Bivalent Metal Complexes of *N*,*N*-Bis(2-hydroxyethyl)glycine

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Complexes of *N*,*N*-bis(2-hydroxyethyl)glycine(BHEG) with a bivalent cation (Cu(II), Ni(II), Co(II), Zn(II), Fe(II), Cd(II), and Pb(II)) have been prepared and investigated by means of infrared absorption spectra, powder surface diffuse reflection spectra, electronic spectra, magnetic susceptibility, and thermal analysis. They can be classified into two types: (A) $ML_2 \cdot nH_2O$ and (B) $ML \cdot X \cdot nH_2O$, (M: metal, L: $BHEG^-$, X: Cl^- or NO_3^-). Ni(II), Co(II), Zn(II), and Fe(II) complexes are of type A, and those of Cd(II) and Pb(II) of type B. In the case of Cu(II) complexes, a blue A type complex (Cu(II)-A) has been prepared from a basic solution and a green B type one (Cu(II)-B) from an acidic solution. From detailed assignments of IR spectra, BHEG is found to have a zwitter ion structure. From magnetic moment data and reflection spectra, we presume that the A type complexes have a *trans* octahedral structure and the B type complexes a tetrahedral structure.

BHEG seems to have the properties of both an amino acid and an amino alcohol, since it has a *N*-substituted amino, a carboxyl, and two hydroxyl groups as coordinating groups in one molecule. Chaberek *et al.*[1)] investigated bivalent metal chelates of BHEG in aqueous solution and discussed the coordination of the hydroxyl group, besides the amino and carboxyl groups. However, no metal complex of BHEG in solid state has yet been studied. Krause[2)] synthesized nickel(II) and cobalt(II) complexes with *N*-(2-hydroxyethyl)imino diacetic acid, which is similar to BHEG, and reported that there are complexes in which the metal is coordinated with a hydroxyl and one carboxyl group, in addition to the normal complexes in which the metal is coordinated with a imino nitrogen and two carboxyl groups.

Many studies have been carried out on amino alcohol complexes.[3–5)] Kida[6)] studied the influence of pH on the coordination of a hydroxyl group.

In the present work, the bivalent metal complexes of BHEG have been prepared and investigated, and detailed assignments for the infrared absorption bands of BHEG and its complexes have been made. Discussion is given on how the hydroxyl group influences the coordination with the metal.

Experimental

Preparation of Compounds. Nickel(II) complex was prepared by adding 0.005 mol of nickel chloride hexahydrate to a hot solution containing 0.005 mol of BHEG and 0.005 mol of sodium hydrogencarbonate. The mixture was then stirred in a water bath. After the solution was condensed, a blue precipitate formed was filtered, washed with ethyl alcohol several times, and dried.

Cobalt(II) and copper(II)-B (green) complexes were prepared by the same procedure as for the nickel(II) complex.

Zinc(II), cadmium(II), lead(II), iron(II), and copper(II)-A(blue) complexes were prepared by means of almost the same procedure as that for the nickel(II) complex, except that: a) the condensed solution was poured into ethyl alcohol in the case of the zinc(II) and cadmium(II) complexes and into acetone in the case of the lead(II) complex; b) the iron(II) complex was prepared from iron(II) sulfate heptahydrate at room temperature and dried *in vacuo*; and c) in the case of the copper(II)-A complex, sodium hydroxide was used instead of sodium hydrogencarbonate in order to keep the pH of the solution high.

Deuteration of Compounds. The deuterated BHEG and its complexes were prepared by dissolving these compounds in 99.9% deuterium oxide and drying *in vacuo*. The NH and OH groups were deuterated by this method.

Thermal Analysis. Thermal analysis was carried out in the air with a Rigaku Denki TG-DTA M-8075 from room temperature to 400 °C. It was found that cadmium(II), lead(II), and iron(II) complexes have one molecule of water.

Magnetic Studies. Magnetic moments were obtained for the solid samples by the Gouy method at room temperature, using $Hg[Co(SCN)_4]$ as a calibration standard.

Powder Diffuse Reflection Spectra. Powder diffuse reflection spectra were observed from 700 nm to 400 nm for copper(II)-A, copper(II)-B, nickel(II), and cobalt(II) complexes with a Hitachi 624 digital spectrophotometer equipped with a standard Hitachi reflection attachment.

