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An Infrared Spectroscopic Study of the Metal Binding in some Valine Chelates

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The IR spectra of some metal–valine chelates have been investigated from 3600–250 cm^{-1} and empirical assignments for observed bands relevant to the chelation binding have been accomplished. The configurations of the chelates have been deduced. From the variations in the metal–nitrogen stretching and NH_2 stretching frequencies, the periodic series trend in metal–nitrogen bond strengths is shown to be Co(II) < Ni(II) < Cu(II) > Zn(II), in accord with the Irving–Williams order. The group variation, Zn(II) < Cd(II) < Hg(II), reflects an increase in metal–nitrogen bond strengths with increasing softness of the metal ion. Using the frequency separation for the carboxylate stretching vibrations, the soft Hg(II) and Cd(II) are shown to bind relatively weakly with oxygen whereas the relatively hard Co(II) is more strongly bound.

Introduction

The significance of chelation phenomena in biological processes is firmly established and there is an increasing awareness of the potential for the employment of transition metal chelates in therapeutic applications [1]. Among several factors influencing the coordination tendencies of transition metal ions *in vivo* are the binding strengths of the ions with different ligand groups, especially with oxygen, nitrogen, and sulfur donor groups [2]. When generalizations regarding these binding tendencies are applied to biological systems it is important that the extent of the interactions of the metal ions with different donor groups in polydentate ligands be distinguished. Bulk properties such as thermodynamic stability constants do not furnish this information. However, IR spectroscopy provides, through the use of appropriate spectral criteria, useful information regarding the relative strengths of individual metal–ligand bonds in such chelates.

In this study several chelates of DL-valine with divalent transition metal ions have been prepared and investigated. The relative strengths of the metal–nitrogen bonds and, to a limited extent, the metal–oxygen bonds have been determined using established spectral criteria. From these results, together with some data from a previous study [3], periodic trends in the metal binding with the individual ligand groups have been discerned.

Experimental

Preparation of Compounds

Bis(DL-valinato)nickel(II) dihydrate was prepared using the method of Neuberg *et al.* [4]. The pale blue solid was washed several times with hot water and dried *in vacuo* over $CaSO_4$ for several hours. Product purity was established by comparing the IR spectrum with published data [3].

Anhydrous bis(DL-valinato)nickel(II) was obtained by heating the hydrate at 110 °C *in vacuo* for 3 hours. The anhydrous nature of this light green solid was demonstrated spectroscopically by the absence of the broad OH_2 stretching band found in the IR spectrum of the hydrate. This compound readily reverts to the blue dihydrate upon exposure to the atmosphere.

Bis(DL-valinato)mercury(II) was prepared as follows. 45 ml of 1.0 *N* NaOH was added dropwise to 100 ml of a solution containing 0.0500 mol (5.86 g) of DL-valine and 0.0250 mol (6.79 g) of $HgCl_2$ at 70 °C over a period of one hour. The solution was digested for an additional hour and the white crystalline product precipitated upon cooling. The product was recrystallized and dried *in vacuo* over $CaSO_4$ for several hours. *Anal.* Calcd. for $Hg[(CH_3)_2CHCH(NH_2)CO_2]_2$: C, 27.74; H, 4.67; N, 6.47. Found: C, 27.66; H, 4.54; N, 6.71.

Bis(DL-valinato)cobalt(II) monohydrate was prepared using essentially the same procedure described for the Hg(II) chelate. The purple crystalline solid was washed several times with water and dried *in vacuo* at 80 °C for several hours. Attempts to dehydrate the compound resulted in decomposition. *Anal.* Calcd. for $Co[(CH_3)_2CHCH(NH_2)CO_2]_2 \cdot H_2O$: C, 38.83; H, 7.18; N, 9.06. Found: C, 38.98; H, 7.43; N, 9.11.

