

was added gradually in small quantities with thorough shaking till a blue precipitate appeared. The precipitate was filtered, washed thoroughly with methanol till the blue tint was removed leaving behind a green amorphous complex. It was washed with ether and dried *in vacuo*. The purity of the isolated compound was established by estimating metal and halogen by standard methods. (Found: Cu, 10.13%; I, 41.05% [Cu( $\gamma$ -pic)<sub>3</sub>I<sub>2</sub>·H<sub>2</sub>O] requires Cu, 10.34%; I, 41.38%.) Conductance measurement was carried out in 0.001 M acetone solution using a Toshniwal Conductivity Bridge and magnetic susceptibility was determined on solid specimens using Gouy method. I.R. spectra were recorded on Nujol mulls using a Unicam SP-200 spectrophotometer. Chloroform solution (0.01 M) of the compound was used to record the electronic spectra in the visible range. I.R. and electronic spectral data are given below:

* I. R. spectra (cm <sup>-1</sup> )	Electronic spectra
728s, 825vs, 970w, 1040s, 1075s, 1235s, 1520m, 1630s, 3500br (742s, 823s, 1015vs, 1060m, 1235s, 1430w, 1460w, 1610vs)	$\gamma_{\max.}$ (cm <sup>-1</sup> ) ( $\epsilon$ ) 14,800 (31)

\*The free ligand ( $\gamma$ -picoline) absorption bands are given in parenthesis.

Cupric iodide is unstable and gets converted to cuprous iodide and iodine. Complexes of copper (II) iodide are known with chelating ligands<sup>4-6</sup>. The nature of the compounds CuI<sub>2</sub>·*n*NH<sub>3</sub> [*n* = 2, or 6] is not well known<sup>7</sup>. Goodgame and co-workers<sup>8</sup> reported [Cu(imidazole)<sub>4</sub>I<sub>2</sub>] and its structure has been determined by X-ray diffraction. Bose *et al.*<sup>9</sup> have described a similar complex with benzimidazole having the composition [Cu(bzd)<sub>4</sub>I<sub>2</sub>].

The green amorphous complex having the composition [Cu( $\gamma$ -pic)<sub>3</sub>I<sub>2</sub>·H<sub>2</sub>O] reported in the present investigation is soluble in acetone, in which medium it is a nonelectrolyte,  $\Lambda_m$  being 16.4 mhos. It is paramagnetic in the solid form, indicating the presence of one unpaired electron ( $\mu_{\text{eff}} = 1.84$  B.M.) and hence the copper atom is in the divalent state. Infra-red spectra show the presence of a broad band at 3500 cm<sup>-1</sup> indicating the presence of co-ordinated water molecule. Some ligand absorption bands are shifted indicating the bonding of the ligand ( $\gamma$ -picoline) to the metal. Absorption spectrum of a chloroform solution in the visible range showed a broad absorption band at 14800 cm<sup>-1</sup> region. Hence a tetragonally distorted octahedral

configuration with weakly bonded iodide ions along the tetragonal axis, as in the corresponding imidazole<sup>8</sup> and benzimidazole<sup>9</sup> complexes, is suggested for the present compound. This is yet another example of a cupric ion stabilised in presence of an iodide ion by complexing.

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### COMPLEXES OF 5, 5'-THIODISALICYLIC ACID WITH SOME *d*<sup>10</sup>-TRANSITION METAL IONS

THIS communication describes the isolation and characterisation of complexes of Ag (I), Hg (II), Th (IV) and UO<sub>2</sub> (VI) with 5, 5'-thiodisalicylic acid, an industrially<sup>1-4</sup> important compound. Mode of co-ordination of the ligand has been deduced from the infrared spectroscopic data. Earlier references cited in the literature on complexation reactions of 5, 5'-thiodisalicylic acid (abbreviated hereafter as TDSA) with some transition metal ions relate to the studies in solution<sup>5-6</sup>.

