

Synthesis & Structural Studies on the Complexes of V(V), Cu(II), Fe(II), Fe(III), Cr(VI) & Ti(IV) with 1-(*o*-Hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole

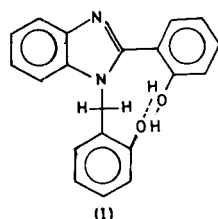
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Complexes of 1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole with V(V), Cu(II), Ti(IV), Fe(II), Fe(III), Cr(VI) have been prepared. The complexes have been characterised on the basis of analytical, conductance and magnetic susceptibility data and thermal, electronic spectral and infrared spectral studies.

Imidazole and its derivatives are known to play an extremely crucial part in the functioning of a number of biologically important molecules by virtue of their being coordinated to metal ions. Our interest in synthesizing the transition metal complexes of 1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole is due to the presence of intramolecular hydrogen bonding between the two hydroxyl groups of the phenyl and benzyl rings in the ligand (structure I) which may endow it with unusual coordination



behaviour. The presence of intramolecular hydrogen bonding leads to the participation of tertiary nitrogen atom in coordination (the hydroxy group on the phenyl ring coordinates with the metal ion in the absence of this intramolecular hydrogen bonding). Herein we report the results of our investigations on the preparation and characterisation of Ti(IV), V(V), Cr(VI), Fe(II & III) and Cu(II) complexes with the title ligand.

Materials and Methods

All the chemicals used in the present study were BDH reagents or reagents of equivalent grade. 1-(*o*-Hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole (HBHPB), the ligand, was prepared according to the method reported in literature¹.

Copper(II) complexes

Addition of methanolic solution of copper(II) nitrate (0.003 mol, 150 ml) to that of the ligand (0.002 mol)

solution at 80°C produced a green solution of copper(II) nitrate complex. This solution was refluxed and excess of solvent was distilled off *in vacuo* till the volume reduced to half of the original. The solid that separated on cooling was filtered, washed with aqueous methanol and dried *in vacuo*. A red coloured sulphate complex was prepared in an analogous manner using copper(II) sulphate as the starting material.

Iron(II) and iron(III) complexes

Iron(II) and iron(III) complexes were prepared by the addition of ligand (0.003 mol in 200 ml MeOH) to a refluxing solution of iron(II) or iron(III) sulphate (0.04 mol in 200 ml). The refluxion was continued for about 3 hr and the resulting solution concentrated to half the original volume *in vacuo*. The solids that separated were washed with aqueous methanol and dried *in vacuo* over P₄O₁₀.

Vanadium(V) complex

A methanolic solution of ammonium metavanadate(V) (0.003 mol in 150 ml) was added to a hot methanolic solution of ligand (0.002 mol in 150 ml) and the contents were refluxed for 3 hr. The green solid that separated was filtered and washed with aqueous methanol. It was recrystallized from ethanol and dried *in vacuo* over P₄O₁₀ for 24 hr.

Titanium(IV) complex

Titanium(IV) complex was prepared by mixing methanolic solutions of titanium(IV) sulphate (0.003 mol) and the ligand (0.002 mol). The contents were refluxed at 80°C on a water-bath for 3-4 hr. The resulting light yellow coloured solution was concentrated to half the original volume by distilling off the excess of methanol *in vacuo*. The yellow precipitate so obtained was filtered, washed with aqueous methanol and dried *in vacuo* over P₄O₁₀ for 24 hr.

Chromium(VI) complex

A hot methanolic solution of potassium dichromate (0.003 mol, 150 ml) was mixed with the methanolic solution of the ligand (0.002 mol) and the contents were refluxed for 3 hr on a water-bath. The resulting yellowish-green solution was reduced to half the original volume by distilling off the excess solvent under reduced pressure. The yellow precipitate that separated was washed with aqueous methanol and dried *in vacuo* over P_4O_{10} for 24 hr.

Elemental analyses (C,H,N) for the complexes were carried out at the Analytical Division, RRL, Hyderabad. Metal contents in the complexes were determined volumetrically according to literature². IR spectra were recorded in both nujol mull and KBr pellets on a Perkin Elmer 983 G IR spectrophotometer. UV and visible spectra were recorded on a PYE Unicam SP-100 UV/VIS spectrophotometer. TG and DTA were recorded on ULAC SINKU-RIKU TA-1500 thermal analyser at the Indian Institute of Science, Bangalore. Magnetic susceptibilities of the solid compounds were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The molar conductances of the complexes were determined by using a Systronics direct reading conductivity meter 303.

Results and Discussion

The analytical data, magnetic susceptibilities and molar conductances of the complexes are recorded in

Table 1. Analytical data indicate formation of the complexes of the types $[NH_4VO_3L] \cdot H_2O$, $[TiL_3(SO_4)_2] \cdot 5H_2O$, $[CrO_3L_3] \cdot 4H_2O$, $[FeL_3SO_4] \cdot 2H_2O$ and $[(FeL)_2O(SO_4)_2] \cdot 4H_2O$, $[CuL(NO_3)]NO_3 \cdot 2H_2O$ and $[CuLSO_4] \cdot H_2O$.