Electronic Spectra. Electronic spectra of metal complexes in 1M $NaClO_4$ solution were obtained from 900 nm to 190 nm with the same spectrophotometer described above. Since nickel(II) complex is insoluble in 1 M $NaClO_4$ solution, its spectra could not be obtained. The results of the elemental analysis and the values of magnetic moments, reflection spectra, and electronic spectra are given in Table 1.

Infrared Absorption Spectra. Infrared absorption spectra from 4000 cm^{-1} to 300 cm^{-1} were obtained with Hitachi EPI-G2 and EPI-L spectrophotometers, which were calibrated with polystyrene and atmospheric water vapor. Samples were prepared as potassium bromide discs and Nujol mulls. The observed absorption frequencies and the assignments for BHEG and the metal complexes are given in Table 2.

Results and Discussion

From the results of elemental analysis and infrared spectra, the eight complexes prepared can be divided into two types, nickel(II), cobalt(II), zinc(II), iron(II) complexes belonging to type A ($ML_2 \cdot nH_2O$), and cadmium(II) and lead(II) complexes to type B ($ML \cdot X \cdot H_2O$). As for copper(II) complexes, a blue A type complex (copper(II)-A) can be prepared from a basic solution and a green B type one (copper(II)-B) from an acidic solution.

Electronic Spectra and Magnetic Moments. Copper(II)-A and copper(II)-B complexes have magnetic moments of 1.86 B.M. and 1.90 B.M. respectively, which are the same as those for $Cu(gly)_2 \cdot H_2O$.[7)]

In copper(II)-A, the reflection spectrum shows a band at 630 nm, and the electronic spectrum in 1M

TABLE 1. ANALYTICAL DATA AND PHYSICAL PROPERTIES OF BHEG COMPLEXES

Complex	Found (calcd) %					Magnetic moment	Color	Reflection spectra	Electronic spectra
	C	H	N	M	Cl	μ_{eff}		nm	nm
$Ni[C_6H_{12}O_4N]_2$	36.64	6.23	7.02	15.50	0	3.36 B.M.	blue	752, 615, 365	
	(37.63)	(6.32)	(7.31)	(15.33)	0	(2.83)[a]			
$Co[C_6H_{12}O_4N]_2$	37.33	5.74	7.31	15.39	0	4.56	pink	480, 463, 440	505, 487
	(37.61)	(6.31)	(7.31)	(15.38)	0	(3.87)			
$Zn[C_6H_{12}O_4N]_2$	37.26	6.09	7.16	16.50	0	dia	white	—	—
	(36.98)	(6.21)	(7.19)	(16.78)	0	(0)			
$Fe[C_6H_{12}O_4N]_2 \cdot H_2O$	36.17	6.88	6.88	14.03	0	5.52	pale green	>700	
	(36.20)	(6.58)	(7.04)	(14.03)	0	(4.90)			
$Cu[C_6H_{12}O_4N]_2$	36.66	6.10	7.07	16.02	0	1.86	blue	630	610, 602
	(37.16)	(6.24)	(7.22)	(16.38)	0	(1.73)			
$Cu[C_6H_{12}O_4N]Cl$	27.17	4.53	5.40	23.77	13.40	1.90	green	>700	760
	(27.59)	(4.63)	(5.36)	(24.33)	(13.57)	(1.73)			
$Cd[C_6H_{12}O_4N]Cl \cdot H_2O$	22.06	4.21	4.36	34.61	11.57	dia	white	—	—
	(21.97)	(4.30)	(4.27)	(34.26)	(10.81)	(0)			
$Pb[C_6H_{12}O_4N]NO_3 \cdot H_2O$	16.09	3.08	6.27	45.61	0	dia	white	—	—
	(16.04)	(3.14)	(6.23)	(46.11)	0	(0)			

a) Spin only value.

$NaClO_4$ solution shows a peak at 610 nm assigned to $^2E_g \rightarrow {}^2T_{2g}$. Laurie[8] investigated the reflection spectra of several forms of bis(tyrosinato)copper(II) complexes and concluded that the blue form of Cu(II)-DL-tyrosine complex, which shows a peak at 625 nm, has a *trans* configuration. Graddon[9] studied the electronic spectra for anhydrous copper(II) complexes of amino acids and found that copper(II) complexes, which have a peak in the region near 621 nm, have *trans* octahedral configurations. Therefore, we can assume that the copper(II)-A complex has a *trans* octahedral configuration.

