

3. Bovet, D and Bovet Mitti, F., In *Medicaments die Systeme Nervous Vegetalis*, Karger Basel, 1948, p. 222.
4. Werner, L. H. and Barrett, W. E., In *Antihypertensive Agents*, E. Schlittler, ed., Academic Press, New York, 1967, p. 177.
5. Ratouis, R., Boissier, J. R. and Dumont, C., *J. Med. Chem.*, 1965, , 271.
6. Prasad, R. M., Hawkins, L. R. and Tietze, K., *J. Med. Chem.*, 1968, 11, 1144.
7. Pollard, C. B. and MacDowell, L. G., *J. Am. Chem. Soc.*, 1934, 56, 2199.
8. — and Wicker, T. H., *Ibid.*, 1954, 76, 1853.
9. Change, E. and Jain, V. K., *J. Med. Chem.*, 1966, 9, 433.
10. Smith, G. W., *Progress in Medicinal Chemistry*, 1967, 1, 1.

V(III), Cr(III), Mn(III) AND Fe(III) COMPLEXES OF DISALICYLALDIMINE OXAMIDE, -MALONAMINE AND -SUCCINAMIDE

K. K. NARANG AND U. S. YADAV

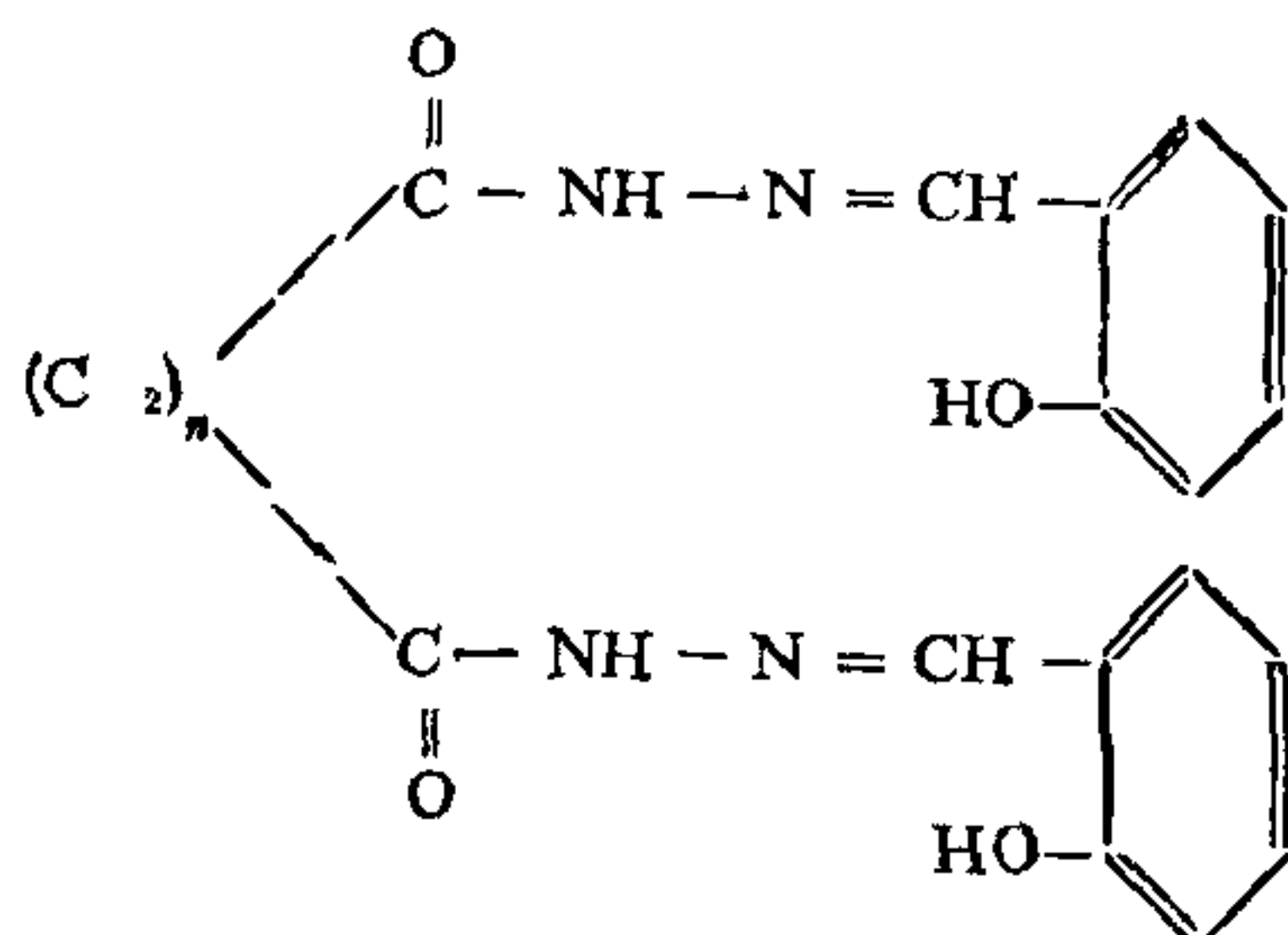
Chemistry Department, Banaras Hindu University, Varanasi 221 005, India

