

TABLE 1—GAMMA AND X-IRRADIATION OF CHLORAMINE-T AND ANHYDROUS CHLORAMINE-T.
DOSE RATES ARE GIVEN IN RADS/MIN AND ABSORBED DOSE IN EV/GM $\times 10^{19}$.

Compound	CAT (Gamma irradiation)		CAT (X-irradiation)		Anhydrous CAT (Gamma irradiation)		Anhydrous CAT (X-irradiation)			
	870		10,660		256		870		603	
Dose rate No.	Absorbed dose	G _{-CAT}	Absorbed dose	G _{-CAT}	Absorbed dose	G _{-CAT}	Absorbed dose	G _{-CAT}	Absorbed dose	G _{-CAT}
1	9.18	286.0	5.95	216.0	2.88	246.0	9.04	114.0	2.63	527.0
2	18.36	370.7	12.52	186.3	5.76	246.0	18.08	80.0	5.10	826.0
3	24.48	373.3	19.40	206.0	11.52	830.7	48.20	71.0	6.77	820.0
4	48.96	309.4	36.56	223.4	17.28	977.0	60.26	80.0	—	—
5	61.20	262.3	56.34	196.2	—	—	72.30	129.0	—	—
6	73.44	286.4	—	—	—	—	—	—	—	—

The high G-values observed for the solids (Table 1) indicate that there is a chain mechanism operative in the radiation decomposition of CAT. Probably, the only other well known example of compounds showing a similar behaviour is the gamma decomposition of solid choline chloride and choline bromide³⁻⁵, with G values of the order of 10^4 . A chain mechanism has been assumed in these cases and e.s.r. studies⁴ have identified the biradical which interacts with the substrate to produce the free radical precursor for initiating the chain reaction. In gamma irradiated CAT, e.s.r. studies³ have revealed the presence of a free radical in which the odd electron is moving in a delocalized π orbital. However, a mechanism of decomposition of solid CAT can be worked out after a complete analysis of the radiolytic products.

Acknowledgement

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References

1. E. BISHOP and V. J. JENNINGS, *Talanta.*, 1958, **1**, 197.
2. D. S. MAHADEVAPPA and ANANDA MURTHY, *J. Indian Chem. Soc.*, 1971, **48**, 683.
3. R. L. COLLIN, *J. Amer. Chem. Soc.*, 1957, **79**, 6086.
4. R. O. LINDBLOM, R. M. LEMMON and M. CALVIN, *J. Amer. Chem. Soc.*, 1961, **83**, 2484.
5. R. M. LEMMON, M. A. PARSONS and D. M. CHIN, *J. Amer. Chem. Soc.*, 1955, **77**, 4139.

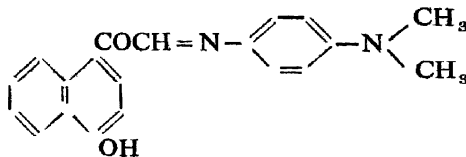
Study in Chelates of Some 3d Transition Elements and *p*-Dimethyl Aminoanil of 4-Hydroxyl 1-Naphthyl Glyoxyl

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GOOD amount of work¹⁻⁸ has been done on the transition metal chelates of anils from *p*-dimethyl-aminoaniline and nonsubstituted glyoxals (aliphatic and aromatic). In the present communication attempt is being made to study the chelates of *p*-dimethyl-aminoanil of 4-hydroxyl 1-naphthyl glyoxal (*), in extension.



Ligand (L), *p*-dimethylaminoanil of 4-hydroxyl 1-naphthyl glyoxal explores possibility of chelation at hydroxyl, carbonyl and azomethine groups. Most probably hydroxyl group is not participating in complexation as it is at a remotor position than that of carbonyl and azomethine adjacent groups. This paper deals with the stoichiometry and the electrolytic nature of the complexes.

Experimental

Preparation of ligand : Alcoholic solutions of 4-hydroxy 1-acetyl naphthalene⁷ (15%, w/v) and selenium

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dioxide (12-15%, w/v) were mixed in 3 : 1 ratio (v/v) and boiled, after adding 15-25 ml water in 200 ml solution, it was refluxed for 2-3 hrs and then concentrated. Decanted liquid was poured in to hot 1.5 lit water and refluxed for 15-30 minutes. Dirty orange glyoxal was collected on Buckner funnel and recrysta-

Results and Discussion

Results of elemental analysis noted in Table 1 established metal-ligand interaction ratios 1 : 2 and 1 : 1 in Mn (II), Cr (III), Fe (III) and Co (II), Cu(II) complexes, respectively.

