Inorg. Chem. **1980**, *19*, 175–180

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Preparation, Structure, and Spectral Characterization of Bis[D-β-(2-pyridyl)-α-alaninato]nickel(II), Ni(D-Pyala)$_2$

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Received June 5, 1979

The complex [Ni(D-Pyala)$_2$]·2H$_2$O was prepared by reaction of NiCO$_3$ with D-$^+$H$_3$NCH(CH$_2$C$_5$H$_4$N)CO$_2$$^-$, D-PyalaH, the tridentate analogue of histidine. It was established from three-dimensional X-ray diffraction data that of the three possible isomeric forms the configuration of the complex in the crystalline state is that in which the amino nitrogen atoms are mutually trans. The crystals were monoclinic, of space group $P2_1$, with $a = 14.942$ (4) Å, $b = 12.091$ (2) Å, $c = 10.090$ (2) Å, $\beta = 90.3$ (3)°, $V = 1815.58$ Å^3, $d_{\text{calcd}} = 1.556$ g/cm^3, $Z = 4$, $\mu = 11.1$ cm^{-1} for Mo Kα, and $R = 0.084$. The visible spectrum of the complex suggests that the ligands remain tridentate in aqueous solution, and the circular dichroism spectrum is consistent with the complex having the same configuration as in the solid state. The structural and spectral results are discussed in the context of related complexes.

Introduction

Earlier work has shown that β-(2-pyridyl)-α-alanine, $^+$H$_3$NCH(CH$_2$C$_5$H$_4$N)CO$_2$$^-$ (PyalaH), binds to transition-metal ions to form M(Pyala)$_2$ with a large degree of enantioselectivity.[1] For example, the formation constant for Ni(D-Pyala)(L-Pyala) is nine times larger than that for Ni(D-Pyala)$_2$. Our purpose was to examine this stereoselective effect in greater depth.

When only one enantiomer of the ligand is present, e.g., D-Pyala$^-$, the resulting octahedral M(D-Pyala)$_2$ complexes may exist in any of three geometrical isomers (Figure 1). We have reported the preparation and structure of the most stable complex of cobalt(III), Co(D-Pyala)$_2$$^+$, which has the trans-carboxylate configuration (Figure 1a).[2] The cis arrangement of the pyridine rings was surprising since it was beleived that sterically these groups should occupy trans positions. Indeed, the trans imidazole was found to be the observed structure for the bis complexes of L-histidine with Co(II),[3] Ni(II),[4,5] and Co(III).[6] In the present study we extended our investigations to the labile Ni(II) complex in solution and in the crystalline state to further explore the factors which determine the most stable structures of the M(Pyala)$_2$ complexes.

Experimental Section

Materials. Racemic β-(2-pyridyl)-α-alanine (PyalaH) was prepared and resolved as described previously.[7] Nickel carbonate was purchased from Allied Chemical.

Preparation of Bis[D-β-(2-pyridyl)-α-alaninato]nickel(II) Dihydrate, [Ni(D-Pyala)$_2$]·2H$_2$O. To an aqueous solution of D-PyalaH (1.0 g, 6.1 mmol) was added powdered NiCO$_3$ (0.36 g, 3.0 mmol), and the mixture was heated (60 °C) and stirred for 2 h. The dark blue solution was allowed to cool to room temperature, and the unreacted NiCO$_3$ was filtered from the ligand. The volume was reduced to about 3 mL under reduced pressure. Slow evaporation over phosphorus pentoxide in a desiccator yielded well-formed deep blue crystals suitable for X-ray analysis. More crystals were obtained by allowing a layer of ethanol to diffuse into the aqueous phase. The yield was 54%. Anal. Calcd for [Ni(C$_8$H$_9$N$_2$O$_2$)$_2$]·2H$_2$O: C, 45.21; H, 5.22; N, 13.18. Found: C, 44.93; H, 5.37; N, 13.21.

Spectra. Infrared spectra were recorded on a KBr disk and on a D$_2$O solution of the complex by using a Beckman IR 4250 spectrophotometer. The visible and circular dichroism spectra from 650 to 350 nm were recorded on aqueous solutions at room temperature by using a Jasco ORD/UV/CD-5 spectrophotometer. At wavelengths longer than 650 nm, the visible spectrum was measured with the Cary Model 14 spectrophotometer.

Crystal Data. [Ni(C$_8$H$_9$N$_2$O$_2$)$_2$]·2H$_2$O: mol wt 425.08, monoclinic $P2_1$, $a = 14.942$ (4) Å, $b = 12.091$ (2) Å, $c = 10.090$ (2) Å, $\beta = 90.3$ (3)°, $V = 1815.58$ Å^3, $d_{\text{calcd}} = 1.556$ g/cm^3, $Z = 4$, $\mu = 11.1$ cm^{-1} for Mo Kα.

