Table V. Absolute Torsion Angles (deg) around the Silicon Backbone in $Si_9(CH_3)_{16}$

Atoms	Torsion angle In molecule A	Torsion angle In molecule B
In Ring I		
Si(9)-Si(1)-Si(2)-Si(3)	33.5	37.4
Si(4)-Si(3)-Si(2)-Si(1)	0.3	4.3
Si(5)-Si(4)-Si(3)-Si(2)	0.6	1.5
Si(9)-Si(5)-Si(4)-Si(3)	32.0	32.0
Si(4)-Si(5)-Si(9)-Si(1)	69.9	68.4
Si(5)-Si(9)-Si(1)-Si(2)	70.5	70.4
In Ring II		
The average absolute torsion angle is 56.5 ± 0.5°.		
Between Both Rings		
Si(8)-Si(1)-Si(2)-Si(3)	91.4	87.9
Si(7)-Si(8)-Si(1)-Si(2)	66.2	66.4
Si(6)-Si(5)-Si(4)-Si(3)	91.8	92.1
Si(7)-Si(6)-Si(5)-Si(4)	65.6	63.0

Table VI. Absolute Torsion Angles (deg) Involving Eclipsed Methyl Groups in $Si_9(CH_3)_{16}$

Atoms	Torsion angle In molecule A	Torsion angle In molecule B
C(1)-Si(1)-Si(2)-1C(2)	33.0	32.4
1C(2)-Si(2)-Si(3)-1C(3)	7.2	3.3
2C(2)-Si(2)-Si(3)-2C(3)	4.5	0.7
1C(3)-Si(3)-Si(4)-1C(4)	3.0	0.6
2C(3)-Si(3)-Si(4)-2C(4)	3.9	1.9
1C(4)-Si(4)-Si(5)-C(5)	31.3	28.0

Table VII. Distances (Å) between Methyl Carbon Atoms around Ring I Which Are Less Than 4.0 Å

Atoms	Dist in molecule A	Dist in molecule B
C(1)-1C(2)	3.61 (2)	3.58 (4)
1C(2)-1C(3)	3.38 (3)	3.55 (4)
2C(2)-2C(3)	3.49 (3)	3.52 (3)
1C(3)-1C(4)	3.50 (3)	3.39 (3)
2C(3)-2C(4)	3.56 (3)	3.63 (4)
1C(4)-C(5)	3.57 (2)	3.71 (3)

molecules occupying positions A(x, y, z), B(x, y, z), A($x, {}^1/_2 - y, {}^1/_2 + z$), and B($x, {}^1/_2 - y, {}^1/_2 + z$) may be thought of as chains of molecules whose centers all have a y coordinate of approximately ${}^1/_4$. The centrosymmetric mates of the molecules produce a similar array; the centers of these molecules all lie on an approximate plane at $y = {}^3/_4$. Hence, Figure 3 is a composite of these two planes. The closest contact between neighboring molecules is 3.83 Å and occurs between 2C(6)A and 2C(7)A and again between 1C(9)A and 1C(7)B, indicative of the fact that the crystal is held together almost exclusively by van der Waals forces. The closest approach between methyl groups of neighboring molecules in $Si_6(CH_3)_{12}$[4] has been reported as 3.98 Å.

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Registry No. $Si_9(CH_3)_{16}$, 37249-25-5.

Supplementary Material Available: Table I, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Acetate Dihydrate, $[Ni(NH_2CH_2CH_2NH_2)_3](O_2C_2H_3)_2 \cdot 2H_2O$

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The crystal structure of $[Ni(en)_3](O_2C_2H_3)_2 \cdot 2H_2O$ has been determined by single-crystal x-ray diffraction techniques. After least-squares refinement using anisotropic thermal parameters for the nonhydrogen atoms and isotropic ones for hydrogens, the conventional R index converged at 0.033. The purple crystals form in the monoclinic space group $P2_1/c$ with $a = 10.936$ (1) Å, $b = 13.132$ (3) Å, $c = 15.151$ (3) Å, $\beta = 116.16$ (1)°, and $Z = 4$. The divalent nickel is hexacoordinated and exhibits the usual distortion from octahedral symmetry found in tris(ethylenediamine) complexes. A twist angle of 50.4 ± 1.0° exists between trigonal planes formed by the coordinating nitrogen atoms. The centric cell contains complex cations in both the $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$ configurations. Disorder about the metal center is attributed to a superposition of $\Delta\lambda\lambda\lambda$ over $\Lambda\delta\delta\delta$ and is estimated to occur about 14% of the time. An extensive network of hydrogen bonding is described between the cation and anion, the anion with H_2O, and the cation with H_2O. The effect of hydrogen bonding on the observed structure is discussed and a new parameter which considers anion size is postulated as influencing the occurrence of λ rings in tris(ethylenediamine) complexes.

Introduction

We have been interested in studying the ring conformations of ethylenediamine (en) chelates in solution and in a recent paper[1] we examined the effect of various anions on ring conformational equilibria. From the temperature dependence of the NMR contact shifts of $[Ni(en)_3]^{2+}$ in the presence of nitrate, acetate, and benzoate we argued that the formation at low temperature of multiple hydrogen bonds between cation and anion would favor the $\Lambda\delta\delta\lambda$ conformation for the complex. At higher temperatures each of these three systems yielded a second equilibrium in which ΔH and ΔS showed a strong correlation with the Lewis base strength of the anion; the strongest base, acetate, produced the largest thermodynamic values.

Solid-state observations of mixed conformations like $\Lambda\delta\delta\lambda$ are rare. Even though the oxygens of the nitrates in crystalline $[Ni(en)_3](NO_3)_2$[2] and $[Co(en)_3](NO_3)_3$[3] form two simultaneous hydrogen bonds to amine protons, as we have hypothesized occurs in solution, the x-ray crystal analysis revealed the usual $\Lambda\delta\delta\delta$ conformation for both salts. Raymond et al.[4,5] reported some of the few examples of non $\Lambda\delta\delta\delta$ conformations in crystal studies of $[Cr(en)_3]^{3+}$ with the anion $[Ni(CN)_5]^{3-}$ producing both $\Lambda\delta\lambda\lambda$ and $\Lambda\delta\delta\lambda$ and the anion $[Co(CN)_6]^{3-}$ giving $\Lambda\lambda\lambda\lambda$. They suggested[6] that the formation of λ rings was induced by strong hydrogen-bonding interactions between amine protons and the anions or waters of crystallization.