Table 1

Sl. No.	Complexes	Analysis						Δ_M (Mhos)
		Metal (%)		Nitrogen (%)		Chlorine (%)		
		Found	Calcd.	Found	Calcd.	Found	Calcd.	
1.	MnL ₂ Cl ₂	7.30	7.21	7.29	7.35	9.23	9.30	1.18
2.	CoLCl ₂	13.00	13.16	6.18	6.25	15.74	15.83	0.84
3.	CuLCl ₂	13.92	14.04	6.09	6.19	15.75	15.67	3.15
4.	CrL ₂ Cl ₃	6.72	6.85	7.30	7.38	9.30	9.34	21.94
5.	FeL ₂ Cl ₃	7.40	7.32	7.24	7.34	9.37	9.29	18.58

lised from alcohol; m.p. 185° (Found : C, 71.21 ; H, 3.90 ; O, 24.89. Required : C, 72.00 ; H, 4.00 ; O, 24.00).

p-Dimethylaminoaniline was mixed in excess to equimolar quantity of glyoxal in alcohol and the resulted solution was concentrated over water bath. The anil was precipitated from the cold solution by adding small volume of water. Excess amine was washed with ether and the product was recrystallised from acetone; m.p. 210° (Found : C, 75.00 ; H, 5.57 ; N, 8.69. Required : C, 75.54 ; H, 5.62 ; N, 8.81). In the i.r. spectra of anil appearance of bands at 1667 Cm^{-1} and 1613 Cm^{-1} , which could only be assigned⁸ to $>\text{C}=\text{O}$ and $>\text{C}=\text{N}$ stretching vibrations, confirm the presence of these groups.

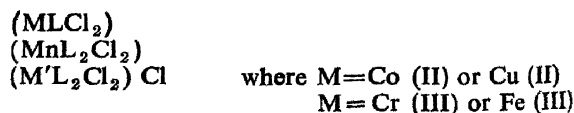
Isolation of complexes : All the complexes under study have been isolated from the method of Upadhyay⁹ et al.

Analysis and conductometric measurements : Analysis was performed by C. D. R. I. Lucknow. Chlorine was estimated as AgCl and metal components were determined gravimetrically¹⁰.

Molar conductance (Δ_M) in nitrobenzene was determined with Toshniwal's conductivity bridge. Ligand solution was prepared in acetone by dissolving accurately weighed quantity, directly. Metal chloride (BDH Analar) solutions were also prepared in acetic medium and standardised¹⁰ before use.

Molar conductance (Δ_M) values of the chelates (Table 1) in nitrobenzene explore¹¹ nonelectrolytic and 1 : 1 electrolytic nature of divalent and trivalent metal chelates respectively. Silver nitrate treatment of the adducts in ethanol also verified the above conclusions.

Taking in to account the above results, most probable formulae assigned to the chelates are :



Above formulae satisfy maximum coordination numbers, 6 for Mn (II), Cr (III), Fe (III) and 4 for Co (II), Cu (II) in their Complexes.

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References

1. R. C. SAXENA, Ph. D. Thesis, Roorkee University, Roorkee, 1968.
2. P. SINGH, Ph. D. Thesis, Meerut University, Meerut, 1971.
3. R. K. UPADHYAY, Ph. D. Thesis, Meerut University, Meerut, 1972.

- R. K. UPADHYAY, and R. C. SAXENA., *Indian J. Chem.*, 1973, 11, 697.
- R. K. UPADHYAY, R. C. SAXENA and R. R. SHARMA., *Indian J. Chem.*, 1973, 11, 736.
- R. K. UPADHYAY and RASHMI RANI BANSAL., *J. Indian Chem. Soc.*, 1974, Communicated.
- M. A. KRAM and R. D. DESAI., *Proc. Indian Acad. Sci.*, 1940, 49, II.
- J. R. DYER., "Applications of Absorption Spectroscopy of Organic Compounds", Prentice Hall of India, New Delhi, 1969.
- R. K. UPADHYAY, V. P. SINGH and S. C. SHARMA., *J. Indian Chem. Soc.*, 1974, Communicated.
- A. I. VOGEL., "A Text Book of Quantitative Inorganic Analysis" Longman Group Ltd., London, 1969.
- M. M. JONES., "Elementary Coordination Chemistry" Prentice Hall, Inc, N. J., 1964.

Acetato-N, N'-Ethylenebis (5-bromosalicylideneiminato)-manganese(III)

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RECENTLY some Schiff bases with more than one coordinating centres have been used to stabilize Mn(III) ion as the metal chelates.¹⁻¹² We have isolated a Mn(III) complex of the dibasic quadridentate Schiff base derived from 5-bromo-salicylaldehyde and ethylene-diamine (BRSALEN-H₂), the preparation and properties of which are described here.