It was found that the reflection spectrum of copper(II)-B has a peak above 700 nm and the electronic spectrum in 1 M $NaClO_4$ solution has an absorption maximum at 760 nm. Hare *et al.*[10] studied the effect of pH on the electronic spectra of a number of copper(II)-amino acid complexes and found that all species of Cu(aminoacidato)$^+$ have maximum extinction coefficients of about 30 at 724 nm, while those of bis(amino acidato)copper(II) have maximum extinction coefficients between 60 and 75 at 621 nm. We can thus assume that the copper(II)-B complex has a Cu(aminoacidato)$^+$ ion.

Nickel(II) complex has a magnetic moment of 3.36 B.M. The three peaks in its reflection spectrum are given in Table 1. The spectrum is similar to that of $Ni(gly)_2 \cdot H_2O$[11] in solution and the absorption peaks are assigned to $^3A_{2g} \rightarrow {}^1E_g$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P).

Cobalt(II) complex is a high spin complex with a magnetic moment 4.56 B.M. It seems that these nickel(II) and cobalt(II) complexes have the same octahedral structure as that of copper(II)-A complex.

The iron(II) complex is pale green and has a magnetic moment of 5.52 B.M., which is the same as that of the iron(II) ion itself.

It seems that the iron(II) complex is a high spin complex. Zinc(II), cadmium(II), and lead(II) complexes are diamagnetic and their electronic spectra show no peaks in the visible region. These eight complexes in 1 M $NaClO_4$ solution have absorption peaks below 300 nm, which are assigned to the electron transfer of BHEG.

Infrared Absorption Spectra. The assignments for BHEG and its metal complexes have been based on a comparison of the observed spectra with those of glycine,[12,13] betaine,[14] other α-amino acid,[15,16] NTA,[17] triethanolamine,[3] HIDA,[2] and their metal complexes, which have been throughly studied.

BHEG: The broad bands at 3186 and 3089 cm^{-1} are assigned to the OH stretching vibrations, because of their disappearance on deuteration and the absence of bands in this region for betaine. Since these OH vibrations have lower frequencies than those of free OH vibration, it seems that OH forms a hydrogen bonding.[18]

The fine bands from 2985 to 2843 cm^{-1} are due to CH_2 stretching vibrations. The N^+–H stretching vibration which is supposed to appear at about 3000 cm^{-1} is difficult to distinguish as it overlaps the OH and CH_2 stretching vibrations.

The very strong band at 1639 cm^{-1} is assigned to the COO^- antisymmetric stretching and N^+–H deformation vibrations. On deuteration, the N^+–H deformation vibration shifts to 1275 cm^{-1} and appears as the N^+–D deformation vibration. Moreover, BHEG has no carboxy(C=O) stretching vibration at 1700 cm^{-1}, which is characteristic of acid. Thus BHEG, like glycine, has a zwitter ion structure in solid state.

The bands at 1401 and 699 cm^{-1} are due to the COO^- symmetric stretching and scissors vibrations. The bands at 1207 and 737 cm^{-1}, which shift on deuteration, are assigned to OH in plane and out of plane deformation vibrations, since they are not observed in betaine and glycine.

Metal Complexes: Nickel(II), cobalt(II), and zinc(II) complexes show similar spectra. The spectrum of lead(II) complex differs slightly from the spectrum of cadmium(II) complex, because of the presence of a NO_3^- ion.

Table 2. Assignments of infrared absorption spectra of BHEG complexes (cm^{-1})

