

bands of medium to strong intensity in the complex salts. Tartaric acid shows the OH deformation vibration at 1275 cm^{-1} which disappears in uranium(IV) ditartarate indicating that the OH groups are coordinated to uranium(IV) ion. The $\nu_s(\text{OCO})$ band as reported above in this compound is relatively broader than all other complex salts which further implies that this band arises due to a combination of several superimposed bands.

In complex salts the observed bands in this region appear on both higher as well as lower frequency side of 1275 cm^{-1} band and clearly imply that the OH groups are dissimilar and most probably only one of the OH group is coordinated to uranium(IV) ion. In addition to the above spectral data, the spectra of d-tartaric acid show a peak at 1097 cm^{-1} which arises due to C-O stretching vibration of the secondary alcoholic group (C-OH). In uranium(IV) ditartarate and its complex salts this band shifts to a lower frequency region $1085\text{--}1049\text{ cm}^{-1}$ and appears as a doublet. The splitting indicates that both the (C-OH) groups are dissimilar in these compounds.

It appears from the above discussion that tartarate ion coordinates through two carboxylate groups and a hydroxy group to a uranium(IV) ion and the secondary hydroxy group being coordinated to a neighbouring uranium(IV) ion. The splitting of the (C-OH) stretching band appears due to differences in vibrational energies of the coordinated OH group in the chelate ring and the coordinated OH group with the neighbouring uranium(IV) ion.

Acknowledgement

The authors thank Dr. B. Sahoo, for his interest in the work. Thanks are also due to Prof. S. Pani, Head of the Chemistry Department, Sambalpur University for facilities.

References

1. K. C. SATPATHY and B. SAHOO, *Curr. Sci.*, 1967, 36, 320.
2. K. C. SATPATHY and S. C. BISWAL, *J. Indian Chem. Soc.*, 1975, 52, 327.
3. K. C. SATPATHY and A. K. PATNAIK *J. Indian Chem. Soc.*, 1975, 52, 1012.

Some Ni(II) Complexes of 4-Thiazolidinone Derivatives

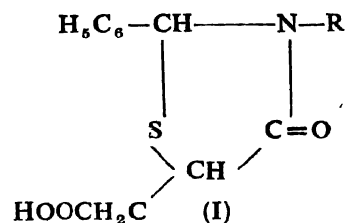
L. D. DAVE, S. K. THAMPY and S. K. THULASIDAS
University Department of Chemistry, Bhavnagar University,
Bhavnagar

Manuscript received 19 July 1980, revised 18 July 1981,
accepted 11 August 1981

WE describe in this paper the preparation and characterisation of some Ni(II) complexes with 2-phenyl-5-carboxymethyl-4-thiazolidinone derivatives¹, having phenyl, *p*-chlorophenyl and *p*-methoxyphenyl groups in position 3.

Experimental

The three ligands (I) have been prepared by the condensation of proper Schiff bases with thiomalic acid following the procedures described in literature^{1,2,3}.



Where R = phenyl, *p*-chlorophenyl or *p*-methoxyphenyl.

Equimolar quantities of nickel chloride in distilled water and the ligands in rectified spirit were mixed and the pH was adjusted between 6 to 6.5 by means of acetate buffer. The mixture was refluxed for 1 hr. Separated solids were filtered, washed with hot water and then with alcohol. The complexes were dried in vacuum at room temperature. All the complexes were insoluble in water and common organic solvents and were only partially soluble in DMF. Data on elemental analysis, thermal analysis, magnetic moment at room temperature, electronic and ir spectra are stated in Table 1.

Results and Discussion

Elemental analysis shows the complexes to be 1:2::M:L with two water molecules. Thus the ligands behave as bidentate monobasic groups and with two water molecules give a six-coordinate Ni(II) complex. The low conductivity (about 10 mhos) indicates the non-electrolytic nature of the complexes. The T.G.A. residues are in accordance with the suggested composition of the molecules. DTA curves show an endothermic peak between $140\text{--}175^\circ$ which suggests the presence of water; decarboxylation sets in at around 320° in all these complexes.

The values of the experimental magnetic moments of the complexes are found to lie in the range of 3 to 3.2 B.M. suggesting an octahedral stereochemistry⁴. All the complexes show absorption bands at around 360 nm and 420 nm which are also present in the ligands. They further show three more bands which are weak. These bands could be due to the following idealised (O_h symmetry) transitions. The bands at 450 nm ($\epsilon=770$), 530 nm ($\epsilon=300$) and 640 nm ($\epsilon=120$) could be ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transitions respectively.