Bis(DL-valinato)zinc(II) was prepared by adapting a general method reported by Berezina *et al.* for the preparation of Mn(II)–amino acid chelates [5]. A solution (100 ml) containing 0.0110 mol (3.16 g) of $ZnSO_4 \cdot 7H_2O$ was added to a suspension of 0.0110 mol (4.07 g) of barium valinate at 70 °C. The suspen-

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TABLE I. Infrared Frequencies (cm^{-1}) and Assignments (500–250 cm^{-1}) for DL-valine and Metal–Valine Chelates.[a]

LH	CdL_2	HgL_2	$CoL_2 \cdot H_2O$	$NiL_2 \cdot 2H_2O$	NiL_2	ZnL_2	Assignments
473m	439m	431w	439w,b	473w	464w 439w	486m 469w	CC_3 def.
425m	406w	400w	416w	418m	416w 393w	437w 424w	CC_3 asymmetric def.
	399w	474w	358w,b	365sh	371w,b	371w,b	M–N antisymmetric str.
363s,b	374m	372m	315m,b	316s,b	330sh	285m	CC_3 asymmetric def.
					318s,b	305sh	M–N symmetric str.
		323vw					
			291m,b	302s,b			OH_2 libration
276m	255m,b	286w,b	246w	245w		253m	CCCN def.

[a]Abbreviations: LH = DL-valine; s = strong; m = medium; w = weak; b = broad; sh = shoulder; v = very; str. = stretching; def. = deformation.

TABLE II. NH_2 and Metal–Nitrogen Stretching Frequencies (cm^{-1}).

	Series Variations			Group Variations		
Metal:	Co(II)	Ni(II)*	Cu(II)**	Zn(II)	Cd(II)	Hg(II)
NH_2 str.	3332	3326	3297	3324 3306	3359	3191
	3273	3270	3250	3265 3252	3257	3161
M–N anti. str.	358	365	394	371	399	474

*Dihydrate. **Data from ref. 3.

sion was digested for one hour, cooled, filtered to remove $BaSO_4$, and evaporated to dryness. The white crystalline product was washed several times with water and dried *in vacuo* over $CaSO_4$ for several hours. *Anal.* Calcd. for $Zn[(CH_3)_2CHCH(NH_2)CO_2]_2$: C, 40.34; H, 6.79; N, 9.41. Found: C, 39.51; H, 6.63; N, 9.28.

Bis(DL-valinato)cadmium(II) was prepared using the same procedure described for the Zn(II) chelate except that the suspension was digested for 3 days at room temperature prior to removing the $BaSO_4$. *Anal.* Calcd. for $Cd[(CH_3)_2CHCH(NH_2)CO_2]$: C, 34.84; H, 5.86; N, 8.13. Found: C, 33.49; H, 5.70; N, 7.83.

Deuteration Procedures

The N-deuterated chelates were prepared by the prolonged mixing of each complex with 99.5% deuterium oxide in a sealed tube at 60 °C. The deuterated Ni(II) chelate was dehydrated in the same fashion as was the protonated compound. Attempts to prepare D_2O solutions of these deuterated complexes for spectroscopic study were unsuccessful due to their very low solubilities.

Absorption Measurements

IR spectra were obtained using a Perkin-Elmer Model 621 spectrophotometer. Most of the samples were run as KBr and CsI discs; all such spectra were checked using Nujol mulls. Spectra of the anhydrous nickel(II) complexes were obtained as Nujol and fluorocarbon oil mulls. Wave number calibration was accomplished by comparison with polystyrene, water vapor, and carbon dioxide standard peaks.

Other Measurements

The magnetic susceptibility of the anhydrous bis(DL-valinato) nickel(II) was obtained using a Cahn Model 7500 Electrobalance DTL-Faraday Magnetic Susceptibility apparatus. The determination was performed at 23 °C using $HgCo(SCN)_4$ as the standard. The effective magnetic moment of the complex was determined to be 2.9 B.M.

Elemental analyses were accomplished using a Model 185 F & M Carbon, Hydrogen, Nitrogen

TABLE III. Carboxylate Stretching Frequencies and Frequency Separations (cm^{-1}) for N-deuterated Chelates.

	Series Variations			Group Variations		
Metal:	Co(II)	Ni(II)*	Cu(II)**	Zn(II)	Cd(II)	Hg(II)
COO^- anti. str.	1643	1592	1613	1593	1574	1587
COO^- sym str.	1363	1389	1380	1428 1401	1394	1397
ΔCOO^-	280	203	233	192	180	190

*Dihydrate. **Data from ref. 15.

Analyzer. Cyclohexanone-2,4-dinitrophenylhydrazone was the calibration standard.

