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 ohm^{-1} cm^{-2} 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[3]. 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[4] or have a small temperature independent paramagnetism (TIP)[5]. 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. νM-O in the complexes appear as very weak bands in the region 450-500 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[6] to higher frequencies (865-880 cm^{-1}) and the lowering of ν_{as} and ν_s NH (3400 and 3300 cm^{-1}) of the ligand. The medium intensity νM-N vibrations appear at 400 [Pm(III)], 390 [Eu(III)], 400 [Tb(III)], 375 [Pd(II)], 380 [Pt(II)] and 360 cm^{-1} [Ir(II)] (ref. 1). The band occurring in the range 1615-1580 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 cm^{-1} (ref. 7). The band in the present complexes around 730 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 [PdBr$_4$]$^{2-}$ and [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 cm^{-1}); $^1A_{1g}{\rightarrow}^1B_2{\rightarrow}^1B_{1g}$ (22,000 cm^{-1}) and $^1A_{1g}{\rightarrow}^1E_{1g}$ (26,410 cm^{-1}). The remaining two bands which appear at 36,000 and 46,500 cm^{-1} may be allowed charge-transfer bands. The large spacing of 10,500 cm^{-1} between the two charge-transfer bands may indicate ligand to metal charge-transfer[8].

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Co(II), Ni(II), Cu(II), Zn(II) & Cd(II) Chelates of
o-(N-α-Methyl-2-hydroxybenzylideneimino)-benzene Sulphonic Acid & 2-(N-α-Methyl-2-hydroxybenzylideneimino)-ethane Sulphonic Acid

B. R. SINGHVI & R. K. MEHTA

Department of Chemistry, University of Jodhpur, Jodhpur

The chelates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) formed with o-(N-α-methyl-2-hydroxybenzylideneimino)benzene sulphonic acid (H$_2$NB) and 2-(N-α-methyl-2-hydroxybenzylideneimino)ethane sulphonic acid (H$_2$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°±0·05° and 35°±0·05°. The order of stability is Cu(II)$>$Ni(II)$>$Co(II)$>$Zn(II)$>$Cd(II), which is in accordance with the Irving-William rule. The values of overall changes in $\Delta G°$, $\Delta H°$, $\Delta S°$ 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-α-methyl - 2 - hydroxybenzylideneimino) benzene sulphonic acid (H$_2$NB) and 2-(N-α-methyl-2-hydroxybenzylideneimino)ethane sulphonic acid (H$_2$NE) derived from o-aminobenzenesulphonic acid or 2-aminoethanesulphonic acid and o-hydroxyaceto-

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TABLE 1 — ANALYTICAL DATA* OF THE COMPLEXES

Complex	N (%)		Metal (%)	
	Found	Calc.	Found	Calc.
Pm[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_3$. 2H$_2$O	16·00	16·25	18·11	18·31
Eu[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_3$. 2H$_2$O	16·15	16·10	19·21	19·42
Tb[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_3$. 2H$_2$O	16·00	15·81	20·00	20·13
Pd[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_2$	16·55	16·71	21·11	21·16
Pt[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_2$. 2H$_2$O	13·40	13·39	31·00	31·10
Ir[C$_6$H$_2$(NO$_2$)$_2$(NH$_2$)O]$_2$. 2H$_2$O	13·20	13·45	30·44	30·78

*Satisfactory C, H analyses have been obtained.

phenone have not been studied[1]. These Schiff bases containing -SO$_3$H, -CH = N-groups are structurally similar and thus are expected to behave as biprotic tridentate ligands. This is borne out by the results presented in this note. In the present paper chelates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with these Schiff bases have been studied potentiometrically in aqueous medium at $\mu = 0\cdot1M$ (NaClO$_4$) employing Calvin-Bjerrum titration technique.

The ligands were synthesized according to the literature procedure[2]. The solutions of H$_2$NB, H$_2$NE and metal nitrates (BDH, AR) were prepared in conductivity water and standardized. Carbonate-free potassium hydroxide solution was prepared by the method of Allen and Low[3].

*p*H-*Titration procedure* — Calvin's extension of Bjerrum's method[4] was followed to determine the dissociation constants of H$_2$NB and H$_2$NE and stability constants of their metal chelates. H$_2$NB and H$_2$NE were titrated with standard alkali in the absence and in the presence of the metal ions at $25 \pm 0\cdot05°$ and $35 \pm 0\cdot05°$.

The proton-ligand formation curves were obtained by plotting Bjerrum's formation function ($\bar{n}_A$) of the proton-ligand complexes against *p*H.*p*K$_1$ and *p*K$_2$ were found from these curves at $\bar{n}_A = 1\cdot5$ and $0\cdot5$. These values were also calculated by algebraic methods[5] and the average values of *p*K$_1$ and *p*K$_2$ obtained are shown in Table 1.

For the determination of the metal ligand stability constants by Calvin's extension of Bjerrum's method, formation curves were obtained by plotting $\bar{n}$ versus $-\log$ [A^{2-}].

