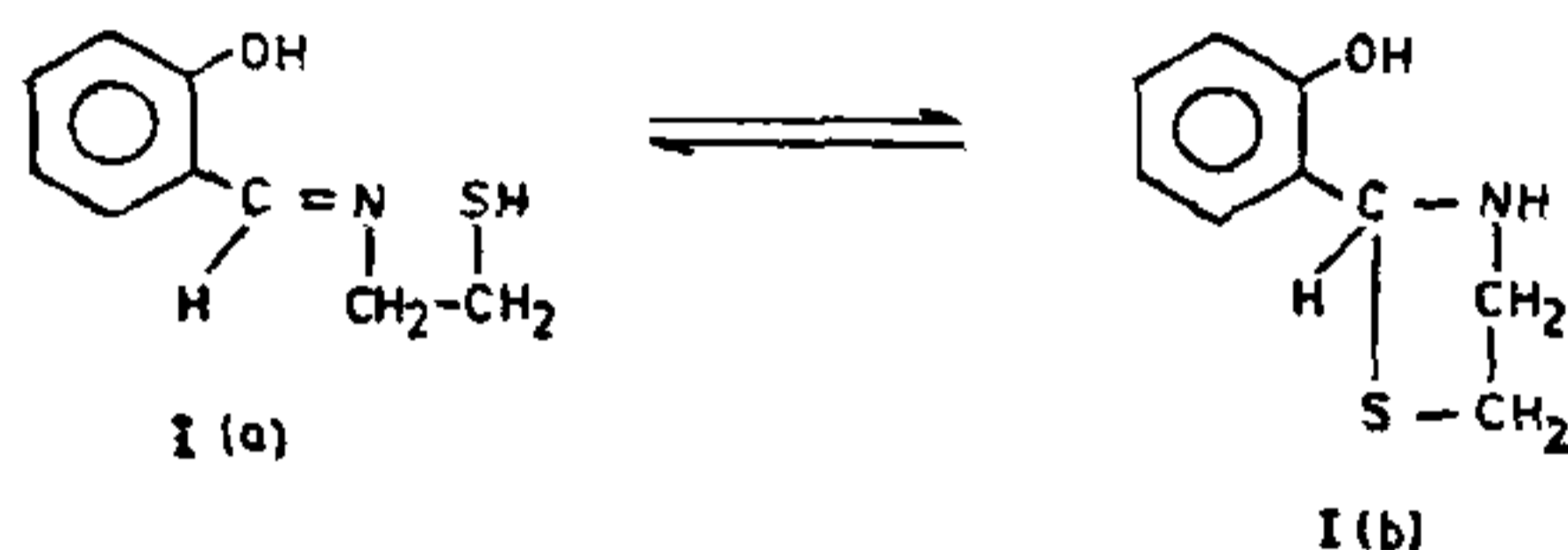


ALUMINIUM, GALLIUM AND INDIUM COMPLEXES OF SULPHUR CONTAINING SCHIFF BASES

(Miss) M. AGRAWAL, J. P. TANDON AND R. C. MEHROTRA

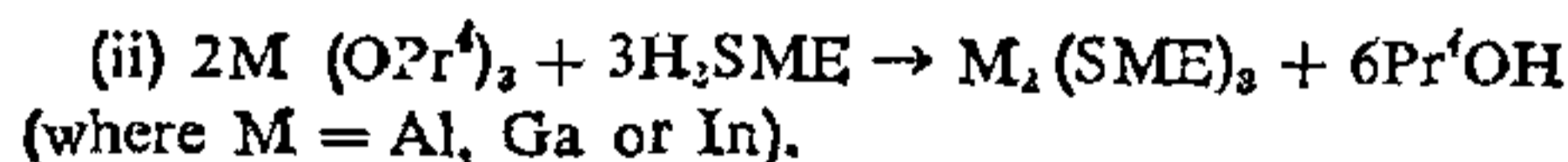
Department of Chemistry, University of Rajasthan Jaipur, 302004, India

MULTIDENTATE ligands having the amine and the mercaptide groups have been reported to form quite stable chelate compounds with transition metals^{1,2}. The amine and the mercapto groups in 1, 2 position behave as competitive nucleophiles, usually resulting in the formation of thiazolines. Suvorcka *et al.*³ have reported that the reaction of salicylaldehyde or its halogen derivatives with β -mercaptoethylamine produces a large percentage of the Schiff base rather than a thiazoline (Fig. 1). In contrast to the transition metals very little work of non-transition metals has been reported.

