

were attached to the complexes by primary valency. The structures are supported by ir spectral data. Metal-nitrogen frequencies were observed at 640 and 635  $\text{cm}^{-1}$  in sulphaguanidine-cupric chloride and sulphaguanidine-silver nitrate, respectively. Similarly, metal-oxygen frequencies were observed at  $685 \pm 5 \text{ cm}^{-1}$ . Two bands were observed near 3430 and 3330  $\text{cm}^{-1}$  of strong and very strong intensity in the ligand with Cu and Ag complexes, indicating that aniline  $\text{NH}_2$  group is not altered in any way. A characteristic frequency at 1570  $\text{cm}^{-1}$  was observed indicating the formation of a six-membered heterocyclic ring. Strong vibration of ligand is modified to weak or medium in complexes.

It is observed that particle size of sulphaguanidine complexes is smaller than sulphaguanidine. This indicates that metal complexes are capable of being absorbed more readily than sulphaguanidine.

Bacteriostatic studies of complexes were carried out using *E. coli*, *S. aureus*, *B. proteus*, *B. pyocyaneus*, *S. typhi* and *S. paratyphi* A. Results indicate that copper complex is slightly reactive on *S. paratyphi*, resistance on *B. pyocyaneus* and very slightly reactive on other pathogens. Silver complex is mildly reactive on *S. aureus*, *B. pyocyaneus*, *S. typhi* and slightly reactive on other pathogens, while sulphaguanidine is resistant to all pathogens.

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### Complexes of Zinc(II), Cadmium(II) and Mercury(II) with 2-Thio-3-benzoylhydantoin

S. SHARMA\*

Department of Chemistry, S. S. College, Jehanabad  
and

M. KUMAR and T. SHARMA

Inorganic Research Laboratory, P. G. Department of Chemistry, Bihar University, Muzaffarpur

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accepted 29 October 1985

SEVERAL complexes of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  with nitrogen donors have been reported<sup>1,2</sup>.

Some complexes of group II B metals have also been reported in which the ligand coordinates through sulphur as well as nitrogen<sup>3</sup>. Some workers<sup>4</sup> have also studied the variation of M—N and M—O stretching frequencies in complexes of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ . However, complexes of these metals with ligands containing sulphur, nitrogen and oxygen donors together have not been studied. Hence, it appeared worthwhile to study the chelating behaviour of 2-thio-3-benzoylhydantoin (TBHNH) with  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ .

#### Experimental

The ligand was prepared by a literature method<sup>5</sup>. For the preparation of metal chelates, a hot ethanolic solution of the metal chloride and that of ligand were mixed in 1 : 2 molar ratio and the resulting solution was refluxed for 2 h. The zinc complex precipitated immediately. The cadmium and mercury complexes precipitated when pH of the solution was raised to 8 by adding dilute sodium hydroxide solution. The precipitate formed was washed successively with water, alcohol and ether. It was dried in a desiccator.

#### Results and Discussion

Analytical data of the three chelates have been given in Table 1.

Molar conductivity was measured in acetone solution. Molar conductivity value of  $\text{Zn}^{2+}$  chelate falls in the range of 1 : 2 electrolytes<sup>6</sup>, whereas  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  chelates are non-electrolytes. All the three compounds are diamagnetic as expected.

Infrared spectrum of the ligand exhibits several absorption bands. A medium band at 3280  $\text{cm}^{-1}$  is assigned to stretching vibration of NH group<sup>7</sup>. In the region 1750-1600  $\text{cm}^{-1}$ , the ligand displays two bands, one very strong at 1740  $\text{cm}^{-1}$  and the other at 1690  $\text{cm}^{-1}$  which are assignable to C = O of  $\text{C}_6\text{H}_5\text{C}=\text{O}$  and the other to C = O group<sup>8</sup>, respectively of the ligand. The strong absorption at 1450  $\text{cm}^{-1}$  may be assigned<sup>10</sup> to C = S.

