Asian Journal of Chemistry Vol. 8, No. 3 (1996), 557–559

NOTE

Spectral, Magnetic and Microbial Activity of 2-Hydroxy Benzohydroxamioxydiacetic Acid Complexes of Some Transition Metal Ions

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Potentiometric evidences have been cited for the formation of 1:1:1 mixed ligand complexes in the system M(II)-HBHODA [M = Cu(II), Ni(II), Co(II) and ligand is 2-hydroxybenzohydroxamioxydiacetic acid]. Formation constants, thermodynamic parameters and stability constants were calculated from these data. The solid complexes were characterized by elemental analyses, molar conductance, magnetic measurement, IR and electronic spectral data.

Ternary complexes of transition metals with the ligand possessing nitfrogen and oxygen donor atoms have been investigated by various physico-chemical techniques[1–3]. Different ligand parameters were also calculated to ascertain the geometry of the resulting complexes. The ligand and its metal complexes were screened *in vitro*, against two bacteria (*B. pumilus and B. subtilis*).

Solutions of all the chemicals (AR, BDH/E. Merck) used were prepared in double distilled water. Synthesis of the ligand was done according to the reported procedure[4, 5].

Digital pH-meter type DPH-77 (Unitech), equipped with a glass-calomel electrode assembly, was used for pH-metric titrations. Measurements were made according to Calvin-Bjerrum's method[6] at 25, 35 and 45°C (μ=0.01 M, 0.05 M and 0.01M $NaClO_4$). Titration curves were found to follow the standard trend.

The IR spectra of the ligand and the corresponding complexes were recorded on a Perkin-Elmer 521 Spectrophotometer and electronic spectra were recorded on Shimadzu UV-240 Spectrophotometer. The magnetic measurements were made by Guoy method. Molecular weight of the complex was determined by cryoscopic method using DMSO as solvent.

Formation curves of the metal-ligand systems were obtained by plotting $\bar{n}$ *vs* $-\log [A^{-2}]$ and stability constant values were refined by various computational methods (interpolation at various $\bar{n}$ values, correction term, convergence formula and successive approximation method etc.). Stability order was found to be in agreement with Irving-Williams rule[7] [Cu(II) > Ni(II) > Co(II)]. The values of $\Delta G°$, $\Delta H°$ and ΔS^0 have been evaluated using Gibbs-Helmholtz equation. The formation of mixed ligand species is favoured due to the positive entropy values in all cases.

The solid complexes do not possess sharp melting point and decompose on heating below 250°C. Elemental analyses and molecular weight determination data of the metal complexes reveal 1 : 1 : 1 M (HBHODA)·$2H_2O$ stoichiometry.

The conductivity ratio in DMSO (3.0–4.5 $ohm^{-1} cm^2 mol^{-1}$) indicate their non-electrolytic nature.

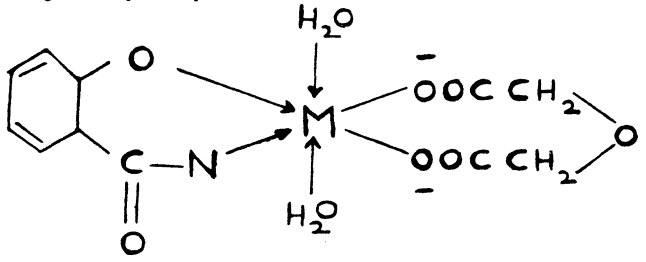
The magnetic moments of copper, nickel and cobalt complexes have been found to be around 2.00, 3.10 and 4.90 BM respectively, corrected for diamagnetism by Pascal's constant.

The copper complexes exhibit one broad band at 13400–14100 cm^{-1} which is in good agreement with the absorption frequency observed in a distorted octahedral[8] copper complex. The nickel complexes exhibit three bands around 9800, 14470 and 25100 cm^{-1} leading to transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ in an octahedral geometry. ν_2/ν_1 ratio also confirms the octahedral geometry of the complex. Dq, B, β, F_4, F_2, η and LFSE were also calculated and reported in Table-1. The lowering in the values of Racah inter-electronic repulsion parameter (B) in comparison to the free ion value of nickel suggests the partial covalent nature of the complex. The cobalt complexes show three bands around 8110, 17590 and 20900 cm^{-1} which may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_2)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$, respectively. The ligand field parameters along with magnetic moment values suggest octahedral environment around cobalt ion[8].

Ligand shows the carboxylic stretching vibrations around 1685 cm^{-1}. These bands are lowered by 20–30 cm^{-1} in the spectra of metal complexes which indicate the coordination through carboxylic oxygen[9, 10]. Band around 3370–3200 cm^{-1} in the spectra was assigned to —CONH and was found to be lowered by 30–40 cm^{-1}, indicating the coordination through the nitrogen atom of the —CONH group[11]. A distant band in the range 3370–3350 cm^{-1} correspond to ν(OH) (phenolic). In all the metal chelates, the band disappeared, indicating the deprotonation of phenolic —OH and its participation in complexation.

The coordinated water molecules are confirmed by the appearance of a broad band in the region 3300–3100 cm^{-1} in all the complexes. However, some new bands are observed in the spectra of metal complexes in the region 870–710, 500–480 and 415–400 cm^{-1} which are probably due to the coordinated water molecule[12] and the formation of M—N and M—O bond respectively[13, 14].

On the basis of analytical and IR data, the structure (Fig. 1) may be proposed for the resulting ternary complexes.



M = Cu(II), Ni(II), Co(II)

The detailed data in terms of diameter of zone of inhibition (mm) of the ligand and its bivalent chelates as summarised in Table-2 reveals that the metal chelates

under study possess comparatively higher activity than the ligand itself. The antibacterial efficacy of these chelates had been found to be in the order Ni(II) > Co(II)) > Cu(II).

TABLE-1
ELECTRONIC SPECTRAL DATA OF Co(II), Ni(II) AND Co(II) COMPLEXES

Metal Ion	Band maxima cm^{-1}	Dq cm^{-1}	B cm^{-1}	β	ν_2/ν_1	F_4	F_2	η	Covalency %	LFSE kcal $mole^{-1}$
Co(II)	8110	811	944	0.76	21.68	113.54	1511.70	0.149	0.31	13.78
	17590									
	20900									
Ni(II)	9800	9800	678	0.62	1.47	90.07	1128.35	0.282	0.61	31.31
	14470									
	25100									
Cu(II)	13400	1340	—	—	—	—	—	—	—	24.31

TABLE-2
MICROBIAL ACTIVITY OF THE LIGAND AND ITS BIVALENT CHELATES

Compound	Diameter of zone of inhibition in mm	
	B. subtilis	*B. pumilus*
Ligand (L)	9.4	6.2
Co(II) (L)	12.5	8.6
Ni(II) (L)	14.4	10.3
Cu(II) (L)	10.2	7.0

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(*Received*: 11 July 1995; *Accepted*: 20 February 1996) AJC-1091