A crystal of the title compound of dimensions 0.2 × 0.2 × 0.3 nm was mounted on a glass fiber and subsequently placed on a goniometer head. From four preliminary ω-oscillation photographs at various χ and ϕ settings, 15 independent reflections were input to the automatic indexing program ALICE.[8]

The resulting reduced cell and reduced cell scalars indicated $P2_1$ (monoclinic) symmetry, which was confirmed by inspection of axial ω-oscillation photographs. The observed layer spacings on these photographs were equal within experimental error to those predicted for this cell by the indexing program. The lattice constants were obtained from a least-squares refinement based on the precise $\pm 2\theta$ ($|2\theta| > 30°$) measurement of 17 strong independent reflections. At 27 °C with Mo Kα reflection ($\lambda = 0.709\,54$ Å), they are $a = 14.942$ (4) Å, $b = 12.091$ (2) Å, $c = 10.090$ (2) Å, and $\beta = 90.3(3)°$.

Collection and Reduction of X-ray Intensity Data. The data were collected at 27 °C with graphite-monochromated Mo Kα radiation on an automated four-circle diffractometer designed and built at Ames Laboratory and previously described by Rohrbaugh and Jacobson.[9] All data (7275 reflections) within a 2θ sphere of 50° ($(\sin\theta)/\lambda = 0.596$ Å^{-1}) in the hkl, $hk\bar{l}$, $h\bar{k}\bar{l}$, $h\bar{k}\bar{l}$ were measured by using an ω-stepscan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured every 75 reflections. These standard reflections were not observed to have varied significantly throughout the data collection period (~6 days). Examination of data revealed systematic absences of $0k0$ reflections for $k = 2n + 1$, thus uniquely defining the space group $P2_1$.

The intensity data were corrected for Lorentz and polarization effects; no absorption correction was made since the transmission factors were 0.76 ± 0.04. The estimated error in each intensity was calculated by $\sigma_I^2 = C_{\mathrm{T}} + K_{\mathrm{t}}C_{\mathrm{B}} + (0.03C_{\tau})^2 + (0.03C_{\mathrm{B}})^2$ where C_{T}, K_{t}, and C_{B} represent the total count, a counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method.[10] Equivalent data were averaged and yielded 5957 reflections with $I_0 > 3\sigma(I)$ which were retained for structural solution and refinement.

Solution and Refinement of the Structure. The positions of the two nickel atoms in the asymmetric unit were obtained from an analysis of a standard sharpened three-dimensional Patterson function. The remaining nonhydrogen atoms were found by successive structure factor and electron density map calculations.[11] The atomic positional parameters were refined by using anisotropic thermal parameters by

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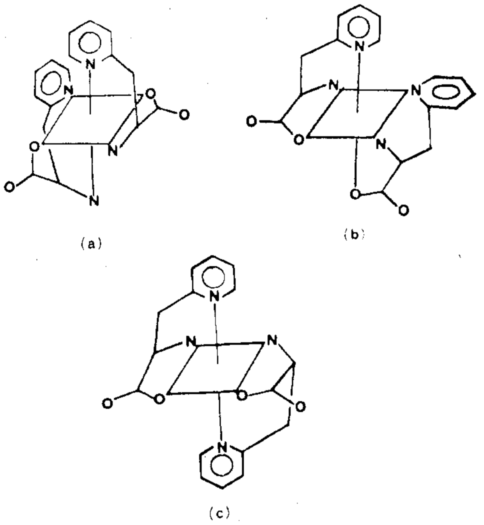

Figure 1. The three possible isomers of Ni(D-Pyala)$_2$: (a) trans carboxylate; (b) trans amino; (c) trans pyridyl.

a block matrix least-squares procedure,[12] with final refinement using a full matrix least-squares procedure and minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$ to a conventional residual index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.084$ and the associated weighted index $R_w = 0.109$. the scattering factors were those of Hanson et al.,[13] modified for the real and imaginary parts of anomalous dispersion.[14]

The solution and refinement of the structure were completed without attempting to refine the absolute configuration of the molecule. The final structure of the optically active molecule was based on the known[1] configuration of D-Pyala$^-$.

The final positional and thermal parameters for one of the two molecules in the asymmetric unit are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-square cycle.

Results

Description and Discussion of the Structure. The asymmetric unit of the crystal contains two molecules of bis[D-β-(2-pyridyl)-α-alaninato]nickel(II). In each molecule the nickel is octahedrally coordinated to two nitrogen atoms and an oxygen atom of each D-Pyala$^-$ group (Figure 2). Since the structures of the two molecules in the asymmetric unit are identical, only one set of bond distances and angles are given here (Tables II and III). The arrangement of the donor atoms about the nickel ion confers the trans-amino configuration (structure b in Figure 1) upon the complex according to the convention used in the Introduction.

A comparison of the corresponding bond distances and angles between the two D-Pyala$^-$ ligands shows only small differences which are within the accuracy of the determination. The bond lengths observed within the ligands compare quite well with other similar amino acid groups.[2,15] The average Ni–N(amino) and Ni–O distances of 2.084 (7) Å and 2.062 (6) Å correspond with those found in other octahedral complexes of nickel(II) involving amino nitrogen or carboxylate oxygen atoms.[15-19] The Ni–N(pyridine) distances (average 2.108 (7) Å) are very similar to values reported for other structures containing a nickel–pyridine bond (average 2.111 Å).[20-22]

