pletely vanishes on dehydration. Similarly, the strong band measured at *ca.* 1660 cm^{-1} in the monohydrato isoleucine complexes probably arises from the bending mode of *coordinated* water in both species. Interestingly, the absence of an absorption in this region for $Cu(gly)_2\cdot 2H_2O$ may indicate that the water molecules exist in the lattice of this crystal rather than coordinated to the copper ion.[36]

Acknowledgment. We appreciatively acknowledge several conversations with Professor C. R. Hare of the University of Miami that stimulated our interest in the problem discussed in this manuscript.

[36] The bending mode of lattice water should appear in the range 1600–1630 cm^{-1} (see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 156), and in $Cu(gly)_2\cdot 2H_2O$ it is assigned to a very strong absorption at 1608 cm^{-1}, unresolved from the NH_2 scissors.

Laser-Raman and Infrared Spectra of Amino Acids and Their Metal Complexes. III. Proline and Bisprolinato Complexes

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Abstract: The laser-Raman spectra of DL-proline and L-proline in the solid state and in aqueous solutions of pH 1.0, 6.0, and 11.0 are investigated, and bands characteristic of the cationic, zwitterionic, and anionic forms of the amino acid residue are discriminated. The infrared spectra of solid DL-proline and L-proline have been measured in the region between 4000 and 200 cm^{-1} and the infrared and Raman spectra of proline in D_2O solutions are also reported. Vibrational modes that principally contribute to the observed frequencies are empirically assigned on the basis of spectral changes resulting from N-deuteration and pH variation and through comparison with a Urey–Bradley force-field analysis of glycine[2] and with the spectrum of pyrrolidine.[3] The infrared spectra of anhydrous, monohydrato, and dihydrato forms of the bis-DL-prolinatocopper(II) complex and the dihydrate of bis-DL-prolinatonickel(II) were carefully examined in order to infer structural differences in these complexes and to detail the effects of variable hydration on their infrared spectra. Similarities in the positions of the metal–nitrogen and metal–oxygen stretching modes indicate that the trans configuration is maintained in all four complexes, and spectral features resulting from removal of the groups occupying axial coordination positions are discussed. Contrasting with this result for the DL-proline complexes, the anhydrous and hydrated forms of bis-L-prolinatocopper(II) appear to adopt cis geometries.

The molecular structure of bis-DL-prolinatocopper(II) dihydrate as determined by Mathieson and Welsh[4] using X-ray diffraction techniques is interesting because it presumably closely resembles the coordinated species in aqueous solution.[5,6] The copper ion is located in a tetragonally distorted octahedral environment with the prolines bidentately coordinated in a trans configuration and with two water molecules bonded axially.[4] This complex can apparently be dehydrated to form $Cu(DL\text{-}pro)_2\cdot H_2O$[7] and $Cu(DL\text{-}pro)_2$, and the effects on the vibrational spectra of the series of complexes of variable hydration and, concomitantly, of groups occupying the fifth and sixth coordination positions, can be examined. Laurie[8] has noted the possible hazards in employing vibrational criteria that ignore these effects to distinguish geometrical isomers of Cu(II)–amino acid complexes. However, the perturbations on the spectra due to such structural changes in the metal–ligand stretching regions are minimal, and the previously developed criterion[9] based on symmetry arguments regarding the number of Cu–N and Cu–O stretching absorptions appears to be valid (at least for this test case). Identification of metal–ligand and chelate ring modes in $Ni(DL\text{-}pro)_2\cdot 2H_2O$, $Cu(DL\text{-}pro)_2$, $Cu(DL\text{-}pro)_2\cdot H_2O$, $Cu(DL\text{-}pro)_2\cdot 2H_2O$, $Cu(L\text{-}pro)_2$, and $Cu(L\text{-}pro)_2\cdot XH_2O$ is based on a comparison with spectrum of the free amino acid and on analogies to the spectrum of bisglycinatocopper(II) monohydrate.[9,10] Utilizing our vibrational criterion[9] and through comparison of the spectra with that of *trans*-$Cu(pro)_2\cdot 2H_2O$ it is concluded that the complexes formed from the racemic amino acids adopt a trans structure. The present study also shows that copper(II) complexes synthesized with the optically active amino acid are cis isomers, and the recent suggestion[11] that stereoselective crystal packing effects operate to stabilize this configuration for bis-L-prolinato complexes is most probably correct.

