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Metal chelates of some Schiff base ligands. Chelating tendencies of 2,5-pyrrolediylbis[*N*-(*o*-hydroxyphenylaldimine)] (SBH_2)

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Abstract

The synthesis, acid–base equilibria and metal-ion chelating tendencies of 2,5-pyrrolediylbis[*N*-(*o*-hydroxyphenylaldimine)] (SBH_2) are reported. From potentiometric equilibrium measurements of hydrogen-ion concentration at 10, 20, and 30°C and ionic strength 0.10 M KNO_3 in 75% (v/v) dioxan–water medium, the stability constants and the thermodynamic parameters (free energy, enthalpy and entropy) of SBH_2 complexes with transition, non-transition and lanthanide ions have been evaluated. The higher values of free energy ΔG, enthalpy ΔH and entropy ΔS of copper(II) complexes compared with those of other metal complexes were attributed to the unique electron configuration d^9 of Cu(II) ions, which is subject to the Jahn–Teller effect. The relation between the thermodynamic parameters of lanthanide complexes and the reciprocal of the cationic radius ($1/r$) of lanthanide cations was not linear, as would be expected from the ionic model. The use of SBH_2 as an analytical reagent for spectrophotometric determination of copper, nickel, cobalt, and uranium is discussed.

INTRODUCTION

Little work has been done on the Schiff bases from aldehydes of pyrrole. The Schiff bases derived from the condensation of 2-pyrrole carboxaldehyde [1] or 2,5-pyrrole dicarboxaldehyde and *o*-aminophenol were recently used by Tayim [2,3], as novel chelating agents. These ligands show high affinities towards various transition, post-transition [2] and lanthanide ions [3]. The Schiff base 2,5-pyrrolediylbis[*N*-(*o*-hydroxyphenylaldimine)] (SBH_2) reacts as a tetradentate dianion without deprotonation of pyrrole [2]. The investigation of SBH_2 solid complexes was performed [1–3] through elemental analysis and infrared spectra. In order to complete the study of this important chelating agent, we report here the acid–base and metal–ligand equilibrium constants and the thermodynamic parameters associated

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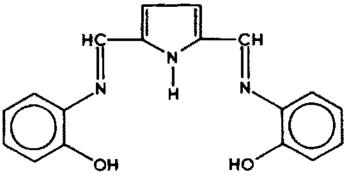
with the chelation of SBH_2 with transition, post-transition and f-transition metal ions.



The structure of SBH_2.

EXPERIMENTAL

Preparation of the solid ligand (SBH_2)

2,5-Pyrrole dicarboxaldehyde was synthesized according to the method described in the literature [4]. The aldehyde was condensed with freshly purified *o*-aminophenol in hot water. The yellow Schiff base thus obtained (SBH_2) was recrystallized from hot benzene: m.p. 184–185°C. Found: C, 70.72; H, 4.89; N, 13.63: $C_{18}H_{15}N_3O_2$ requires C, 70.82; H, 4.92; N, 13.77.

Reagents and materials

Stock solutions of the metal nitrates were prepared and standardized using EDTA in the presence of a suitable indicator [5]. Purification of dioxan was carried out as described earlier [6].

Procedures

Potentiometric titrations and the experimental conditions are essentially the same as described previously [5].

RESULTS

Potentiometric results

Representative plots for the titration curves of SBH_2 ligand in absence and presence of some metal ions are plotted in Fig. 1. No conclusions about the protic nature, or the stepwise dissociation, of the phenolic groups could be drawn from the titration curve of the free ligand (Fig. 1). The protic nature of the ligand is substantiated from the metal–ligand titration curves; only two protons are liberated as indicated by the inflection point at $m = 2$ (m, moles of base added per mole of metal). This indicates that under these conditions the ligand behaves as a diprotic species.