For preparing the complexes, an alcoholic solution of TDSA (0.1 M, 100 ml) was added in each case to aqueous solution of the metal ion (0.1 M, 25 ml) concerned and the mixture was refluxed for about an hour. The precipitated complex was filtered, washed with water, alcohol and acetone and dried in an electric oven at 80° C. The analysis gave the formulae, shown in Table I, for the compounds thus obtained.

The complexes did not dissolve either in water or in common organic solvents suggesting their polymeric nature. No cryoscopic or conductometric measurements could, therefore, be made.

Magnetic measurements on solid complexes were made by Guoy's method using mercury

TABLE I

Complexes	Colour	M.P.* (°C)	% M		% S		% C		% H	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
H[Ag(C <sub>14</sub> H <sub>8</sub> O <sub>6</sub> S)].2H <sub>2</sub> O	.. White	190	24.05	23.80	7.12	7.28	37.41	37.50	2.89	2.40
[Hg(C <sub>14</sub> H <sub>8</sub> O <sub>6</sub> S)(H <sub>2</sub> O) <sub>2</sub> ]	.. "	285	37.10	36.40	5.94	5.82	..	..	..	..
[Th(C <sub>14</sub> H <sub>8</sub> O <sub>6</sub> S) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	.. Yellow	280	25.43	24.81	7.01	6.82	36.84	37.10	2.63	2.10
[UO <sub>2</sub> (C <sub>14</sub> H <sub>8</sub> O <sub>6</sub> S)(H <sub>2</sub> O) <sub>2</sub> ].3H <sub>2</sub> O	Orange	300	35.84	35.90	4.82	5.01	25.30	25.31	2.71	2.80

\*Complexes decomposed on heating above the temperature mentioned.

(II) tetrathiocyanatocobaltate (II) ( $X_p = 16.44 \times 10^{-6}$  c.g.s. units) as calibrating agent. Silver, mercury and uranyl complexes showed a diamagnetic nature (susceptibilities being  $-1.21 \times 10^{-6}$ ,  $-5.60 \times 10^{-6}$  and  $-1.64 \times 10^{-6}$  respectively in c.g.s. units) as expected for the filled  $d^{10}$  electron-configuration. The thorium complex was found to be slightly paramagnetic ( $X_{Meff} = 286.7 \times 10^{-6}$  c.g.s. units). For several reasons<sup>7</sup>, the interpretation of magnetic data in actinides is rather difficult. However, the observed paramagnetism does not seem to have much significance.