A broad band occurring in the range 3400-3300 cm^{-1} in the IR spectra of the ligand and all the complexes is attributed to the phenolic νOH involving intramolecular hydrogen bonding³⁻⁵. The $\nu(C-O)$ frequency observed in the 1240-1250 region⁶ in the spectrum of the ligand remains at the same position in the spectra of the complexes indicating the non-participation of phenolic oxygen in the coordination. This is further corroborated by another sharp band at 1390-1400 cm^{-1} , which is due to $\nu(OH)$ bending vibration, in the ligand as well as in all complexes⁷. The only frequency in the ligand which is lowered on complex formation is the $\nu(C=N)$ frequency, shift varying between 10 and 20 cm^{-1} . Thus, the infrared spectra of the complexes indicate that the coordination site is the tertiary nitrogen of the imidazole moiety.

In sulphate complexes of Cu(II), Fe(II), Fe(III) and Ti(IV), the coordinated nature of the sulphate groups is indicated by the presence of bands at 1150-1170, 1040, 740 and 810 cm^{-1} which are assigned to the ν_3 , ν_4 , ν_1 mode of SO_4^{2-} ion under C_{2v} symmetry. The difference $\nu_1-\nu_4$ (70 cm^{-1}) clearly indicates the chelating nature of SO_4^{2-} group i.e. its bidentate bonding to the same metal ion. A survey of literature showed that the

Table 1 — Analytical, Magnetic Moment and Molar Conductance Data of Complexes

Complex	Found (Calc.), %				Molar conductance		μ_{eff} (B.M.)
	H	N	C	Metal	Solvent	Λ_m	
$[CuLNO_3]NO_3 \cdot 2H_2O$	3.54	10.35	44.31	10.99	DMF	101.88	1.73
	(3.73)	(10.45)	(44.81)	(11.85)	DMSO	53.00	
					MeOH	109.43	
$[CuLSO_4] \cdot 2H_2O$	2.94	5.52	48.21	12.95	DMF	—	1.62
	(3.64)	(5.67)	(48.63)	(12.86)	DMSO	—	
					MeOH	—	
$[FeL_2SO_4] \cdot 2H_2O$	5.08	9.54	65.65	6.82	DMF	161.19	5.12
	(6.09)	(10.24)	(67.82)	(6.81)	DMSO	—	
					MeOH	—	
$[(FeL)_2O(SO_4)_2] \cdot 4H_2O$	3.21	5.46	46.93	10.92	DMF	200.00	6.11
	(3.37)	(5.56)	(47.63)	(11.09)	DMSO	—	
					MeOH	—	
$[CrO_3L_3] \cdot 3H_2O$	4.68	7.46	65.64	4.05	DMF	1.50	Diamagnetic
	(4.90)	(7.62)	(65.39)	(4.71)	DMSO	2.70	
					MeOH	0.03	
$[NH_4VO_3L] \cdot H_2O$	4.57	9.05	53.00	10.55	DMF	3.30	Diamagnetic
	(4.87)	(9.31)	(53.22)	(11.29)	DMSO	—	
					MeOH	—	
$[TiL_3(SO_4)_2] \cdot 5H_2O$	4.50	5.98	55.43	2.96	DMF	—	Diamagnetic
	(4.54)	(6.57)	(56.38)	(3.70)	DMSO	—	
					MeOH	—	

Table 2— Thermal Data of the Complexes

Complex	% H ₂ O		% Anion		% Ligand		% Metal		Initial dec. temp. T _d (°C)	Infl. temp. T _b (°C)	T _{max}
	Calc. (Temp. °C)	Exp. range	Calc. (Temp. °C)	Exp. range	Calc. (Temp. °C)	Exp. range	Calc. (Temp. °C)	Exp. range			
[CuLNO ₃]NO ₃ .2H ₂ O	6.99 (< 70)	6.72	22.00 (70-340)	15.00	59.01 (340-360)	76.95	11.85 (> 360)	5.03	70	360	330
[CuLSO ₄].2H ₂ O	3.60 (< 230)	5.00	19.45 (230-410)	19.00	64.00 (410-540)	68.00	12.86 (> 540)	7.16	-30	540	440
[FeL ₃ SO ₄].2H ₂ O	4.30 (< 70)	4.00	11.70 (70-280)	10.00	77.00 (280-470)	77.08	6.81 (> 470)	7.30	70	470	430
[(FeL) ₂ O(SO ₄) ₂].4H ₂ O	5.35 (< 75)	6.00	19.05 (75-410)	19.00	62.71 (410-480)	61.00	11.07 (> 480)	11.08	75	480	450
[NH ₄ VO ₃ L].H ₂ O	4.00 (< 120)	3.00	10.67 (230-450)	9.00	70.23 (450-500)	71.00	11.32 (> 500)	7.28	120	500	470
[CrO ₃ L ₃].3H ₂ O	4.90	6.00	92.00 (200)	—	90.46	—	—	—	200	540	450
[TiL ₃ (SO ₄) ₂].5H ₂ O	7.00 (< 90)	7.00	15.00 (90-320)	16.00	74.20 (320-520)	73.00	2.96 (> 520)	3.70	90	520	480

bridging SO₄²⁻ (C_{2v}) gives a difference ($\nu_1-\nu_4$) of the order of 200 cm⁻¹.