The strong hydrogen-bonding ability of the acetate anion plus the similar oxygen–oxygen distances in nitrate and acetate led us to suspect that the double equilibrium we found in solution was the result of the formation at low temperature of a mixed conformation in aqueous $[Ni(en)_3](ac)_2$. We undertook this crystal and molecular structure determination of $[Ni(en)_3](ac)_2{\cdot}2H_2O$ in order to understand better the hydrogen-bonding scheme and its influence on the chelate ring conformations.

It should be recognized here that the optically active $[M(en)_3]^{n+}$ complexes usually occur as racemic mixtures. For example, in most of the solid-state studies discussed above centrosymmetric space groups were found so that there were always an equal number of metal ions of Δ and Λ configurations. Such complexes have eight possible isomers: $\Lambda\delta\delta\delta$, $\Lambda\delta\delta\lambda$, $\Lambda\delta\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\delta\delta\delta$, $\Delta\lambda\delta\delta$, $\Delta\lambda\lambda\delta$, $\Delta\lambda\lambda\lambda$; however, for the sake of brevity only the Λ metal ion configuration is usually discussed. Thus the following discussion will be limited to only the first four isomers in the above list, but it must be realized that all arguments apply equally well to the appropriate mirror image, as must be the case in a nonchiral medium.

Experimental Section

Preparation of $[Ni(en)_3](O_2C_2H_3)_2$. To an aqueous solution of 2.85 g (11.5 mmol) of $Ni(O_2C_2H_3)_2{\cdot}4H_2O$ was added 2.5 ml of 98–100% ethylenediamine (37 mmol). The solution was cooled and precipitation was induced on addition of acetone. The light violet powder gave elemental analysis for 33.81% C, 8.47% H, and 22.76% N; calculated values for $[Ni(en)_3](O_2C_2H_3)_2$ are 33.64% C, 8.47% H, and 23.53% N. Electronic spectra obtained on a Cary Model 14 for an aqueous solution of the product showed agreement with solid $[Ni(en)_3](ClO_4)_2$.[7] The powder was hygroscopic and appeared to decompose over a period of weeks.

Collection and Reduction of Intensity Data. Dark purple crystals of $[Ni(en)_3](O_2C_2H_3)_2{\cdot}2H_2O$ were obtained by cooling a saturated aqueous solution at 5°C. The flat, oblong crystals tended to melt when left open to air and several were lodged and sealed in thin-walled capillary tubes and examined under a polarizing microscope before an apparent single crystal was selected. The 0.12 × 0.20 × 0.43 mm crystal was bathed in a small volume of mother liquor throughout the data collection. After data collection the crystal, still sealed in the capillary, was placed on a shelf in the sunlight and it melted.

A Syntex four-circle computer-controlled diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0.70926; $K\alpha_2$, 0.71354 Å) and with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections. The cell constants at 20°C for $[Ni(en)_3](O_2C_2H_3)_2{\cdot}2H_2O$ are a = 10.936 (1) Å, b = 13.132 (3) Å, c = 15.151 (3) Å, and β = 116.16 (1)°; V = 1953.0 (6) Å^3. The compound crystallizes in a monoclinic lattice with $P2_1/c$ symmetry and four molecules per unit cell. The calculated density ρ_{calcd} = 1.3370 (4) g cm^{-3} is in good agreement with the density measured by flotation in a chloroform–benzene solution of ρ_{measd} = 1.330 (3) g cm^{-3}.

Diffraction intensities were collected by the θ–2θ scan technique at a scan rate varying from 5°/min in 2θ to 24°/min in such a way that more time was spent on weaker reflections to improve their standard deviations. Most reflections were observed at the slowest scan rate. All 1834 unique reciprocal lattice points for which $2\theta <$ 40° were examined and only the 1480 showing intensities greater than 3 times their standard deviations were used in the structure refinement.

A time equal to half the scan time for each reflection was spent counting the background at each end of the scan range. A set of three check reflections was measured periodically during data collection and the average total change in intensity was 3%. The appropriate decay correction was performed and a new data set generated. Absorption corrections were made using the Cartesian coordinates of three points on each of the nine crystal faces and the compound's linear absorption coefficient, calculated to be 10.29 cm^{-1}. Transmission coefficients ranged from 0.8138 to 0.8407.

Standard deviations were assigned according to the formula

$$\sigma(I) = \{w^2[\mathrm{CT} + 0.25(t_c/t_b)^2(B_1 + B_2)] + (pI^2\}^{1/2}$$

where CT is the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = w[\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability. The net counts were then corrected for Lorentz and polarization effects.

The principal computer programs used in this study were those previously described.[8] Atomic scattering factors[9] for Ni^+, N^0, O^0, C^0, and H (bonded)[10] were used, with that for the Ni ion modified to account for the real part of the anomalous dispersion correction.

Solution and Refinement of Structure. The positions of the nickel ion and two nitrogen atoms were determined from a three-dimensional Patterson function. Successive cycles of Fourier refinement with phases based initially on the three atoms found in the Patterson analysis revealed the location of the remaining 20 nonhydrogen atoms of the molecule. Full-matrix least-squares refinement with isotropic thermal parameters for all nonhydrogen atoms converged at R_1 = 0.092 and R_2 = 0.107 where

$$R_1 = (\Sigma|F_o - |F_c||)/\Sigma F_o$$
$$R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^{\,2})^{1/2}$$

Full-matrix least-squares anisotropic refinement of all nonhydrogen positions gave R_1 = 0.064 and R_2 = 0.068. At this point a difference Fourier synthesis revealed chelate ring hydrogens. All ring hydrogen coordinates were then cross-checked by calculation[11] assuming tetrahedral geometry and 1.08-Å bond lengths. These 24 hydrogens were given isotropic temperature factors of 6.00 and refined isotropically using full-matrix least-squares techniques until convergence at R_1 = 0.052 and R_2 = 0.057 was reached. The R factor ratio is 1.19 and is much greater than the limiting value of 1.06 calculated for a 99% confidence level.[12]

