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Complexes of Nickel(II), Copper(II), Zinc(II) and Cadmium(II) with 4-Hydroxy-L-proline

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Complexes of four bivalent metals with 4-hydroxy-L-proline have been prepared and characterized by means of infrared absorption, powder diffuse reflection, electronic spectra, magnetic susceptibility, and thermal analysis. The complexes appear to be of three distinct types. The first type includes $ML_2 \cdot nH_2O$ *(M = Ni, Zn, Cu, L = 4-hydroxy-L-prolinato anion), and* $CuClL \cdot H_2O$ *is a second type. In both the ligand chelates metal ions through the nitrogen atom of the pyrrolidine ring and the oxygen atom of the carboxylato group.* CuL_2 *appears to adopt a* cis *geometry, and in the second type a chloride ion seems to bridge to two copper(II) ions.* $CdCl_2HL$ *is a third type, in which the cadmium ion is coordinated through the oxygen atom of the carboxylato group and chloride ions, but is not coordinated through the nitrogen atom.*

Introduction

The investigation of the syntheses, spectral properties and crystal structures of the metal complexes of various amino acids and their derivatives is the program in our laboratory. The present study, of the metal complexes with 4-hydroxy-L-proline, is part of that program.

There is much interest in the formation of bivalent metal complexes with 4-hydroxy-L-proline, which has a pyrrolidine ring containing a hydroxyl group. Many studies have been reported on the stability constants [1–4] and the circular dichroism spectra [5–7] of 4-hydroxy-L-proline metal complexes in aqueous solution. However, there are few reported studies on metal complexes with this ligand in solid state. Kollmann *et al.* [8] isolated $[Au(HL)_2][AuCl_4]$ and PdL_2 (L = 4-hydroxy-L-prolinato anion), and thought that the gold(I) was coordinated with only one nitrogen atom in one pyrrolidine ring. Sicignato [9] has discussed the crystal and molecular structure of bis(hydroxy-L-prolinato)calcium(II) pentahydrate. He reported that the calcium coordination for the bis(hydroxyl-L-prolinato) complex is seven-fold, and is comprised of two carboxyl oxygen atoms, two imino nitrogen atoms, and three water molecules, and that the coordination geometry can be described as a pentagonal bipyramid with a carboxyl oxygen atom and a nitrogen atom as the two extended vertices.

In the present work, we have prepared the bivalent metal complexes of 4-hydroxy-L-proline and have investigated the spectral and thermal properties in solid state. In addition, from the detailed assignments for the infrared absorption bands of this ligand and its metal complexes, the structures of these complexes have been discussed.

Experimental

Preparation of Compounds

Nickel(II) complex was prepared by adding 2.5 mmol of nickel(II) chloride hexahydrate to a hot solution containing 5 mmol of 4-hydroxy-L-proline and 5 mmol of sodium hydrogencarbonate. The mixture was then stirred in a water bath. After the solution was condensed, the mixed solution was poured into an ethyl alcohol/acetone mixture. The pale blue precipitate which formed was filtered, washed with ethyl alcohol and acetone several times, and dried.

Copper(II)-A and zinc(II) complexes were prepared by the same procedure as the nickel(II) complex.

Copper(II)-B and cadmium(II) complexes were prepared by means of almost the same procedure as that for the nickel(II) complex, except that no sodium hydrogencarbonate was used.

The deuterated 4-hydroxy-L-proline and its metal complexes were prepared by the same procedure as DL-serine and its complexes [10]. The NH and OH groups were deuterated by this method.

Magnetic Studies

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

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TABLE I. Analytical Data and Physical Properties of 4-Hydroxy-L-proline Complexes.