ABSTRACT

The solid complexes of type $M(L-2H)X$ where $M = Cr(III)$, $Mn(III)$ and $Fe(III)$, $X = Cl$ or CH_3COO and $V(L-H)SO_4$ with some flexidentate dihydrazide Schiff bases (L) have been prepared and characterized by elemental analyses, U.V., visible, i.r. and magnetic susceptibility data. The complexes are coloured, insoluble in common organic solvents and melt or decompose above $250^\circ C$. All the complexes have octahedral stereochemistry around the metal ion. The ν M-X bands are consistent with bonded X in hexacoordinate stereochemistry. The ligands coordinate through enolized carbonyl and azomethine groups.

INTRODUCTION

BONDING potentialities of acylhydrazones especially those derived from hydroxy aldehydes and ketones provide a reasonable model for the mechanism of mono amine oxidase (MAO) enzyme inhibition by hydrazine derivatives¹. The coordination behaviour of acylhydrazones, exhibiting keto-enol tautomerism, depends on the nature of ligand, metal ion, reaction medium and the temperature²⁻⁴. Recently, we have reported preparation and characterization of aluminium(III) complexes⁵ with the title ligands. As a part of a systematic study, we report, hereunder, the behaviour of these ligands (Fig. 1) towards some trivalent transition metal ions.



where $n = 0, 1$, or 2 .

FIG. 1

EXPERIMENTAL

The ligands were prepared as described earlier⁵. Vanadium(III) sulphate prepared by literature method⁶ was dissolved in dry ethanol and reacted with solid ligands for 6–8 hours. Chromium(III) complexes were prepared by refluxing aqueous solution of metal acetate (metal excess) with solid ligands for 7–8 hours. For manganese(III) complexes, ethanolic solution of freshly prepared manganese(III) acetate⁷ was refluxed with solid ligands for 5–6 hours. Iron(III) complexes were obtained by mixing aqueous solution of iron(III) chloride with alkaline solution of ligands (made neutral with acetic acid) and the mixture was warmed gently. Resulting products in all the above cases were filtered, washed with ethanol or mixture of acetic acid and ethanol and dried at $\sim 110^\circ C$. Metal contents, chloride and sulphate were estimated by following the standard literature procedures⁸. Instruments used for physico-chemical studies were same as reported earlier⁵. The data are summarized in Table I.

