

## Complexes of Dithioamide with Some Divalent Metal Salts

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**A**MONG the ligands having  $>C=O$  group as the donor site, the amides and lactams are particularly interesting since these molecules possess also an amine group, which potentially may act as a donor to the metal ion. However, with transition metal ions thus far only compounds have been isolated that contain oxygen co-ordinated lactams and amides. This was concluded from IR spectra (shift to lower frequencies of the  $C=O$  stretching vibration). We have earlier synthesized<sup>1-4</sup> a number of simple and mixed ligand complexes involving oxygen-nitrogen, oxygen-sulfur and oxygen-nitrogen-sulfur co-ordination. In our attempt to study the complexes with the ligands containing both sulfur and nitrogen as the bonding sites, we now report complexes of dithioamide with several divalent metal ions.

### Experimental

All the chemicals used are of AnalaR grade. Ethanolic solution of metal salts and dithioamide (1:2 ratio) were refluxed for 15 mins to 1 hr (depending on different salts) and the resulting solutions were concentrated by evaporation in air when crystalline compounds separated out. These were filtered under suction, washed with ethanol and ether and dried in a vacuum dessicator.

Metals in the complexes were estimated by EDTA titration method and halogen, thiocyanate and sulfur by standard gravimetric methods. Conductance was measured in  $10^{-3}M$  acetone solution of the complexes. Magnetic susceptibility measurements were made over solid specimens by Gouy method. IR spectra were recorded on nujol mulls by Unicam SP-200 and Perkin-Elmer model 521 spectrophotometer. Electronic spectra were recorded using  $M/100$  (chloroform-ligand) solution of complexes by a Hilgerwatt UVISPECK spectrophotometer. All the relevant analytical, conductance, magnetic susceptibility and IR spectral data are recorded in Table 1.

### Results and Discussion

Complexes reported in the present investigation have the general composition  $[ML_2X_2]$  where  $M =$

$Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Zn(II)$ ,  $Cd(II)$  and  $Hg(II)$ ;  $L$  is dithioamide and  $X = Cl^-$  or  $SCN^-$ .  $Zn(II)$ ,  $Cd(II)$  and  $Hg(II)$  complexes are brown,  $Mn(II)$  complexes are chocolate,  $Co(II)$  complexes deep violet,  $Ni(II)$  and  $Cu(II)$  complexes are black in colour. These have fairly low melting points, are soluble in acetone, in which medium the  $\Delta_M$  values are very low indicating non-electrolytic nature of the complexes. Magnetic susceptibility measurements indicate  $Mn(II)$ ,  $Co(II)$  and  $Cu(II)$  complexes to be paramagnetic,  $\mu_{eff}$  value suggests a possible octahedral environment whereas nickel(II) complexes are diamagnetic.

IR spectra of dithioamide and its complexes have been studied in detail. Usually thiocarbonyl absorption occurs<sup>5</sup> in the  $1020-1250\text{ cm}^{-1}$  region, but the carbon is also linked to nitrogen, several other bands appear in the  $1560-700\text{ cm}^{-1}$  region due to coupling of  $C=S$  and  $C-N$  absorption bands. In the present case dithioamide has prominent bands in the  $3200-3100$ ,  $1500-1600$ ,  $1205$  and  $700-800\text{ cm}^{-1}$  region. In the complexes there are several bands in the  $3300-3100\text{ cm}^{-1}$  region due to modification and splitting of  $\nu(N-H)$  indicating co-ordination through the nitrogen of the  $-NH_2$  group. Also the band at  $1205\text{ cm}^{-1}$  attributable to  $\nu(C=S)$  appear at lower frequency region in complexes suggesting co-ordination through the sulfur atom of the thiocarbonyl group. Further, the two sharp bands at  $1600$  and  $1580\text{ cm}^{-1}$  region go to higher frequency region in the complexes. Bonding through sulfur and nitrogen has been substantiated by observation<sup>6</sup> of  $\nu(M-N)$  and  $\nu(M-S)$  at  $\sim 350\text{ cm}^{-1}$  and  $\sim 260\text{ cm}^{-1}$  regions respectively of the low frequency IR spectra.

In the case of thiocyanato complexes, observation of  $\nu(C\equiv N) \sim 2090\text{ cm}^{-1}$  region indicates<sup>7</sup> terminal N-bonding of the thiocyanato group.

In the u. v. spectra of the ligand and complexes, two bands appear in the  $215$  and  $312\text{ nm}$  region presumably due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  transitions in the  $C=S$  group usually occurring in the  $250-320\text{ nm}$  region. In addition, there may be bands due to  $n \rightarrow \pi^*$  transition of the thiocarbonyl group. Since the two bands obtained are broad, it might have been due to all these three possible transitions.