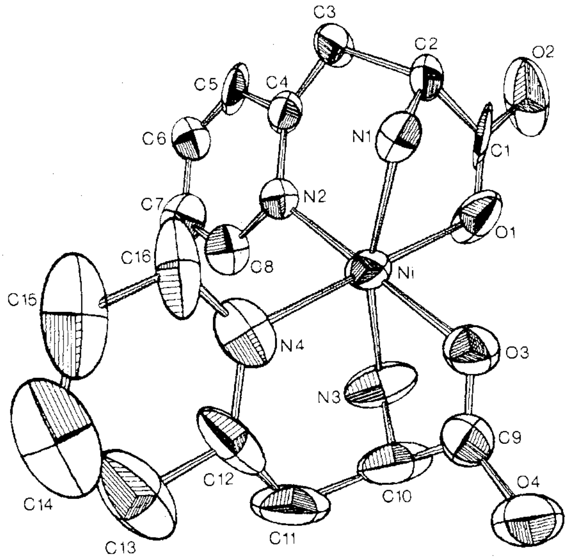

Figure 2. Structure of Ni(D-Pyala)$_2$·2H$_2$O. The water molecules are not shown.

The corresponding N(amino)–Ni–N(pyridine), N(amino)–Ni–O and N(pyridine)–Ni–O bond angles for each of the two ligands differ only slightly. Distortions from ideal octahedral geometry about the nickel atom are readily apparent. The largest deviations occur for N(amino)–Ni–O in the five-membered chelate ring (average 79.4 (3)°) and for N1–Ni–N4, N3–Ni–N2 (average 101.0 (3)°). The remainder of the angles about the nickel ion are very near the expected values of 90 and 180°. The departure of the N(amino)–Ni–O angles in the five-membered chelate rings from the ideal value is the result of the invariant distance between the N(amino) and the O(carboxylate) donor atoms in the ligand itself. Freeman[15] noted that if one imagines a triangle whose corners are M, N(amino), and O(carboxylate), then the constancy of the N···O distance requires that the angle N–M–O decrease if the sides M–N and M–O are lengthened. Indeed, a plot of the angle N–M–O vs. the average M–donor bond length yielded a straight line from distances of 2.0 (angle of 84°) to 2.5 Å (angle of 64°). If the present structure is compared to that for Co(D-Pyala)$_2^+$, this generalization is shown to hold true for the D-Pyala$^-$ ligand. The corresponding average distances and angles are as follows: Co–N(amino) = 1.947 (7) Å, Co–O = 1.893 (6) Å, N–Co–O = 85.4 (3)°; Ni–N(amino) = 2.084 (6) Å, Ni–O = 2.062 (6) Å, N–Ni–O = 79.5 (3)°. The angle found in the amino acid five-membered chelate ring (N–Ni–O) is very close to that found in the structure of bis(histidino)nickel(II) (79.7 (5)°) which has equal numbers of Ni(D-His)$_2$ and Ni(L-His)$_2$ both in the trans-imidazole configuration.[23] In the present structure, the large angles N1–Ni–N4 and N3–Ni–N2 seem to be a consequence of the smaller N–Ni–O five-membered chelate ring angle.

The distances from the nickel atom to the least-squares planes of the pyridine rings are −0.25 and −0.30 Å. These are similar to the displacement of the cobalt atom from one of the pyridine rings in Co(D-Pyala)$_2^+$ (0.32 Å).[2] The dihedral angle between the least-sqaures planes of the two pyridine rings is 89.3°. Neither of these planes are coincident with the plane

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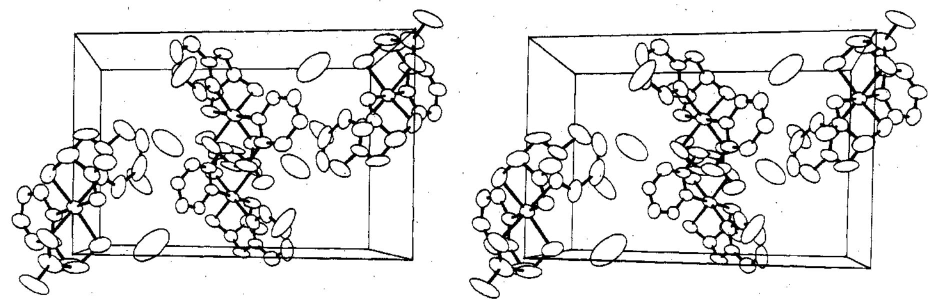

Figure 3. View of the unit cell with the *a* axis horizontal and the *c* axis vertical.

defined by O1–O3–N2–N4–Ni but make dihedral angles with it of 58.7° (for ring containing N2) and 60.6° (for ring containing N4). As can be seen from Table IV, the least-squares plane derived from atoms Ni–O1–O3–N2–N4 is very well-defined. (The largest deviation is –0.01 Å.) Contrary to this is the fact that the other two planes defined by the coordination sphere and containing N1 and N3 show much larger deviations (plane 2, –0.14 Å; plane 3, 0.11 Å). This is at least in part a consequence of the small bite of the five-membered amino acid ring.

Figure 3 illustrates the packing of molecules in the crystal lattice. Hydrogen bonding both within and between the asymmetric units stabilizes the crystal structure. Very strong interactions occur between water molecules (Ow1···Ow2, 2.45 (2) Å; Ow3···Ow4, 2.53 (1) Å) with weak and strong bonds between the water and Ni(D-Pyala)$_2$ molecules. The N–H···O interactions appear to be weak (3.13 (1) and 3.19 (2) Å) with a much stronger carboxylate–water interaction (2.698 (9), 2.776 (9), 2.706 (13) Å).

