

the lower state of which may be $B(^3D)$. The system $D \rightarrow B(^3D)$ being not observed in absorption also indicates that the ground state $X(^1\Sigma^+)$ is not involved in the electronic transition. The ν_0 value for the present system indicates that the upper state (D) must lie in the region 53062.23 cm^{-1} . The nature of the upper state can be studied by rotational analysis only.

The newly observed system $D \rightarrow B(^3D)$ of InI molecule is an addition to similar systems observed in case of monohalides of the same group reported by previous workers. In case of TII molecule system $E \rightarrow A^3\Pi_0$ was observed by A. Terenin³ with maximum at 3475\AA with the position of E state at $\nu_0 = 54000 \text{ cm}^{-1}$. Analogous system $D \rightarrow A^3\Pi_0$ was reported for TIBr molecule by H. G. Howell⁴ with upper state D

at $\nu_0 = 54500 \text{ cm}^{-1}$. For TlCl molecule system $D \rightarrow A^3\Pi_0$ in the region $\lambda\lambda 4180\text{--}4283 \text{ \AA}$ has been reported by P. T. Rao⁵.

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SYNTHETIC AND STRUCTURAL STUDIES ON SOME MIXED LIGAND COMPLEXES OF MANGANESE(II)

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ABSTRACT

The present work deals with the study of mixed ligand complexes of manganese oxalate with nine ligands. The complexes are obtained by the action of manganese oxalate on the ligand in alcoholic solutions and have the general formulae $\text{MnC}_2\text{O}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$. Physicochemical properties such as magnetic susceptibility, electronic and infrared spectra, thermogravimetric analysis, etc., of these complexes have been investigated with a view to determine their structure. These complexes are polymeric in nature containing bidentate bridging oxalate groups and have octahedral symmetry.

INTRODUCTION

MIXED ligand complexes of divalent manganese containing hetero donor atoms have been studied by earlier workers,¹⁻³ in which primary ligands were halogens or pseudohalogens. The use of carboxylate as a primary ligand for the first row of the transition elements has also been described⁴⁻⁶. Though the thermal properties of 3d metals (including manganese²⁺) oxalate mixed ligand complexes with hydrazine⁷ have been reported, exhaustive work on manganese oxalate complexes is lacking. Further, it would be interesting to study the stereochemical and structural behaviour of such mixed ligand complexes. Thus the mixed complexes of manganese oxalate with amides and heterocyclic bases are described in this communication.

MATERIALS AND METHODS

The reagents used were AR in grade. The compounds were synthesised by suspending manganese oxalate ($\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$) in ethanol to which an excess of the ligand was added. The mixture was

stirred and refluxed on a hot plate. The reaction required four to six days for completion and the compounds thus obtained were washed with alcohol and ether and dried in vacuum. In a few cases (DMF and DMSO), ethanol was replaced by methylcyanide as these medium of reaction. These compounds are almost insoluble in organic solvents.

Manganese and sulphur were estimated by the conventional methods⁸ and nitrogen by micro analysis. Magnetic susceptibilities were measured at 30°C by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the standard. I.R. spectra were taken, in nujol mulls; the electronic spectra were taken in solid phase with a Cary-14 model spectrophotometer.

RESULTS AND DISCUSSION

The analytical results and magnetic moments, given in Table I, show 1 : 1 stoichiometry and the formula can be written as $\text{MnC}_2\text{O}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$. The magnetic moments of the complexes fall between 5.86–6.01 B.M. and indicate that these are spin-free octahedral complexes of manganese(II) having five unpaired electrons. However, in spite of repeated efforts,

the replacement of other H₂O molecule was not possible.

The mode of bonding in these complexes can be discussed with the help of the i.r. data (Table II). Thus in the urea complex the C=O absorption shows negative shift of $\approx 140 \text{ cm}^{-1}$ and a positive shift of 25 cm^{-1} in the N-C-N frequency which indicate coordination through oxygen as suggested earlier^{9,10}. Similarly for the thiourea complex the band at 740 cm^{-1} in ligand is attributed mainly to $\nu(\text{C-S})$ shifts to a lower frequency at 705 cm^{-1} in the complex; showing thereby a metal-sulphur bond formation¹¹.