Another difference Fourier map revealed six peaks of 0.77 e/Å^3 that were centered in pairs around the nickel ion. In addition four water hydrogens and one methyl hydrogen were located; following calculation of the other two methyl hydrogen positions, these new hydrogens were isotropically included in the refinement. Excessive thermal disorder at the second methyl group precluded the positioning of any of the three hydrogens. Analysis of interpositional distances indicated that the six anomalous peaks around the nickel center should be treated as nitrogen atoms resulting from general disorder in the unit cell. A series of full-matrix least-squares refinements was undertaken on the initial isotropic thermal parameter of 4.20 for both the old nitrogen and new nitrogen positions. Alternately, a similar series of full-matrix least-squares refinements on the occupancy value of each of these positions was performed. Final convergence yielded R_1 = 0.042 and R_2 = 0.045 and indicated an average occupancy of 86% and 14%, for the disordered nitrogen positions. Since the ratio 0.057/0.045 > 1.02, this decrease in R can be considered significant at better than the 99% confidence level.[12]

Finally, all atomic positions were included and the anisotropic positions were allowed to refine for three more cycles while the isotropic positions were refined once more. The final calculation of the structure factors and error functions yielded R_1 = 0.033 and R_2 = 0.034. The goodness of fit, $\{[\sum w(F_o - |F_c|)^2]/(m - s)\}^{1/2}$, is 0.902. The number of reflections m = 1480 and the total parameter number s = 356 give an overdetermination ratio of 4.16. A final difference Fourier synthesis had an estimated standard deviation in electron density of 0.069 e/Å^3

Table I. Final Positional and Anisotropic Thermal Parameters with Standard Deviations[a]

Atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	7 460.1 (0.5)	474.6 (0.4)	2284.3 (0.4)	65.3 (0.6)	44.0 (0.4)	38.5 (0.3)	7.6 (0.7)	48.1 (0.6)	3.8 (0.6)
N1	6 264 (4)	348 (3)	3051 (3)	83 (4)	64 (3)	55 (3)	3 (6)	79 (6)	−8 (5)
N2	8 790 (4)	1259 (3)	3575 (3)	88 (5)	44 (3)	58 (3)	−4 (5)	72 (6)	−8 (4)
N3	6 488 (4)	1849 (3)	1587 (3)	90 (5)	48 (3)	60 (3)	15 (6)	59 (6)	10 (4)
N4	8 670 (4)	811 (3)	1539 (3)	82 (5)	63 (3)	55 (3)	11 (6)	72 (6)	16 (4)
N5	6 108 (4)	−508 (3)	1146 (3)	85 (4)	71 (3)	48 (2)	28 (6)	48 (5)	2 (5)
N6	8 510 (4)	−931 (3)	2831 (3)	79 (5)	48 (3)	47 (3)	10 (5)	41 (5)	2 (4)
C1	6 844 (5)	1051 (4)	3904 (4)	139 (7)	84 (4)	62 (3)	9 (8)	129 (8)	−15 (6)
C2	8 361 (5)	995 (4)	4339 (3)	127 (6)	71 (3)	51 (3)	−9 (7)	71 (7)	−24 (5)
C3	7 018 (5)	2138 (4)	886 (3)	135 (7)	66 (3)	61 (3)	25 (7)	78 (8)	46 (5)
C4	8 499 (5)	1904 (4)	1315 (4)	120 (6)	79 (4)	73 (3)	−21 (7)	106 (8)	37 (6)
C5	6 248 (5)	−1568 (4)	1520 (4)	134 (6)	47 (3)	76 (3)	0 (7)	49 (7)	−17 (5)
C6	7 958 (5)	−1681 (4)	2039 (4)	115 (7)	61 (3)	68 (3)	34 (7)	58 (8)	−9 (5)
O1	3 043 (4)	−114 (3)	677 (3)	170 (5)	64 (3)	141 (4)	5 (6)	200 (7)	−39 (5)
O2	3 581 (4)	1449 (3)	890 (5)	119 (5)	71 (3)	268 (3)	17 (7)	214 (9)	16 (7)
C7	2 788 (4)	768 (4)	774 (3)	84 (5)	61 (4)	51 (3)	−5 (7)	63 (6)	−3 (4)
C8	1 410 (5)	1068 (4)	705 (5)	120 (6)	88 (4)	141 (5)	16 (8)	172 (10)	−24 (8)
O3	11 573 (3)	769 (3)	3936 (3)	112 (4)	124 (3)	90 (3)	9 (6)	101 (6)	−19 (5)
O4	11 282 (4)	−428 (3)	2848 (3)	104 (4)	103 (3)	109 (3)	−20 (7)	108 (7)	−20 (6)
C9	12 000 (5)	207 (4)	3472 (4)	95 (6)	74 (4)	58 (3)	10 (8)	63 (8)	37 (6)
C10	13 463 (5)	320 (5)	3670 (4)	83 (5)	107 (5)	104 (4)	−3 (8)	90 (7)	5 (7)
O5	7 838 (5)	3457 (3)	3282 (3)	258 (6)	54 (2)	118 (3)	−13 (6)	185 (8)	−6 (4)
O6	7 105 (5)	−1532 (3)	4206 (3)	321 (8)	66 (2)	89 (3)	−47 (7)	161 (8)	2 (4)

[a] Values are given $\times 10^4$. The esd is given in units of the least significant digit given for the corresponding parameter. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

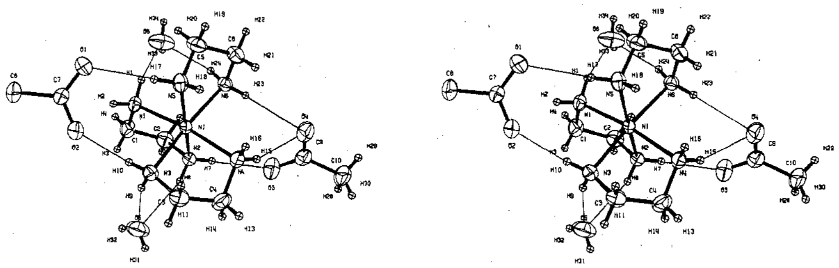

Figure 1. Stereoview of the asymmetric unit showing the hydrogen bonds in $[Ni(en)_3](O_2C_2H_3)_2\cdot 2H_2O$; the atom labeling is consistent with that in the tables. Ellipsoids of 30% probability are used. Excessive disorder precluded refinement of the methyl hydrogens at C8.[31]

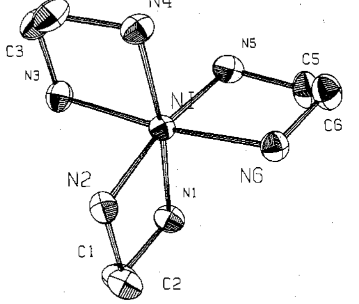

Figure 2. ORTEP drawings of the $[Ni(en)_3]^{2+}$ coordination sphere showing the Λδδδ configuration. Ellipsoids of 30% probability are used. The coordinates in Table I have been rotated 0° on x, −65° on y, and 90° on z to give this view.

and revealed only one area of residual electron density equal to as much as 0.410 e/Å^3 around the unresolved methyl hydrogens of C8. All other peaks in this map were less than 0.256 e/Å^3. The final cycle of full-matrix least-squares refinement yielded shifts that were less than their standard deviations.