Discussion. It is of interest to know whether the amino acid, D-Pyala$^-$, in Ni(D-Pyala)$_2$ retains its tridentate nature in solution or becomes a bidentate ligand. Two techniques are available for distinguishing the atoms in the coordination sphere of the nickel(II) ion. It has been noted previously[1] that log K_1 (7.1) for the binding of Pyala$^-$ to nickel(II) is 1.9 units larger than for the case of 2-(2-aminoethyl)pyridine (5.2), suggesting coordination of the carboxylate group to the nickel(II) ion. This value for Pyala$^-$ (7.1) is also larger than those reported for glycine (5.9) and phenylalanine (5.2), indicating that the pyridine nitrogen adds to the coordinating ability of Pyala$^-$. Complexation through only the carboxylate oxygen and pyridine nitrogen atoms seems unlikely since a less favorable seven-membered chelate ring would be formed.

The rule of average environment, first proposed by Jørgensen,[24] has been used quite extensively by investigators of nickel(II) complexes containing oxygen and nitrogen donors. Since the spectra of the nickel complexes for any given combination of *n* amine and 6 – *n* oxygen donor atoms are similar, the number of each type of donor atom can be estimated. The visible spectrum of Ni(D-Pyala)$_2$·H$_2$O in water is shown in Figure 4. The maxima of the complex (563, 780, 962 nm) agree very well with those of an NiN$_4$O$_2$ chromophore (e.g., Ni(en)(gly)$_2$: 561, 781, 952 nm).[25] These comparisons suggest that the ligands in Ni(D-Pyala)$_2$ are tridentate in solution as well as in the solid state.

The infrared spectrum of the crystals in the KBr disk compares quite well with other bis(amino acidato)nickel(II) complexes.[26] The asymmetric and symmetric N–H stretching absorptions of the coordinated amine appear at 3290 and 3242 cm^{-1}, respectively. Coordination through the carboxylate group is indicated by the position of the asymmetric and symmetric –CO$_2^-$ stretches at 1600 and 1405 cm^{-1}. The M–N stretch occurs at 342 cm^{-1} with the M–O band lying outside the range of the instrument. The infrared solution spectrum taken in D$_2$O has the –CO$_2^-$ stretches in the same position as in the KBr disk spectrum.

As has been shown, the nickel(II) ion is coordinated to the carboxylate oxygen atom, the amino nitrogen atom, and the pyridine nitrogen atom of each D-Pyala$^-$ ligand. For a determination of which of the three geometrical isomers of the bis complex predominates in solution, the circular dichroism was taken for comparison with other bis(amino acidato)-

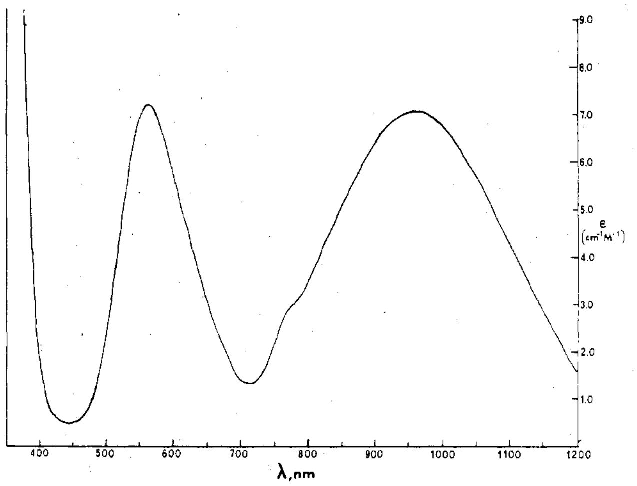

Figure 4. Absorption spectrum of trans amino Ni(D-Pyala)$_2$·2H$_2$O in water.

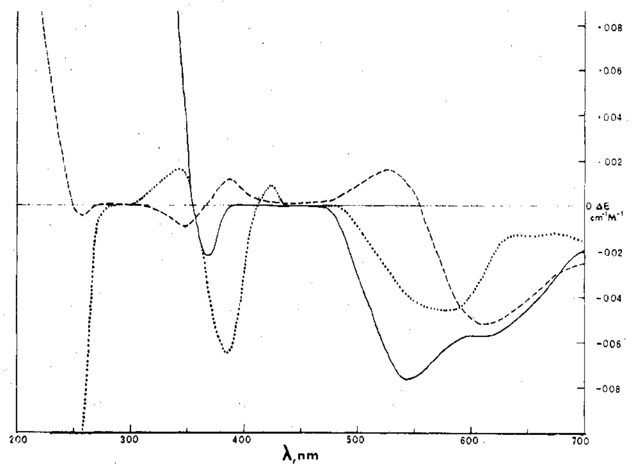

Figure 5. Circular dichroism spectra of Ni(D-Pyala)$_2$·2H$_2$O (—), with the inverse of Ni(L-His)$_2$·H$_2$O (---) and Na$_2$[Ni(D-Asp)$_2$]·5H$_2$O (···) (×5) taken from ref 27.