The C=O stretching frequency is lowered by 40 cm^{-1} in the DMF complex of manganese(II) oxalate compared to the free ligand providing additional evidence that the oxygen of the C=O group forms one of the coordinating site¹². Also, the $\nu(\text{S=O})$ band in the DMSO complex appears at a lower frequency of 990 cm^{-1} as a strong band (1055 cm^{-1} in the ligand) which shows coordination through oxygen¹³.

The bands due to $\nu(\text{C}\cdots\text{C})$ and $\nu(\text{C}\cdots\text{N})$ in the region $1600\text{--}1500 \text{ cm}^{-1}$ are shifted to slightly higher frequencies for pyridine and methyl pyridine (3- or 4-pic) complexes in comparison with the free ligand as observed by earlier workers^{2,3,14}. Further, there are noticeable changes¹⁵ at $\approx 600 \text{ cm}^{-1}$ (in plane ring deformation) and at $\approx 400 \text{ cm}^{-1}$ (out of plane ring deformation). These bands undergo a positive shift by nearly $50\text{--}80 \text{ cm}^{-1}$ in the mixed ligand complexes. Similar shifts are observed for the quinoline complex.

TABLE I
Analytical data for $\text{MnC}_2\text{O}_4 \cdot L \cdot \text{H}_2\text{O}$ complexes

Ligand (L)	% found (cal.)			Magnetic moment B.M. (at 303° K)
	Mn	N	S	
Urea (U)	23.88 (24.88)	12.69 (12.67)	..	5.91
Thiourea (TU)	22.83 (23.18)	11.66 (11.81)	13.26 (13.49)	5.94
Dimethylformamide (DMF)	23.74 (23.49)	5.51 (5.98)	..	5.86
Dimethylsulfoxide (DMSO)	23.38 (23.01)	..	13.48 (13.39)	5.87
Pyridine (Py)	22.79 (22.42)	5.66 (5.83)	..	5.96
4-picoline (4-pic.)	21.55 (21.65)	5.58 (5.51)	..	5.99
3-picoline (3-pic.)	21.53 (21.65)	5.46 (5.51)	..	5.98
Quinoline (quin.)	18.91 (18.96)	4.71 (4.83)	..	5.93
Morpholine (mor.)	20.96 (21.17)	5.98 (5.90)	..	6.01

TABLE II
Relevant i.r. bands (cm^{-1}) for the mixed ligand manganese oxalate complexes and the ligands (in parentheses)

Compound	$\nu(\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{N})$	$\nu(\text{C}\cdots\text{O}, \text{C}\cdots\text{S})$ and others	$\nu(\text{M-L})$
$\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$..	1650sh, 1600b and 1300s and $\delta(\text{O-C-O})$ at 790s (oxalate)	
$\text{MnC}_2\text{O}_4 \cdot \text{U} \cdot \text{H}_2\text{O}$	1495sh (1471m)	1545m (1683s)	380m
$\text{MnC}_2\text{O}_4 \cdot \text{TU} \cdot \text{H}_2\text{O}$	(1476m)	705m (740s)	245m
$\text{MnC}_2\text{O}_4 \cdot \text{DMF} \cdot \text{H}_2\text{O}$..	1640m (1680s)	390m
$\text{MnC}_2\text{O}_4 \cdot \text{DMSO} \cdot \text{H}_2\text{O}$..	990s (S=O, 1055s)	400w
$\text{MnC}_2\text{O}_4 \cdot \text{Py} \cdot \text{H}_2\text{O}$	1610b, 1560sh, 1490m (1589s, 1555w, 1486b)	..	245m
$\text{MnC}_2\text{O}_4(4\text{-pic.}) \cdot \text{H}_2\text{O}$	1605,b 1585sh, 1505w (1610s, 1570m, 1498m)	..	230w
$\text{MnC}_2\text{O}_4(3\text{-pic.}) \cdot \text{H}_2\text{O}$	1600-1700b, 1590, 1515m (1625, 1600, 1580, 1505)	..	240m
$\text{MnC}_2\text{O}_4 \cdot \text{Quin.} \cdot \text{H}_2\text{O}$	1645b, 1600b, 1590sh (1620s, 1600m, 1585m)	..	270m
$\text{MnC}_2\text{O}_4 \cdot \text{Mor}^q \cdot \text{H}_2\text{O}$	1645sh, 1600b, 1590sh (1620s, 1600, 1585m)	$\nu(\text{N-II})$ 3360m (3440s)	298m

b = broad, sh = sharp, w = weak, m = medium, s = strong

The N-H stretching vibration, in morpholine occurs at 3440 cm^{-1} and in the complex it is coupled with the $\nu(\text{O}-\text{H})$ band; this band is lowered by 80 cm^{-1} showing coordination through the nitrogen of the ligand¹⁶.