The spectral study of the metal complexes necessitated a comprehensive investigation and assignment of the

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Table I. Infrared and Raman Spectra of Proline[a,b]

Infrared spectra		Raman spectra					
				Aqueous solutions			
DL-pro (solid)	L-pro (solid)	DL-pro (solid)	L-pro (solid)	pH 1.0	pH 6.0	pH 11.0	Assignment
3182 (vs)	3050 (vs, br)	3183 (w)					
							N–H stretching
3130 (sh)		3119 (w)	3051 (m, br)	3032 (m, br)	3027 (w, br)		
3022 (sh)	3006 (m)	3008 (m)	3007 (s)	3002 (s)	2997 (m)	2983 (s)	
3002 (sh)	2982 (s)	2991 (w)					
2978 (s)	2975 (m)	2979 (w)	2976 (m)	2976 (w)	2978 (w)	2966 (w)	
2955 (s)	2955 (m)	2965 (m)	2950 (s)	2962 (w)	2961 (w)	2942 (m)	C–H str
2920 (sh)	2935 (sh)	2942 (m)	2952 (w)	2944 (m)	2944 (m)	2921 (w)	
2880 (s)	2920 (sh)	2908 (m)	2919 (w)	2921 (w)	2918 (w)	2895 (m)	
2825 (w)	2875 (w)	2882 (w)	2878 (w)	2893 (w)	2891 (w)	2877 (w)	
				1734 (s)			
							C=O str
				1716 (m)			
1611 (vs)	1619 (vs)	1643 (w)		1656 (m)	1639 (w)	1656 (w)	
							COO^- asym str
		1622 (w)	1624 (w)	1614 (m)	1616 (w)	1619 (w)	
1598 (vs)	1555 (vs)	1595 (e)	1550 (w)	1548 (vw)	1549 (vw)		
							NH_2^+ scissor
1578 (sh)						1525 (vw)	
1483 (m)	1472 (s)	1484 (m)	1471 (w)	1481 (m)	1476 (m)	1482 (m)	
1461 (s)		1465 (w)	1451 (m)	1457 (s)	1457 (s)	1456 (s)	CH_2 bend
1449 (s)	1447 (s)	1450 (m)	1441 (w)				
1412 (m)	1402 (s, br)	1411 (vw)	1409 (w)	1416 (w, br)	1424 (w)	1422 (w, br)	
							COO^- sym str, CO str
					1411 (s, br)	1396 (s)	
1381 (sh)		1385 (w)	1373 (s)	1382 (w)	1388 (w)		NH_2^+ twist
1365 (w)	1375 (s, br)	1361 (w)	1349 (w)	1357 (w)	1354 (m)	1354 (m)	C–H bend
1340 (s)	1340 (sh)	1345 (w)			1333 (m)		CH_2 twist
1316 (s)	1317 (s)	1306 (w)	1320 (vw)	1329 (m)	1316 (m)	1317 (w)	C–H bend
1291 (m)	1292 (s)	1280 (m)	1285 (m)	1298 (w)	1295 (w)	1301 (w)	
							CH_2 twist
	1289 (s)			1274 (m)	1274 (m)	1281 (w)	
1259 (m)	1253 (m)	1257 (w)	1264 (m)				
							CH_2 wag
1235 (m)	1225 (sh)	1235 (m)	1239 (m)	1244 (m)	1242 (m)	1244 (m)	
1186 (m)		1192 (w)	1192 (vw)	1191 (m)	1194 (w)	1186 (m)	NH_2^+ wag, NH bend for pH 11.0 spectrum
1168 (s)	1168 (s)	1162 (w)	1173 (m)	1173 (w)	1171 (w)		
							CH_2 twist
			1164 (w)				
						1112 (vs)	
							CH_2 rock
1089 (w)	1083 (m)	1091 (w)	1082 (m)	1093 (w)	1090 (w)	1090 (w)	
1049 (m)	1051 (w)	1054 (s)	1056 (m)	1046 (s)	1045 (s)	1043 (m)	
							CH_2 wag
	1033 (m)		1033 (m)				
996 (m)	979 (m)	994 (w)	994 (w)	993 (w)	992 (w)	986 (m)	
			984 (m)				
							CCN and CC str
950 (m)	945 (m)	943 (m)	951 (m)	947 (w)	944 (w)	953 (w)	
921 (m)	911 (w)	920 (vs)	919 (vs)	911 (vs)	909 (vs)	915 (vs)	
887 (m)	900 (w)	898 (vs)	898 (vs)	891 (w)	889 (w)	875 (s)	NH_2^+ rock, N–H bend for pH 11.0 spectrum
	880 (w)						
855 (m)	860 (sh)	854 (m)	866 (w)	868 (m)	864 (s)	853 (m)	
833 (m)	846 (s)	834 (vs)	842 (s)	848 (m)	845 (m)		CH_2 rock
	830 (sh)			834 (m)		833 (m)	
783 (w)	791 (m)	783 (w)	795 (m)	777 (w)	785 (w)	785 (m)	
							Skel def
		748 (w)		748 (m)			
678 (m)	688 (w)	677 (w)	698 (w)	677 (w)	681 (w)	683 (w)	COO^- scissor
653 (m)	661 (sh)	654 (w)	667 (w)	633 (w)	636 (w)	646 (w)	Skel def
626 (m)	639 (s)	626 (m)	641 (m)	597	609 (w)	621 (w)	COO^- wag
575 (vw)	569 (w)	595 (w)			580 (w)	582 (w)	
							Skel def
		577 (w)	577 (w)	565 (w)	556 (w)	556 (w)	
461 (s)	450 (s)	461 (s)	448 (m)	455 (s, br)	454 (s, br)	453 (s, br)	COO^- rock
386 (vs)	369 (vs)	389 (m)	377 (w)	336 (m, br)	344 (m)	346 (w)	CCN bend
285 (w)	292 (m)	289 (m)	298 (w)	292 (w)	312 (w)	320 (w)	
							Skel def
245 (w)		258 (w)			227 (vw)	274 (vw)	