Results and Discussion

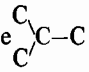
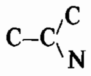
The observed absorption frequencies and assignments from 500 cm^{-1} to approximately 250 cm^{-1} for the ligand and the metal chelates are given in Table I. Selected frequencies sensitive to the extent of the metal–ligand binding in the chelates are listed in Tables II and III.

Spectral Assignments

In general, two types of spectra have been observed throughout the region studied: (1) the relatively simple spectra exhibited by the Cd(II), Hg(II), Co(II), and hydrous Ni(II) chelates; (2) the more complicated spectra of the Zn(II) and anhydrous Ni(II) compounds. In the spectral region from 3600 to approximately 500 cm^{-1} the proper assignments for the chelates are easily determined so only those data and assignments pertaining to the extent of the metal–ligand binding are presented and dicussed. A more detailed discussion of assignments in the low frequency region is presented.

In the region 3600–2000 cm^{-1} the only absorption bands are those due to hydrogen stretching vibrations of the NH_2, OH_2, CH_3, and CH groups. Of these, only the amino hydrogen atoms exchange with deuterium under the deuteration conditions employed. Thus, the NH_2 stretching bands (see Table II) are identified upon a comparison of the spectra of the complexes with those of the corresponding N-deuterated compounds.

In the approximate range 1600–1400 cm^{-1} the relatively intense bands due to the carboxylate antisymmetric and symmetric stretching vibrations appear. The antisymmetric stretching band usually overlaps a band due to the NH_2 scissors vibration. This complication is avoided by considering the carboxylate stretching frequencies for the N-deuterated chelates, which are listed in Table III.

In the low frequency region of the spectrum (see Table I) the spectra of the chelates should contain bands due to the metal–nitrogen stretching vibrations of the coordinated NH_2 groups [3, 6–8] in addition to bands due to skeletal deformation vibrations analogous to those observed for the ligand. Metal–oxygen stretching and chelate ring deformation vibrations are expected to appear at frequencies below the range studied [7–9] and were not observed. The ligand bands observed at 473, 425, and 363 cm^{-1} may be approximately described as CC_3 skeletal deformation vibrations, *i.e.*, deformations of the  ${}^{C}_{C}\!\rangle C{-}C$ (left) portion of the valine skeleton*. A newly-observed ligand band at 276 cm^{-1} is attributed to a CCCN skeletal deformation vibration, *i.e.*, a deformation of the  $C{-}C\langle^{C}_{N}$ (right) portion of the valine skeleton.

Among those chelates which exhibit relatively simple absorption patterns, the spectrum of the Cd(II) compound is found to contain a single new band at 399 cm^{-1} upon comparison with the ligand spectrum. This band is attributed to the M–N antisymmetric stretching vibration, as are the bands at 365 and 358 cm^{-1} in the spectra of the hydrous Ni(II) and Co(II) chelates, respectively. The spectra of these two hydrates, which are very similar, also contain a second new band at 302 (Ni) and 291 (Co) cm^{-1}. This band disappears upon dehydration of the Ni(II) complex and is thus ascribed to a libration of the water of hydration in both compounds. The spectrum of the Hg(II) chelate contains two new low frequency bands at 474 and 323 cm^{-1}, the latter band being very weak. The higher frequency absorption is assigned to the M–N antisymmetric stretching vibration on the basis of the very low NH_2 stretching frequencies observed for this complex, since these data suggest that the M–N bonds in the Hg(II) chelate are relatively strong. In treating the considerably

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*A more detailed description of these modes, based on a normal coordinate analysis, is given in reference 3.

more complicated spectra of the anhydrous Ni(II) and Zn(II) chelates, assignments of the M–N antisymmetric stretching vibration are based on a comparison of these similar spectra with that of the hydrous Ni(II) chelate. Additional bands at 318 (Ni) and 305 (Zn) cm^{-1} are attributed to the M–N symmetric stretching vibration using an approximate normal coordinate analysis which suggests that the separation of the M–N antisymmetric and symmetric stretching frequencies should be approximately 60–70 cm^{-1} [6].

Configurations of the Chelates

The spectral data strongly support a *trans*-planar configuration of the coordinating groups about the central metal ion for the Cd(II), Hg(II), Co(II), and hydrous Ni(II) chelates in view of the following considerations. (1) The general simplicity of the spectra throughout the entire region studied suggests that these complexes have a center of symmetry. Specifically, in the region 500–250 cm^{-1} only one absorption band which may be reasonably assigned to a metal-nitrogen stretching mode is observed. For complexes with lower symmetries both the metal–nitrogen antisymmetric and symmetric stretching modes are IR active and both have been observed for *cis* chelates of amino acids [6, 10]. (2) These spectra are similar to that of bis (DL-valinato)platinum(II) for which the *trans*-planar configuration has been demonstrated chemically [3].