FIG. 1. Salicylaldehyde-2-mercaptoethylamine (H_2SME)

EXPERIMENTAL

The ligand was synthesized by refluxing salicylaldehyde and 2-aminoethanethiol in unimolar ratio in benzene and the metal complexes by refluxing 1 : 1 or 2 : 3 molar ratios in dry benzene and continuously removing isopropanol in the azeotrope⁴⁻⁶. These reactions can be represented by the following equations :



The $(OPr^t)M(SME)$ complexes also undergo exchange reaction with *t*-butanol (Table II).

RESULTS AND DISCUSSION

All these newly synthesized metal complexes are obtained by the deprotonation and coordination of the ligand moiety and on the basis of spectral studies these may be classed as metal Schiff base derivatives (Table I). These are yellow solids, soluble in most of the common organic solvents. A comparative study^{7,8} of these complexes has revealed the following

interesting facts : (i) All the derivatives with mono-isopropoxy or monobutoxy groups are essentially dimeric. (ii) In general, the reactivity goes on decreasing with the increase in the atomic weight of the central metal atom, i.e., $Al(OPr^t)_3$ is much more reactive than $Ga(OPr^t)_3$ or $In(OPr^t)_3$. (iii) The hydrolytic as well as the thermal stabilities increase with the atomic number of the metal atom and in view of their dimeric nature, the following tentative structure (II in Fig. 2) has been suggested for these complexes with the central metal atom being in the uncommon pentacoordination state⁹⁻¹¹.

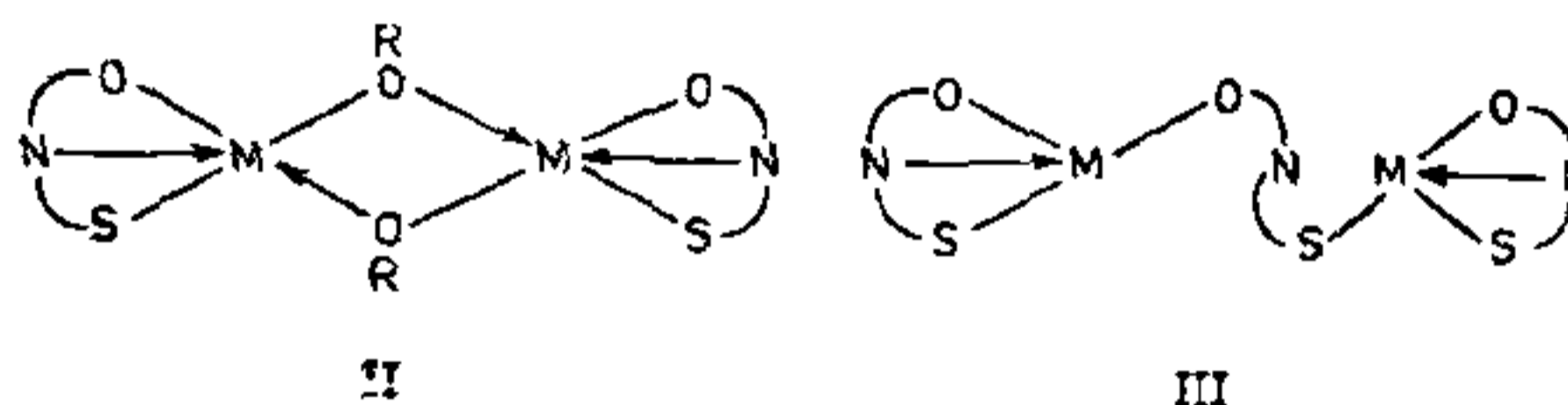


FIG. 2

(where $M = Al, Ga$ or In ; ONS unit represents the donor sites of the Schiff base unit and $R = Pr^t$ or Bu^t).

However, the 2 : 3 reaction products are quite stable towards hydrolysis and keeping in view the monomeric nature of these complexes, the structure (III) has been proposed with stable four coordinated central metal atom.

When some of the above derivatives were subjected to hydrolysis with aqueous benzene the original ligand could be separated and then confirmed by T.L.C. and I.R. spectral measurements. The electronic spectrum of the ligand (H_2SME) is fully consistent with the typical spectrum of the Schiff bases⁴⁻⁶. The 2 : 3 reaction products show considerable bathochromic shift in the band corresponding to $n - \pi^*$ transition.