Complex	Found (Calcd) %					Magnetic moment	Color	Reflection spectra	Electronic spectra	
	H	C	N	M	Cl	μ_{eff}/μ_B		λ/nm	λ/nm	log ε [b]
$Ni(C_5H_8O_3N)_2 \cdot 3\frac{1}{2}H_2O$	6.15	31.90	7.30	15.0	0	3.18	pale blue	621	615	0.78
	(6.07)	(31.44)	(7.33)	(15.4)	(0)	(2.83)[a]		373	370	1.08
$Zn(C_5H_8O_3N)_2 \cdot \frac{1}{2}H_2O$	5.20	35.85	8.33	19.8	0	dia	white	–	–	–
	(5.12)	(35.89)	(8.37)	(19.5)	(0)	(0)[a]				
$Cu(C_5H_8O_3N)_2$	5.02	36.89	8.59	19.3	0	1.83	blue	650	611	1.84
Cu(II)-A	(4.98)	(37.09)	(8.65)	(19.6)	(0)	(1.73)[a]				
$CuCl(C_5H_8O_3N) \cdot H_2O$	4.19	24.26	5.64	25.9	14.20	1.89	light blue	769	680	1.52
Cu(II)-B	(4.07)	(24.30)	(5.67)	(25.7)	(14.34)	(1.73)[a]				
$CdCl_2(C_5H_9O_3N)$	2.86	19.08	4.49	35.9	22.40	dia	white	–	–	–
	(2.88)	(19.10)	(4.45)	(35.8)	(22.55)	(0)[a]				

[a] Spin only value. [b] ε is given in $mol^{-1}\ dm^3\ cm^{-1}$.

Powder Diffuse Reflection Spectra

Powder diffuse reflection spectra were observed from 800 nm to 400 nm with a Hitachi 624 digital spectrophotometer equipped with a standard Hitachi reflection attachment and a magnesium oxide standard.

Electronic Spectra

Electronic spectra of metal complexes in 1 mol dm^{-3} $NaClO_4$ solution were obtained from 900 nm to 370 nm with the spectrophotometer described above.

Infrared Absorption Spectra

Infrared absorption spectra from 4000 cm^{-1} to 200 cm^{-1} were obtained with Hitachi spectrophotometers, type EPI-G2 and type EPI-L, and a JIR-O3F FT-IR spectrophotometer from JEOL. These spectra were calibrated with polystyrene and atmospheric water vapor. Samples were prepared as potassium bromide discs and nujol mulls.

Thermal Analysis

The simultaneous TG-DTA measurements were carried out with a Rigaku Denki M8075 using a sample weighing about 10 mg in each operation, with a heating rate of 5 °C min^{-1} under static air, using α-alumina as the reference.

Results and Discussion

The results of elemental analyses and infrared spectra suggest that there are three distinct types of complexes: the first type includes $NiL_2 \cdot 3\frac{1}{2}H_2O$, $ZnL_2 \cdot \frac{1}{2}H_2O$, and CuL_2; $L=\underline{CH(COO^-)CH_2CH(OH)CH_2NH}$. The $CuClL \cdot H_2O$ is a second type and the $CdCl_2HL$ is a third type. To distinguish between the copper(II) complexes, we call the first type copper(II)-A(blue) and the second one copper(II)-B (light blue) for convenience.

Electronic Spectra and Magnetic Moments

The results of elemental analyses and electronic and reflection spectra, and the magnetic moments are listed in Table I.

The electronic spectrum of the nickel(II) complex contains two peaks at 615 and 370 nm. They are assigned to d–d transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in an O_h approximation. This spectrum is similar to the electronic spectra determined for the corresponding nickel(II) complexes of proline [11, 12] and DL-2-azetidinecarboxylic acid [13]. As the reflection spectrum also has the same two peaks in the above regions, the structure of the nickel(II) complex in solid state appears to have the same structure as it has in 1 mol dm^{-3} $NaClO_4$ solution. For the nickel(II) complex, the magnetic moment is within the ranges expected for octa-

TABLE II. Temperature Range of Decomposition and Mass Loss.

Complex	Temperature range °C	Thermal reaction	Mass loss %	
			Obsd	Calcd
Ni(II)	50–160	endo	9.59	9.43[a]
	260–345	exo		
	345–400	exo	78.34	80.45[b]
Zn(II)	263–386	endo		
	386–497	exo	76.04	75.68[b]
Cu(II)-A	210–290	exo	75.49	75.44[b]
Cu(II)-B	140–170	endo	7.57	7.28[a]
	180–690	exo	31.94	32.19[b]
Cd(II)	230–280	endo		
	280–520	exo		
	520–600	endo		
	600–960	exo	0	0[c]

[a] Two and one molecules of water have been released in these steps. [b] The metal oxides have been formed as a residue in these steps. [c] All residual material in turn sublimates in this step.

hedral complexes (2.80–3.50 B.M. for nickel(II)). Therefore, this nickel(II) complex has an octahedral structure.