[a] Spectra recorded as Nujol and hexachlorobutadiene mulls. [b] v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad. All frequencies in tables in cm^{-1}.

Table II. Spectra of N-Deuterated DL-Proline

Infrared		Raman
Solid[a,b]	D_2O solution	D_2O solution
		3028 (w)
	3010 (sh)	2992 (s)
	2986 (m)	2982 (w)
	2956 (m)	2964 (w)
		2943 (m)
	2924 (sh)	2919 (w)
	2885 (m)	2889 (w)
	2850 (sh)	
2720 (w)		
2660 (w)		
2630 (sh)		
2370 (s)		
2280 (sh)		
2240 (m)		
1998 (s, br)		
1925 (m)		
1900 (s, br)		
1604 (vs, br)	1608 (vs)	1615 (w)
1588 (sh)		
1483 (w)	1475 (sh)	1480 (w)
	1457 (s)	1456 (w)
		1432 (w)
	1401 (s)	1402 (vs, br)
	1360 (s)	1355 (w)
1328 (m)	1326 (m)	1327 (m)
1305 (m)	1308 (s)	1305 (m)
1295 (m)		
1268 (w)	1270 (w)	1270 (m)
1259 (sh)		1256 (w)
1246 (w)	1236 (w)	
1184 (sh)	1193 (m)	
1168 (m)		1175 (w)
1119 (m)		1104 (w)
1096 (m)	1098 (s)	1086 (w)
1048 (w)		1046 (m)
		1031 (w)
1009 (vw)	1010 (vw)	1009 (m)
998 (vs)		
972 (w)	971 (w)	
935 (m)	931 (m)	932 (s)
912 (m)	914 (w)	913 (s)
	900 (w)	893 (m)
858 (sh)	870 (m)	878 (m)
846 (m)	840 (sh)	851 (s)
836 (sh)		
824 (sh)	823 (m)	829 (s)
		791 (m)
771 (m)	768 (m)	773 (w)
766 (sh)		
747 (m)		755 (w)
653 (s)		678 (w)
638 (s)		657 (w)
611 (s)		612 (w)
		573 (vw ?)
536 (vw)		539 (w)
447 (s)		451 (s)
435 (w)		432 (w)
348 (vs)		381 (vw)
		317 (m)
275 (w)		286 (w)

[a] Nujol mull only. [b] Abbreviations as in Table I.

vibration fundamentals of proline. Low-resolution infrared spectra[12–14] and a partial Raman spectrum[15] of this amino acid have been reported, but the assignment of observed frequencies to vibrational modes was not attempted. In order to argue our empirical assignment as closely as possible, measurements include the infrared and laser-Raman spectra of the zwitterionic and N-deuterated solids and a study of changes occurring in the Raman spectra of solutions upon pH variation and deuteration.

