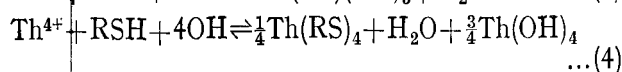
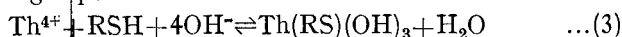


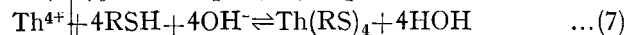
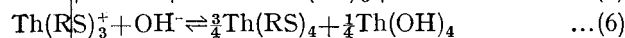
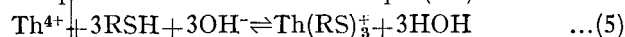
Fig. 2 — Formation curves of  $UO_2^{2+}$ -RSH system at 20° and 30°

suggests the formation of either  $Th(RS)(OH)_3$  or  $Th(RS)_4$  and  $Th(OH)_4$  in accordance with the following equations:



The appearance of a precipitate during titration rules out the possibility of the formation of hydroxo metal complexes<sup>6</sup> and supports the formation of  $Th(RS)_4$  and  $Th(OH)_4$ .

The inflexion at  $m \approx 1.33$  and 1.0 when the ratio of metal to ligand is 1:3 and 1:4 respectively confirms the formation of  $Th(RS)_4$  as the highest complex in accordance with Eqs. (5-7).



Conductometric titrations of RSH in the absence and presence of metal ions, mixed in different ratios, against standard NaOH, yielded breaks in the curves corresponding to the formation of  $UO_2(RS)_2$  and  $Th(RS)_4$  as the highest complex species, as obtained from pH titrations.

Calvin and Melchior's<sup>7</sup> extension of Bjerrum's<sup>8</sup> method (using graphical method) has been employed for the determination of stability constants of the complexes. The pH titrations of RSH solution at  $\mu = 0.1M$  ( $NaClO_4$ ) in the absence and presence of metal ions were carried out at 20° and 30° against 0.1M NaOH and the concentration of the bound ligand, calculated from the horizontal distance between the corresponding curves was divided by the total [metal ion] to obtain  $\bar{n}$  values. At any pH, the value of free ligand concentration [A], was calculated from the relation

$$[A] = \frac{[RSH]_{total} - [RSH]_{bound}}{[H]^+ / K_a + 1}$$

where  $K_a$ , the dissociation constant of RSH, determined polarographically, is  $3.98 \times 10^{-10}$ . The formation curves obtained by plotting  $\bar{n}$  against  $-\log[A]$  (Fig. 2) reveal the formation of 1:1 and 1:2 complexes for uranyl ion and 1:3 and 1:4 complexes in case of thorium ions, whose stability values ( $\log K$ )

determined by graphical method are:

Temp. °C	$UO_2^{2+}$ complex		$Th^{4+}$ complex	
	(1:1)	(1:2)	(1:3)	(1:4)
20	7.02	6.30	7.55	6.30
30	7.12	6.47	7.53	6.04

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### Pm(III), Eu(III), Tb(III), Pd(II), Pt(II) & Ir(II) Complexes of Picramic Acid

R. C. AGARWALA & S. P. GUPTA

Department of Chemistry, D.N. College, Meerut 250002

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**Pm(III), Eu(III), Tb(III), Pd(II), Pt(II) and Ir(II) complexes with picramic acid have been prepared and characterized on the basis of analytical, conductance, magnetic moment, electronic and IR spectral data. While the rare earth metal ions form 1:3 complexes (metal : ligand), Pd(II), Pt(II) and Ir(II) form 1:2 complexes. Picramic acid acts as a monovalent bidentate ligand coordinating through phenolic oxygen and amine nitrogen atoms.**

**I**N continuing project<sup>1,2</sup> concerning studies on the spectral and magnetic properties of some rare earth metal complexes of picramic acid, the preparation and characterization of Pm(III), Eu(III), Tb(III), Pd(II), Pt(II) and Ir(II) complexes with picramic acid are reported in this note.

The rare earth nitrates were prepared from the corresponding oxides of specpure quality. Pd(II) and Ir(II) chlorides procured from Johnson-Matthey were used as such. The ligand and chloroplatinic acid were of AR grade.

*Lanthanide picramates* — These were prepared in 60-70% yield by the procedure described earlier<sup>1</sup>.

*Pd(II) complex* — An yellowish brown precipitate was obtained when aqueous solutions of sodium picramate (100 ml, 0.02M) and Pd(II) chloride (25 ml, 0.02M) were mixed together. It was digested, filtered, and successively washed with water, ethanol and ether and dried, yield 80%.

*Pt(II) complexes* — A brown solution was obtained on mixing 4 moles of sodium picramate (0.02M aqueous solution) with 1 mole of chloroplatinic acid (0.02M aqueous solution). The reaction mixture was concentrated and kept in a refrigerator for a couple of days. The black coloured crystals,

which separated out, were filtered off and washed thoroughly with water, ethanol, ether and dried, yield 82%.

**Ir(II) complex** — A steel-grey solution was obtained when 75 ml of a 0.02M ethanolic solution of iridium chloride was added to 450 ml of an equimolar aqueous solution of sodium picramate. Concentration of the solution yielded steel-grey coloured crystals which were washed with water, ethanol, ether and dried, yield 65%.

The elemental analyses (Table 1) indicate a 1:3 (M:L) stoichiometry in each of the rare earth complexes, whereas this ratio is 1:2 for the Pd(II), Pt(II) and Ir(II) complexes. Molar conductance of the complexes in acetone ( $<12 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mole}^{-1}$ ) show that they are non-electrolytes. All the complexes decompose with explosive violence when heated between 260° and 290°.