The reflection and electronic spectra of copper(II)-A show single peaks at 650 and 611 nm, respectively. The electronic spectra are similar to that of bis(L-prolinato)copper(II) dihydrate [7, 14], which shows an absorption band at about 610 nm and is characteristic of an octahedral configuration about the copper(II) ion with the two water molecules occupying axial positions and with the amino acid ligand occupying equatorial positions [15]. Then in aqueous solution copper(II)-A seems to have a same octahedral structure as bis(L-prolinato)copper(II) dihydrate has.

Copper(II)-B complex has an absorption band at longer wave lengths than that of the copper(II)-A complex. Allan *et al.* [16] has reported that bis(isonicotinic acid) copper(II) dichloride has an octahedral environment, since it has an absorption band at 699 nm and its magnetic moment is 1.89 B.M. Therefore copper(II)-B seems to have an octahedral structure.

Thermal Analysis

The temperature range and the mass loss obtained from TG and DTA curves of complexes are summarized in Table II.

The nickel(II) and copper(II)-B complexes give endothermic reactions below about 170 °C, as shown in Table II. The percentages of mass loss for both complexes in these reactions are in good agreement with the values which have been calculated by assuming that two and one molecules of water respectively have been released in these steps.

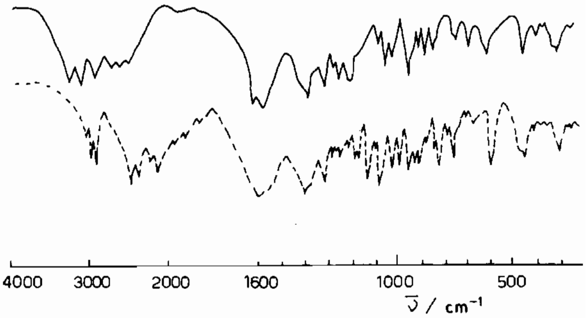

Fig. 1. Infrared absorption spectra of 4-hydroxy-L-proline (——) and its deuterated compound (------) in KBr discs.

The TG and DTA curves of the cadmium(II) complex show a steep mass loss over 230–280 °C by an endothermic reaction. Then, after two stages of mass loss by exothermic reactions, an endothermic reaction occurs from 520 to 600 °C. Finally all residual material in turn sublimates and the vessel becomes empty around 960 °C.

Infrared Absorption Spectra

The infrared spectral data are listed in Table III. The assignments of observed spectra have been made by referring to those of poly-(hydroxy-L-proline) [17, 18], DL-2-azetidinecarboxylic acid [13], proline [17, 19], pyrrolidine [20], serine [10], other α-amino acids [21, 22] and their metal complexes.

4-hydroxy-L-proline: X-ray [23] and neutron [24] diffraction techniques have shown that 4-hydroxy-L-proline is in the zwitterion form. We have assigned the spectra of the ligand on the basis of these results. The strong bands at 3277 and 3130 cm^{-1} disappear on deuteration and shift to 2444 and 2335 cm^{-1} respectively for the deuterated compound, as shown in Fig. 1. Deveney *et al.* [17] have assigned the bands at 3284 and 3134 cm^{-1} of 4-hydroxy-L-proline and the band at 3055 cm^{-1} of L-proline to NH_2^+ vibrations. It is well known that in N-substituted amino acids the NH_2^+ group absorbs at lower frequency region than where the NH_3^+ group absorbs and that the intermolecular hydrogen bonded OH vibration appears at 3400–3200 cm^{-1} [25]. Therefore it is difficult to assign these two bands, but we assigned both bands tentatively as shown in Table III. The bands at 2728 and 2600 cm^{-1} also disappear on deuteration. As there are no bands due to the metal complexes in this region, these bands are associated with NH_2^+ stretching vibrations. The most important absorption bands of this ligand are the asymmetric and symmetric stretching bands of the carboxylato group. These bands occur at 1587 and 1401 cm^{-1}. Since the bands at 1637,