Experimental Section

A. Preparation of Compounds. 1. DL-Proline ($NHCH_2CH_2CHOOH$), purchased as the monohydrate from Cyclo Chemical Corp. (Los Angeles, Calif.), was purified by recrystallization from aqueous solution after treatment with activated charcoal and dried *in vacuo* over P_2O_5 for several hours at 60°. L-Proline (California Biochemical Research Co., Los Angeles, Calif.) was used without further purification. DL-Proline was N-deuterated by repeated recrystallization from 99.5% deuterium oxide under vacuum conditions.

2. ***trans*-Cu(DL-pro)$_2\cdot$2H_2O** was prepared by a method similar to that described by Neuberg, *et al.*[16] The soluble dihydrate precipitated as blue crystals from a solution of small volume, and these were not washed with organic solvents since this may lead to dehydration. *Anal.*[17] Calcd: Cu, 19.24; C, 36.37; H, 6.72; N, 8.49; H_2O, 1.09. Found: Cu, 20.36; C, 35.63; H, 6.04; N, 9.91; H_2O, 1.15. Cu(DL-pro)$_2\cdot H_2O$ was obtained as purple crystals upon gently heating the dihydrate. Intensities of the H_2O stretching and bending modes in the infrared spectrum of this complex are approximately half those of the dihydrate, and one water per molecule appears to be lost discretely. The anhydrous, blue copper complex was obtained by heating Cu(DL-pro)$_2\cdot$2H_2O *in vacuo* at 120° for 2 hr. Prolonged heating of the dihydrate in a KBr matrix above 100° produced a complex exhibiting an identical spectrum.

3. **Cu(L-pro)$_2\cdot xH_2O$** was prepared by the method described for Cu(DL-pro)$_2\cdot$2H_2O. The anhydrous material was obtained only with considerable difficulty, requiring heating *in vacuo* at 120° for 24 hr, and this material was very hygroscopic. Prolonged heating of the hydrate in a CsI matrix above 100° produced a complex exhibiting an identical spectrum.

4. **Ni(DL-pro)$_2\cdot$2H_2O** was prepared as a light blue powder according to the method used for the analogous copper complex, followed by heating *in vacuo* at 60° for 3 hr. *Anal.* Calcd: Ni, 18.08; C, 36.99; H, 6.83; H_2O, 1.11. Found: Ni (from ash), 18.62; C, 37.55; H, 6.52; H_2O, 1.01. A rusty orange anhydrous complex was prepared from the dihydrate by heating *in vacuo* at 100° for several hours. The possibility of significant decomposition upon dehydration was dismissed since the spectrum of the dihydrate formed by rehydration of Ni(DL-pro)$_2$ was identical with that of the original Ni(DL-pro)$_2\cdot$2H_2O.

B. Spectral Measurements. The infrared spectra were measured from 4000 to 200 cm^{-1} using a carefully calibrated Perkin-Elmer Model 621 infrared spectrophotometer equipped with an air-dryer accessory. The spectra were recorded for samples as KBr and CsI pellets and as mulls supported on CsI plates. The reported spectra are those of the potassium bromide disks, except for those cases in which the mull and pellet spectra are not in good agreement. Nujol and hexachlorobutadiene mull spectra are recorded in that event. The infrared spectrum of N-deuterated DL-proline dissolved in D_2O was measured as a thin film supported on KRS-5 plates. Frequencies are accurate to $\pm 2\ cm^{-1}$.

The Raman spectra were measured with a modular instrument employing a Spex Model 1400 double monochromator spectrometer, a ITT FW-130(S-20) photomultiplier, and dc amplification with a Spectra-Physics Model 112 helium–neon laser as the excitation source (monitored power 45 mW at 632.8 nm). The frequency scale was calibrated in the region 0–4000 cm^{-1} using known frequencies of chloroform, carbon tetrachloride, benzene, and certain atomic neon lines. The reported Raman frequencies are

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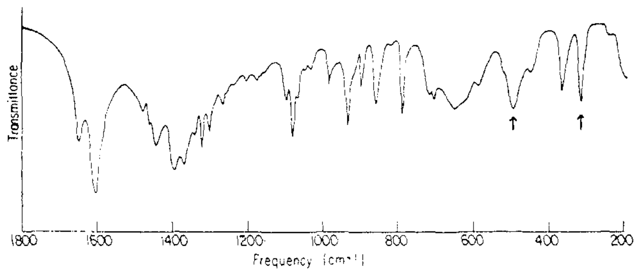