The observed magnetic moments at room temperature, for the picramates of Pm(III), Eu(III) and Tb(III) are 3.00, 3.94 and 9.70 BM which are in fair agreement with those reported earlier for typical lanthanide sulphates<sup>3</sup>. The picramates of platinum and iridium are diamagnetic in nature. Palladium(II) has the  $d^8$  configuration and mostly forms low-spin square-planar complexes which are diamagnetic<sup>4</sup> or have a small temperature independent paramagnetism (TIP)<sup>5</sup>. The complex under study reveals a value of 0.81 BM.

A comparison of the IR spectra of ligand and its complexes shows that the stretching and deformation modes of the phenolic —OH group disappear in the spectra of the complexes, indicating coordination through phenolic oxygen.  $\nu\text{M-O}$  in the complexes appear as very weak bands in the region 450-500  $\text{cm}^{-1}$  (ref. 1). That the coordination also takes place through the amine nitrogen is revealed by the shift of —NH rocking and twisting modes<sup>6</sup> to higher frequencies (865-880  $\text{cm}^{-1}$ ) and the lowering of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  NH (3400 and 3300  $\text{cm}^{-1}$ ) of the ligand. The medium intensity  $\nu\text{M-N}$  vibrations appear at 400 [Pm(III)], 390 [Eu(III)], 400 [Tb(III)], 375 [Pd(II)], 380 [Pt(II)] and 360  $\text{cm}^{-1}$  [Ir(II)] (ref. 1). The band occurring in the range 1615-1580  $\text{cm}^{-1}$  due to phenyl ring vibrations in the ligand remains practically unchanged in the complexes. Coordinated water is reported to give bands in the region 880-650  $\text{cm}^{-1}$  (ref. 7). The band in the present

complexes around 730  $\text{cm}^{-1}$  which is not present in the ligand may, therefore, be assigned to coordinated water.

**Electronic spectrum of Pd(II) picramate** — The electronic spectrum of complex closely resembles those of  $[\text{PdBr}_4]^{2-}$  and  $[\text{PdCl}_4]^{2-}$  which have a square-planar stereochemistry. Five bands have been observed of which three bands may be due to spin-allowed  $d-d$  transitions  $^1A_{1g} \rightarrow ^1A_{2g}$  (17,000  $\text{cm}^{-1}$ );  $^1A_{1g} \rightarrow ^1B_2 \rightarrow ^1B_{1g}$  (22,000  $\text{cm}^{-1}$ ) and  $^1A_{1g} \rightarrow ^1E_{1g}$  (26,410  $\text{cm}^{-1}$ ). The remaining two bands which appear at 36,000 and 46,500  $\text{cm}^{-1}$  may be allowed charge-transfer bands. The large spacing of 10,500  $\text{cm}^{-1}$  between the two charge-transfer bands may indicate ligand to metal charge-transfer<sup>8</sup>.

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### Co(II), Ni(II), Cu(II), Zn(II) & Cd(II) Chelates of *o*-(*N*- $\alpha$ -Methyl-2-hydroxybenzylideneimino)-benzene Sulphonic Acid & 2-(*N*- $\alpha$ -Methyl-2-hydroxybenzylideneimino)-ethane Sulphonic Acid

B. R. SINGHVI & R. K. MEHTA

Department of Chemistry, University of Jodhpur, Jodhpur

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The chelates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) formed with *o*-(*N*- $\alpha$ -methyl-2-hydroxybenzylideneimino)benzene sulphonic acid ( $\text{H}_2\text{NB}$ ) and 2-(*N*- $\alpha$ -methyl-2-hydroxybenzylideneimino)ethane sulphonic acid ( $\text{H}_2\text{NE}$ ) have been studied potentiometrically by Calvin's extension of Bjerrum's method in aqueous medium in the presence of 0.1 M sodium perchlorate at  $25^\circ \pm 0.05^\circ$  and  $35^\circ \pm 0.05^\circ$ . The order of stability is  $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Zn(II)} > \text{Cd(II)}$ , which is in accordance with Irving-William rule. The values of overall changes in  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $E$  have also been evaluated at 30°. The electronic absorption spectra and magnetic moments of the chelates favour distorted octahedral stereochemistry around Co(II), Ni(II) and Cu(II) ions in solution.

THE metal chelates of the Schiff bases *o*-(*N*- $\alpha$ -methyl-2-hydroxybenzylideneimino)benzene sulphonic acid ( $\text{H}_2\text{NB}$ ) and 2-(*N*- $\alpha$ -methyl-2-hydroxybenzylideneimino)ethane sulphonic acid ( $\text{H}_2\text{NE}$ ) derived from *o*-aminobenzenesulphonic acid or 2-aminoethanesulphonic acid and *o*-hydroxyaceto-

TABLE 1 — ANALYTICAL DATA\* OF THE COMPLEXES

Complex	N (%)		Metal (%)	
	Found	Calc.	Found	Calc.
$\text{Pm}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_3 \cdot 2\text{H}_2\text{O}$	16.00	16.25	18.11	18.31
$\text{Eu}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_3 \cdot 2\text{H}_2\text{O}$	16.15	16.10	19.21	19.42
$\text{Tb}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_3 \cdot 2\text{H}_2\text{O}$	16.00	15.81	20.00	20.13
$\text{Pd}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_2$	16.55	16.71	21.11	21.16
$\text{Pt}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_2 \cdot 2\text{H}_2\text{O}$	13.40	13.39	31.00	31.10
$\text{Ir}[\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\text{O}]_2 \cdot 2\text{H}_2\text{O}$	13.20	13.45	30.44	30.78

\*Satisfactory C, H analyses have been obtained.