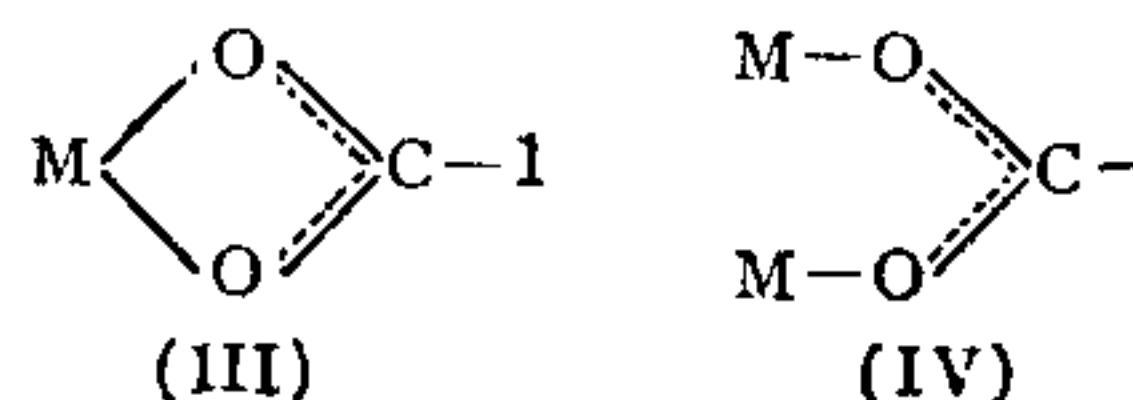
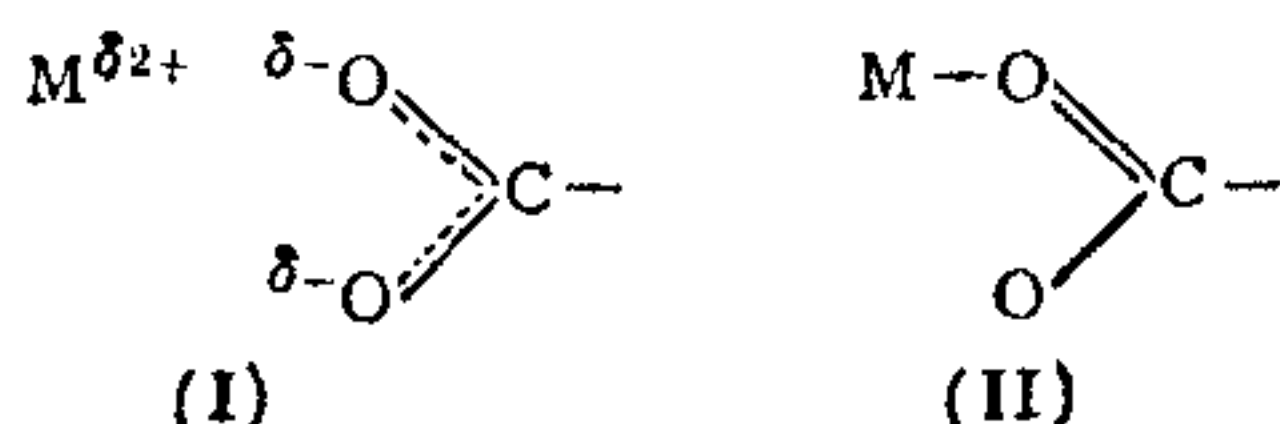
The infrared spectra of the ligand and the complexes under investigation were recorded from their KBr-pellets on a 'Perkin Elmer-521' spectrophotometer in the range  $4000 \text{ cm}^{-1}$  —  $250 \text{ cm}^{-1}$ . The absorption bands of diagnostic value and their tentative assignments are given in Table II. Infrared spectral data indicate co-ordination through the carboxylic group only.

TABLE II

Silver complex ( $\text{cm}^{-1}$ )	Mercury- complex ( $\text{cm}^{-1}$ )	Thorium- complex ( $\text{cm}^{-1}$ )	Uranyl- complex ( $\text{cm}^{-1}$ )	TDSA ( $\text{cm}^{-1}$ )	Assignments
1540	1560	1500	1550	1660	$\nu \text{C}=\text{O}$ (asym.)
1600	1600	1610	1600	1600	$\nu \text{C}=\text{O}$ (sym.)
1150	1165	1150	1150	1200	$\delta \text{C}=\text{O} + \nu \text{C}-\text{O}$
*	*	435	400	..	$\nu \text{M}-\text{O}$

\* The range could not be covered in these cases.

Out of the following possible modes<sup>8</sup> of co-ordination for carboxylic group,



the data obviously favours structure (II) for the complexes under study.

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### STRUCTURE OF SOME CRYSTALLINE COMPONENTS OF SALACIA PRENOIDES

In continuation of our earlier<sup>1</sup> brief note on some terpenoid components from *Salacia prenoides* D.C., we report now on the structures of three more components from the same source. One of these has been proved to be friedel-1-ene-3-one (I) by means of a two-way correlation with friedelin (friedelane-3-one) (II). Another has been proved to be friedelane-1, 3-dione-7 $\alpha$ -ol (III) by transforming it into friedelane-3, 7-dione (IV) which is already known as a natural product under the name putranjivadione<sup>2</sup>. The third compound has been shown to be friedelane-1, 3-dione-24-al (V)