

for N-salicylidene- $\alpha$ -amino acid complexes of cobalt(II) appears to be applicable in the case of the present complexes involving schiff bases derived from  $\alpha$ -,  $\beta$ - and  $\gamma$ -amino acids. The experimental data are also in agreement with a dimeric structure.

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## Mixed Chelate Complexes of Manganese(III)

B. PRADHAN &amp; D. V. RAMANA RAO\*

Department of Chemistry, Regional Engineering College, Rourkela 769 008

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Five mixed chelate complexes of manganese(III), viz.  $Mn(tsc)_2(acac)$ ,  $Mn(tsc)_2(pyca)$ ,  $Mn(tsc)_2(et_2dte)$ ,  $Mn(acac)_2(pyca)$  and  $Mn(acac)(pyca)_2$ , where  $tscH$  = thiosemicarbazide,  $acacH$  = acetylacetone,  $pycaH$  = picolinic acid,  $et_2dte$  = diethyldithiocarbamate, have been isolated. The thiosemicarbazido complexes have been obtained on oxidation of manganese(II) by air in alkaline medium whereas the other two mixed chelates have been obtained from manganese(III) compounds by substitution reactions. The compounds have been characterized on the basis of their elemental analyses, molecular weight, molar conductance, magnetic susceptibility, infrared and electronic spectral data.

THE 3+ oxidation state of manganese has been well-characterized by the preparation of a number of anionic, cationic and neutral complexes and a good number of mixed chelate and mixed ligand complexes<sup>1-6</sup>. The complexes were generally obtained starting from the manganese(III) compounds. In the present investigation besides the usual method for isolating Mn(III) complexes, a method involving

oxidation of divalent to trivalent manganese in the presence of ligands has been used.

(i) *Preparation of  $Mn(tsc)_2(acac)$ ,  $Mn(tsc)_2(pyca)$  and  $Mn(tsc)_2(et_2dte)$* —Ethanol solutions of manganese(II) chloride, acetylacetone/picolinic acid/sodium salt of diethyldithiocarbamic acid and thiosemicarbazide in 1 : 1 : 2 molar ratio were reacted. Ethanol sodium hydroxide solution was added to it till faintly alkaline and then air was bubbled through the resulting solution for one hour when the colourless solution darkened and the compounds separated out. These were filtered, washed with ethanol, ether and dried *in vacuo*.

(ii) *Preparation of  $Mn(acac)_2(pyca)$* —Tris (acetylacetonato)manganese(III),  $Mn(acac)_3$ , in chloroform and picolinic acid in ethanol were refluxed in 1 : 1 molar ratio for one hour. The volume was reduced to one-third by suction and the contents kept overnight when the compound separated out. It was filtered, washed with ethanol, ether and dried *in vacuo*.

(iii) *Preparation of  $Mn(acac)(pyca)_2$* —Tris (acetylacetonato)manganese(III),  $Mn(acac)_3$ , in chloroform and picolinic acid in ethanol were mixed in 1 : 2 molar ratio and refluxed for 15 min when the compound separated out. It was filtered, washed with ethanol, ether and dried *in vacuo*.

Elemental analyses (Table 1) carried out by standard methods were consistent with the formulations of the compounds. The molar conductances for  $\sim 10^{-3}$  M solutions of the complexes in nitrobenzene medium range between 2.1 and 2.9 mho  $cm^2$  mole<sup>-1</sup> indicating the non-electrolytic nature of the compounds.

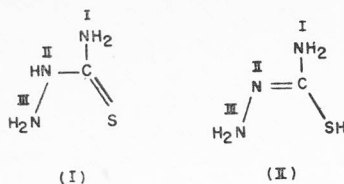
The magnetic moment values (determined using Gouy method) of 4.92-5.08 B.M. (Table 1) indicate the presence of four unpaired electrons corresponding to high-spin manganese(III) state with <sup>5</sup>E<sub>g</sub> ground term. The molecular weight measurements (Rast method using camphor) indicate that the compounds are monomeric.

Thiosemicarbazide exists in the tautomeric forms (I) and (II) and can act as a neutral or charged chelating group<sup>7</sup>.

Haines and Sun<sup>8</sup> have reported that in thiosemicarbazido complex, the band at 1049  $cm^{-1}$  for free thiosemicarbazide becomes very weak and a new strong band appears at 960  $cm^{-1}$ . Such features can

TABLE 1 — ANALYSES, COLOUR, MELTING POINTS, MAGNETIC SUSCEPTIBILITY AND MOLECULAR WEIGHTS DATA OF MIXED CHELATE MANGANESE(III) COMPLEXES

| Compound             | Colour        | m.p. (°C) | Found (Calc.) %  |                  | $\mu_{eff}$ (B.M.) | Mol. wt found (calc.) |
|----------------------|---------------|-----------|------------------|------------------|--------------------|-----------------------|
|                      |               |           | Mn               | S                |                    |                       |
| $Mn(tsc)_2(acac)$    | Chocolate     | >300      | 16.04<br>(16.44) | 18.70<br>(19.19) | 5.05               | 356.2<br>(335.9)      |
| $Mn(tsc)_2(pyca)$    | Grey          | >300      | 15.11<br>(15.38) | 17.43<br>(17.95) | 5.0 <sup>d</sup>   | 338.1<br>(357.2)      |
| $Mn(tsc)_2(et_2dte)$ | Greyish-brown | >300      | 14.43<br>(14.32) | 33.01<br>(33.43) | 4.93               | 369.8<br>(357.2)      |
| $Mn(acac)_2(pyca)$   | Grey          | 150       | 14.43<br>(14.63) | —                | 4.92               | 349.0<br>(375.2)      |
| $Mn(acac)(pyca)_2$   | Pink          | 160       | 13.74<br>(13.79) | —                | 5.08               | 437.1<br>(398.2)      |



