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NOTES

Synthesis and Structural Studies on Mn(II) Complexes with Some β-ketoimines

S. K. AGARWAL* and MUKESH KUMAR
Chemistry Department
Lajpat Rai (P.G.) College
Sahibabad-201 005, India
and
SUBHASH CHAND
Chemistry Department
Marathwada Institute of Technology, Aurangabad-431 005, India.

Mn(II) complexes having the formulae $Mn(L)_2$, where L=4-p-dimethyl amino-anilino-3-penten-2-one, 4-(β-mercapto) ethyl amino-3-penten-2-one, 4-(4-phenyl thiazole-2) amino-3-penten-2-one, 4-(2-hydroxy-penten)-3-pyridyl ketoimine and O-(4-imino-3-penten-2-one) benzene sulphonic acid have been prepared. The complexes show non-electrolytic behaviour. All the complexes have either octahedral or high spin tetrahedral geometries.

Several transition metal complexes of β-ketoimines[1-6] have been prepared and physico-chemical properties investigated. A thorough survey of the literature reveals that comparatively little is known about the complexes of Mn(II) with β-ketoimines. Here we report the synthesis and structural characterization of some Mn(II) complexes with β-ketoimines such as 4-p-dimethyl amino-anilino-3-penten-2-one ($C_{13}H_8NO$), 4-(β-mercapto) ethyl amino-3-penten-2-one ($C_7H_{13}NOS$), 4-(4-phenyl thiazole-2) amino-3-penten-2-one ($C_{14}H_{14}NOS$), 4-(2-hydroxy-penten)-3-pyridyl ketoimine ($C_{10}H_{12}NO$) and 0-(4-imino-3-penten-2-one) benzene sulphonic acid ($C_{11}C_{13}NSO_4$).

Ligands were synthesized as described earlier[6-8]. $MnCl_2.4H_2O$ used was of AR Grade.

The metal chelates were prepared by the gradual addition of appropriate quantities of hot methanolic solution of the respective ligand to the aqueous solution of metal salt. The precipitates were obtained at pH-8. The precipitates were digested on water bath for about ½ hr. at *ca* 50°C. The separated solids were filtered, washed with distilled water and ethanol and finally with ether and dried in vacuum over P_4O_{10}. Elemental analyses showed 1 : 2 (M : L) stoichiometry in the isolated complexes.

*III-E, 7/9, Nehru Nagar, Ghaziabad (India).

Low molar conductance values 1.30–2.80 ohm^{-1} cm^2 mole^{-1}) in nitrobenzene solution (*ca* 10^{-3}M) are suggestive of their non-ionic nature. Magnetic moment values (5.66–5.67 B.M.) of $Mn(C_{13}H_{17}NO)_2$, $Mn(C_{14}H_{13}NOS)_2$ and $Mn(C_{11}H_{12}NSO_4)_2$ correspond to the high-spin (sp^3) tetrahedral configuration while the values 5.91 and 5.92 B.M. of $Mn(C_7H_{12}NOS)_2$ and $Mn(C_{10}H_{11}NO)_2$ reveal the octahedral environment around the central metal ion. Further, the electronic spectra of $Mn(C_{13}H_{17}NO)_2$ and $Mn(C_{14}H_{13}NOS)_2$ and $Mn(C_{11}H_{12}NSO_4)_2$ show a band at 24,400–24,600 cm^{-1} ($^4T_1 \rightarrow {}^6A_1$) and a charge transfer band at 36,000–36,150 cm^{-1} corresponding to tetrahedral structure but in $Mn(C_7H_{12}NOS)_2$ and $Mn(C_{10}H_{11}NO)_2$, five bands corresponding to octahedral stereochemistry have been observed at 17,480–17,600 cm^{-1} [$^6A_{1g} \rightarrow T_{1g}(G)$], 21,250–21,280 [$^6A_{1g} \rightarrow T_{2g}(G)$], 23,460–23,540 [$^6A_{1g} \rightarrow E_g(G)$], 26,510–26,560 [$^6A_{1g} \rightarrow T_{2g}(D)$], 28,730–28,740 [$^6A_{1g} \rightarrow E_g(D)$].