In the visible electronic spectrum five absorption bands are noticed in case of  $Mn(II)$  complexes  $\sim 320$ ,  $380$ ,  $410$ ,  $450$  and  $560\text{ nm}$  regions. Extinction co-efficient values are very low being  $0.04$  for the third band whereas for others it is around  $0.02$ . Magnetic moments are  $\sim 5.9$  B.M. suggesting a possible high-spin octahedral configuration for these complexes. Cobalt(II) complexes give rise to two absorption bands  $\sim 550$  ( $16$ ) and  $\sim 1210$  ( $12$ ) nm regions attributable<sup>8</sup> to  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$  transitions respectively. The other

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TABLE 1—ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND IR SPECTRAL DATA

Compound	%Metal		%Sulfur		%Nitrogen		$\Delta m$ mhos $cm^{-2}$	$\mu_{eff}$ B.M.	$\nu(C=\epsilon)$	$\nu(N-H)$
	Found	Reqd.	Found	Reqd.	Found	Reqd.				
$MnL_2Cl_2$	14.95	15.008	15.39	17.51	7.52	7.68	8.5	5.90	1200	3300
$MnL_2(SCN)_2$	13.16	13.35	30.81	31.17	13.58	13.61	12.0	5.85	1190	3150
$CoL_2Cl_2$	15.36	15.50	16.59	16.87	7.16	7.36	10.5	4.8	1195	3200
$CoL_2(SCN)_2$	13.98	14.19	30.57	30.88	13.24	13.48	10.00	4.9	1190	3200
$NiL_2Cl_2$	15.74	15.87	17.16	17.30	7.46	7.57	7.5	—	1200	3300
$NiL_2(SCN)_2$	13.96	14.14	30.72	30.84	13.35	13.49	8.0	—	1195	3100
$CuL_2Cl_2$	16.72	16.99	16.90	17.12	7.25	7.49	10.5	1.79	1200	3150
$CuL_2(SCN)_2$	15.08	15.13	30.23	30.49	13.16	13.34	12.5	1.78	1150	3200
$ZnL_2Cl_2$	17.28	17.36	16.80	16.99	7.35	7.43	10.0	—	1195	3250
$ZnL_2(SCN)_2$	15.37	15.50	30.16	30.35	12.07	12.28	11.0	—	1190	3300
$CdL_2Cl_2$	26.37	26.53	14.94	15.11	6.50	6.61	8.5	—	1190	3150
$CdL_2(SCN)_2$	23.72	23.98	27.16	27.31	11.83	11.94	12.5	—	1195	3100
$HgL_2Cl_2$	39.05	39.21	12.32	12.50	5.38	5.47	10.5	—	1200	3250
$HgL_2(SCN)_2$	35.87	36.03	22.54	22.98	11.25	11.49	8.0	—	1190	3300

L=dithioamide.

band is not noticed. Magnetic moment values of 4.8 B.M. indicate a possible octahedral or distorted-octahedral configuration for these complexes.

Nickel(II) complexes show one absorption band ~ 500 (54) nm region typical of planar complexes. Diamagnetic nature of the complex from magnetic measurement supports the planar configuration.

One broad absorption band is observed in case of copper(II) complexes ~ 550 (3) nm region indicating a tetragonally distorted-octahedral stereochemistry. Magnetic moment values are ~ 1.79 B.M.

From the analysis, conductance and IR spectral data, zinc, cadmium and mercury(II) complexes have presumably an octahedral environment around the metal ions.

#### References

1. BIPIN B. MAHAPATRA, B. K. MAHAPATRA and S. GURU, *J. Indian Chem. Soc.*, 1978, 55, 1012.
2. BIPIN B. MAHAPATRA, B. K. MAHAPATRA and S. GURU, *Indian J. Chem.*, 1978, 16A, 445.
3. BIPIN B. MAHAPATRA, R. P. MISHRA and S. GURU, *Curr. Sci.*, 1978, 48, 34.
4. BIPIN B. MAHAPATRA, N. C. MISHRA and S. GURU, *J. Indian Chem. Soc.*, 1978, 55, 437.
5. S. M. SILVERSTEIN and G. C. BASLER, "Spectrophotometric Identification of Organic Compounds", John Wiley, New York, 1967.
6. J. R. FERRARO, "Low frequency vibrations of Inorganic and Co-ordination Compounds", Plenum Press, New York, 1971.
7. A. TRAMER, *J. Chem. Phys.*, 1962, 59, 232.
8. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.

#### Fluoroindates of Some Bivalent Metals

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MANY papers have been published on the fluoro compounds of indium<sup>1-4</sup>. In view of the large number of fluoro complexes known for related elements, aluminium and gallium, it is reasonable to expect similar fluoroindates. Since the electronegativity for indium is 1.3, the In-F bond may be expected to be about 90% ionic<sup>5</sup>, and the radius ratio gives a maximum coordination number of eight for indium towards fluorine. Such highly coordinated complex should be stabilised by the triple charge on indium ion but mutual repulsion between adjacent fluorine atoms could decrease the maximum coordination number. That's why many hexafluoro indium compounds having the composition  $M^I M^{II} InF_6$  are known<sup>6,7</sup> whereas the only known pentafluoro compound<sup>8</sup> containing bivalent metal is  $CoInF_5 \cdot 7H_2O$ . The present work deals with the isolation and study of a number of pentafluoroindates of some other bivalent metals.

*Preparation of fluoroindates:*  $InF_3 \cdot 3H_2O$  was prepared by evaporating the solution of freshly precipitated  $In(OH)_3$  in dilute HF.  $InF_3 \cdot 3H_2O$  (1 gm) was dissolved in water slightly acidified with dilute HF. A solution of the desired bivalent metal carbonate in very dilute HF was added to the first solution with constant stirring. The mixture was then evaporated on a water-bath to crystallisation. The crystals were filtered and recrystallised from their aqueous solutions faintly acidified with dilute HF. The crystals were filtered, washed with a little water and dried in air.