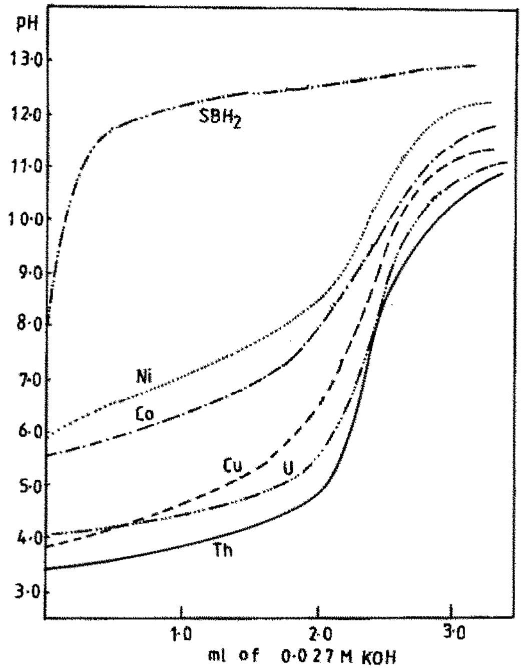


Fig. 1. Potentiometric titration curves for 30 ml SBH_2 (0.002 M) in absence and presence of 0.001 M metal ion ($t = 30°C$; $\mu = 0.10$ M KNO_3).

The SBH_2 curves obtained with 2:1 molar ratios of ligand to Cu(II), Ni(II), Co(II), Zn(II), Fe(III), UO_2(II) and Th(IV) give inflection points at $m = 2$ corresponding to the formation of a 1:1 complex

$$H_2L + M^{n+} \rightleftarrows ML^{(n-2)+} + 2H^+ \qquad (1)$$

For SBH_2 curves in the presence of lanthanide ions (Ln^{3+}) the curves show a long buffer region between $m = 0$ and $m = 4$, followed by an inflection point at $m = 4$ due to the formation of bis-chelates as a higher complex type

$$2H_2L + Ln^{3+} \rightleftarrows ML_2^- + 4H^+ \qquad (2)$$

The formation of bis-chelates is in accordance with the higher coordination number of lanthanide elements.

From the above, SBH_2 does indeed retain the pyrrole N–H bond during its reaction with all the metal ions in the present study, in agreement with previous studies on SBH_2–metal ion complexes in the solid state [2,3]. The values of the protonation constants K_1^H and K_2^H of the two phenolic groups were calculated using the relationship [7]

$$\frac{1}{K_1^H}\frac{[H^+]}{(2-F)}F - K_2^H = [H^+]\frac{(1-F)}{(2-F)} \qquad (3)$$

TABLE 1

Stability constants of metal chelates of SBH_2 at different temperatures ($\mu = 0.10$ M KNO_3; 75% dioxan–water)

Cation	lg K_1 [a]			M^{3+}	lg K_1 [b]			lg K_2 [b]
	10°C	20°C	30°C		10°C	20°C	30°C	30°C
H^+	13.22	12.86	12.50	La	12.39	12.09	11.69	10.07
lg K_2	14.09	13.50	12.91	Pr	14.32	13.78	13.38	12.29
Cu^{2+}	21.24	20.25	19.07	Nd	14.52	13.98	13.54	12.74
Ni^{2+}	14.78	14.23	13.13	Sm	14.66	14.20	13.67	12.99
Co^{2+}	16.27	15.09	14.94	Eu	14.80	14.25	13.77	13.01
Zn^{2+}	16.13	15.46	14.86	Gd	14.73	14.15	13.75	12.89
Mn^{2+}	13.24	12.76	12.18	Tb	15.02	14.23	13.85	12.81
VO^{2+}			18.44	Dy	15.18	14.38	14.00	13.64
Fe^{3+}	18.82	18.68	18.48	Ho	15.34	14.58	14.24	12.76
UO_2^{2+}	19.99	19.37	18.93	Er	15.44	14.85	14.48	13.04
Th^{4+}	21.00	20.37	19.69	Tm	15.61	15.11	14.81	13.25
				Yb	15.50	15.29	15.36	13.48
				Lu	15.55	15.36	15.22	13.55

[a] ±(0.01–0.08).