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Table I. Final Atomic Parameters

(a) Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

atom	x	y	z	atom	x	y	z
Ni[b]	58.0 (6)	0.0	2142.6 (8)	O22	5681 (5)	8145 (5)	5731 (6)
O1	−656 (5)	−882 (5)	747 (7)	O23	4143 (5)	8624 (4)	7482 (6)
O2	−1046 (8)	−809 (7)	−1363 (9)	O24	6023 (7)	8047 (6)	3588 (7)
O3	867 (4)	−1345 (4)	2494 (5)	N21	4194 (7)	6920 (6)	5463 (8)
O4	1189 (5)	−2575 (7)	4051 (6)	N22	5761 (5)	5881 (5)	6754 (6)
N1	799 (6)	343 (5)	435 (7)	N23	4197 (5)	6410 (6)	8605 (8)
N2	−750 (5)	1398 (5)	1772 (6)	N24	5706 (5)	8081 (7)	8587 (7)
N3	−680 (5)	−793 (7)	3615 (9)	C21	5908 (7)	5419 (6)	5558 (8)
N4	806 (4)	863 (7)	3572 (7)	C22	6555 (6)	4582 (6)	5412 (9)
C1	−576 (9)	−505 (7)	−433 (11)	C23	7025 (6)	4209 (8)	6449 (10)
C2	81 (9)	377 (8)	−618 (9)	C24	6873 (6)	4684 (9)	7675 (10)
C3	−308 (10)	1539 (8)	−596 (8)	C25	6240 (6)	5511 (8)	7809 (9)
C4	−904 (7)	1827 (6)	570 (8)	C26	5360 (9)	5732 (7)	4372 (10)
C5	−1537 (8)	2678 (7)	407 (10)	C27	4920 (10)	6883 (7)	4381 (9)
C6	−2056 (7)	3039 (7)	1475 (10)	C28	5604 (9)	7772 (8)	4565 (9)
C7	−1889 (6)	2605 (9)	2684 (11)	C29	3744 (7)	5506 (8)	8134 (13)
C8	−1221 (6)	1747 (8)	2828 (9)	C210	3102 (8)	4975 (10)	8887 (17)
C9	735 (6)	−1770 (8)	3593 (8)	C211	2960 (8)	5339 (11)	10185 (21)
C10	−1 (7)	−1278 (10)	4445 (11)	C212	3471 (8)	6254 (10)	10719 (12)
C11	391 (10)	−433 (12)	5408 (9)	C213	4092 (6)	6756 (9)	9851 (9)
C12	906 (6)	488 (11)	4846 (10)	C214	4269 (8)	9032 (8)	8585 (9)
C13	1531 (11)	1038 (16)	5686 (14)	C215	4986 (7)	8596 (8)	9486 (9)
C14	2036 (9)	1936 (19)	5199 (29)	C216	4585 (8)	7735 (10)	10418 (9)
C15	1887 (7)	2297 (13)	3920 (20)	Ow1	2203 (11)	2265 (10)	314 (16)
C16	1263 (6)	1735 (10)	3106 (14)	Ow2	3266 (7)	1929 (10)	8505 (14)
Ni2	4950.1 (7)	7270.6 (9)	7134.2 (9)	Ow3	1753 (8)	5355 (8)	3484 (13)
O21	3802 (6)	9840 (6)	9048 (6)	Ow4	2764 (10)	4961 (10)	5436 (14)