TABLE III. Assignments of Infrared Absorption Spectra (cm^{-1}).[a]

ligand	Ni(II)	Zn(II)	Cu(II)-A	Cu(II)-B	Cd(II)	Assignments
				3488 s	3477 s	OH str.
	3370 sh					
		3335 s				
3277 s	3273 sb	3290 s				
		3237 s		3247 s		NH str.
			3216 sb			NH str. + OH str.
		3198 sh		3100 sb	3198 m	OH str.
3130 s					3120 sh	
					3099 sh	NH_2^+ str.
					3047 s	
3036 w			3009 vw			
3034 w						
2984 w		2964 w		2965 vw	2972 m	CH_2 + CH str.
2948 s	2954 w	2950 w	2946 sh	2953 vw	2961 m	
2923 sh b	2923 w	2937 w	2929 sh	2920 m		
			2910 m			
		2881 m				
		2877 m	2862 sh			
2728 m						NH_2^+ str.
2600 m						
2504 vw						
2456 w						
1637 sb						NH_2^+ scissors for the ligand
		1617 sh	1622 sh			NH bending
1587 sb	1577 sb	1591 sb	1592 sb	1592 sb	1609 sb	COO^- asym. str.
				1567 s	1573 wsh	
					1532 sb	NH_2^+ scissors for the Cd(II)
		1445 s	1437 sh	1453 sh	1441 sh	CH_2 scissors
				1444 m	1430 m	
1429 m						NH_2^+ wagging for the ligand
1401 s	1428 m	1422 s	1407 s	1407 m	1409 s	COO^- sym. str.
	1388 msh	1399 msh		1393 m		
					1360 m	NH_2^+ wagging for the Cd(II)
				1348 sh		
1362 w	1331 wb	1335 m	1326 m	1335 m	1337 w	CH_2 twisting
1319 m		1313 m	1311 m	1323 m	1319 m	CH bending
				1304 sh	1301 w	
1297 m					1272 m	OH in plane def.
1260 m	1268 vwsh	1269 w	1266 w	1269 m		CH_2 twisting
1232 m		1205 w	1212 vw	1234 w	1235 m	CH_2 wagging
1211 m	1212 wb	1240 w	1236 w	1219 m		OH in plane def.
	1195 vwsh	1189 w	1194 vw		1198 m	CH_2 rocking
					1174 m	
		1096 m	1116 m	1101 m		
1085 m	1077 vwsh	1084 m	1080 m	1075 m	1079 sh	C–OH str. + C–C str. + ring mode (in plane)
1054 m	1055 m	1063 m	1064 w		1071 s	
		1046 m	1051 m	1052 m	1052 s	
		1041 sh				
		986 w	989 w	991 m		
960 m	960 m	969 vw	965 w	960 w	955 s	ring mode (in plane)
		953 m				
917 m	929 m	927 m	938 m	922 m	937 sh	ring breathing mode
	912 sh	908 w			908 m	
882 m					870 m	NH_2^+ rocking for the ligand and Cd(II)
		871 m	870 w	861 m		

(continued on facing page)

TABLE III. *(continued)*

ligand	Ni(II)	Zn(II)	Cu(II)–A	Cu(II)–B	Cd(II)	Assignments
		860 w	858 w			ring mode (in plane)
850 sh	856 m	850 w			852 w	CH_2 rocking
842 m					821 w	
765 sh	788 wsh	797 m	793 w	799 w	791 w	ring mode (in plane)
		767 m	778 sh	760 m		
753 m	761 w	757 m			751 vw	COO^- scissors
		731 m		717 m	699 wb	skel. def.
	718 w	714 m	712 w			
699 m		680 m				OH out of plane def.
		660 wsh		657 vw	640 w	
640 sh		630 w	627 vw			skel. def.
612 m	600 sh	600 vw		597 w	600 m	COO^- wagging
		556 m			542 m	
	520 w			528 m	513 m	
			516 w			M–N str.
		490 w	489 w			M–N str.
459 m	450 vw	448 vw	455 w	467 m	438 w	COO^- rocking
421 w	433 vwsh			433 w		skel. def.
		417 w			418 w	
				411 w		M–N str.
396 vw	398 sh	403 w	399 w	395 w	397 sh	skel. def. + ring torsion
			366 w	345 w	353 w	
327 mb		328 w	320 m			CCN bending
				306 w		
		302 w	298 mb			M–O str.
	261 w	281 w	278 msh	261 w	260 w	M–O str.
				283 w		M–Cl str.
				277 w		
240 mb		245 m	239 vw	238 w	227 msh	skel. def.
		216 m			209 mb	

[a] *Abbreviations:* s = strong; m = medium; w = weak; v = very; sh = shoulder; b = broad.