The final positional and thermal parameters for the atoms refined anisotropically are given in Table I. Table II lists the positional and thermal parameters for the isotropically refined atoms. Bond lengths are given in Table III while Tables IV and V contain bond angles. A listing of observed and calculated structure factors is also available.[13] A stereoview of the asymmetric unit is shown Λδδδ Figure 1. Figure 2 illustrates a metal ion with the Λδδδ configuration. Since the crystal is centric and racemic, an equal number of ΔλλΛ metal ions are present. Figure 3 gives a stereoview of the contents of one unit cell. The numbering scheme for the atoms in the tables is consistent with that used in the figures.

Description and Discussion of Structure

All of the refined atoms of the asymmetric unit are shown in Figure 1. Each of the three ethylenediamine ligands acts as a bidentate chelate and the six coordinating nitrogens form a distorted octahedron centered around the divalent nickel ion. The average chelate bite distance of 2.786 (7) Å effects the distortion by compressing to about 82° the N–Ni–N angle of

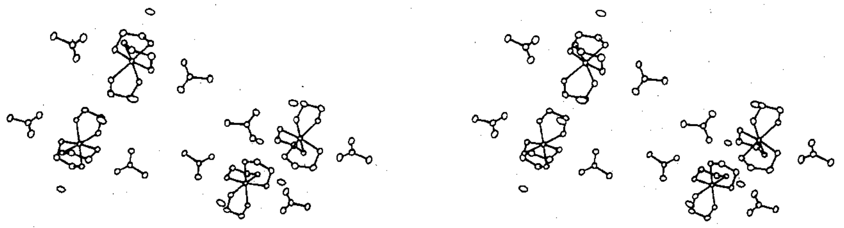

Figure 3. Stereoview (ORTEP) of the contents of a unit cell of $[Ni(en)_3](O_2C_2H_3)_2\cdot 2H_2O$. Ellipsoids of 20% probability are used. The orientation is the same as that shown in Figure 1 where the view was obtained by rotating the coordinates given in Table I 0° on x, −169° on y, and 160° on z. Here the hydrogens have been eliminated for the sake of clarity.

Table II. Isotropic Atom Positions and Thermal Parameters[a]

Atom[b]	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	B, Å^2
H1	6 330 (52)	−327 (42)	3274 (38)	6.3 ± 1.2
H2	5 392 (49)	518 (39)	2659 (36)	6.0 ± 1.1
H3	6 644 (50)	1665 (40)	3723 (36)	6.3 ± 1.1
H4	6 599 (35)	850 (27)	4338 (26)	3.1 ± 0.7
H5	8 736 (41)	279 (32)	4567 (29)	4.6 ± 0.9
H6	8 719 (50)	1353 (40)	4805 (36)	5.8 ± 1.1
H7	9 600 (49)	1101 (39)	3762 (35)	5.8 ± 1.1
H8	8 708 (42)	1903 (32)	3513 (29)	4.0 ± 0.9
H9	6 685 (55)	2306 (43)	2032 (38)	6.2 ± 1.2
H10	5 608 (60)	1765 (45)	1318 (42)	7.1 ± 1.4
H11	6 859 (45)	2786 (37)	720 (32)	5.8 ± 1.0
H12	6 557 (43)	1822 (33)	321 (31)	4.8 ± 0.9
H13	8 802 (55)	2069 (42)	943 (39)	6.6 ± 1.2
H14	9 087 (48)	2282 (37)	1895 (35)	5.8 ± 1.1
H15	9 450 (53)	646 (41)	1884 (38)	5.9 ± 1.2
H16	8 378 (59)	445 (46)	1026 (42)	6.9 ± 1.3
H17	5 275 (51)	−382 (40)	1010 (37)	6.3 ± 1.2
H18	6 292 (60)	−490 (47)	559 (44)	6.7 ± 1.4
H19	6 140 (47)	−2014 (38)	1012 (34)	6.0 ± 1.0
H20	6 051 (44)	−1786 (34)	1958 (31)	5.1 ± 0.9
H21	8 274 (43)	−1500 (34)	1569 (31)	5.1 ± 0.9
H22	8 178 (47)	−2349 (37)	2277 (33)	5.7 ± 1.0
H23	9 372 (57)	−830 (44)	3045 (40)	7.3 ± 1.3
H24	8 307 (49)	−1168 (38)	3333 (35)	5.6 ± 1.1
H28	13 985 (84)	691 (68)	4257 (64)	12.0 ± 2.1
H29	13 789 (62)	−277 (50)	3736 (46)	8.0 ± 1.5
H30	13 523 (77)	727 (61)	3204 (58)	11.1 ± 1.9
H31	8 022 (61)	3825 (50)	2946 (50)	6.4 ± 1.4
H32	7 564 (114)	3622 (92)	3583 (90)	14.6 ± 3.2
H33	7 523 (51)	−1374 (42)	4702 (37)	5.5 ± 1.1
H34	6 927 (60)	−2087 (49)	4186 (42)	7.6 ± 1.4
D1	6 365 (24)	1540 (19)	2835 (17)	4.0 ± 0.5
D2	8 698 (21)	185 (16)	3804 (15)	3.1 ± 0.4
D3	6 249 (25)	1013 (20)	808 (19)	3.8 ± 0.5
D4	8 766 (26)	1613 (20)	2334 (19)	5.9 ± 0.5
D5	6 025 (26)	−751 (20)	2149 (19)	4.7 ± 0.5
D6	8 367 (25)	−650 (19)	1840 (19)	3.0 ± 0.5

[a] Fractional coordinates $\times 10^4$ are given. The esd is in the units of the least significant digit given for the corresponding parameter. [b] D denotes a disorder position which was treated as a nitrogen.