[b] ±(0.04–0.08).

where

$$F = \{C_A + [H^+] - [OH^-]\}/C_t$$

$$C_A = TN/(V + V_T); \quad C_t = w \times 10^3/M(V + V_T)$$

where w is the weight taken, M is the molecular weight, V is the volume of

TABLE 2

Thermodynamic functions of SBH_2–metal complexes at 30°C ($\mu = 0.10$ M KNO_3; 75% dioxan–water)

Cation	$-\Delta G_1$	$-\Delta H_1$ [a]	ΔS_1 [b]	Cation	$-\Delta G_1$	$-\Delta H_1$ [a]	ΔS_1 [b]
H^+	17.34	14.10	10.7	Nd^{3+}	18.78	19.22	−1.5
	17.91	23.11	−17.2	Sm^{3+}	18.96	19.38	−1.4
Cu^{2+}	26.45	42.46	−52.8	Eu^{3+}	19.10	20.19	−3.6
Ni^{2+}	18.21	32.19	−46.1	Gd^{3+}	19.07	19.23	−0.5
Co^{2+}	20.72	26.28	−18.4	Tb^{3+}	19.21	23.01	−12.5
Zn^{2+}	20.61	24.89	−14.1	Dy^{3+}	19.42	23.21	−12.5
Mn^{2+}	16.90	20.74	−12.7	Ho^{3+}	19.75	21.64	−6.2
Fe^{3+}	25.64	6.65	62.7	Er^{3+}	20.09	18.85	4.1
UO_2^{2+}	26.26	20.80	18.0	Tm^{3+}	20.54	15.71	15.9
Th^{4+}	27.31	25.65	5.5	Yb^{3+}	20.93	8.03	42.6
La^{3+}	16.22	13.72	8.3	Lu^{3+}	21.11	6.48	48.3
Pr^{3+}	18.56	18.44	0.4				

[a] ±(0.15–0.76) kcal mol^{-1}.

[b] ±(0.5–1.5) cal mol^{-1} deg^{-1}.

solvent used for dissolving the sample, V_T is the volume of the titrant added, C_A is the concentration of K^+ and N is the normality of the alkali added.

The calculation of the stability constants of the complexes formed was carried out as described previously [8]. The values of the protonation constants and of the stability constants at 10, 20, and 30°C are presented in Table 1.

The values of ΔG, ΔH, and ΔS given in Table 2 were calculated using temperature coefficients and Gibbs–Helmhotz equations. The values of ΔH are calculated in each case by a least-squares fit of the data to the relation

$$\log K = -(\Delta H/2.303RT) + \text{constant} \tag{4}$$

Least-squares analysis was also used to calculate the probable errors in ΔH terms.

DISCUSSION

Protonation equilibria

The values of the two protonation constants of SBH_2 listed in Table 1, are consistent with the structure of this ligand. The higher value of pK_2^H compared with pK_1^H is attributed to the electron-donating action of O^-, in addition to the formation of a hydrogen bond between O^- and the second phenolic proton. The pK_1^H and pK_2^H values in different dioxan compositions are according to the following order: 75% > 60% > 50% > 30% > 20% > 10% (v/v) dioxan–water. The relation between pK_1^H or pK_2^H and $1/D$ (D is the dielectric constant of the medium) show two straight lines, the first one is between 0% and 60%, and the second is between 60% and 75% (v/v) dioxan–water.

It has been shown by Kole and Chaudhury [9] that the protonation constants in mixed aqueous solvents decrease with (a) increasing the dielectric constant (D) of the solvent; (b) decreasing the extent of hydrogen bonding in water by organic solvent and (c) increasing the proton solvation by the organic solvent. These effects are prominent at solvent contents greater than 60% (v/v) dioxan–water. In this region (> 60%) the aqueous solvation shell is dispersed by the interposition of the organic solvent molecules and then participation of the organic solvent molecules in the solvation of H_3O^+ can not be ignored. It has been indicated also [10] that dioxan molecules progressively break down the hydrogen bonding of water. This effect, in addition to the low dielectric constant of dioxan solvent, would perhaps explain the relative pK^H values of SBH_2 in different dioxan–water mixtures as shown in Table 3.