Figure 1. Infrared spectrum (1800–200 cm^{-1}) of Cu(DL-pro)$_2$·2H_2O. Metal–ligand bands are indicated by arrows.

averages obtained from values measured in at least three of the best spectra. The spectra were analyzed with the aid of a Du Pont Model 310 curve resolver, and the estimated maximum frequency error is ±5 cm^{-1} for the spectra of the solids. For the solutions, the spectral bands are characteristically broader, and resolution of band envelopes is more difficult; consequently, the possible frequency error may be ±10 cm^{-1} for weak, broad peaks. The Raman spectra of solid DL-proline and L-proline were recorded from pressed multicrystalline pellets supported by a goniometer head at an angle of 20° to the incident laser beam. Saturated aqueous solutions of proline of pH 1.0, 6.0, and 11.0 and in D_2O were treated with activated charcoal to reduce fluorescence and immediately passed through sintered glass or Millipore filters directly into the sample cell.

Results

The laser-Raman spectra of solid DL-proline, solid L-proline, and saturated solutions of DL-proline at pH 1.0, 6.0 and 11.0 are tabulated in Table I, and the spectra of the solutions are associated with the cationic, zwitterionic, and anionic forms of the free acid, respectively. The spectra of solutions of DL- and L-proline are identical, and variations in the spectra of the two solids must arise from crystalline effects. The infrared spectra of solid DL- and L-proline are also contained in Table I. Raman and infrared spectra of N-deuterated DL-proline are recorded in Table II.

Proline belongs to the trivial point group C_1, and all 45 vibrational modes are both Raman and infrared active. The spectrum of the amino acid is sensitive to hydrogen-bonding effects, and the assignments made in Table I are those for the zwitterionic acid in the solid state, except where specifically noted. In arriving at approximate descriptions of normal modes that are principal contributors to the observed frequencies, we have assumed that the vibrations associated with the substituted pyrrolidinyl ring would lie close to the values found for pyrrolidine,[3] while those of the carboxylate group would bear analogy to the assignments established for glycine.[2] Six frequencies attributable to NH_2^+ motions may be described as the symmetric (3130 cm^{-1}) and asymmetric (3182 cm^{-1}) N–H stretches, and the NH_2^+ scissoring (1598 cm^{-1}), twisting (1381 cm^{-1}), wagging (1186 cm^{-1}) and rocking (887 cm^{-1}) modes. These peaks disappear on N-deuteration, and peaks ascribable to the ND_2^+ group motions appear at 2370, 2240, 1009, 972, 846, and 743 cm^{-1}. Similarly, N-deuteration permits the identification of the symmetric (1611 cm^{-1}) and asymmetric (1412 cm^{-1}) carboxylate stretches, which are probably strongly coupled to NH_2^+ modes in the protonated form, of the carboxylate scissoring mode (678 cm^{-1}), which mirrors its behavior in glycine[2] in shifting to 653 cm^{-1} upon deuteration, and of the COO^- wagging (626 cm^{-1}) and rocking (461 cm^{-1}) modes.

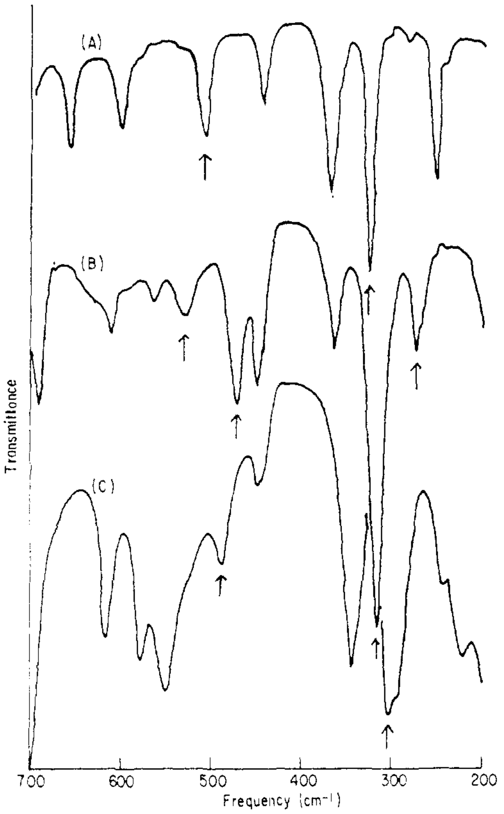

Figure 2. Low-frequency infrared spectra of (A) Cu(DL-pro)$_2$ in CsI pellet, (B) Cu(L-pro)$_2$ in CsI pellet, and (C) Ni(DL-pro)$_2$.2H_2O as Nujol mull on CsI plates. Metal–ligand bands are indicated by arrows.