Table III. Bond Distances (Å) and Standard Deviations

	Coordination Sphere		
Ni-N1	2.104 (4)	Ni-N4	2.131 (4)
Ni-N2	2.119 (4)	Ni-N5	2.139 (4)
Ni-N3	2.124 (4)	Ni-N6	2.138 (4)
	Chelate Rings		
N1-C1	1.485 (6)	N6-C6	1.462 (6)
N2-C2	1.470 (6)	C1-C2	1.492 (7)
N3-C3	1.466 (6)	C3-C4	1.487 (7)
N4-C4	1.469 (7)	C5-C6	1.510 (7)
N5-C5	1.486 (6)		
	Acetate Ions		
C7-O1	1.215 (7)	C9-O3	1.245 (7)
C7-O2	1.203 (6)	C9-O4	1.245 (7)
C7-C8	1.515 (7)	C9-C10	1.500 (7)
	Amine Hydrogens		
N1-H1	0.94 (5)	N4-H15	0.81 (5)
N1-H2	0.90 (5)	N4-H16	0.85 (6)
N2-H7	0.83 (5)	N5-H17	0.86 (5)
N2-H8	0.85 (4)	N5-H18	0.99 (6)
N3-H9	0.86 (5)	N6-H23	0.86 (6)
N3-H10	0.87 (6)	N6-H24	0.93 (5)
	Methylene Hydrogens		
C1-H3	0.85 (5)	C4-H13	0.80 (5)
C1-H4	0.85 (4)	C4-H14	0.97 (5)
C2-H5	1.02 (4)	C5-H19	0.91 (5)
C2-H6	0.79 (5)	C5-H20	0.97 (4)
C3-H11	0.88 (5)	C6-H21	0.95 (4)
C3-H12	0.88 (4)	C6-H22	0.94 (5)
	Disordered Nitrogens		
Ni-D1	2.23 (2)	Ni-D4	2.05 (3)
Ni-D2	2.13 (2)	Ni-D5	2.19 (3)
Ni-D3	2.16 (3)	Ni-D6	2.05 (3)
	Disordered Rings		
D1-C1	1.60 (2)	D4-C4	1.49 (3)
D2-C2	1.48 (2)	D5-C5	1.62 (3)
D3-C3	1.68 (3)	D6-C6	1.50 (3)
	Hydrates		
O5-H31	0.79 (7)	O6-H33	0.72 (5)
O5-H32	0.68 (12)	O6-H34	0.75 (6)
	Methyl Hydrogens		
C10-H28	0.95 (9)	C10-H30	0.91 (8)
C10-H29	0.85 (6)		

each ligand from the 90° value expected for pure octahedral symmetry. The distorted octahedron of coordinating nitrogens is actually a trigonal antiprism[14] in which the twist angle between the equilateral trigonal planes defined by N1–N3–N5 and N2–N4–N6 is 50.4 ± 1.0°.

The five-membered rings formed by each chelate are not flat as evidenced by the axial and equatorial distinction between the positions of the methylene hydrogens. The dihedral angles, θ_i, listed in Table VI for these hydrogens are in good agreement with $\theta_{ax} = 76 \pm 4°$ found for $[Ni(en)_3]^{2+}$ from a treatment[15] of the paramagnetic NMR contact shifts of the axial and equatorial hydrogens. The parameter ω, the dihedral angle between the planes defined, for example, by N1–C1–C2 and C1–C2–N2, has been suggested[16] as a measure of ring pucker. The average ω of the three rings in this structure is $58.0 \pm 0.2°$ and this agrees well with $\omega = 56°$ calculated for $[Ni(en)_3]SO_4$.[16]

The type of ring puckering found in this tris chelate can be determined[17] from the illustration shown in Figure 2. The configuration about the illustrated metal center is Λ, and since all three C–C bonds are parallel to the C_3 axis of the complex ion, each ring is present as the δ conformer. Because of the symmetry of the crystal there are an equal number of Λδδδ and Δλλλ configurations positioned in pairs across inversion centers in the unit cell. Due to some disorder we have observed what appears to be Δλλλ superimposed on the Λδδδ configuration. Since the arrangements of the carbon and nickel atoms are identical for both configurations, the only evidence for the superposition was an "extra set" of six nitrogens. Refinement of the occupancy parameters for all the nitrogen atoms indicated that this disorder occurs to an extent of 14%.

Both acetate anions are planar and approach the complex ion along its C_3 axis from opposite directions. In both cases the carboxyl end of the anion is nearest the amine hydrogens of the cation. It is interesting to note that the O3–O4–C9–C10 acetate which shows the larger deviations from the plane in Table VII also has a slightly longer set of C–O bonds than does the first acetate. These small structural differences could perhaps be a result of the hydrogen bonding to be discussed later. The two waters of hydration have similar positions in that each is nested between two chelate rings. Also, Figure 1 shows O5 below and O6 above the same N1–N2 chelate ring.

Hydrogen Bonding

Examination of the data listed in Table VIII reveals a hydrogen-bonding network which involves a variety of interactions. Five amine hydrogens are strongly interacting with the oxygens of the acetate anions as evidenced by the short A–B distances and the AHB angles of nearly 180°. The O4 atom sets up simultaneous hydrogen bonds with H15 and H23 while each of the other acetate oxygens acts as a base for only one amine hydrogen. In addition, four other amine hydrogens are H bonded to the two waters of hydration.

These nine interactions have been included visually in Figure 1 as single, solid lines, and under stereoviewing several interesting features of the H-bonding scheme become evident.