The IR spectral data and high solubilities of complexes indicate that the sulphate group is chelating in all the complexes and not bridging.

The nitrate groups in the Cu(II) complexes showed bands at 1500 and 1510 cm⁻¹ (NO₂ asymmetric stretch), 1270 (NO₂ symmetric stretch) and at 1040 cm⁻¹ (NO stretch) respectively⁸. The positions of symmetric and asymmetric stretches and the difference of about 240 cm⁻¹ in their positions is characteristic of a bidentate nitrate group⁹. A peak expected at 1380-1390 cm⁻¹ for the ionic nitrate could not be identified due to the presence of ligand vibrations (phenolic -OH).

The appearance of a weak broad absorption at 1400 cm⁻¹ in the V(V) complex, which is absent in the ligand and other complexes, may be due to NH₄⁺ vibration in accordance with the observations of earlier workers¹⁰. A medium band at 540 cm⁻¹ can be attributed to ν (Ti-N) frequency on the basis of similar observations of Issleib *et al.*¹¹. In the case of Fe(II) and Fe(III) complexes the metal-nitrogen¹²⁻¹⁵ stretching frequency is observed around 300 cm⁻¹.

The molar conductances of the complexes in DMF, DMSO and MeOH are presented in Table 1. Cu(II) nitrate complex ionises as 1:1 electrolyte whereas the molar conductances of Fe(II) and Fe(III) indicate their 1:2 and 1:3 electrolytic nature in DMF.

V(V), Ti(IV) and Cr(VI) complexes showed diamagnetic behaviour as expected. The room temperature magnetic moment values of the complexes are shown in Table 1. The low values of the magnetic moment of [CuLSO₄].H₂O complex may be

attributed to metal-metal or super exchange interaction¹⁶. In the case of Fe(II) and Fe(III) complexes, the μ_{eff} values of 5.12 and 6.11 B.M., respectively, correspond to 4 and 5 unpaired electrons indicating their +2 and +3 oxidation states.

The ligand shows electronic spectral bands in the regions 41666; 35330; and 32051 cm⁻¹ which are assigned to $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi_1^*$, and $\pi \rightarrow \pi_2^*$ transitions respectively^{17,18}. On complexation with Cu(II) ion, the $\sigma \rightarrow \sigma^*$ band disappears and the $\pi \rightarrow \pi_1^*$ band remains unchanged. The $\pi \rightarrow \pi_2^*$ transition shifts towards lower energy side and appears at 26315 cm⁻¹. The shifting or disappearing of $\pi \rightarrow \pi_2^*$ towards lower energy side indicates the involvement of ligand in coordination.

Further, the Cu(II) complexes display two bands in the visible region at 14286 cm⁻¹ ($^2A_{1g} \rightarrow ^2B_{1g}$), and 21000 cm⁻¹ (charge transfer band). Thus, it can be concluded that Cu(II) complex has square-planar geometry which is consistent with the observations of earlier workers^{19,20}.

The band positions in the electronic spectra of Fe(II) complex at 40000, 34000, 21000, 12500 ($^5T_{2g} \rightarrow ^5E_g$) and of Fe(III) at 38910, 35460 cm⁻¹, 22222 ($^6A_{1g} \rightarrow ^4A_{1g}$), 12500 ($^5T_{2g} \rightarrow ^5E_g$) confirm the interaction of the ligand with Fe(II) and Fe(III) and octahedral environment around metal ions²¹. Since the electronic spectra are recorded in DMSO medium, a solvent molecule may be coordinating to the metal ion in solution state. The electronic spectrum of Cr(VI) complex shows bands at 39062, 35062; that of V(V) at 30215, 34965 and 30959 cm⁻¹.

The thermal decomposition data are presented in Table 2. All the hydrated chelates showed mass loss below 70°C due to loss of water. In vanadium(V)

complex an extra step, which is not observed in other cases, is due to the decomposition of NH_4^+ ion which occurs in the range 120-320°C.

Extrapolation of fairly linear portions of the pyrolysis curves at high and low temperatures and taking the intersection of decomposition temperature leads to the following order of thermal stabilities:

Cu(II) nitrate > Cu(II) sulphate > iron(II) sulphate > iron(III) sulphate > titanium(IV) > vanadium(V) > chromium(VI).

In the differential thermal analysis of the complexes, the first endotherm obtained in all the hydrated compounds below 70°C may be associated with the loss of water of hydration as shown by TGA curve also. Since no sharp exothermic or endothermic peaks are observed below 500°C, it can be concluded that the oxidation-reduction of the metal does not take place. The temperatures (T_{max}) of the decomposition peak maxima were used in determining the relative thermal stabilities of the chelates. A comparison of thermal stabilities from DTA (T_{max}) and TGA (procedural decomposition temperatures) show that they are in good agreement with each other.

Based on the above observations and experimental findings, the compositions of these complexes are as given in Table 1.

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