TABLE 1

Chelates	Colour	M.p. °C	Analysis % : Found/(Calcd.)						$\Delta_m$ $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$
			M	C	H	N	S	Cl	
[Zn(TBHNH) <sub>2</sub> ]Cl <sub>2</sub>	Dull white	215	11.28 (11.25)	51.49 (51.47)	2.77 (2.82)	9.89 (9.83)	11.11 (11.00)	12.32 (12.28)	129
[Cd(TBHN) <sub>2</sub> ]	Yellow	200	20.28 (20.20)	43.47 (43.49)	2.89 (1.58)	10.14 (10.00)	11.55 (11.50)	—	8
[Hg(TBHN) <sub>2</sub> ]	Reddish brown	270	31.38 (31.29)	37.47 (37.41)	2.49 (1.38)	8.73 (8.62)	9.98 (9.92)	—	8.5

In the ir spectra of Zn<sup>II</sup> chelate the  $\nu_{NH}$  band of the ligand remained unaffected while in Cd<sup>II</sup> and Hg<sup>II</sup> chelates it disappeared. This obviously shows that unlike in Zn<sup>II</sup> chelate, coordination occurs through deprotonated nitrogen in Cd<sup>II</sup> and Hg<sup>II</sup> chelates. In the spectra of Zn<sup>II</sup> chelate, a very strong band appears at 1705 cm<sup>-1</sup> with a weak shoulder at 1690 cm<sup>-1</sup>, which shows that C = O of C<sub>6</sub>H<sub>5</sub> C = O has taken part in coordination. In the spectra of Cd<sup>II</sup> and Hg<sup>II</sup> chelates, there is no marked change in the  $\nu_{C=O}$ , which shows that carbonyl groups are free. The band at 1450 cm<sup>-1</sup> ( $\nu_{C-S}$ ) in the free ligand, however, is shifted to lower frequency in all the three chelates. It shows that sulphur is coordinated in all the three chelates. Coordination through oxygen and sulphur in Zn<sup>II</sup> chelate may further be substantiated by the appearance of two bands at 545 (M—O) and 315 cm<sup>-1</sup> (M—S). The non-electrolytic nature of Cd<sup>II</sup> and Hg<sup>II</sup> chelates confirms coordination through deprotonated nitrogen.

Tetrahedral structure is suggested to all the three chelates as it is the most preferred geometry for a d<sup>10</sup> system.

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**Potentiometric Studies of some Mixed Ligand Chelates of Samarium(III) with Phenolic Hydroxy Compounds as Secondary Ligands**

A. R. RAUT and T. H. MIHASKE\*

Department of Chemistry, Vidarbha Mahavidyalaya, Amravati-444 604

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RECENTLY, there has been considerable interest on the studies of mixed ligand complexes of lanthanides by pH-metric methods<sup>1-4</sup>. The importance of mixed ligand complexes in environmental chemistry<sup>5</sup>, medicinal chemistry<sup>6</sup>, analytical chemistry<sup>7</sup> and industrial chemistry<sup>8</sup> has led to large number of reports on the formation and stabilities of mixed ligand complexes<sup>9</sup>. The rare earth ions<sup>1,10,11</sup> expand their coordination number more than commonly assumed six.

In the present paper an attempt has been made to study log K<sub>MAL</sub><sup>MAL</sup> of Sm<sup>III</sup> systems, where M = Sm<sup>III</sup>; A = nitrilotriacetic acid (NTA), N-hydroxyethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), cyclohexanediaminetetraacetic acid (CDTA); and L = hydroquinone (HQ), 1-hydroxynaphthaic acid (1-HNA), 3-hydroxynaphthaic acid (3-HNA), and alizarin red S (ARS). The stability constants at 25 and 35°, and at constant ionic strength ( $\mu = 0.1 M NaClO_4$ ), have been determined employing a modified form of Irving and Rossotti<sup>12</sup> potentiometric titration technique.

**Experimental**

A stock solution (0.01 M) of samarium perchlorate was prepared in calculated quantity of perchloric acid and its metal content was estimated by spectrophotometric method<sup>13</sup>. Solutions of 0.05 M each of NTA (B.D.H.), HEDTA (Sigma), Na<sub>2</sub>EDTA (Sigma) and CDTA (Kochlight) and 0.01 M each of HQ and ARS (Loba-chemie) were prepared in double distilled water; 0.01 M each of 1-HNA and 3-HNA (Loba-chemie) were prepared in purified alcohol. All the solutions were stan-