Table IV. Bond Angles (deg)[a] and Standard Deviations

N1-Ni-N3	92.60 (0.14)	N1-C1-C2	108.57 (0.40)	D1-Ni-D3	89.8 (0.9)
N3-Ni-N5	95.45 (0.15)	N3-C3-C4	109.39 (0.39)	D3-Ni-D5	93.2 (0.9)
N5-Ni-N1	91.14 (0.15)	N5-C5-C6	108.15 (0.38)	D5-Ni-D1	90.9 (0.9)
N2-Ni-N4	93.11 (0.15)	C1-C2-N2	108.61 (0.37)	D2-Ni-D4	89.4 (0.9)
N4-Ni-N6	91.79 (0.14)	C3-C4-N4	107.84 (0.38)	D4-Ni-D6	96.2 (1.0)
N6-Ni-N2	91.68 (0.14)	C5-C6-N6	108.79 (0.37)	D6-Ni-D2	93.3 (0.9)
N1-Ni-N2	82.53 (0.16)			D1-Ni-D2	84.1 (0.8)
N3-Ni-N4	81.49 (0.16)	O1-C7-O2	122.51 (0.50)	D3-Ni-D4	84.2 (1.0)
N5-Ni-N6	81.61 (0.14)	O1-C7-C8	120.53 (0.46)	D5-Ni-D6	82.6 (1.0)
N1-Ni-N6	94.35 (0.15)	O2-C7-C8	116.91 (0.51)	D1-Ni-D4	90.5 (1.0)
N3-Ni-N2	92.02 (0.15)	O3-C9-O4	123.91 (0.48)	D3-Ni-D6	93.5 (1.0)
N5-Ni-N4	93.90 (0.16)	O3-C9-C10	117.48 (0.49)	D5-Ni-D2	93.3 (0.9)
N1-Ni-N4	172.56 (0.14)	O4-C9-C10	118.60 (0.47)	D1-Ni-D6	172.8 (0.9)
N3-Ni-N6	172.50 (0.15)	H31-O5-H32	123.2 (11.1)	D3-Ni-D2	171.1 (0.9)
N5-Ni-N2	170.43 (0.15)	H33-O6-H34	111.0 (6.0)	D5-Ni-D4	177.1 (1.0)
Ni-N1-C1	107.48 (0.27)	H28-C10-C9	112.6 (5.4)	Ni-D1-C1	97.8 (1.1)
Ni-N2-C2	106.54 (0.28)	H29-C10-C9	106.7 (4.2)	Ni-D2-C2	105.7 (1.1)
Ni-N3-C3	108.02 (0.28)	H30-C10-C9	109.7 (5.0)	Ni-D3-C3	99.0 (1.2)
Ni-N4-C4	106.21 (0.29)			Ni-D4-C4	109.5 (1.4)
Ni-N5-C5	107.15 (0.29)			Ni-D5-C5	99.9 (1.2)
Ni-N6-C6	107.89 (0.26)			Ni-D6-C6	110.8 (1.4)

[a] For a listing of angles involving ring hydrogens see Table V.

Table V. Bond Angles (deg) and Standard Deviations for Chelate Ring Hydrogens

Ni-N1-H1	107.8 (3.1)	H7-N2-H8	109.4 (4.4)
Ni-N1-H2	110.6 (3.3)	H15-N4-H16	107.8 (5.6)
Ni-N3-H9	107.9 (3.5)	H23-N6-H24	111.0 (5.0)
Ni-N3-H10	109.4 (3.8)	H3-C1-C2	105.5 (3.4)
Ni-N5-H17	111.3 (3.4)	H4-C1-C2	108.1 (2.4)
Ni-N5-H18	111.5 (3.3)	H5-C2-C1	113.4 (2.3)
Ni-N2-H7	112.9 (3.4)	H6-C2-C1	112.4 (3.9)
Ni-N2-H8	112.7 (2.8)	H11-C3-C4	111.3 (3.1)
Ni-N4-H15	109.1 (3.7)	H12-C3-C4	111.9 (2.9)
Ni-N4-H16	107.4 (4.0)	H13-C4-C3	110.2 (3.9)
Ni-N6-H23	108.9 (4.0)	H14-C4-C3	116.8 (3.0)
Ni-N6-H24	108.9 (3.1)	H19-C5-C6	105.6 (3.0)
H1-N1-H2	111.2 (4.4)	H20-C5-C6	108.9 (2.6)
H9-N3-H10	107.4 (5.2)	H21-C6-C5	105.8 (2.8)
H17-N5-H18	113.1 (4.6)	H22-C6-C5	109.3 (2.8)

Table VI. Dihedral Angles[a] Formed by Methylene Hydrogens

Defining plane of atoms	Hydrogen	Angle, deg[b]	Description
Ni-N1-C1	H3	75.2	Axial
Ni-N2-C2	H5	77.5	Axial
Ni-N3-C3	H12	85.1	Axial
Ni-N4-C4	H14	80.7	Axial
Ni-N5-C5	H20	79.8	Axial
Ni-N6-C6	H21	71.7	Axial
Ni-N1-C1	H4	157.7	Equatorial
Ni-N2-C2	H6	168.2	Equatorial
Ni-N3-C3	H11	161.7	Equatorial
Ni-N4-C4	H13	168.6	Equatorial
Ni-N5-C5	H19	157.8	Equatorial
Ni-N6-C6	H22	162.9	Equatorial

[a] T. Ottersen, MOLGE computer program, University of Hawaii, 1973. [b] Standard deviations are approximately ±3.0°.

Table VII. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

Plane 1		Plane 2	
O1	*−3*	O3	*−15*
O2	*−5*	O4	*−15*
C7	*13*	C9	*54*
C8	*−5*	C10	*−24*
H1	3371	H7	−3371
H2	2459	H8	−12552
H9	1177	H15	−18294
H10	361	H16	−24446
H17	305	H23	7051
H18	−400	H24	13840
q_{bxc}	−824	q_{bxc}	−668
q_b	1225	q_b	−6929
q_c	9890	q_c	7179
D	0.695	D	2.474
δ	8	δ	31

[a] Italic deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom position lies between that plane and the origin. The direction cosines (× 10^4), q, are with respect to orthogonal axes. D is the distance (in Å) from the plane to the origin as calculated in MOLGE. The rms of the italic deviations (Å × 10^3) from the plane is δ.

All of the hydrogens associated with the acetates are equatorial to the five-member chelate ring and point along the C_3 axis of the complex. Another equatorial amine hydrogen, H2, which apparently has no H-bonding interaction points directly into the delocalized electron cloud of the O1–C7–O2 moiety; however, the shortest distance, H2–O2, of 2.82 Å is too long to suggest hydrogen bonding with the π-electron cloud. All of the hydrogens associated with water oxygens are axial with respect to the chelate ring. More significantly, water oxygens achieve a tetrahedral arrangement via their acceptance of hydrogen bonds from the amine protons on two different chelate rings. The two other axial amine hydrogens, H16 and H18, are not involved with water but are important in linking cations together.