(b) Final Thermal Parameters (×10^4) and Their Estimated Standard Deviations (in Parentheses)[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	48.9 (4)	52.2 (7)	75.7 (9)	−13.4 (5)	−7.4 (5)	7.5 (6)
O1	97 (5)	47 (4)	165 (9)	−8 (3)	−59 (6)	8 (5)
O2	180 (9)	123 (8)	200 (12)	70 (7)	−126 (9)	−87 (8)
O3	52 (3)	67 (4)	88 (6)	−11 (3)	−1 (3)	4 (4)
O4	99 (5)	122 (7)	99 (7)	45 (5)	−13 (4)	26 (6)
N1	94 (5)	45 (4)	86 (7)	−7 (4)	26 (5)	−4 (4)
N2	65 (4)	50 (4)	81 (6)	−8 (3)	−12 (4)	−9 (4)
N3	43 (3)	113 (8)	179 (11)	5 (4)	10 (5)	77 (8)
N4	40 (3)	99 (7)	104 (8)	2 (4)	5 (4)	−32 (6)
C1	127 (9)	37 (5)	161 (14)	32 (6)	−69 (9)	−46 (8)
C2	144 (10)	55 (6)	86 (9)	26 (7)	9 (8)	−9 (6)
C3	180 (11)	57 (6)	67 (8)	53 (7)	7 (8)	6 (6)
C4	99 (7)	35 (5)	84 (8)	7 (4)	−28 (6)	−4 (5)
C5	102 (7)	38 (5)	142 (11)	−1 (5)	−45 (7)	−10 (6)
C6	75 (6)	62 (6)	131 (11)	1 (5)	−20 (6)	−2 (7)
C7	56 (5)	88 (8)	162 (13)	−10 (5)	15 (6)	−8 (8)
C8	58 (5)	86 (7)	119 (10)	−7 (5)	−4 (5)	1 (7)
C9	57 (5)	77 (7)	92 (9)	6 (4)	−12 (5)	8 (6)
C10	68 (6)	130 (11)	133 (12)	25 (6)	31 (7)	72 (10)
C11	141 (11)	152 (13)	67 (9)	58 (10)	22 (8)	28 (9)
C12	60 (5)	165 (12)	110 (11)	50 (6)	−28 (6)	−79 (10)
C13	107 (11)	249 (23)	219 (19)	122 (14)	−109 (13)	−167 (18)
C14	57 (7)	250 (25)	572 (59)	62 (10)	−93 (16)	−326 (36)
C15	42 (5)	162 (16)	400 (34)	−19 (7)	20 (10)	−196 (22)
C16	49 (5)	118 (10)	289 (23)	−26 (6)	43 (9)	−114 (13)
Ni2	66.7 (6)	39.0 (6)	85.3 (11)	−9.3 (5)	−24.1 (6)	2.3 (6)
O21	130 (6)	75 (5)	100 (7)	10 (5)	12 (5)	−16 (5)
O22	108 (5)	39 (4)	108 (7)	−10 (3)	−3 (5)	−1 (4)
O23	99 (4)	47 (4)	87 (6)	0 (3)	−22 (4)	1 (4)
O24	149 (7)	84 (6)	113 (8)	30 (5)	36 (6)	18 (5)
N21	116 (6)	52 (5)	124 (10)	3 (4)	−74 (7)	−2 (5)
N22	63 (4)	43 (4)	90 (7)	−6 (3)	−7 (4)	6 (4)
N23	53 (4)	56 (5)	143 (10)	−1 (3)	−25 (5)	17 (5)
N24	71 (4)	83 (6)	116 (8)	−17 (4)	−24 (5)	−16 (6)
C21	95 (6)	39 (5)	76 (8)	−4 (4)	−12 (5)	9 (5)
C22	61 (5)	43 (5)	132 (10)	−8 (4)	9 (6)	8 (6)
C23	52 (5)	95 (8)	127 (11)	−7 (5)	7 (6)	−18 (8)
C24	50 (4)	103 (9)	133 (11)	9 (5)	−8 (5)	29 (8)
C25	47 (4)	96 (7)	95 (9)	−1 (5)	−12 (5)	1 (7)
C26	152 (10)	51 (6)	112 (11)	32 (7)	−59 (8)	−12 (7)
C27	160 (11)	46 (6)	89 (10)	23 (7)	−70 (9)	−17 (6)
C28	131 (9)	52 (6)	82 (9)	46 (6)	4 (7)	11 (6)
C29	57 (5)	60 (7)	265 (20)	−10 (5)	−48 (8)	60 (10)
C210	61 (6)	83 (9)	292 (23)	9 (6)	−24 (9)	62 (13)

Table I (*Continued*)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C211	55 (6)	92 (11)	359 (35)	12 (6)	−15 (12)	112 (17)
C212	72 (6)	120 (11)	193 (16)	12 (7)	−6 (8)	82 (11)
C213	66 (5)	98 (8)	111 (10)	8 (5)	−18 (6)	46 (8)
C214	106 (7)	58 (7)	90 (10)	−11 (5)	−1 (7)	6 (7)
C215	74 (6)	83 (7)	103 (10)	−28 (5)	−21 (6)	−6 (7)
C216	98 (7)	126 (11)	88 (10)	−31 (7)	−37 (7)	25 (9)
Ow1	268 (13)	92 (9)	490 (27)	−13 (10)	205 (16)	−35 (13)
Ow2	123 (7)	234 (15)	474 (27)	102 (9)	165 (12)	223 (17)
Ow3	150 (8)	124 (9)	357 (21)	50 (7)	−149 (11)	−81 (11)
Ow4	236 (12)	121 (10)	378 (23)	41 (10)	−161 (14)	−26 (13)

[a] The positional parameters are presented in fractional unit cell coordinates (×10⁴). [b] The *y* positional parameter was not varied. [c] The β_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Interatomic Distances (Å) and Their Estimated Standard Deviations (in Parentheses)

	molecule			molecule	
	A	B		A	B
Ni–O1	2.066 (6)	2.074 (6)	Ni–O3	2.058	2.061 (6)
Ni–N1	2.087 (7)	2.078 (7)	Ni–N3	2.081 (7)	2.097 (7)
Ni–N2	2.111 (7)	2.105 (7)	Ni–N4	2.105 (7)	2.130 (7)
C1–O1	1.28 (1)	1.27 (1)	C9–O3	1.24 (1)	1.23 (1)
C1–O2	1.23 (1)	1.21 (1)	C9–O4	1.27 (1)	1.29 (1)
O1–O2	2.211 (10)	2.223 (9)	O3–O4	2.217 (8)	2.217 (9)
C1–C2	1.46 (2)	1.49 (2)	C9–C10	1.52 (1)	1.50 (1)
N1–C2	1.51 (1)	1.54 (2)	N3–C10	1.44 (2)	1.54 (2)
C2–C3	1.52 (1)	1.54 (1)	C10–C11	1.53 (2)	1.52 (1)
C3–C4	1.51 (1)	1.50 (1)	C11–C12	1.47 (2)	1.51 (2)
C4–C5	1.41 (1)	1.41 (1)	C12–C13	1.43 (2)	1.41 (1)
C5–C6	1.40 (1)	1.34 (1)	C13–C14	1.41 (3)	1.45 (2)
C6–C7	1.35 (1)	1.38 (1)	C14–C15	1.38 (3)	1.40 (2)
C7–C8	1.45 (1)	1.38 (1)	C15–C16	1.42 (2)	1.38 (2)
C8–N2	1.34 (1)	1.36 (1)	C16–N4	1.34 (1)	1.37 (1)
N2–C4	1.34 (1)	1.35 (1)	N4–C12	1.37 (1)	1.33 (1)
N1–Ow1	3.127 (14)		Ow3–Ow4	2.532 (14)	
N1B–Ow4	3.190 (17)		O2[b]–Ow3	2.776 (9)	
O4–Ow3[a]	2.698 (9)		O2[b]–Ow1	3.076 (16)	
O4B–Ow2	2.706 (13)		Ow1–Ow2[c]	2.449 (16)	