The vibrations due to oxalate show significant changes in these mixed ligand complexes. Thus $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$ band shifts to higher frequencies, viz., $1660 \pm 5\text{ cm}^{-1}$ and symmetric stretching frequency shifts to lower by 10 to 15 cm^{-1} , thereby indicating coordination. The band at 790 cm^{-1} in the i.r. of manganese oxalate is attributed to a bridging (bidentate) oxalate group¹⁹ as is evident from the infrared data (Table III) of oxalate ion¹⁷.

The complexes studied by us invariably show the presence of a strong band in the region $800 \pm 15\text{ cm}^{-1}$.

That one water molecule is also coordinated to the metal atom is shown by the presence of a medium band at $\approx 690\text{ cm}^{-1}$ due to the rocking mode of coordinated water¹⁸. The thermogravimetric results for four representative compounds are given in Table IV. The manganese oxalate trihydrate²⁰ loses total water in $30\text{--}125^\circ\text{C}$ region whereas in all the

mixed adducts the loss in weight corresponding to water occurs at comparatively higher temperature. This shows the presence of a strongly coordinated water although less firmly than the ligand since the ligand species are only given off at higher temperature (column 2 of Table IV). However, for the pyridine complex, the weight loss due to water as well as the ligand is almost in the same region ($30\text{--}290^\circ\text{C}$). The decomposition temperature of anhydrous manganese oxalate is also given in Table IV. The observation at still higher temperatures are not significant to the metal-ligand or metal-water coordination and hence not discussed.

The reflectance electronic spectra of a few representative complexes were recorded in nujol (Table V). The ground state for Mn(II), a d^5 configuration in octahedral field is ${}^6\text{A}_g$. The $d-d$ transitions for Mn(II) in an octahedral field are all spin-forbidden and hence give rise to very weak absorptions. The complexes are shown to possess an octahedral symmetry¹⁶ (O_h) since they absorb at nearly 27000 , 22700 and 16200 cm^{-1} which is in good agreement with the observation by Liptay and Burger¹. Thus on the

TABLE III
Infrared bands (cm^{-1}) of oxalate ion

Assignment	Ionic	Bridging (bidentate)	Chelate	Bridging (bidentate)	
$\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$	1640vs	1640vs	1720sh 1610vs	1567vs	1562vs
$\nu_s(\text{O}-\text{C}-\text{O})$	1335s 1316s	1335m 1315m	1433s 1305s	1351m 1300s	1365m 1310s
$\delta(\text{O}-\text{C}-\text{O})$	774	795m	775s	740s	760s

TABLE IV
TGA data for hydrated manganese oxalate²⁰ and its adducts

Compound	% loss in weight (temperature range)		
	(1) loss of water	(2) loss of ligand	(3) decomposition of MnC_2O_4
$\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$	(30–125° C)	..	(270–420° C)
$\text{MnC}_2\text{O}_4 \cdot \text{U} \cdot \text{H}_2\text{O}$	8.26 (30–190° C)	35.36 (190–290° C)	(290–520° C)
$\text{MnC}_2\text{O}_4 \cdot \text{py} \cdot \text{H}_2\text{O}$	(30–290° C)	40.36 (30–290° C)	(290–520° C)
$\text{MnC}_2\text{O}_4 \cdot (4\text{-pic})\text{H}_2\text{O}$	7.23 (30–280° C)	43.86 (280–310° C)	(310–520° C)
$\text{MnC}_2\text{O}_4 \cdot \text{DMSL} \cdot \text{H}_2\text{O}$	7.56 (30–240° C)	40.26 (240–350° C)	(350–510° C)

basis of foregoing discussion the compounds may be assigned a polymeric octahedral structure containing bridging (bidentate) oxalate groups as shown in Fig. 1.