The spectrum of the isoelectric pH 6.0 solution is virtually identical with those of the solids, but a new band that may be described as the C=O stretching mode of the cation appears at 1734 cm^{-1} in the spectrum of the pH 1.0 solution. The spectrum of the proline anion (pH 11.0 solution) differs from that of the zwitterion principally in the absence of NH_2^+ peaks at 3027, 1549, and 1388 cm^{-1}, while spectral features at 1186 and 875 cm^{-1} arise from N–H bending motions in this molecule.

The infrared frequencies listed in Table III are those observed for metal–proline chelates, and the spectra are assigned by direct comparison with the spectra of DL- and L-proline and congruent with a normal coordinate analysis of metal–glycine complexes.[10] The infrared spectrum (1800–200 cm^{-1}) of *trans*-Cu(DL-pro)$_2$·2H_2O is shown in Figure 1, and Figure 2 presents a comparison of the spectra of Cu(DL-pro)$_2$, Cu(L-pro)$_2$, and Ni(DL-pro)$_2$·2H_2O in the region between 700 and 200 cm^{-1}. The modifications in the proline spectrum upon chelation are similar to the spectral behavior observed upon increasing solution basicity, and they arise from partial deprotonation of the NH_2^+ group upon metal binding. Only a single, strong absorption is measured for the complexes in the N–H stretching region, and peaks at 1598 and 1381 cm^{-1} in the spectrum of solid DL-proline have disappeared. Otherwise, the predominant new features in the spectrum occur below 600 cm^{-1}, and these are attributable to metal–ligand stretching modes and chelate ring deformations. The metal–nitrogen and metal–oxygen modes in Cu(DL-pro)·2H_2O are assigned at 489 and 319 cm^{-1},

Table III. Infrared Spectra of Metal–Proline Chelates[a]