[a] Symmetry operation: $x, y - 1, z$. [b] Symmetry operation: $-x, {}^1/_2 + y, -z$. [c] Symmetry operation: $x, y, z - 1$.

Table III. Bond Angles (deg) and Their Estimated Standard Deviations (in Parentheses)

	molecule			molecule	
	A	B		A	B
N1–Ni–N3	163.6 (3)	163.5 (3)			
O1–Ni–N4	178.6 (3)	178.6 (3)	O3–Ni–N2	178.9 (2)	179.1 (2)
O1–Ni–O3	90.9 (2)	91.0 (3)	N2–Ni–N4	91.7 (3)	92.2 (3)
O1–Ni–N1	79.2 (3)	80.6 (3)	O3–Ni–N3	79.8 (3)	80.0 (3)
O1–Ni–N2	89.7 (2)	88.9 (2)	O3–Ni–N4	87.7 (3)	87.8 (3)
O1–Ni–N3	88.6 (3)	87.5 (3)	O3–Ni–N1	89.4 (3)	88.9 (3)
N1–Ni–N2	89.8 (3)	90.2 (3)	N3–Ni–N4	91.2 (3)	91.5 (3)
N1–Ni–N4	100.7 (3)	100.3 (3)	N3–Ni–N2	101.2 (3)	100.9 (3)
Ni–O1–O1	113.8 (6)	113.8 (7)	Ni–O3–C9	113.0 (5)	112.4 (6)
Ni–N1–C2	102.1 (6)	101.4 (6)	Ni–N3–C10	103.3 (5)	103.0 (5)
Ni–N2–C4	124.8 (6)	125.9 (5)	Ni–N4–C12	122.6 (7)	124.2 (6)
Ni–N2–C8	114.2 (5)	115.1 (5)	Ni–N4–C16	114.9 (7)	114.1 (7)
O1–C1–O2	123.4 (13)	127.5 (12)	O3–C9–O4	124.0 (8)	123.2 (10)
O1–C1–C2	116.0 (8)	115.9 (10)	O3–C9–C10	117.3 (8)	121.1 (9)
O2–C1–C2	120.4 (12)	116.6 (9)	O4–C9–C10	118.7 (8)	115.7 (8)
C1–C2–N1	111.6 (8)	111.8 (7)	C9–C10–N3	109.9 (8)	106.5 (7)
N1–C2–C3	106.7 (8)	109.4 (9)	N3–C10–C11	111.7 (9)	111.1 (9)
C1–C2–C3	114.5 (11)	111.0 (10)	C9–C10–C11	110.1 (9)	109.5 (8)
C2–C3–C4	116.6 (8)	117.2 (7)	C10–C11–C12	117.6 (7)	119.6 (8)
C3–C4–N2	120.8 (8)	121.5 (8)	C11–C12–N4	123.7 (9)	123.3 (9)
C3–C4–C5	118.1 (8)	118.3 (8)	C11–C12–C13	117.9 (13)	115.1 (10)
C4–C5–C6	120.7 (8)	121.5 (8)	C12–C13–C14	120.1 (16)	116.4 (13)
C5–C6–C7	118.1 (9)	118.3 (9)	C13–C14–C15	118.7 (12)	120.7 (12)
C6–C7–C8	119.9 (9)	119.8 (9)	C14–C15–C16	119.9 (17)	118.2 (13)
C7–C8–N2	120.3 (8)	121.6 (8)	C15–C16–N4	120.6 (15)	121.5 (13)
C8–N2–C4	120.3 (8)	118.7 (7)	C16–N4–C12	122.1 (10)	121.4 (9)
N2–C4–C5	120.5 (9)	120.1 (8)	N4–C12–C13	118.5 (14)	121.6 (10)