Experimental

Manganese (III) acetate dihydrate was prepared as described previously.⁽¹⁰⁾ The Schiff base, BRSALEN-H₂, was prepared by warming 5-bromo-salicylaldehyde and ethylenediamine in methanol on water bath. The yellow coloured Schiff base recrystallised from methanol melted at 189°-192° (lit.¹³ m.p. 192-194°). All other solvents and chemicals were purified as described previously.¹⁰ The molar conductance, electronic spectra, infrared spectra, and magnetic susceptibility were measured and elemental analyses were performed as described previously.¹⁴

Preparation of the Mn (III)-Schiff base complex : An equimolar mixture of the Schiff base (4.26 g, 0.01 mole) and manganese (III) acetate dihydrate (2.68 g, 0.01 mole) in methanol (~ 200 ml) was refluxed (1 hr). The resulting solution was filtered and concentrated by passing air through it whereby the dark brown separated out. The complex was filtered off, washed with cold benzene and dried in avacuum desiccator over P₂O₅. (Found : Mn, 10.29 ; N, 5.20% ; calc. for [Mn(BRSALEN)(CH₃COO)] : Mn, 10.21 ; N, 5.21%). $\Lambda_M = 2.2$ ohm⁻¹ cm² mole⁻¹ (conc. 6.58 x 10⁻⁴ M in acetonitrile), $\mu_{eff} = 4.92$ B.M. (31°C) ; ν_{max} at 24, 150 cm⁻¹ (log $\epsilon \approx 3.5$) and at 20, 490 cm⁻¹ (log $\epsilon \approx 3.0$) (in acetonitrile) ; I. R. spectral data are discussed in results and discussion.

Results and Discussion

Elemental analyses of the compound correspond to the formula [Mn(BRSALEN)(CH₃COO)] (where, BRSALEN-H₂ = a molecule of the dibasic quadridentate Schiff base) and its paramagnetic moment of 4.92 B. M. is close to the spin-only value for high spin d⁴ system. It is moderately soluble in methanol and acetonitrile and is practically nonconducting in acetonitrile. The molar conductance value supports the coordination of acetate ion, which is further substantiated by infrared spectral data. The medium intensity bands observed at 1600 and 1351 cm⁻¹ are due to the asymmetric and symmetric COO⁻ stretching frequency respectively in the complex. The difference of 249 cm⁻¹ between the two bands and their positions indicate monodentate nature of the acetate group.¹⁵ The C=N and phenolic C-O stretching frequencies in the free ligand are observed at 1647 and 1284 cm⁻¹ respectively. These two bands in the Mn(III) complex have been shifted to 1639 and 1304 cm⁻¹ respectively. The lowering of the C=N stretching frequency is an indication of the coordination of imine nitrogen atom.¹⁶ The shift of phenolic C-O frequency in the complex in the complex is due to the change of hydrogen bonded structure to covalent mental bonded structure.¹⁶

The electronic spectra of the Mn(III) complex in acetonitrile show two bands, one at 24, 150 cm⁻¹ (log $\epsilon \approx 3.5$) and the other broad band at 20,490 cm⁻¹ (log $\epsilon \approx 3.0$). Usually the high-spin Mn (III) complexes¹⁷ with octahedral geometry give one charge transfer band around 25,000 cm⁻¹ (log $\epsilon \approx 3.5$) and a spin-allowed d-d transition band, ⁵E_g → ⁵T_{2g} around 20,000 cm⁻¹ (log $\epsilon \approx 2.5$). The high energy band observed in this compound may be considered as a charge transfer band, while the band at 20,490 cm⁻¹ may be assigned to d-d transition. This broad band occurring at lower frequency with increased intensity, suggests the lowering of the octahedral symmetry.

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References

- B. C. SARMA, K. R. RAY, R. E. SIEVERS and J. C. BAILAR, Jr., *J. Amer. Chem. Soc.*, 1964, 86, 14.
- A. EARNSHAW, E. A. KING and L. F. LARKWORTHY., *J. Chem. Soc.*, (A), 1968, 1048.
- C. P. PRABHAKARAN and C. C. PATEL., *J. Inorg. Nuclear Chem.*, 1969, 31, 3316.
- B. C. SARMA and C. C. PATEL., *Indian J. Chem.*, 1970, 8, 94.
- A. VAN DEN BERGEN, K. S. MURRAY, M. J. O'CONNOR and B. O. WEST, *Austral. J. Chem.*, 1969, 22, 39.
- B. C. SARMA and C. C. PATEL., *Indian J. Chem.*, 1970, 8, 747.
- J. LEWIS, F. E. MABBS and H. WEIGOLD., *J. Chem. Soc.* (A), 1968, 1699.
- K. DEY and K. C. RAY., *J. Indian Chem. Soc.*, 1973, 50, 66.
- K. DEY, R. L. DE and K. C. RAY., *Indian J. Chem.*, (In press).