BHEG	Ni(II)	Co(II)	Zn(II)	Fe(II)	Cu(II)-A	Cu(II)-B	Cd(II)	Pb(II)	Assignments
				3361ssh			3526 s		OH str.
3186vsb	3271vs	3283vs	3271vs	3287sb	3306vs		3346sb	3272sb	
				3169mb	3160 s		3272sb		
3089vs	3063mb	3046mb	3072mb	3053mb		3025sb			
2985w	2984wsh	2976wsh	2980wsh	2976wsh	2993w				CH_2 str.
					2979vw				
2973w	2964m	2963m	2962m	2964vw	2968w	2960 s	2974wsh		
	2954m	2954w	2954w	2957vw	2955w		2955w	2957w	
	2922w	2920w	2927w	2944w	2940w	2935 s	2930w		
2904m	2893w	2889w	2894sh	2914w	2923w	2891wsh	2913w		
2843m	2841w	2851w	2847w	2866w	2894w	2817w	2892w	2899w	
				2830wb	2840w		2853w	2851w	
				2761wb	2797wsh	2779w			
2742w	2723mb	2717mb	2727mb			2720m			
2660w	2673wsh	2667w	2657w	2697w		2662w			
	2627wsh	2627w				2607w			
1639vsb	1599vsb	1586vsb	1605vsb	1583vsb	1621vsb	1578vsb	1570vsb	1593vsb	COO^- asym. str., N^+–H def. (for ligand)
					1611vsb				
1495w	1486w	1488w	1487w	1485w	1487w	1489m	1479w	1484w	CH_2 scissors
1487sh					1462sh	1480sh			
1453m	1453msh	1455msh	1454msh	1454msh	1450w	1463w	1448m	1468m	
1444sh	1435 s	1434 s	1433 s	1434m	1430m	1452m	1438m		
1401 s	1412 s	1410 s	1408 s	1413 s	1402 s	1406 s	1409 s	1406vsb	COO^- sym. str.
1387 s	1387m	1389m	1383m	1389m			1383sh	1385 s	NO_3^- asym. str. for Pb
1358 s	1368w	1370w	1369w		1367w	1376m			CH_2 wagging and CH_2 twisting
						1369sh			
1314sb	1326m	1327m	1327w	1330m	1328w	1337m	1332 s		
	1304 s	1311 s	1309m	1304m	1300m	1320m	1306w	1315w	
	1290sh	1299sh	1299sh	1288w	1281m	1283m	1283w	1289 s	
	1277m	1282m	1280m	1268vw	1271vwsh	1266m	1262m		
				1252vw					
1237vw				1245w					
1207m	1223m	1230m	1226m	1225w	1219m	1235w	1230m		OH in plane def. + C–OH str.
1139vw	1160vw	1160vw	1158vw	1159m	1150vw	1156w	1142m	1153w	C–N str.
1115w	1135w	1138w	1132w	1136w	1124w	1121m	1128m	1127m	
1096 s		1096sh	1093sh	1103w				1088 s	C–C str.
1077w	1070 s	1072 s	1071 s	1074 s	1074 s	1080m		1079 s	CCN asym. str.
		1068wsh	1067wsh						
	1061 s	1061 s	1060 s	1064 s	1057 s	1061 s	1064 s	1059m	
1046 s	1045 s	1047 s	1044 s	1048 s	1054 s	1042m	1050vw	1049vw	
					1041 s	1035m	1033m	1039m	
1026w	1028 s	1031 s	1029 s	1029 s	1023 s	1016 s	1011 s	1008m	C–OH str. for ligand
1003m									
972m	980m	984m	981m	995m	975w	985w	984w	981vw	
				987w					
				975vw					
	959 s	961 s	959 s	964m	955 s		959vw	938m	
				938vw					
933m	932 s	936 s	929m	930m	934 s		937m	911m	CH_2 rocking
903m						908m	905m	901m	
887m	892 s	893 s	891 s	889m	883m	895 s	881m	891sh	CCN sym. str.
856w				840w			862w	844w	
								829m	
	822m	827m	823w	812w				821m	
	807sh	811sh	806vw	801vw	818w	804m	793wb	802wsh	
797wb					793w				
699m	749 s	755 s	753 s	741m	748 s	739m	734m	715mb	COO^- scissors
					703m				
737mb	642w	633w	638w	637w	645w	620m	604w		OH out of plane def.
				615m					
583m				583w					
565w	563w	562w	563w	564w	567m	565m	577w		COO^- wagging

Table 2. (Continued)

BHEG	Ni(II)	Co(II)	Zn(II)	Fe(II)	Cu(II)-A	Cu(II)-B	Cd(II)	Pb(II)	Assignments
546m	536m	521m	530m	539w	537m		546w	545w	COO^- rocking
	522m	516m	514m	516m	512m	511m		507w	
				488vw					
477m				458w		480m			
424m	443w	436vw	435vw	432vw	444w	421w	448wb	443w	
	420vw	419vw	420vw	407w			430w	420w	
387w	387m	385w	376w	365sh	393m	372w	390w		M-N str. for Cu-A
	354m	356m	358w	360sh	360m				CCN asym. def.
	345m	346m	329m	345m		340m			M-N str. for Ni, Co, Zn, Fe and Cu-B
	338sh								
	330w	335vw	335sh	337m					
303w	313m	302m	304w	305w	308w	317m	303w		

Abbreviations: s=strong, m=medium, w=weak, sh=shoulder, b=broad.