Conclusions regarding the configurations of the anhydrous Ni(II) and Zn(II) chelates are more tentative. The complexity of both spectra is, in general, consistent with either the *cis*-planar or tetrahedral configurations for the chelates. For the Ni(II) complex a *cis* configuration is unlikely in view of the ease of the interconversion of the *trans* hydrous and the anhydrous compounds. In addition, the magnetic moment of 2.9 B.M. for this complex does not support a regular, or nearly regular, tetrahedral arrangement. For such 'tetrahedral' Ni(II) complexes, moments in the range 3.5–4.0 B.M. are expected [11]. A reasonable proposal is that the configuration is intermediate between tetrahedral, in which the dihedral angle between the two chelate rings is 90°, and planar, in which this angle is zero. Thus, it is suggested that dehydration is accompanied by a rotation of one chelate ring relative to the other. Magnetic moments for such distorted complexes are characteristically in the range 3.0–3.5 B.M. [11]. For the Zn(II) chelate, the diamagnetism of this d^{10} ion precludes the use of magnetic moment data to distinguish possible structures. However, in view of the similarity of the spectra of the Zn(II) and anhydrous Ni(II) chelates it is reasonable to propose that their structures are similar.

Metal–Ligand Binding

The metal–nitrogen bonds

In the absence of strong solid-state effects, the NH_2 stretching frequencies have been a generally reliable criterion of the relative strengths of the metal–nitrogen bonds in a series of metal complexes of the same amino acid [3, 6, 7]. These frequencies decrease with increasing metal–nitrogen bond strengths, expressed in terms of the M–N bond-stretching force constants. The NH_2 stretching frequencies, together with the M–N antisymmetric stretching frequencies for several metal–valine complexes, are given in Table II. In considering the series variations in the M–N antisymmetric stretching frequencies, trends in these frequencies should accurately reflect the trends in the M–N bond-stretching force constants since the reduced masses are not very different. Thus, both spectral criteria demonstrate that the series trend in the metal–nitrogen bond strengths is Co(II) $<$ Ni(II) $<$ Cu(II) $>$ Zn(II). The M–N stretching frequency data show that the group trend in M–N bond strengths is Zn(II) $<$ Cd(II) $<$ Hg(II). Since the reduced masses for the M–N stretching vibrations increase in the same order, so must the bond-stretching force constants. Although the NH_2 stretching frequencies suggest approximately equal M–N bond strengths for the Zn(II) and Cd(II) chelates, this criterion is considered to be less reliable than the M–N stretching frequencies because of possible differences in intermolecular interactions due to the different structures of the two chelates.

The series trend in metal–nitrogen bond strengths follows the familiar Irving–Williams order of stability [12] and may be attributed to the variations in the inherent strengths of the metal ions as Lewis acids, arising in part from a decrease in ion size across the series and in part from variations in ligand field stabilization energies. The group trend in bond strengths reflects the increasing softness of the metal ions from zinc to mercury resulting in the soft Hg^{2+} and Cd^{2+} preferentially forming stronger bonds with the softer amino nitrogen rather than with the carboxylate oxygen.

The metal–oxygen bonds

Nakamoto *et al.* have concluded that the separation of the carboxylate antisymmetric and symmetric stretching frequencies is a reliable criterion of the relative metal–oxygen bond strengths in a series of related amino acid complexes provided that the spectral comparisons are made using compounds in the same physical state: anhydrous solid, hydrated solid, or D_2O solution, [13]. Of the three, data obtained using D_2O solutions appear to be the most reliable [13, 14]. In the absence of such solution data, carboxylate stretching frequencies for the N-deuterated solids are compared in Table III. The absence of any clear periodic trends is not unexpected since two of the solids are hydrates and the others are anhydrous. However, the data indicate that the soft Hg^{2+} and Cd^{2+} ions bind rather weakly with the relatively hard carboxylate oxygen whereas the harder Co^{2+} ion is a substantially stronger oxygen binder.

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