Table IV. Equations of Least-Squares Planes[a]

atom	D^b	atom	D
Plane 1: Ni-O1-O3-N2-N4			
$-0.63211X - 0.30453Y + 0.71252Z - 1.47256 = 0$			
Ni	0.0070	N2	−0.0099
O1	0.0065	N4	0.0065
O3	−0.0103		
Plane 2: Ni-N1-N2-N3-O3			
$0.56757X + 0.54161Y + 0.62009Z - 1.31177 = 0$			
Ni	0.0833	N3	−0.1375
N1	−0.1362	O3	0.1094
N2	0.0809		
Plane 3: Ni-N1-N3-N4-O1			
$0.62692X - 0.77293Y + 0.09761Z - 0.36158 = 0$			
Ni	−0.0903	N4	−0.0519
N1	0.1099	O1	−0.0761
N3	0.1084		
Plane 4: N2-C4-C5-C6-C8			
$0.69496X + 0.69489Y + 0.18479Z - 0.7148 = 0$			
N2	0.0151	C7	0.0192
C4	−0.0121	C8	−0.0192
C5	0.0151	Ni[c]	−0.2502
C6	−0.0180		
Plane 5: N4-C12-C13-C14-C15-C16			
$-0.71939X + 0.61850Y + 0.31612Z - 0.91761 = 0$			
N4	−0.0101	C15	0.0107
C12	0.0038	C16	0.0027
C13	0.0092	Ni[c]	−0.3033
C14	−0.0164		

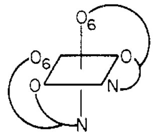
[a] Planes are defined as $C_1X + C_2Y + C_3Z + C_4 = 0$, where X, Y, and Z are Cartesian coordinates. [b] D is the distance (Å) of the given atom from the fitted plane. [c] These atoms were not included in the calculation of the plane.

nickel(II) complexes. The CD spectrum of an aqueous solution of the complex [Ni(D-Pyala$_2$]·2H$_2$O along with those of Na$_2$[Ni(D-Asp)$_2$]·5H$_2$O and the inverse of [Ni(L-His)$_2$]·H$_2$O are shown in Figure 5.

Contributions to the optical activity of these three complexes arise from (1) the vicinal effect of the asymmetric carbon, (2) the conformational effect of the chelate rings formed, and (3) the overall configuration of the complex. The first contribution should be similar to those for other amino acids, e.g., Ni(D-ala)$_2$, and is expected to be small.[27] Although there are more chelate rings formed in these tridentate amino acid complexes when compared to bidentate amino acid complexes, the same conformation (δ for D enantiomer) is imposed on the amino acid ring because of the steric requirements of the ligand. This contribution is also expected to be small and very similar in the histidinate, asparate, and Pyala$^-$ complexes. Thus, the major contribution arises from the overall configuration imposed on the complex by the particular geometrical isomer that is formed. The circular dichroism curves for Ni(D-Pyala)$_2$, Na$_2$[Ni(D-Asp)$_2$], and Ni(D-His)$_2$ (equal to the inverse of Ni(L-His)$_2$) should be very similar if the arrangements of the chelate rings in the complexes are the same.

It has been suggested that the trans-imidazole configuration is the predominant isomer of Ni(L-His)$_2$ in aqueous solution.[27,28] In Figure 5 it can be seen that the circular dichroism spectrum of Ni(D-Pyala)$_2$ differs considerably from the inverse of the Ni(L-His)$_2$ spectrum (this should be equal to the CD of Ni(D-His)$_2$). Both spectra have two maxima in the long wavelength region (450–700 nm); however, the maxima for Ni(D-Pyala)$_2$ are of the same sign (negative) while those of Ni(D-His)$_2$ are of opposite sign (one positive and one negative). This suggests that the structure of Ni(D-Pyala)$_2$ differs from that of Ni(D-His)$_2$ in aqueous solution.

On the basis of the signs of the maxima and shape of the circular dichroism spectrum, a predominance of the trans-(O5),cis(N5) isomer of Ni(D-Asp)$_2^-$

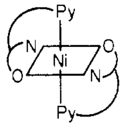


in aqueous solution was suggested.[27] The arrangement of the chelate rings in trans(O5),cis(N5) Ni(D-Asp)$_2^-$ is the same as in trans-carboxylate Ni(D-Pyala)$_2$ (Figure 1a). The large difference between the circular dichroism spectra of Ni(D-Pyala)$_2$ and Ni(D-Asp)$_2^-$ suggests that Ni(D-Pyala)$_2$ does not have the analogous trans-carboxylate structure (Figure 1a). This conclusion leaves the trans-amino configuration as the most likely isomer in solution, as well as in the solid state.

Conclusion

Although it is not clear why Ni(D-Pyala)$_2$ adopts the trans-amino structure in the solid state and presumably also in solution, it appears that in the limited number of crystal structures of other octahedral 2:1 amino acid complexes of nickel(II), the majority also has the trans-amino configuration. This is in contrast to the related Co(D-Pyala)$_2^+$ complex whose most stable structure is the trans carboxylate.

Assuming the trans-amino isomer of Ni(D-Pyala)$_2$ to be the most stable in solution, the higher formation constant for Ni(D-Pyala)(L-Pyala) as compared to Ni(D-Pyala)$_2$[1] may be readily rationalized. A preference for trans-amino groups requires that the pyridyl groups be cis to each other in Ni(D-Pyala)$_2$. On the other hand, Ni(D-Pyala)(L-Pyala) with trans-amino groups would have the structure



in which the bulky pyridyl groups are trans to each other, which could favor the formation of this complex over Ni(D-Pyala)$_2$.

Acknowledgment. This work was supported by National Institute of General Medical Sciences Research Grant GM 12626 and by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

Registry No. [Ni(D-Pyala)$_2$]·2H$_2$O, 72002-38-1.

Supplementary Material Available: A table listing observed and calculated structure factors (15 pages). Ordering formation is given on any current masthead page.

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