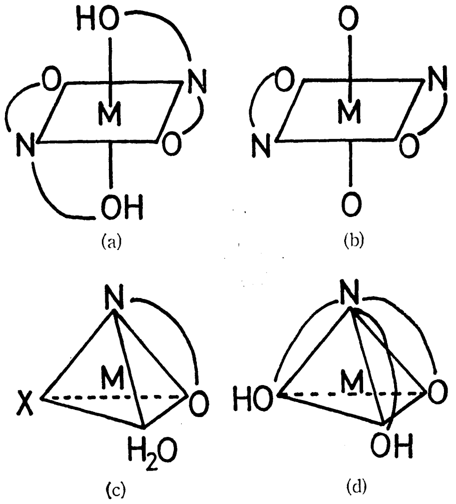

Fig. 1. Four possible configurations for BHEG complexes.
(a) Ni(II), Co(II), Zn(II), and Fe(II). (b) Cu(II)-A. (c) Cd(II) and Pb(II) (X=Cl^- for Cd(II), NO_3^- for Pb(II)). (d) Cu(II)-B.

The broad bands above 3000 cm^{-1} for all complexes are assigned to OH stretching vibrations. In nickel(II), cobalt(II), zinc(II), and iron(II) complexes, one of these two OH stretching vibrations shifts *ca.* 100 cm^{-1} towards higher frequencies and the others towards lower frequencies as compared with those of the ligand. In the case of copper(II)-A, cadmium(II), and lead(II) complexes, all the vibrations shift to higher frequencies. This can be explained as follows. The OH vibration, which is at a lower frequency in the ligand due to hydrogen bonds, seems to become strong by the breaking of the hydrogen bonding when a complex is formed. When the OH group coordinates to a metal, the OH bond becomes weak and the OH stretching vibration shifts to lower frequencies. Therefore, in nickel(II), cobalt(II), zinc(II), and iron(II) complexes, one of these two OHs in one molecule does not coordinate, and the other slightly coordinates and forms a *trans* octahedral structure (Fig. 1-a).

On the other hand, in copper(II)-A, cadmium(II), and lead(II) complexes, neither of the OH groups coordinates. Copper(II)-A has a *trans* octahedral structure which extends above and below the basal plane like the alanine copper(II) complex[15] (Fig. 1-b), while cadmium(II) and lead(II) complexes take a tetrahedral structure with ligand, water, and anion (Fig. 1-c). In the copper(II)-B complex, the OH vibration markedly shifts to a lower frequency and the two OH groups seem to be coordinated to the metal to form a tetrahedral structrue with only one ligand (Fig. 1-d).

The bands at 1600 cm^{-1} assigned to COO^- antisymmetric stretching vibrations are observed at frequencies lower than those of the ligand. In the ligand the vibration shifts to higher frequencies because of the hydrogen bond, while in the complexes the hydrogen bonds are broken and the O–M bonds have a stronger ionic character. Fairly strong ionic coordination bonds are observed in NTA complexes.[17]

From 500 to 300 cm^{-1}, absorption bands which cannot be observed in the ligand appear in the complexes and are assigned to M–N stretching vibrations by comparison of the spectrum of the ligand with those of the metal complexes with glycine[12] and betaine.[14]

The frequency separation of the COO^- antisymmetric and symmetric stretching vibrations of the complexes in the same physical state increases in the order cobalt(II)<nickel(II)<zinc(II)<copper(II)-A (Table 1). The trend is the same as that in the corresponding series of complexes with various aliphatic α-amino acids, showing the corresponding order in the strengths of the metal-oxygen bond.

The copper(II)-A complex has a octahedral structure, like the glycine–copper(II) complex.[12] Nickel(II), cobalt(II), zinc(II) and iron(II) complexes have a *trans* octahedral structures, since BHEG acts as a tridentate ligand. However, cadmium(II) and lead(II) complexes have a four-coordinated structure with a 1 : 1 ratio of ligand to metal, differing from the *trans* octahedral structure of alanine–cadmium(II) complex.[15] The size and position of the CH_2CH_2OH group and the ionic radius of Cd^{2+} and Pb^{2+} seem to affect the formation of complexes.

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