Approximate values of log K_1 and log K_2 were read directly from the formation curves at $\bar{n} = 0\cdot5$ and $1\cdot5$ respectively. Their refinement was done by computational method[6] and the average values obtained are summarized in Table 1.

The values of overall changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying chelation have been evaluated by standard thermodynamic relations (Table 2). The energy of activation (E) (Table 2) of chelation was calculated from Eq. (1).

$$\log \frac{K_2}{K_1} = \frac{E}{2\cdot303R} \left[\frac{T_2 - T_1}{T_2 T_1}\right] \qquad \ldots(1)$$

In the case of H$_2$NB and H$_2$NE chelates of Co(II), Ni(II) and Cu(II), values of $\bar{n} > 1\cdot5$ indicate the formation of 1:1 and 1:2 chelates whereas for Zn(II) and Cd(II) values of $\bar{n} < 1\cdot5$ show the formation of 1:1 chelates only. log K_1 and log K_2 of H$_2$NE chelates are found slightly higher than those of H$_2$NB, which may perhaps be due to the difference in the *p*H at which chelation takes place and the steric factors in the latter.

In all the chelates log β_2 values at 35° are greater than those at 25° indicating that higher temperature is favourable for the formation of these chelates. The order of stability at 25° and 35° is Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II), which is in ac-

TABLE 1 — DISSOCIATION CONSTANTS OF H$_2$NB AND H$_2$NE AND AVERAGE STABILITY CONSTANTS OF Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) CHELATES

Metal ion	Dissociation/ stability constants	Av. values		
		25°	30°	35°
	H$_2$NB			
—	*p*K$_1$	3·650	3·529	3·410
	*p*K$_2$	9·191	9·098	8·991
	H$_2$NE			
—	*p*K$_1$	8·080	8·003	7·9127
	*p*K$_2$	9·890	9·827	9·7717
	CHELATES WITH H$_2$NB			
Cu^{2+}	log K_1	5·676	5·461	5·247
	log K_2	5·063	5·059	5·038
Ni^{2+}	log K_1	4·437	4·480	4·519
	log K_2	3·975	3·992	4·005
Co^{2+}	log K_1	4·1212	4·160	4·211
	log K_2	3·6208	3·658	3·703
Zn^{2+}	log K_1	3·775	3·851	3·920
Cd^{2+}	log K_1	3·375	3·404	3·430
	CHELATES WITH H$_2$NE			
Cu^{2+}	log K_1	11·400	11·420	11·451
	log K_2	3·850	3·160	3·901
Ni^{2+}	log K_1	6·179	6·357	6·5278
	log K_2	3·7170	3·803	3·8662
Co^{2+}	log K_1	6·0232	6·106	6·1934
	log K_2	3·5168	3·573	3·6306
Zn^{2+}	log K_1	4·550	4·796	5·020
Cd^{2+}	log K_1	3·600	3·981	4·350

TABLE 2 — THERMODYNAMIC PARAMETERS* OF THE BIVALENT CHELATES OF H$_2$NB AND H$_2$NE

Metal ions	$\Delta G°$ (kcal/mole)		$\Delta H°$ (kcal/mole)	$\Delta S°$ (cal/deg/ mole)	E_a (kcal/mole)	μ_{eff} (30°) BM
	25°	35°				
		CHELATES WITH H$_2$NB				
Cu^{2+}	−14·640	−14·500	−18·90	−14·29	−18·90	1·88
Ni^{2+}	−11·480	−12·010	4·926	55·01	4·926	2·92
Co^{2+}	−10·550	−11·150	7·224	59·67	7·224	4·96
Zn^{3+}	−5·147	−5·526	6·091	37·73	6·091	Diamagnetic
Cd^{2+}	−4·602	−4·835	2·311	23·20	2·311	do
		CHELATES WITH H$_2$NE				
Cu^{2+}	−20·790	−21·640	4·285	84·26	4·285	1·90
Ni^{2+}	−13·500	−14·650	20·91	115·40	20·91	2·90
Co^{2+}	−13·010	−13·850	11·93	83·70	11·93	4·94
Zn^{2+}	−6·204	−7·076	19·74	87·08	19·74	Diamagnetic
Cd^{2+}	−4·909	−6·132	31·51	122·20	31·51	do

*Values at 30°.

cordance with Irving-William rule[7]. A relation between log K_n and second ionization potential is noted in the present case. This potential suggests that the d-orbitals are involved in chelation. $\Delta G°$ values of all the chelates excepting the Cu(II)-H_2NB, have more negative values at 35° than at 25°. It is further observed that $\Delta H°$ is positive in all cases, suggesting that the reactions are endothermic. The positive values of $\Delta S°$ for all the chelates indicate that entropy term is favourable for their formation. The energy of activation is found positive in all cases confirming the endothermic nature of the reactions.