be explained if the band is indeed a N-N vibration. In a symmetrical molecule, the N-N vibration is infrared forbidden. In the neutral ligand it should be allowed but is probably very weak. For the uni-negative ligand, however, the vibration becomes more intense and this is explained by the X-ray studies<sup>10</sup> which show that the C=N double bond is almost completely localized in the C-N<sup>II</sup> region. Hence, the N<sup>II</sup> and N<sup>III</sup> atoms are very much different. The position of the band at lower energy is also consistent with the observed lengthening of the N<sup>II</sup>-N<sup>III</sup> bond. In all the three thiosemicarbazido complexes, in addition to bands due to  $\delta(\text{NH})$ , amide,  $\nu(\text{CN}) + \delta(\text{NH}_2)$  and  $\nu(\text{C}=\text{S})$ , a sharp band appears at  $950\text{ cm}^{-1}$  indicating uninegative bidentate nature of the ligand<sup>8,9</sup>. Dithiocarbamate can behave as a bidentate or a monodentate ligand. The former exhibits  $\nu(\text{CS})$  near  $1000\text{ cm}^{-1}$  as a single band, whereas the latter shows a doublet in the same region<sup>11</sup>. Also the  $\nu(\text{C}=\text{N})$  of the former (above  $1485\text{ cm}^{-1}$ ) is higher than that of the latter (below  $1485\text{ cm}^{-1}$ )<sup>12</sup>. In the present case, the ligand dithiocarbamate exhibits  $\nu(\text{C}=\text{N})$  band at  $1505\text{ cm}^{-1}$  and a singlet at  $1005\text{ cm}^{-1}$  due to  $\nu_{\text{as}}(\text{CS})$  indicating that the chelate is coordinated to manganese(III) ion through both the sulphur atoms as a uninegative bidentate ligand. Similar observations for manganese tris (dithiocarbamates) have been reported by Prabhakaran and Patel<sup>13</sup> and Das and Ramana Rao<sup>14</sup>. In the acetylacetonato complexes, the bands due to  $\nu(\text{C} \cdots \text{O})$  and  $\nu(\text{C} \cdots \text{C})$  were obtained at  $\sim 11600$  and  $1520\text{ cm}^{-1}$  respectively indicating the uninegative bidentate coordination of the ligand as suggested by Graddon<sup>15</sup>. In the compounds containing picolinate group, the band due to free carboxyl group at  $1710\text{ cm}^{-1}$  was found to be absent. Other bands due to  $\nu_{\text{as}}(\text{CO}_2)$  and pyridine ring were found to be present indicating the coordination of the ligand through the nitrogen and oxygen atoms as an uninegative bidentate one as suggested by Fowles *et al.*<sup>16</sup>.

The electronic spectra of the complexes show three bands at  $\sim 13500$ ,  $\sim 22900$ , and  $\sim 25000\text{ cm}^{-1}$ . Only one spin-allowed transition  ${}^5E_g \rightarrow {}^5T_{2g}$  is expected for weak field octahedral manganese(III) complexes<sup>17,18</sup>. The presence of three bands in these complexes indicates lowering of the  $O_h$  symmetry due to Jahn-Teller distortion. The complexes are expected to be tetragonally distorted with  $D_{4h}$  symmetry and the bands can be assigned to the transitions,  ${}^5B_{1g} \rightarrow {}^5A_{1g}$  ( $\sim 13500\text{ cm}^{-1}$ ),  ${}^5B_{1g} \rightarrow {}^5B_{2g}$  ( $\sim 22900\text{ cm}^{-1}$ ) and  ${}^5B_{1g} \rightarrow {}^5E_g$  ( $\sim 25000\text{ cm}^{-1}$ ) as suggested by Davis *et al.*<sup>19</sup> and Lever<sup>20</sup>. The lowest band of all the complexes was found to be broad which confirms the Jahn-Teller distortion experien-

ced by these complexes. Thus, in the light of the above evidences, it is suggested that the five mixed chelate manganese(III) complexes reported here are six-coordinated with tetragonally distorted octahedral stereochemistries.

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#### Polarographic Studies on Mixed Ligand Complexes Involving Amino Acids : Ternary Systems, Cd- $\alpha$ -Alanine-Oxalate & Cd- $\beta$ -Alanine-Oxalate

ANITA RANI AGGARWAL, K. B. PANDEYA & R. P. SINGH\*  
Department of Chemistry, University of Delhi, Delhi 110 007

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Ternary complexes of cadmium(II) with oxalate as primary ligand and  $\alpha$ - and  $\beta$ -alanines as secondary ligands have been studied polarographically. Formation of three mixed complex species,  $[\text{Cd}(\text{amino acid})(\text{oxalate})]$ ,  $[\text{Cd}(\text{amino acid})(\text{oxalate})_2]$  and  $[\text{Cd}(\text{amino acid})_2(\text{oxalate})]$ , is observed in each case. The reduction is reversible and diffusion-controlled. The stability constants have been evaluated using the method of McMasters. The  $\alpha$ -alanine complexes are found to be more stable than the corresponding  $\beta$ -alanine complexes.