The ir spectra of the complexes show a broad peak around 3500 cm^{-1} confirming the presence of water molecules. A band around 1720 cm^{-1} in all the complexes shows the presence of C=O group. It is not shifted from its position in the ir spectrum of the ligands. Hence we conclude that the C=O group does not enter into complex formation. A very weak band near 750 cm^{-1} could be assigned to rocking vibration of water attached to nickel. The complexes show two sharp bands at $\sim 1600\text{ cm}^{-1}$ and $\sim 1400\text{ cm}^{-1}$ due to the COO^- group. The second bond of ligand to Ni(II)

TABLE I—ANALYTICAL, MAGNETIC, THERMAL AND SPECTRA DATA

No.	Complex	Mol. wt.	% Metal	% Sulphur	% Nitrogen	μ_{eff} B. M.	Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	Thermal Analysis % residue found (NiO)	Electronic spectra (nm)	IR spectra (cm^{-1})
1.	2,3-Diphenyl-5-carboxymethyl-4-thiazolidinone Ni(II).2H ₂ O	735 (718.7)	8.02 (8.17)	3.72 (3.69)	8.74 (8.92)	3.03	8	20.95 (20.6)	360 420 445 530 640	3520 2980 1725 1607 1410 750
2.	2-Phenyl-3-(<i>p</i> -chlorophenyl)*-5-carboxymethyl-4-thiazolidinone Ni(II).2H ₂ O	731 (750.7)	7.56 (7.45)	3.64 (3.73)	8.44 (8.52)	3.2	12	19.2 (19.0)	360 425 450 540 630	3500 3000 1720 1600 1400 750
3.	2-Phenyl-3-(<i>p</i> -methoxyphenyl)-5-carboxymethyl-4-thiazolidinone Ni(II).2H ₂ O	762 (778.7)	7.48 (7.53)	3.72 (3.59)	8.31 (8.22)	3.05	10	19.7 (19.4)	350 425 450 540 650	3500 3000 1730 1600 1390 740

*Cl found 8.7 (8.9)

can be at S, N or O (of CO) site. If the bond is established at sulphur, a six-membered ring will be formed. With either N or O as the donor site, the chelate ring will be seven-membered and hence less stable. On the basis of the structure of the ligand, we suggest Ni-S bonding. The stretching vibration of M-S bond was beyond our ir range. We, therefore, suggest that our complexes are diaquo, octahedral complexes where the ligand binds the metal at S and COO groups.

References

1. G. C. KAMDAR, H.H. PATEL and A. R. PARIKH, *Curr. Sci.*, 1979, 48, 945.
2. A. R. SURREY, *J. Amer. Chem. Soc.*, 1949, 7, 3105.
3. G. REDDELIEN, *Ber.*, 1920, 1913, 2712, 2718, 345.
4. J. LEWIS and R. G. WILKINS "Modern Coordination Chemistry", Interscience, 1960, p. 427.

Chromium(III) Complexes of 2-(*o*-Hydroxyphenyl) Benzoxazole

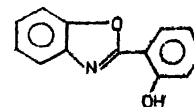
R. L. DUTTA and TAPAS RAY

Department of Chemistry, The University of Burdwan, Burdwan-713 104

Manuscript received 28 May 1981, accepted 11 August 1981

HARKINS *et al*¹ first reported copper(II), nickel(II), cobalt (II) and zinc(II) complexes of 2-(2'-pyridyl) benzoxazole. Oxygen bonded complexes of 2-methylbenzoxazole and of benzoxazole with halides of the above metal ions were studied by Duff and Hughes² and by Duff³. Complexes of some alkyl- and hydroxy-alkyl derivatives of benzoxazoles with silver(I)⁴, niobium pentachloride⁵, palladium(II)⁶ and iridium(III)⁷ have also been reported. We herein report some homo and

and hetero-complexes of chromium(III) with 2-(*o*-hydroxyphenyl) benzoxazole, HL, (I)



HL (I)

Experimental

2-(*o*-Hydroxyphenyl) benzoxazole⁸ and trichloro tris (thiourea) chromium(III)⁹ were prepared by standard procedures.

[CrL₃]4H₂O : A mixture of 0.8 gm (~0.004 mol) of the ligand in alcohol, 0.8 gm (~0.002 mol) of [Cr(tu)₃Cl₃] in 20 ml alcohol and 5 ml water was refluxed on a steam bath for 5 hrs.

After filtration the volume was reduced to 30 ml and was left overnight in the refrigerator. 2 ml water was added and the mixture again left in the refrigerator for the separation of the unreacted ligand. After filtration the solution was reduced to 15 ml and allowed to crystallise. Finally, the green crystalline compound was collected, washed with little water and stored in a desiccator.

[Cr(L)(dipy)(tu)₂]Cl₂ : To a 1:1 alcoholic solution of 1 gm of [Cr(tu)₃Cl₃], 0.8 gm of dipridyl was added and the solution was refluxed for 4-5 hrs. 0.5 gm of benzoxazole dissolved in alcohol was then added and refluxing continued for about 16 hrs. After filtration the volume was reduced, 6 ml water added and left in the refrigerator for a few hrs. The unreacted ligand was removed, the solution was concentrated under a stream of air and then left in the refrigerator for 2 days. The solution was scratched with 10 ml water and the separated brown crystalline product was collected, washed with acetone and stored in a desiccator.