$Cu(DL\text{-}pro)_2 \cdot 2H_2O$[b]	$Cu(DL\text{-}pro)_2 \cdot H_2O$	$Cu(DL\text{-}pro)_2$	$Cu(L\text{-}pro)_2$	$Ni(DL\text{-}pro)_2 \cdot 2H_2O$	Assignment
3418 (vs)	3438 (s)				
	3355 (s)				
3205 (vs)	3190 (s)	3190 (w)	3196 (s, b)	3270 (vs, br)	
					NH str
	3002 (sh)		3101 (s)		
2980 (s)	2978 (m)	2965 (m)	2978 (sh)	2977 (sh)	
2947 (m)	2945 (w)	2942 (m)	2970 (s)	2970 (m)	
2930 (sh)	2930 (sh)	2923 (m)	2955 (sh)	2948 (w)	
					CH str
2903 (w)	2895 (w)	2894 (m)	2910 (m)	2925 (w)	
2875 (m)	2874 (w)	2867 (m)	2873 (m)	2901 (w)	
		2855 (sh)		2872 (w)	
1650 (s)	1637 (sh)			1685 (sh)	H_2O def
1604 (vs)	1606 (vs)	1623 (vs)	1628 (vs)	1601 (vs)	
					COO^- asym str
			1604 (vs)		
1476 (w)	1480 (w)	1483 (w)	1450 (sh)	1473 (sh)	
					CH_2 bend
1457 (sh)	1450 (w)	1451 (w)		1458 (w)	
1444 (m)	1428 (m)	1443 (w)	1441 (m)	1442 (m)	
					COO^- sym str
1390 (s)		1430 (m)	1418 (s)	1402 (s)	
			1397 (s)		
1365 (s)	1352 (s)	1355 (vs)	1375 (m)	1344 (w)	
1342 (w)			1357 (vs)	1322 (m)	
1322 (m)	1326 (m)	1330 (s)	1319 (s)	1302 (m)	
1303 (w)	1299 (w)	1299 (w)	1304 (m)		
	1286 (w)	1292 (w)			
1267 (w)	1262 (w)	1267 (w)	1270 (vw)	1267 (w)	CH_2 twist, wag, and rock, CH bend, and NH bend
1230 (vs)		1258 (w)	1238 (vw)	1230 (sh)	
1200 (w)	1198 (m)	1200 (w)		1203 (vw)	
1176 (w)	1176 (w)	1186 (w)	1186 (s)	1179 (w)	
1097 (m)	1105 (m)	1109 (m)	1096 (m)	1097 (m)	
1082 (m)	1076 (m)	1080 (m)	1079 (w)	1087 (m)	
1047 (w)	1044 (w, br)		1068 (s)	1068 (w)	
1033 (w)		1030 (w)	1041 (s)	1031 (w)	
983 (w)	971 (w)	973 (w)	980 (w)	981 (w)	
937 (m)	937 (m)	942 (m)	970 (vw)	941 (m)	
925 (sh)	927 (w)	924 (w)	936 (m)	929 (sh)	CN str, CC str, CH_2 rock, skel def, and NH_2 bend
918 (w)	901 (w)	903 (w)	926 (s)	916 (vw)	
898 (w)	870 (vw)	864 (w)	899 (sh)	899 (w)	
859 (m)	848 (m)	851 (m)	893 (w)	860 (m)	
814 (vw)	805 (vw)		868 (w)	808 (sh)	
790 (m)	769 (w)	777 (m)	852 (w)	788 (s, br)	
			799 (w)		
			791 (w)		
705 (m)	720 (w)	716 (m)	708 (w)	700 (m)	
					COO^- scissor
			693 (w)		
645 (m, br)	656 (w)	659 (w)	629 (w)		Skel def
580 (w)	604 (w)	602 (w)	609 (w)	616 (m)	COO^- wag
520 (vw)	577 (vw)		563 (vw)	576 (m)	
					Skel def
				549 (m)	
498 (m)	516 (w)	510 (w)	527 (w)	495 (w)	
					Metal–nitrogen str
			470 (m)		
452 (w)	443 (w)	447 (w)	447 (w)	445 (w)	COO^- rock
368 (m)	374 (m)	370 (m)	354 (w)	342 (m)	CCN bend
319 (m)	330 (m)	330 (m)	316 (s)	302 (s)	
					Metal–oxygen str
			274 (w)		
245 (vw)	258 (w)	255 (m)		289 (sh)	
				243 (w)	Skel def
				219 (m)	

[a] Spectra recorded as KBr disks between 4000 and 400 cm^{-1}, and as Nujol mulls supported on CsI plates between 400 and 200 cm^{-1}. [b] Abbreviations as in Table I.

respectively, and in $Ni(DL\text{-}pro)_2 \cdot 2H_2O$ they are measured at 445 and 302 cm^{-1}, respectively, in reasonable agreement with the values assigned in the trans bisglycinato complexes of copper (477, 334 cm^{-1})[8,9] and nickel (439, 290 cm^{-1}).[10] Metal–ligand frequency designations for the remaining complexes follow from those of the dihydrates.

The carboxylate scissoring and wagging modes shift upon coordination to the metal, while the rocking mode is invariant at 450 cm^{-1}. The carboxylate scissoring increases in frequency from 678 cm^{-1} to *ca.* 705 cm^{-1}, but the wagging motion decreases in energy and appears in the complexes at *ca.* 580 cm^{-1}. The frequency displacements are comparable to those observed for these motions in metal–glycine complexes,[10] and they further support our assignment of carboxylate modes in the proline spectra.

Discussion

In a companion paper,[9] the problem of geometrical isomerism in square-planar and pseudo-square-planar bis(amino acidato) complexes of Cu(II) is discussed, and a vibrational criterion is developed that permits distinction between cis and trans forms of these complexes. This criterion is based on consideration of the local symmetry about the copper ion furnished by the binding groups of the amino acids. It is argued that the cis complexes, which do not possess a (local) center of symmetry, should exhibit twice the number of metal–ligand stretching modes that are observed for the locally centrosymmetric trans complexes. Although this argument appears to be valid for a number of complexes whose structures have been determined,[9] Laurie[8] has criticized the use of local-symmetry vibrational criteria of this type because the total molecular symmetry and the effects of groups in the fifth and sixth coordination sites are generally disregarded. He further notes that variable hydration and crystal structural differences could result in deceptive variations in the infrared spectra that are not coupled to conformational modifications.[8] Although the effects of crystal structure and of total molecular symmetry may be significant in vibrational regions sensitive to hydrogen-bonding changes (*i.e.*, regions containing NH_2^+ and COO^- modes), the effects on the metal–ligand stretches are trivial.[9]