RESULTS AND DISCUSSIONS

From the analytical data it is evident that V(III), Cr(III), Mn(III) and Fe(III) form 1 : 1 (M : L) complexes. All the complexes contain one anion of the original metal salt. In the complexes of Cr(III), Mn(III) and Fe(III) deprotonation of the ligands

TABLE I
Analytical, electronic, magnetic moment and some i.r. data of V(III), Cr(III), Mn(III) and Fe(III) complexes

Sl. No.	Complex and Colour	Found (Calcd.) Analysis %			Magnetic moment μ_{eff} B.M.	Electronic bands compound (ligand) λ_{max} nm	I.R. bands (cm^{-1})	
		Metal	Nitrogen	Ligand			ν (C=N)	ν (NCO)
1.	V(disaloxH ₂) · SO ₄ Green	10.78 (10.80)	11.92 (11.86)	69.02 (68.85)	19.8 (20.3)	238, 365, 380, 582 (200, 292, 362)	1615	1528
2.	V(disalmalH ₂) · SO ₄ Shining brown	10.51 (10.49)	11.43 (11.52)	69.78 (69.75)	19.6 (19.7)	255, 300, 335, 370, 575 (238, 245, 290, 340)	1595	..
3.	V(disalsucH ₂) · SO ₄ Dirty green	10.17 (10.20)	11.61 (11.20)	70.48 (70.60)	19.31 (19.20)	215, 245, 300, 375, 570 (210, 278, 325)	1605	1530
4.	Cr(disaloxH ₂) · Ac Light green	11.98 (11.95)	12.88 (12.87)	74.54 (74.48)	..	230, 292, 370, 445, 585	1620	1525
5.	Cr(disalmalH ₂) · Ac Yellow	11.49 (11.55)	12.42 (12.44)	75.05 (75.11)	..	235, 265, 300, 365, 450, 578	1618	1520
6.	Cr(disalsucH ₂) · Ac Light green	11.30 (11.23)	12.22 (12.09)	76.58 (76.02)	..	230, 290, 365, 445, 582	1620	1518
7.	Mn(disaloxH ₂) · Ac Brown	15.59 (14.55)	12.03 (11.78)	74.23 (73.97)	..	240, 315, 430, 548	1595	1525
8.	Mn(disalmalH ₂) · Ac Dark brown	12.21 (12.16)	12.52 (12.39)	74.46 (74.77)	..	220, 245, 265, 428, 555	1600	1530
9.	Mn(disalsucH ₂) · Ac Greenish brown	11.78 (11.80)	12.47 (12.01)	75.38 (75.53)	..	242, 360, 435, 560	1605	..
10.	Fe(disaloxH ₂) · Cl Brown black	13.62 (13.49)	13.60 (13.49)	73.48 (73.25)	8.62 (8.55)	240, 310, 348, 405, 508	1600	1525
11.	Fe(disalmalH ₂) · Cl Black	13.00 (13.05)	13.53 (13.05)	79.08 (78.78)	8.25 (8.27)	220, 245, 350, 400, 502	1590	1520
12.	Fe(disalsucH ₂) · Cl Black	12.70 (12.63)	12.57 (12.64)	78.89 (79.45)	8.21 (8.01)	242, 295, 340, 410, 510	1595	1520

occurs to the extent of two protons while only one proton is liberated in V(III) complexes. It appears that in the case of vanadium(III) complexes, initial reaction between the vanadium(III) sulphate and the ligands liberates H_2SO_4 which, being a strong acid, lowers the pH of the medium and suppresses the lability of the remaining ligand protons. The complexes are insoluble in water and non-polar organic solvents but are sparingly soluble in coordinating solvents like dimethylformamide. Because of their insolubility, molecular weight and conductivity, etc., could not be determined. Some of the complexes melt above 250°C while the majority of them decompose without melting above 300°C . Solubility, decomposition temperature and magnetic behaviour (discussed below) are indicative of their polymeric nature in solid state⁹⁻¹⁰.

Magnetic and Electronic Spectral Studies

The $>\text{C}=\text{O}$, $>\text{C}=\text{N}$ and $-\text{OH}$ groups in ligands perturb the electronic transitions of benzene nuclei, consequently primary (${}^1\text{B}_1\text{U} \leftarrow {}^1\text{A}_{1g}$) and the secondary (${}^1\text{B}_2\text{U} \leftarrow {}^1\text{A}_{1g}$) bands due to benzene nucleus split and shift to longer wavelengths. When two chromophores $-\text{OH}$ and $>\text{C}=\text{O}$ or $>\text{C}=\text{N}$ are present as in salicylaldehyde¹¹ and salicylaldimines, one of the bands is observed even in the U.V. visible border region. The bands at 362, 340 and 235 nm in the ligands (Sl.No. 1, 2, 3) respectively are characteristic of the salicylaldimine group similar to those observed for monoacylhydrazone ligands¹². Chelation of the ligands causes splitting of the U.V. bands which are considerably red shifted due to bonding of ligands with metal ions.