Also listed in Table VIII are the disordered nitrogen positions and their distances to possible hydrogen-bonding sites. In general, these D1 through D6 positions duplicate the scheme found for the other set of nitrogens. This alludes to the equal stability[18,19] of the enantiomers Λδδδ and Δλλλ and indicates that the hydrogen bonding has no preference for either of the two configurations. No such disorder has been reported in other crystal structure determinations involving $[M(en)_3]^{n+}$ chelates.[2,3,20–24]

Finally, there are two kinds of hydrogen bonding occurring between adjacent unit cells and these have been included in Table VIII. Both hydrogens of each water point away from the complex and toward an acetate in another unit cell effecting four strong hydrogen bonds as indicated by the relatively short A–B distances and AHB angles very close to 180°. There is a large amount of uncertainty associated with H32 due to the large thermal parameter found for its position. A second kind of intercellular H bonding appears to occur between the axial amine hydrogen, H16, and an O1 oxygen

Table VIII. Possible A–H· · ·B Bonds with A· · ·B Distances Less than 3.20 Å

A–H	B[a]	A–B, Å	AHB, deg
N2–H7	O3	2.916 (5)	168 (5)
N3–H10	O2	2.922 (6)	171 (6)
N4–H15	O4	3.121 (6)	158 (5)
N5–H17	O1	3.147 (5)	178 (5)
N6–H23	O4	3.092 (5)	153 (5)
N1–H1	O6	2.930 (6)	157 (5)
N2–H8	O5	3.034 (5)	162 (4)
N3–H9	O5	3.144 (6)	164 (5)
N6–H24	O6	3.185 (6)	161 (4)
D1	O2	3.17 (2)	
D2	O3	3.16 (2)	
D3	O2	3.03 (3)	
D4	O3	3.16 (3)	
D5	O1	3.15 (2)	
D6	O4	2.88 (3)	
D1	O5	2.90 (2)	
D2	O6	3.07 (2)	
D4	O5	3.20 (3)	
D5	O6	2.99 (3)	
O5–H31	O4, (3)200	2.730 (6)	170 (7)
O5–H32	O1, (3)100	2.878 (6)	151 (12)
O6–H33	O3, (2)201	2.726 (6)	170 (5)
O6–H34	O2, (3)1–10	2.742 (6)	179 (6)
N4–H16	O1, (2)100	3.172 (6)	154 (5)
D3	O1, (2)100	2.93 (3)	

[a] Where indicated, some B type atoms have been transformed to another unit cell. Thus, O4, (3)200 means that the x, y, z of O4 given in Table I have been transformed to $-x$, $1/2 + y$, $1/2 - z$ and moved to 200 from unit cell 000; O3 (2)201 means that the x, y, z of O3 given in Table I have been transformed to $-x$, $-y$, $-z$ and moved to 201 from unit cell 000.

of an acetate lying in an adjacent unit cell. A similar hydrogen, H18 on N5, also is directed at this same acetate with an AHB angle of 161 (5)°, but the A–B distance of 3.380 (6) Å represents, at best, a very weak hydrogen bond. Again, the disorder positions are found to form a duplicate set of hydrogen bonds in that D3 forms a similar A–B type interaction with O1, (2)100, as does N4.

There is a close approach between molecules within a unit cell as can be observed in Figure 3 where the N1–N2 ring of equivalent position number 1 lies very near the N3–N4 ring of position 4. The distances between carbons on the respective rings are C1–C3 = 3.77 Å and C2–C4 = 4.03 Å. These values are not far from twice the van der Waals radius of 2.0 Å given for a methylene group[25] and suggest that the close packing between cation complexes in this structure is limited only by the repulsive forces of methylene–methylene interactions.

The $\Lambda\delta\delta\delta$ configuration found for $[Ni(en)_3](O_2C_2H_3)_2 \cdot 2H_2O$ is not unusual. It is the only isomer found in Ni(II) complexes and is the common configuration for most tris(ethylenediamine) chelate complexes which is in agreement with theoretical treatments.[18,19] However, a present theory[6] postulates that tris(ethylenediamine) complexes in a strongly hydrogen-bonding environment of anions and hydrate waters tend to favor the higher energy λ ring conformations. For example, the $\Lambda\delta\delta\lambda$ conformer has been found in the presence of three strong hydrogen bonds, ≤3.1 Å, while the $\Lambda\delta\lambda\lambda$ conformer in the same crystal[4] has seven such bonds. The structure of $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$ also fits this pattern as it has the $\Lambda\delta\lambda\lambda$ configuration and eight strong hydrogen bonds.[26] Furthermore, the only known example of the highest energy $\Lambda\lambda\lambda\lambda$ conformer[5] is surrounded by ten strong hydrogen bonds. This theory is inconsistent with our observations on $[Ni(en)_3](O_2C_2H_3)_2 \cdot 2H_2O$. Table VIII lists five strong hydrogen bonds with A···B distance ≤ 3.1 Å, yet the $\Lambda\delta\delta\delta$ conformer prevails. The strong hydrogen bonding is also evident from the extent of ring puckering, which has been postulated[27] to be an indicator of the hydrogen-bonding strength of the surrounding medium. For this complex, this value is 58°, the largest value yet recorded for a tris(ethylenediamine) complex.

In both earlier structures for $[Ni(en)_3]^{2+}$ the $\Lambda\delta\delta\delta$ conformation was reported.[2,20] While the hydrogen bonds in $[Ni(en)_3](NO_3)_2$ were shown[2] to be very weak because of bifurcation, the strong and extensive hydrogen bonding found in the $[Ni(en)_3]SO_4$ determination[20] led Caughlan et al. to qualify the supposed relationship between rings and strong hydrogen bonds.[6] They suggested that if hydrogen-bond acceptor sites were close together, then the resulting multiple hydrogen bonds with amine protons on the complex would stabilize the usual $\Lambda\delta\delta\delta$ conformation. Similar results in the structure determination of $[Co(en)_3](HPO_4)_3 \cdot 9H_2O$ by Duesler and Raymond[22] caused these authors to support the amended theory. The results reported here are also consistent with this more detailed version of the earlier postulate.