The existence of anhydrous, monohydrato, and dihydrato complexes of bis-DL-prolinatocopper(II) provides the possibility of examining the effects of variable hydration and of groups in the axial coordination positions on the low-frequency spectral region. In the structure of $Cu(DL\text{-}pro)_2 \cdot 2H_2O$, both waters are coordinated, and, presumably, upon loss of one of these, a pentacoordinate complex is formed with the copper remaining approximately in the plane formed by the two nitrogens and the two carboxylate oxygens. A five-coordinate structure of this type is present in $Cu(gly)_2 \cdot H_2O$, which was a cis geometry, however.[18] The similarity of the spectra in the far-infrared region and the invariance of the Cu–N and Cu–O stretching frequencies in these complexes indicate that variable hydration and axial coordination do not seriously affect our vibrational criterion.[9] All three spectra contain only one metal–nitrogen and one metal–oxygen absorption, and trans configurations may be inferred for the three complexes.

Gillard, *et al.*,[11] suggest that, in contrast to the trans geometries adopted by complexes prepared from racemic proline, the optically active acid complexes may exist in cis configurations, and that the conformer is stereoselected by the absolute configuration at the asymmetric carbon atom. To test this, $Cu(L\text{-}pro)_2$ and $Cu(L\text{-}pro)_2 \cdot xH_2O$ were prepared and their spectra affirm the probable correctness of the prediction. For both complexes, two copper–nitrogen stretches are measured, at 527, 470 and 525, 471 cm^{-1}, respectively. The spectrum of the hydrated complex exhibits two absorptions (319, 272 cm^{-1}) in the region appropriate for assignment as copper–oxygen asymmetric and symmetric stretches, respectively, and for $Cu(L\text{-}pro)_2$ they fall at 316 and 274 cm^{-1}. Although skeletal deformations probably contribute to the absorption at 274 cm^{-1}, this band does not correspond to the band measured at 255 cm^{-1} in $Cu(DL\text{-}pro)_2$ and attributed to a skeletal deformation in that spectrum. In this regard, a comparison of the spectra of the free amino acids (Table I) with those of the complexes shows that a 245-cm^{-1} skeletal mode is present in DL-pro, shifting to *ca.* 255 cm^{-1} for the complexes. This line is absent in the spectrum of L-pro, and there are no absorptions for L-pro in the 260–290-cm^{-1} region, where we assign Cu–O (symmetrical stretch) for the complexes. The infrared spectra are thus indicative of cis geometries for both the hydrated and anhydrous copper compounds prepared from the optically active amino acid. The difference in conformation for the complexes formed with DL- and L- proline may be responsible for their contrasting circular dichroism spectra.[6,19]

Finally, we have investigated the spectra of Ni(II) complexes formed with DL-pro, since Condrate and Nakamoto's measurements[10] on a series of glycinato complexes suggested that a local symmetry criterion for geometrical isomerism[9] might be extended to amino acid complexes of other metal ions. For $Ni(pro)_2 \cdot 2H_2O$, such an extension does appear valid, and nickel–ligand modes appear at 445 (Ni–N) and 302 cm^{-1} (Ni–O) in comparison with respective values of 439 and 290 cm^{-1} in *trans*-$Ni\text{-}(glycine)_2 \cdot 2H_2O$. No other absorptions characterizable as metal–ligand frequencies appear for $Ni(pro)_2 \cdot 2H_2O$, and it is likely that it exists in a trans configuration. Upon dehydration of this material to an orange-red anhydrous compound, the conclusions that may be drawn from the spectra are more tenuous. A nickel–nitrogen stretch still is measured at 443 cm^{-1} and a nickel–oxygen stretch is found at 300 cm^{-1}. However, moderately intense peaks appear at 532 and 397 cm^{-1}, and there are weak shoulders at 462 and 328 cm^{-1}. Although it is tempting to attribute these to decomposition, the complex may be rehydrated with concurrent disappearance of the anomalous absorptions. It may be that departure from square-planar geometry is severe in this complex, but the present studies cannot resolve this question. It is evident that extension of vibrational arguments concerning geometrical isomerism to complexes of metals other than Cu(II) must be made with care.

Acknowledgment. We thank Professor Curtis Hare of the University of Miami for helpful conversations regarding this problem.

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