Vanadium(III) complexes exhibit the magnetic moment values 2.54–2.62 B.M. The lowering in magnetic moment values is attributed to the polymeric nature of the complexes¹³ as indicated by their insoluble nature and high decomposition temperature. The complexes show two bands in the region 370–380 nm and 570–582 nm assigned to ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transitions, respectively, which are indicative of an octahedral disposition of the donor sites around the $d^2\text{V(III)}$ species^{13,14}.

Magnetic moment values of the chromium(III) complexes lie in the range 3.73–3.84 B.M. and are close to the predicted value of 3.87 B.M. for three unpaired electrons irrespective of five or six coordinate environment around the metal ion¹⁵. The complexes show three bands between 578–582, 445–450 and 265–290 nm similar to those observed for six coordinate chromium(III) complexes. Assuming the octahedral stereochemistry these bands can be assigned¹⁶ to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ in the order of increasing energy.

μ_{eff} values of Mn(III) complexes are in the range 4.67–4.76 B.M. Such a lowering of magnetic moment from spin only value of 4.94 B.M. may be ascribed to the presence of an intramolecular antiferromagnetic interaction in the solid state between neighbouring paramagnetic manganese atoms. This type of interaction could occur if the complex molecules exist as dimers or other associated species¹⁷. The electronic spectra of Mn(III) complexes show bands around 548–560 and 428–435 nm. The band between 548–560 nm may be assigned¹⁸ to ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ transition while the high energy band between 428–435 nm is due to $\text{L} \rightarrow \text{M}$ charge transfer.

Iron(III) complexes show slightly lower magnetic moment values (5.53–5.85 B.M.) than expected value of 5.92 B.M. for a spin-free d^5 system. The lowering in magnetic moment values may be attributed to the presence of antiferromagnetic coupling as reported in several dimeric iron(III) complexes¹⁹. The electronic spectra of the complexes show bands centred between 502–510, 405–410 and 340–350 nm. The bands resemble with those observed in case of six coordinate²⁰ iron(III) complexes. The first two bands may be assigned²¹ to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{A}_2)$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ transitions respectively and the third, a relatively stronger band around 340–350 nm due to $\text{L} \rightarrow \text{M}$ charge transfer.

Infrared Spectra

In ligands, the bands between $3500\text{--}3000\text{ cm}^{-1}$ due to νOH and νNH and between $1700\text{--}1650\text{ cm}^{-1}$ due to $\nu\text{C}=\text{O}$ indicate that the ligands exist in keto-form²². The ligands undergo keto-enol tautomerism and coordinate in either form. In complexes, $\nu\text{C}=\text{O}$ disappears and is replaced by a very sharp band between $1620\text{--}1595\text{ cm}^{-1}$ indicating the presence of coordinated azine ($>\text{C}=\text{N}-\text{N}=\text{C}<$) group⁴ while the $-\text{N}=\text{C}-\text{O}^-$ group vibrations observed between $1530\text{--}1518\text{ cm}^{-1}$ confirm the enolization of amide

O
||
(-C-NH-) group²³.

$\nu\text{C}-\text{O}$ between $1305\text{--}1270\text{ cm}^{-1}$ in the enolized ligands confirms the deprotonation of the ligands in the complexes. In the acetato, chloro and sulphato complexes in the present study, $\delta(\text{OCO})$ carboxylate frequencies, between $655\text{--}645\text{ cm}^{-1}$ are indicative of terminal nonbridging acetate group²⁴, $\nu\text{Fe}-\text{Cl}$ between $325\text{--}310\text{ cm}^{-1}$ are consistent with 6-coordinate complexes²⁵ while bands between $1240\text{--}1040\text{ cm}^{-1}$ indicate bidentate chelating²⁶⁻²⁸ sulphate group in the complexes.