The electronic absorption spectra of Co(II) chelates in benzene show two bands at 15,500 and 20,200 cm^{-1} which can be assigned to the transitions $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$. These bands suggest distorted octahedral stereochemistry of the Co(II) chelates. The absorption spectra of the Ni(II) chelates in benzene shows four bands at 8,700, 13,600, 15,500 and 23,200 cm^{-1}, which may be assigned to the transitions $^3A_{2g} \rightarrow ^3T_{2g}(E)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$, $^3A_{2g} \rightarrow ^1E_g$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ respectively. These bands suggest a distorted octahedral stereochemistry around Ni(II) ion[8,9]. In the case of Cu(II) chelates a broad absorption band around 12200 cm^{-1} was observed which is attributed to the transition $^2E_g \rightarrow ^2T_{2g}$. This transition suggests the distorted octahedral stereochemistry of Cu(II) chelates[9] in term of Jahn-Teller effect[10].

The magnetic moments of Co(II), Ni(II) and Cu(II) chelates of H_2NB and H_2NE in the solid state were determined by Gouy magnetic balance at 303°K and the values, given in Table 2, also suggest the octahedral geometry in the solid state.

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Formation Constants of Pr(III), Nd(III), Sm(III), Gd(III) & Dy(III) Complexes of 2,5-Dimercapto-1,3,4-thiadiazole (Bismuthiol I)

S. A. A. ZAIDI & V. ISLAM

Department of Chemistry Aligarh Muslim University Aligarh

The formation of 1:1 complexes of Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) ions with 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I) has been shown potentiometrically. The stability constants have been determined at 25° and 0.1M ionic strength. The log K values have been estimated and found to be 10.1675, 10.2050, 10.3625, 10.1625 and 10.3475 respectively.

IN continuation of our work[1,2] on the complexing property of Bismuthiol I, we report in this note the results of our studies on the stability constants of Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) complexes of Bismuthiol I in 80% (v/v) alcohol-water medium by Bjerrum-Calvin[3-5] pH titration technique as adopted by Irving and Rossotti[6]. Necessary corrections were made in the pH-meter reading for the non-aqueous solvent used.

Rare earth chlorides taken either directly (PrCl$_3$, NdCl$_3$ and DyCl$_3$) or obtained from oxides (Sm$_2O_3$ and Gd$_2O_3$) were made anhydrous[7]. The appropriate amount of these rare earth chlorides were dissolved in perchloric acid to prevent the hydrolysis of these ions. The solution of Bismuthiol I (m.p. 148°, Koch-Light, AR) was prepared in ethanol. NaOH (BDH), NaClO$_4$ (Riedel) and HClO$_4$ (E. Merck) solutions were prepared in CO$_2$-free doubly distilled water. NaOH and HClO$_4$ solutions were standardized by known method[8]. The pH-titrations were carried out with an ELICO-LI-10 pH-meter (accuracy ± 0.05 units) calibrated against standard buffers, in 80% (v/v) aq. ethanol medium, in CO$_2$-free nitrogen at 25° ± 0.10°.

The experimental procedure involved the titration of the following carbonate-free solutions (total vol. 50 ml) against NaOH (0.2128M): (A) 5 ml of HClO$_4$ (0.101M); (B) 5 ml of HClO$_4$ (0.101M)+25 ml of 0.005M Bismuthiol I; (C) 5 ml of HClO$_4$ (0.101M) containing rare earth ions (0.005M)+25 ml of 0.005M Bismuthiol I. The total ionic strength was kept constant (0.1M).

Proton-ligand formation constant — Bismuthiol I has two ionizable protons. It has been observed that only one proton from the ligand is removed in the acidic range up to $B=6.5$ while other proton dissociates only between pH 9 and 11. The proton-ligand formation number $\bar{n}_A$ was plotted against pH to get the proton ligand formation curve. The approximate value of proton-ligand stability constants (pK_1^H and pK_2^H) were obtained by pointwise calculations using equations (1) and (2):

$$pK_1^H = pH + \log (\bar{n}_A - 1/2 - \bar{n}_A) \text{ in the range}$$
$$1.0 < \bar{n}_A < 2.0 \qquad \qquad \qquad ...(1)$$

$$pK_2^H = pH + \log (\bar{n}_A / 1 - \bar{n}_A) \text{ in the range } 1.0 > \bar{n}_A ...(2)$$

The values (9.348 and 4.090) are in general agreement with those obtained by half integral method (9.350 and 4.100).

Metal-ligand stability constants — For the calculation of stability constants of rare earth complexes very dilute solutions were employed which eliminates the possibility of polymerization.

At pH-meter reading $(B)=6.5$ no hydrolysis occurred as evidenced by a constant value of $\bar{n}$. The complexation reaction between lanthanide (III) ion and Bismuthiol I was obvious from the reagent curve (Fig. 1).

The increase in the $\bar{n}$ values was continuous from $B=4.0$ to $B=5.8$ in most of the cases. The maximum $\bar{n}$ value in most cases was 1.193 at $B=6.5$. This suggests the formation of only 1:1 complex. The most likely coordination site being the deprotonated nitrogen atom. The $\bar{n}$ values changed abruptly beyond $B=6.5$, due to the hydrolysis of