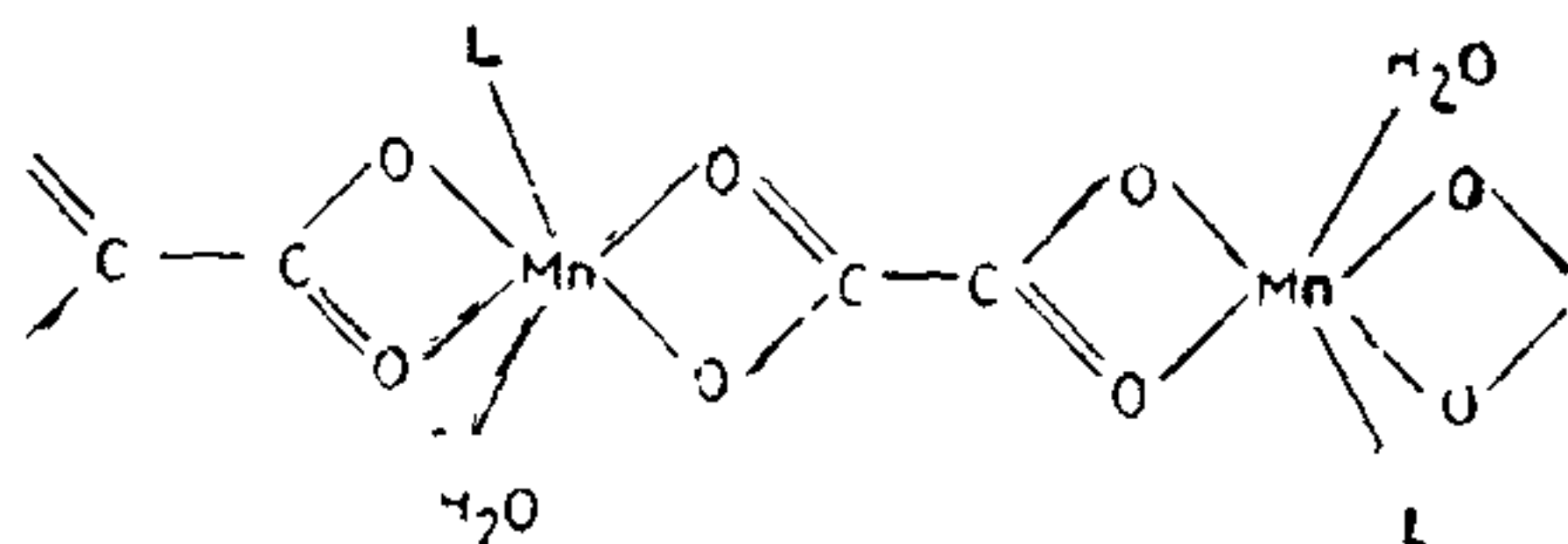


FIG. 1. Structure of MnC₂O₄.L.H₂O

TABLE V

Electronic spectral data for some Mn(II) complexes

Compound	λ_{max} (cm ⁻¹)
MnC ₂ O ₄ . U . H ₂ O	27000, 22730, 16210
MnC ₂ O ₄ . TU . H ₂ O	26800, 22500, 16110
MnC ₂ O ₄ . DMF . H ₂ O	27000, 23100, 16380
MnC ₂ O ₄ . Pj . H ₂ O	27100, 22640, 16220
MnC ₂ O ₄ . Quin . H ₂ O	26800, 21850, 16190

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NEW INDOLYL HYPOTENSIVE AGENTS

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SOME new 2-substituted-3-[[p-(N⁴-aryl-N¹-piperaziny) anilino] methyl] indoles have been prepared by the condensation of 2-substituted indole-3-aldehyde with 1,4-disubstituted piperazines followed by the reduction of the imine linkage by palladium carbon in N,N-dimethyl formamide and hydrazine hydrate to give the title compound. All the compounds were screened for their cardiovascular activity. Some of the compounds possess cardiovascular activity.

The presence of an indole nucleus in both naturally occurring and synthetic antihypertensive compounds¹⁻⁴ and the important role of 5-HT in the cardiovascular disorders have initiated a great spurt in the investigation of a number of analogues for cardiovascular activity⁵⁻⁸. In addition, the clinical efficiency of numerous indole derivatives⁹⁻¹¹ for the treatment of cardiovascular disorders and their ability to lower the blood pressure have prompted the synthesis of 2-substituted-3-[[p-(N⁴-aryl-N¹-piperaziny) anilino] methyl] indoles and evaluated them for their cardiovascular activity.

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