1429, and 882 cm^{-1} shift to 1133, 993, and 670 cm^{-1} on deuteration, they are assigned to NH_2^+ deformation vibrations. The bands at 1211 and 699 cm^{-1}, which also shift in deuteration, are assigned to the OH deformation vibrations by comparing the spectra with L-proline [19] and N-[tris(hydroxymethyl)methyl]glycine [26], since they are not observed in L-proline.

From 1300 to 1000 cm^{-1}, the spectra of the ligand are very different from that of its deuterated compound (as shown in Fig. 1), because the OH deformation and C–O and C–N stretching vibrations are observed in this region.

Metal complexes: 4000–2000 cm^{-1}. For nickel(II), zinc(II) and copper(II)-A the bands at 3130 and about 2700 cm^{-1} which are observed for the ligand disappear and several strong peaks are observed above 3200 cm^{-1}, as shown in Fig. 2. By the formation of the metal complex, the NH_2^+ group in the ligand releases H^+ to become the NH group. As all of these bands shift to about 2400 cm^{-1} on deuteration, it is difficult to assign these bands to OH or NH stretching vibrations.

On the other hand, the spectra of copper(II)-B and cadmium(II) complexes are different from that of the above three complexes. The sharp strong bands at about 3480 cm^{-1} for both complexes are assigned to OH stretching vibrations. The OH vibration, which is at a lower frequency in the ligand due to hydrogen bonds, seems to become stronger and to shift to higher frequencies by the breaking or weakening of the hydrogen bond when a complex is formed. This same behavior has been observed for the cadmium(II) complexes of N-[tris(hydroxymethyl)methyl] glycine [26] and N,N-bis(2-hydroxyethyl)glycine [27].

1700–500 cm^{-1}. Copper(II)-A and zinc(II) complexes have a shoulder or weak bands above 1600 cm^{-1}, but at a lower frequency region than where the NH_2^+ scissors vibration of the ligand appear; they also disappear on deuteration. These are therefore assigned to NH bending vibrations. The cad-

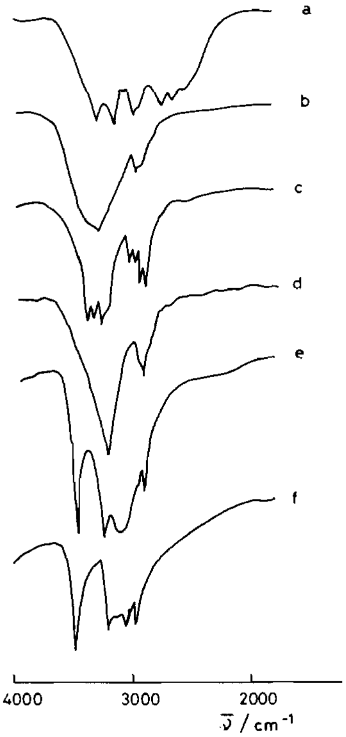

Fig. 2. Infrared absorption spectra of 4-hydroxy-L-proline and its complexes in KBr discs. (a) 4-hydroxy-L-proline, (b) Ni(II), (c) Zn(II), (d) Cu(II)-A, (e) Cu(II)-B, (f) Cd(II).

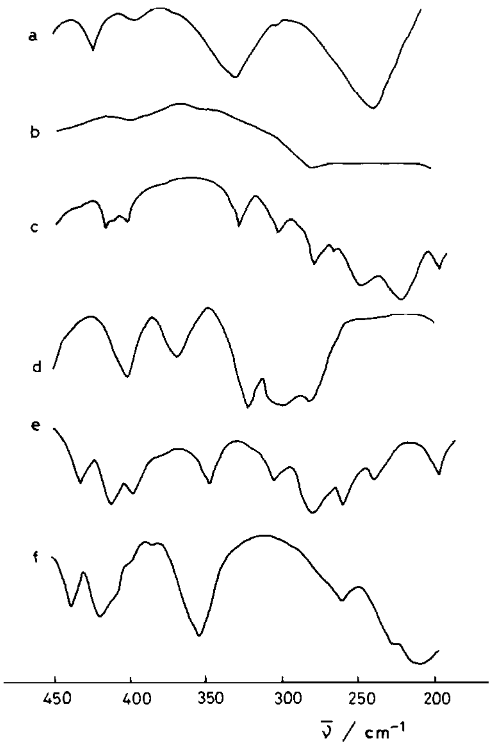

Fig. 3. Infrared absorption spectra of 4-hydroxy-L-proline and its complexes in nujol. (a) 4-hydroxyl-L-proline, (b) Ni(II), (c) Zn(II), (d) Cu(II)-A, (e) Cu(II)-B, (f) Cd(II).