TABLE 3

Acid dissociation constant (pK_1^H and pK_2^H) of SBH_2 in different mixed dioxan–water solvents at 30°C and 0.10 M KNO_3

Solvent composition (%) (v/v)	Mole fraction	Reciprocal of dielectric constant (1/*D*)	$pK_1^{H\,a}$	$pK_2^{H\,a}$
0	0		9.35	9.57
10	0.022	0.0178	9.64	9.85
20	0.048	0.0188	9.75	10.22
30	0.083	0.0195	9.95	10.55
50	0.174	0.0293	10.51	11.55
60	0.240	0.0388	11.17	12.05
75	0.388	0.0699	12.20	13.32

[a] ±(0.02–0.08).

Complexation studies

The SBH_2 ligand shows strong affinity towards various metal ions as is illustrated by the higher values of log K_1 or log K_2 of different complexes given in Table 1. This could be attributed to (a) the higher basicity (ΣpK^H) of the ligand; (b) the stabilization of anionic ligand caused by the coplanarity of the whole conjugated system, due to extensive delocalization of electrons of the skeleton of the planar Schiff-base anion (the intense and dark colours of the complexes which vary between red and brown supports this point) and (c) the ligand contains four coordination sites (two phenolic oxygens and two azomethine nitrogens) so on complexation with different metal ions produces chelates with two five-membered rings.

The order of the stability of metal complexes is $Cu^{2+} > UO_2^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$. Except for the Ni(II) complex, this sequence is in agreement with the well known Irving–Williams rule. The same position of the Ni(II) chelate is also found for the nickel(II) chelates of 2-phenyl-8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline [11] and 2-(*o*-hydroxyphenyl)-benzoxazole [12]. In all of these systems, as in the present study, the stability of nickel(II) chelates is less than that of the corresponding cobalt(II) and zinc(II) chelates. This was attributed to the fact that the tendency of nickel(II) to form planar complexes is being hindered, giving rise to either a strained or distorted planar configuration or possibly even a tetrahedron.

In Fig. 2(a), ΔG_1, ΔH_1 and ΔS_1 are plotted against the atomic number of divalent metal ions. The order of ΔH_1 and ΔS_1 is Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). It is known that these metal ions exist in solution as octahedrally hydrated species and ΔH values reflect the changes in the number and the strength of bonds made and broken during the process of the coordination. ΔH increases from Mn(II) to Cu(II) and then diminishes