ACKNOWLEDGEMENT

The authors thank Prof. B. M. Shukla, Head of the Chemistry Department, Banaras Hindu

University, Varanasi 221 005, for providing laboratory facilities.

1. Weigand, R. G., *J. Am. Chem. Soc.*, 1956, **78**, 5307.
2. Narang, K. K. and Lal, R. A., *Transition Met. Chem.*, 1978, **3**, 272.
3. Biradar, N. S. and Havinala, H., *Inorg. Chim. Acta*, 1976, **17**, 157.
4. Iskander, M. F., El-Aggan, A. M., Refact, L. S. and El-Sayed, L., *Ibid.*, 1975, **14**, 167.
5. Narang, K. K. and Yadav, U. S., *Indian J. Chem.* (in press).
6. Claunch, R. T. and Jones, M. M., *Inorganic Syntheses*, McGraw Hill Book Company, New York, 1963, **7**, 92.
7. Christensen, T., *Z. Anorg. Chem.*, 1901, **27**, 325.
8. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, Longman Green, London, 1962.
9. Marvel, C. S. and Tarkoy, N., *J. Am. Chem. Soc.*, 1957, **79**, 6000.
10. Goodwin, H. A. and Bailar, J. C., *Ibid.*, 1961, **83**, 2467.
11. Rohatgi, K. K. and Sengupta, S. K., *J. Inorg. Nucl. Chem.*, 1972, **34**, 3061.
12. Narang, K. K. and Aggarwal, A., *Inorg. Chim. Acta*, 1974, **9**, 137; *Indian J. Chem.*, 1975, **13**, 1072.
13. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, Elsevier, 1968, p. 269.
14. Clark, R. J. H. and Greenfield, M. L., *J. Chem. Soc. (A)*, 1967, p. 409.
15. Figgis, B. N. and Lewis, J., *Prog. Inorg. Chem.*, 1964, **6**, 37.
16. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968, p. 274.
17. Gerloch, M. and Mabbs, F. W., *J. Chem. Soc. (A)*, 1967, p. 2850.
18. Boucher, L. J. and Coe, C. G., *Inorg. Chem.*, 1975, **14**, 1289.
19. Bertand, J. A., Breece, J. L., Kalyanaraman A. R., Long, C. J. and Baker, W. A., *J. Am. Chem. Soc.*, 1970, **92**, 5233.
20. Sacconi, L. and Bertini, I., *Ibid.*, 1966, **88**, 5180.
21. Cotton, S. A., *Coord. Chem. Rev.*, 1972, **8**, 85.
22. Miyazawa, T., Shimanouchi, T. and Mizushima, S., *J. Chem. Phys.*, 1958, **29**, 64.
23. Mashima, M., *Bull. Chem. Soc. Japan*, 1962, **35**, 332, 338, 2020.
24. Curtis, N. F., *J. Chem. Soc. (A)*, 1968, p. 1579.
25. Clark, R. J. H., *Spectrochim. Acta*, 1965, **21**, 955.
26. Ahuja, I. S. and Singh, R., *J. Inorg. Nucl. Chem.*, 1973, **35**, 2075.
27. Nakamoto, K., Fujita, J., Tanaka, S. and Kobayashi, M., *J. Am. Chem. Soc.*, 1957, **79**, 4904.
28. Ahuja, I. S. and Singh, R., *Spectrochim. Acta*, 1973, **29 A**, 1879.

THIRD INTERNATIONAL CADMIUM CONFERENCE

World experts meet to discuss Cadmium, the third International Cadmium Conference will be held at the Intercontinental Hotel, Miami, Florida, from 3-5 February, 1981. Jointly organized by the Cadmium Association, London, and by the International Lead Zinc Research Organization (ILZRO) and Cadmium Council of New York, the Conference will

be wide ranging and cover economic technical, environmental and health aspects of cadmium.

Registration fee for the three-day conference is \$250.00. For additional information and registration forms please contact: Indian Lead Zinc Information Centre, B-6/7, Shopping Centre, Safdarjung Enclave, New Delhi 110 029.