There is however one structure which does not seem to be in accord with any version of the hydrogen-bonding theory. Only one strong hydrogen bond is found in the structure of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$ where the $Co(en)_3{}^{3+}$ ion has the $\Lambda\delta\lambda\lambda$ configuration, and this hydrogen bond is to the δ ring.[28] This leads us to suggest that another parameter, namely, a size or bulk effect, may be equally as important or more important than the hydrogen-bonding effect in determining which conformer will be observed in the solid state. It has been recognized[6] that a change from the $\Lambda\delta\delta\delta$ to $\Lambda\lambda\lambda\lambda$ configuration involves a general broadening of the metal complex. All of the known examples of $[M(en)_3]^{n+}$ complexes which contain one or more λ rings occur as salts of large counterions such as $[Ni(CN)_5]^{3-}$, $[Co(CN)_6]^{3-}$, $[Cr(CN)_5NO]^{3-}$, and $[Cu_2Cl_8]^{4-}$. These large, complex anions are capable of isolating the cation with enough open space in the lattice for it to assume the less commonly observed, bulkier λ rings. A similar effect has been used,[29] for example, in removing quadrupole splitting in the Mössbauer spectra of $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ by isolating the anion in the lattice with the large $[N(CH_2CH_2NH_3)_3]^{3+}$ ion and thus producing pure octahedral symmetry about Ru(III).

Conclusion

The observed $\Lambda\delta\delta\delta$ structure of $[Ni(en)_3](O_2C_2H_3)_2 \cdot 2H_2O$ cannot be explained with a theory which requires that strong hydrogen bonding stabilizes only λ rings. Out data indicate that the $[Ni(en)_3]^{2+}$ complexes are closely packed and as a result are restricted to the smaller configuration. The five strong hydrogen bonds formed with the amine hydrogens in this complex actually indicate that strong hydrogen bonding is possible with δ as well as λ rings.

In solution where packing effects must be ignored, studies of $[M(en)_3]^{n+}$ have shown that a conformational equilibrium exists. The work of Ho and Reilley[14] with ethylenediamine complexes of Ni(II) has shown that two CH_2 peaks result due to an unequal population of δ and λ ring conformations which are exchanging rapidly on the NMR time scale. Mason and Norman[30] have observed changes in the visible circular dichroism of aqueous $[Co(en)_3]^{3+}$ which are dependent upon anion and have explained the changes as resulting from hydrogen-bonding association of anions with the cations which alters the ring conformational equilibria. While the role of hydrogen bonding in the solid state is in doubt, it is likely that in solution hydrogen bonding of the cation with anions or solvent is a probable mechanism of altering the conformational equilibrium.

Note Added in Proof. The x-ray crystallographic structure determination of $[Ni(en)_3](B(C_6H_5)_4)_2 \cdot 3DMSO$ has recently been completed in this laboratory. The configuration of the complex cation is Λδδλ. A complete discussion of the molecular structure will be forthcoming.

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Supplementary Material Available: Table IX, listing the structure factor amplitudes for $[Ni(en)_3](O_2C_2H_3)]\cdot 2H_2O$ (9 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Hexakis(methyl isocyanide)dipalladium(I) Bis(hexafluorophosphate) Hemiacetone, $[Pd_2(CNMe)_6](PF_6)_2\cdot{}^1/_2Me_2CO$. A Palladium(I) Dimer

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The crystal and molecular structure of the novel palladium(I) dimer hexakis(methyl isocyanide)dipalladium(I) bis(hexafluorophosphate), $[Pd_2(CNMe)_6](PF_6)_2$, has been determined as its hemiacetone solvate by three-dimensional single-crystal x-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ in a cell of dimensions a = 12.281 (2) Å, b = 12.544 (3) Å, c = 10.388 (2) Å, α = 111.03 (1)°, β = 111.12 (1)°, and γ = 75.95 (1)° with two formula weights corresponding to $[Pd_2(CNMe)_6](PF_6)_2\cdot{}^1/_2Me_2CO$ per unit cell (ρ_{exptl} = 1.87 (1) g/cm³; ρ_{calcd} = 1.87 g/cm³). The structure was solved by standard heavy-atom methods and refined (on F) by least squares to final discrepancy factors R_1 and R_2 of 0.045 and 0.057, respectively, for 3249 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. In the cation a metal–metal bond of length 2.5310 (9) Å joins the two Pd atoms, each of which possesses an essentially square-planar coordination geometry with the Pd–Pd bond occupying one of the coordination sites. The complex exhibits approximately D_{2d} symmetry. The Pd–"axial" C bonds are significantly longer than the Pd–"equatorial" C bonds, 2.049 (6) vs. 1.963 (5) Å, and the cis C–Pd–C bond angles average 95.0 (6)°. The bonding in this unusual dimer is discussed following the approach of Elian and Hoffmann to metal carbonyl fragments, and its stereochemical nonrigidity is considered.

Introduction

In recent years the chemistry of the platinum group metals has been vigorously pursued, in large measure stimulated by the ability of their low-valent complexes to form adducts, activate substrates and catalyze reactions.[1-12] An important class of these low-valent complexes is those which contain metal–metal bonds. Within the platinum group elements, metal–metal bonding is most often observed in carbonyl cluster compounds.[13-23] While platinum and palladium form a number of metal–metal bonded systems,[24-37] few of these contain the metal ions in their lower oxidation states.

It was therefore of structural interest when we learned of the synthesis of the Pd(I) cation dimer $[Pd_2(CNMe)_6](PF_6)_2$ by Balch and coworkers.[38] The complex was found to exhibit only a single methyl resonance at room temperature but two proton resonances in the intensity ratio 1:2 below −30°C.[39] In spite of the unusual Pd(I) oxidation state, the complex shows remarkable stability presumably arising from metal–metal bond formation. The stereochemical nonrigidity of the system and its extraordinary stability thus made the complex even more intriguing from a structural standpoint. Herein we report the crystal structure determination of $[Pd_2(CNMe)_6](PF_6)_2$ and a discussion of its bonding.

The complex $[Pd_2(CNMe)_6]^{2+}$ represents one of the few simple M_2L_6 systems known where M is a transition element.[40-46] It is formally isoelectronic with the unstable nickel(I) cyanide system $[Ni_2(CN)_6]^{4-}$ which has been extensively studied because of its interesting chemical and catalytic properties.[47-53] The structure of $[Ni_2(CN)_6]^{4-}$ has been reported[45-46] and the anion shows a short Ni–Ni bond unsupported by cyanide bridges. The title compound is also closely related to palladium(I) and platinum(I) carbonyl halide dimers $[M_2X_4(CO)_2]^{2-}$ [54] which have been reported and whose structures have been suggested on the basis of infrared spectroscopy. The present results will no doubt bear on these proposals.[84]

The structure of $[Pd_2(CNMe)_6](PF_6)_2$ has appeared in a communication.[39]