The characteristic OH and SH absorption bands of the free ligand completely disappear in the corresponding complexes. The $\nu(C=N)$ stretching frequencies (1620 cm^{-1} in the ligand), however, remain almost at the same position in the corresponding complexes¹² (Table I).

In the PMR spectra of complexes, signals at 11.4 and $3.0\ \delta$ (present in the free ligand due to OH and SH protons) disappear and thereby show the deprotonation of the ligand. The azomethine proton in the free ligand ($8.28\ \delta$) also show corresponding shifting (Table I) due to the coordination of the azomethine nitrogen to the central metal atom.

TABLE I
Analytical and spectral data of 1 : 1 and 2 : 3 reaction products

| Sl. No. | Compound | M.P. (°C) | Mol. wt. found (calcd.) | ν (M-O) cm^{-1} | ν (M-N) cm^{-1} | ν (M-S) cm^{-1} | ν (C=N) cm^{-1} | δ C=N H ppm |
|---------|--|-----------|-------------------------|------------------------------|------------------------------|------------------------------|------------------------------|--------------------|
| 1. | (Pr ⁴ O) Al (C ₉ H ₉ ONS) | 270 | 550 (265) | 720, 680 | 530, 435 | 410, 370 | 1620 | 8.40 |
| 2. | (Pr ⁴ O) Ga (C ₉ H ₉ ONS) | 300 | 630 (307) | 630, 550 | 470, 440 | 320, 250 | 1625 | 8.62 |
| 3. | (Pr ⁴ O) In (C ₉ H ₉ ONS) | 310 | 720 (352) | 620, 550 | 500, 450 | 340, 290 | 1620 | 8.45 |
| 4. | Al ₂ (C ₉ H ₉ ONS) ₃ | 250 | 600 (591) | 720, 640 | 520, 420 | 400, 380 | 1630 | .. |
| 5. | Ga ₂ (C ₉ H ₉ ONS) ₃ | 265 | 690 (676) | 680, 570 | 480, 420 | 330, 270 | 1620 | .. |
| 6. | In ₂ (C ₉ H ₉ ONS) ₃ | 280 | 785 (766) | 640, 560 | 470, 410 | 340, 290 | 1625 | .. |

The chemical analysis for the metal, nitrogen and sulphur agreed with the calculated values within the limits of experimental errors.

TABLE II
Analytical data of exchange reaction products

| Sl. No. | Compound | M.P. (°C) | Mol. wt. Found (Calcd.) |
|---------|--|-----------|-------------------------|
| 1. | (Bu ⁴ O) Al (C ₉ H ₉ ONS) → | 270 | 570 (279) |
| 2. | (Bu ⁴ O) Ga (C ₉ H ₉ ONS) → | 270 | 650 (321) |
| 3. | (Bu ⁴ O) In (C ₉ H ₉ ONS) → | 270 | 758 (366) |

ACKNOWLEDGEMENT

The first author thanks U.G.C., New Delhi, for financial assistance under the Special Assistance Programme.

- Hans Jadamus, Quintus Fernando and Henry Freiser, *J. Am. Chem. Soc.*, 1964, 86, 3656.

- Sillen, L. G. and Martell, A. E., *Chem. Soc. Spec. Publ. No. 17*, 1964.
- Zelantsov, V. V. and Suvcrova, K. M., *Zh. Obshch. Khim.*, 1968, 38 (3), 480.
- Agrawal, M., Tandon, J. P. and Mehrotra R. C., *Syn. React. Metal-Org. Chem.*, 1980, 1, 9.
- , — and —, *J. Inorg. Nucl. Chem.*, 1979, 41 (10), 1465.
- , — and —, *Indian J. Chem.*, 1979, 18A, 151.
- Davidson, N. and Brown, H. C., *J. Am. Chem. Soc.*, 1942, 64, 316.
- Coates, G. E. and Hayter, R. G., *J. Chem. Soc.*, 1953, p. 2519.
- Ruff, J. K. and Hawthorne, M. F., *J. Am. Chem. Soc.*, 1960, 82, 2141.
- Beattie, I. R., Gilson, T. and Ozin, G. A., *J. Chem. Soc., A*, 1968, 1092.
- Veidis, M. V. and Palenik, G. I., *Chem. Comm.*, 1969, p. 586.
- Sharma, B. D. and Bailar, J. C. Jr., *J. Am. Chem. Soc.*, 1955, 77, 5476.