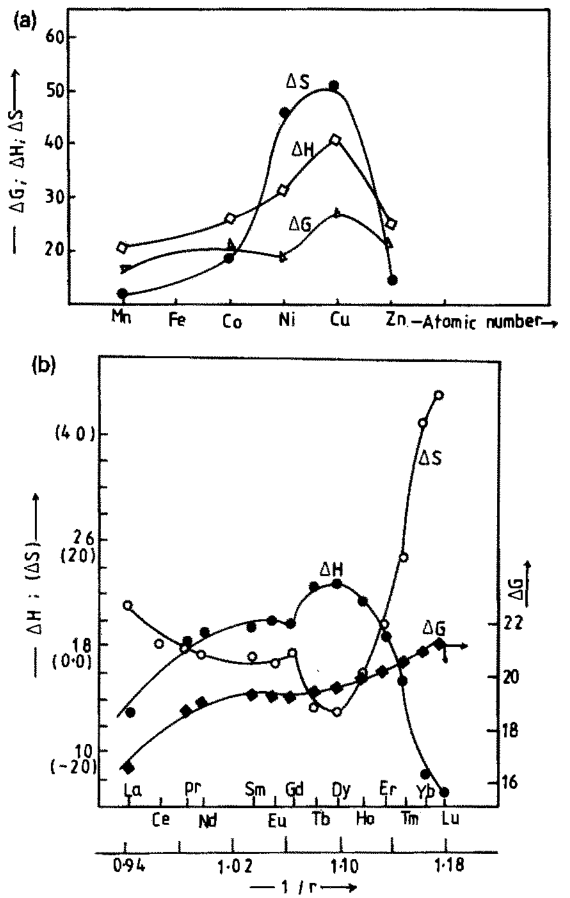


Fig. 2. Variation of the thermodynamic parameters for M^{n+}–SBH_2 chelates. (a) M^{2+}–SBH_2 chelates; (b) Ln^{3+}–SBH_2 chelates.

to Zn(II). As suggested by Frank and Evans [13], the ions in aqueous solution order the water molecules around them so as to form an "iceberg", the process being similar to partial freezing of the liquid. On this picture the removal of the ions from solution, during complex formation between oppositely charged ions (SB^{2-} and M^{n+}), will lead to the breakdown of the "iceberg" and a resulting positive entropy and enthalpy change. Qualitatively the data in Table 2 do not agree with this picture. The higher negative values of ΔH could be explained by the increase of solvent basicity [9] which caused exothermic behaviour for the transfer of metal ion from the aqueous state to dioxan solvent. The ΔH dependence on solvent can be ascribed primarily to different hydration–solvation conditions of the metal ions [14]. The Schiff-base ligand (SBH_2) is expected to be weakly solvated and the extent of charge neutralization on association with metal ions in solution is such that a positive entropy change is not predicted.

Restrictions imposed on rotation and vibration of the ligand upon association will produce a considerable loss of entropy. Thus the complexation of SBH_2 with these metal ions in solution appears to be an enthalpy-driven process.

The higher ΔG and ΔH values of Cu(II) complexes compared to the complexes of other metal ions is attributed to the unique electronic configuration, d^9, of Cu(II) ions which is subject to the Jahn–Teller effect. The tetragonal distortion of octahedra in the XY plane results in two long bonds along the Z axis, the effect of which is to increase the covalent character of the Cu–N and Cu–O bonds, leading to a more negative ΔH. The higher ΔG, ΔH and ΔS values obtained for Th(IV) and UO_2(II) complexes compared to the corresponding values of Ln(III) complexes may indicate the relative roles of 4f and 5f orbitals in the complexation of the two series, respectively. The reduced shielding of 5f orbitals compared to 4f orbitals causes a greater degree of covalency in actinide bonding than in lanthanide bonding. The higher ΔG, ΔH and ΔS of Th(IV) complexes, compared to the corresponding UO_2(II) complexes, could be related to the higher charge and ionization potential of Th(IV).

A favourite relationship of researchers in lanthanide complexation is that between the stability (free energy) constants or some other thermodynamic parameters (ΔH and ΔS) and the reciprocal of the cationic radius ($1/r$) of lanthanide elements. A linear relationship would be expected from a model of purely electrostatic interaction. In Fig. 2(b), the variation with $1/r$ was not linear, instead curves are obtained. The values of ΔG and ΔH show regular increases from La through Eu and a discontinuity at gadolinium. For the ions beyond Gd, however, two distinct behaviours are apparent: (1) a normal further increase in ΔG and ΔS with decreasing radius from Tb to Lu and (2) for ΔH a maximum is noticed in the region Tb–Dy followed by a decrease of enthalpy values with $1/r$ from Ho to Lu. This behaviour was interpreted on the basis of the existence of two different hydration numbers in the lanthanide series [14]. The ions from La to Nd have a similarly sized hydration layer; the ions from Dy to Lu have a larger one. The intermediate ions Sm to Tb represent a transitional group. The entropy changes in Table 2 are in agreement with this idea of three groups of hydrated lanthanide ions. The ΔS terms are lower for La to Nd than for Dy to Lu, reflecting release of fewer water molecules from the smaller hydration sphere of the lighter lanthanides (La–Eu). Spedding et al. [15] first suggested such a model of different sizes of hydration spheres for lanthanide ions.

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