm^{-1} is assignable to the partially π-bonded C–N stretch[6]. In sodium tetrahydroisoquinolinyl-N-carbodithioate, the band assignable to the C–N stretch occurs at 1440 cm^{-1}. In the case of the pyrrolidyl and piperidyl derivatives, the C–N stretch occurs at 1460 and 1470 cm^{-1} respectively. The magnitude of C–N stretch depends on the ability of the substituent on the nitrogen atom to donate electrons. The present studies show that the heterocyclic ring substituents on the nitrogen are in general less electron donating to the C–N bond as compared to the alkyl substituents. The substituent effect is quite marked in the case of the tetrahydroisoquinolinyl derivative. The

TABLE I

Analytical and physical data

Complex	Manganese % Found	Sulphur % Found	Nitrogen % Found	μ_{eff} B.M.	Molar conductance λ_m ohm^{-1} cm^2 mole^{-1}		IR frequencies and their assignments	
					Nitrobenzene	Acetonitrile	Frequency cm^{-1}	Assignments
Sodium tetrahydroisoquinolinyl-N-carbodithioate	..	..	..	..	..	..	1440 s	ν_{C-N}
							960 m	ν_{C-S}
Tris (tetrahydroisoquinolinyl-N-carbodithioate) Mn(III)	7·86 (8·02)	28·09 (28·02)	6·05 (6·13)	4·97	0·2	23·1	1480 s	ν_{C-N}
							965 m	ν_{C-S}
Sodium pyrrolydyl-N-carbodithioate	..	..	..	..	..	..	1460 m	ν_{C-N}
							945 s	ν_{C-S}
Tris (pyrrolydyl-N-carbodithioato) Mn(III)	10·60 (11·14)	39·02 (38·95)	8·48 (8·52)	4·87	0·2	26·9	1470 vs	ν_{C-N}
							960 m	ν_{C-S}
Sodium piperidyl-N-carbodithioate	..	..	..	..	..	..	1470 s	ν_{C-N}
							970 s	ν_{C-S}
Tris (piperidyl-N-carbodithioto) Mn(III)	9·60 (10·27)	36·04 (35·90)	7·64 (7·85)	5·07	0·1	18·2	1480 vs	ν_{C-N}
							960 s	ν_{C-S}

Calculated values are given in parenthesis.

C–S stretching frequencies for the tetrahydroisoquinolinyl, piperidyl and pyrrolydyl derivatives of manganese(III) are located at 965, 960 and 960 cm^{-1} respectively. The complex with lowest ν_{a_1} C–S is the most stable. On this basis, the three complexes under investigation have comparable stability.

The electronic spectra (chloroform) show bands around 28000 cm^{-1} assignable to charge-transfer processes[7]. The spectra also show bands around 20000 cm^{-1} and 16000 cm^{-1} assignable to the *d-d* transitions. Usually, octahedral manganese(III) complexes show only one band assignable to $^5E_g \rightarrow {}^5T_{2g}$. The occurrence of more than one band in the present complexes show a lowering of symmetry from O_h. The tris chelate complexes of the type under study will most probably belong to the point group D_3 because of the disymmetry caused by the chelating agent. In Mn(III) complexes, in addition to this, strong Jahn–Teller distortion is expected to be operative and hence the present complexes may be considered to have a symmetry C_2. The bands observed in the present complexes can be assigned to transition involving the split components of ^5E_g and $^5T_{2g}$ in a low symmetry ligand field.

A thermogravimetric analysis of the complexes show that the complexes are stable upto 200° C, then the decomposition occurs in one stage.

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