IR spectra of the ligands: ($C_{13}H_{18}NO$) and ($C_{10}H_{12}NO$) exhibits characteristic bands at *ca* 3525 and 2780 cm^{-1} due to νOH vibrations. The ligand exists in the enolic form involving intramolecular hydrogen bonding. The νC=N occurs at *ca.* 1650 cm^{-1}. The bands due to νOH vibrations disappear in the complex, suggesting the participation of the hydroxyl oxygen in coordination. νC=N band was shifted to lower frequency region on complexation, showing the participation of the azomethine nitrogen in coordination. In $Mn(C_{10}H_{11}NO)_2$, shifting of the bands due to νC=C and νC=N observed in the corresponding ligand, indicates co-ordination of the pyridinic nitrogen to the metal ion.

In the IR spectra of ligands: ($C_7H_{13}NOS$), ($C_{14}H_{14}NOS$) and ($C_{11}H_{13}NSO_4$), bands characteristic of ν(C=O) and ν(N–H) are observed in the region 1680–1670 cm^{-1} and 3340–3330 cm^{-1} respectively. In ($C_7H_{13}NOS$) a sharp band is observed at 2560 cm^{-1}, due to ν(SH). In complexation, the bands due to νC=O get shifted to lower frequency region, indicating the involvement of carbonyl oxygen in chelation. The band due to ν(NH) in $Mn(C_{14}H_{13}NOS)_2$ and $Mn(C_{11}H_{12}NSO_4)_2$ disappear while the band characteristic of ν(SH) is not appeared in the IR spectrum of the chelate of MEAPO, indicating the deprotonation of the ligand and replacement of hydrogen by metal ion. Some new bands appear in the lower frequency region (460–590 cm^{-1}), which may be assigned due to ν(M-O) and ν(M-N) vibrations, ν(M-S) is observed at 380 cm^{-1} in $Mn(C_7H_{12}NOS)$ complex.

The horizontal line on TG curve upto 240°C indicate the stability of all the compounds. In case of $Mn(C_{13}H_{17}NO)_2$ and $Mn(C_{10}H_{11}NO)_2$, organic part of the molecule gets decomposed abruptly in pure oxygen atmosphere in the temperature range 240°–620°C and Mn_2O_3 is obtained as final product. The observed weight loss correspond to the formation of Mn_2O_3 which might be contaminated with Mn_3O_4. In $Mn(C_7H_{12}NOS)_2$,

$Mn(C_{14}H_{13}NOS)_2$ and $Mn(C_{11}H_{12}NSO_4)_2$, from the TG curve it is seen that the decomposition of organic entity becomes complete in the temperature range 240–670° and the last product is the same as obtained above.

From DT curve exothermal effects are well observed at 320°, 470° and 600°C in $Mn(C_{13}H_{17}NO)_2$ and $Mn(C_{10}H_{11}NO)_2$, while these peaks are seen at 340°, 480° and 650°C in the other compounds, suggesting abrupt oxidation of organic part of the complexes in oxygen atmosphere.

In general, the decomposition of the compounds is represented by the following reactions:

$$MnL_2 \xrightarrow{240\text{–}380^\circ} MnL \xrightarrow{380\text{–}540^\circ} MnL_{1/2} \xrightarrow{540\text{–}620^\circ} MnO \rightarrow Mn_2O_3.$$

(where $L = C_{13}H_{17}NO$ or $C_{10}H_{11}NO$)

$$MnL'_2 \xrightarrow{240\text{–}300^\circ} MnL' \xrightarrow{390\text{–}560^\circ} MnL'_{1/2} \xrightarrow{560\text{–}670^\circ} MnO \rightarrow Mn_2O_3.$$

(where $L' = C_7H_{12}NOS$, $C_{14}H_{13}NOS$ or $C_{11}H_{12}NSO_4$)

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