mium(II) complex has a band at 1532 cm^{-1}, which cannot be observed for the other complexes and which shifts to 1151 cm^{-1} on deuteration. In addition, the two bands at 1360 and 870 cm^{-1} disappear on deuteration. By considering the bands above 3000 cm^{-1}, we think that the NH_2^+ group may be retained in the cadmium(II) complex and that these bands can be assigned to NH_2^+ deformation vibrations.

All complexes have broad strong bands at about 1600 and 1400 cm^{-1}, which are assigned to COO^- asymmetric and symmetric stretching vibrations [28]. The frequency separation of both vibrations increases in the order: nickel(II) < zinc(II) < copper(II)-A for the complexes of the first type. This trend is the same as that in the corresponding series of complexes with various aliphatic α-amino acids [21, 22, 26, 27], and suggests an increase in the degree of interaction of the metal–oxygen bonds for the metal complexes given, in the above order [28].

500–200 cm^{-1}. In this region absorption bands which cannot be observed in the ligand appear in zinc(II) and copper(II)-A complexes. These are assigned to the M–N and M–O stretching vibrations by comparing these spectra with those of metal complexes with proline [19] and glycine [29, 30]. It has been determined using X-ray diffraction techniques that bis(DL-prolinato)copper(II) dihydrate has a tetragonally distorted octahedral structure with a *trans* configuration [31]. Herlinger and Long [19] reported that the anhydrous and hydrated forms of bis(L-prolinato)copper(II) appear to adopt *cis* geometries contrasting infrared absorption spectra of bis(L-prolinato)copper(II) with that of bis (DL-prolinato)copper(II), because the former has twice the bands which are assigned to M–N and M–O stretching vibrations than the latter has. They assigned the bands at 527 and 470 cm^{-1} to M–N stretching vibrations and the bands at 316 and 274 cm^{-1} to M–O stretching vibrations for bis(L-prolinato)-copper(II).

Copper(II)-A has the bands at the same region that bis(L-prolinato)copper(II) has, which are absent in the ligand. For *cis* bis(glicinato)copper(II) monohydrate Kincaid and Nakamoto [29] assigned the bands at 478 and 457 cm^{-1} to M–N stretching vibrations, and the bands at 334 and 284 cm^{-1} to M–O stretching vibrations. Similar assignments were made for *cis* bis(glycinato)copper(II) by Percy [30]. Therefore, copper(II)-A seems to have a *cis* configuration.

For the copper(II)-B complex, there are bands at 411 and 261 cm^{-1}, which seem to be assigned to M–N and M–O stretching respectively. In addition, there are several bands which have not been observed for the ligand at the region of about 270 cm^{-1}. It has been reported that in the square planar halogen-bridge system [32], Cu–Cl stretching vibrations have been observed at about 300 cm^{-1} for a terminal mode and at about 270 to 280 cm^{-1} for a bridging mode. Therefore these bands should be assigned to the bridging Cu–Cl stretching vibration.

For the cadmium(II) complex, it is reasonable that the band at 260 cm^{-1} be assigned to Cd–O stretching vibrations, because we think that the NH_2^+ group may be retained and the nitrogen atom may not coordinate to the cadmium(II) ion. In general, bridging M–Cl stretching frequencies are lower than terminal M–Cl stretching frequencies observed in the region from 400 to 200 cm^{-1} [28, 33]. As there is no new band (except the band at 260 cm^{-1} for cadmium(II) complex), the Cl^- ion appears to bridge to two cadmium(II) ions.

The analyses of the crystal structure of dichloro-(4-hydroxy-L-proline)cadmium(II) and dichloro(L-proline)cadmium(II) have been carried out in our laboratory [34].

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