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Stabilization of the Higher Oxidation States of Nickel.[1] Molecular Structure of Bis(2,6-diacetylpyridine dioximato)nickel(IV)

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The nickel(IV) complex, bis(2,6-diacetylpyridine dioximato)nickel(IV), $Ni(C_9N_3O_2H_9)$, has been examined by single-crystal X-ray structural techniques. The crystallographic data are: Laue symmetry $4/m$; space group, $I4_1/a$; $a = b = 7.745$ (3) Å, $c = 30.510$ (16) Å; $d_m = 1.59$ (2) g/cm³; $d_x = 1.600$ g/cm³ for four monomeric molecules in the unit cell. The 8371 reflections were measured on an automated Picker four-circle diffractometer and gave 702 unique observations for the structural analysis. Full-matrix least-squares analysis including hydrogen atoms gave final discrepancy factors of $R = 0.028$ and $R_w = 0.025$, $S = 0.93$. The crystallographic and molecular symmetry of the molecule is $\bar{4}$ (S_4) with the nickel atom coordinated to two 2,6-diacetylpyridine dioximato ligands *via* the six nitrogen atoms of these ligands. A comparison of these nickel-nitrogen distances with those found in nickel(II) complexes suggests a shortening of 0.17 Å in the Ni(IV)–N bond. This average difference of 0.17 Å for $t_{2g}{}^6$ and $t_{2g}{}^6e_g{}^2$ with a change in formal oxidation number of 2 can be compared with the 0.18-Å difference reported earlier in the $t_{2g}{}^5e_g{}^2$ $Co(NH_3)_6{}^{2+}$ and $t_{2g}{}^6$ $Co(NH_3)_6{}^{3+}$ complexes with a change in formal oxidation number of 1.

Introduction

Complexes reported to contain a nickel atom in a formal oxidation state which is greater than two fall into three categories: (1) planar four-coordinate, (2) "sandwich," and (3) classical six-coordinate compounds in which nickel is coordinated to the electronegative elements, nitrogen, oxygen, and fluorine. Evidence now suggests that the square-planar nickel(IV) complexes are better represented as nickel(II) stabilized radical ligand complexes.[2,3] The only well-characterized "sandwich" complexes containing nickel in the formal oxidation states of III and IV have been the π-(3)-1,2- and π-(3)-1,7-carbollyl systems.[1b,4-6] By far, the majority of the reported nickel(IV) complexes contains a metal ion surrounded by an octahedral field of the electronegative first row elements: oxygen, fluorine, and nitrogen, *e.g.*, heteropolyniobates,[7] heteropolymolybdenates,[8] complexes of the type M_2NiF_6 ($M = Na^+, K^+, Rb^+, Cs^+, NO^+$),[9] and the subject of this investigation, oximes. On the basis of spectroscopic,[10,11] electrophoretic,[12,13] and ion-exchange studies,[14] the monomeric nickel(IV) complex of dimethylglyoxime [$CH_3C(NOH)C(NOH)CH_3 = DMGH_2$] has been formulated as $Ni(DMG)_3{}^{2-}$. Nickel(II) in an aqueous alkaline solution of the related tridentate ligand, 2,6-diacetylpyridine dioxime ($DAPDH_2$), is slowly oxidized by air and various oxidizing agents to give an intensely blue solution from which a violet crystalline complex can be isolated. The product has been characterized[15-17] as a 2:1 oxime ligand to nickel complex, $Ni^{IV}(DAPD)_2$. There is no evidence for the intermediate complex anion, $Ni(DAPD)_2{}^-$, from cyclic voltammetry experiments as would be expected for a cation ligand complex.[3,16-21] It was suggested[17] that one requirement for the stabilization of such highly oxidized forms is the presence of a strong spherical component of the crystal field; and, the interesting value of 1.58 kK for the *Dq* of $Ni(DAPD)_2$ was calculated. This is significantly greater than the value of 1.50 kK calculated for the hypothetical anion, $Ni(CN)_6{}^{4-}$.[22]

We have previously reported the synthesis of a nickel(IV) heteropolyniobate[7] and the structural characterization of a nickel(III) dicarbollide.[1b] As part of our continuing interest in these unusual oxidation states of nickel and in order to investigate the oxidation state in $Ni(DAPD)_2$, we report here the results of a single-crystal structural investigation of $Ni(DAPD)_2$.

Experimental Section

In order to produce crystals of sufficient size for X-ray crystallographic purposes, it was necessary to modify slightly the earlier reported synthesis of $Ni(DAPD)_2$.[16,17] Tetragonal-bipyramidal prisms of reasonable size were grown by cooling the reaction mixture to 0° and adding bromine in carbon tetrachloride over a period of a few hours. The tetragonal axis of the tetragonal-bipyramidal shaped crystals corresponded to [001] and the sides were perpendicular to {101}. The density was determined by flotation in 1,1,2,2-tetrachloroethylene and carbon tetrachloride to be 1.59 (2) g/cc. *Anal.* Calcd for $NiC_{18}H_{18}O_4$: Ni, 13.32; C, 49.02; H, 4.11. Found: Ni, 13.22; C, 48.84; H, 4.18.

Crystal data: $Ni(C_9N_3O_2H_9)_2$ mol wt 441.1; tetragonal with Laue symmetry = $4/m$ and space group, $I4_1/a$; systematic absences $h + k + l = 2n + 1$ for (hkl); $h, k = 2n + 1$ for ($hk0$); $00l$, $l = 4n$; $a =$

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Table I. Positional and Thermal Parameters for Nonhydrogen Atoms in $Ni(DAPD)_2$ Using p/c Weights

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0.25	0.125	0.01249 (7)[b]	0.01249 (7)	0.00048 (1)	0	0	0
N(1)	0	0.25	0.18521 (7)	0.01235 (52)	0.01100 (50)	0.00056 (3)	0.00165 (51)	0	0
C(2)	0.07813 (24)	0.11734 (25)	0.20542 (7)	0.01081 (43)	0.01245 (44)	0.00065 (3)	−0.00016 (44)	−0.00003 (9)	−0.00001 (10)
C(3)	0.07847 (29)	0.11600 (27)	0.25106 (7)	0.01517 (52)	0.01540 (48)	0.00058 (3)	0.00140 (49)	−0.00022 (10)	0.00070 (12)
C(4)	0	0.25	0.27299 (10)	0.01465 (74)	0.02107 (86)	0.00048 (4)	0.00035 (76)	0	0
C(7)	0.15449 (27)	−0.00515 (28)	0.17539 (7)	0.01378 (46)	0.01235 (44)	0.00072 (3)	0.00094 (45)	−0.00038 (10)	0.00001 (10)
N(8)	0.13093 (21)	0.03413 (22)	0.13359 (5)	0.01215 (35)	0.01439 (38)	0.00065 (2)	0.00000 (34)	0.00010 (8)	−0.00064 (8)
O(9)	0.18749 (21)	−0.05684 (19)	0.10265 (4)	0.01984 (37)	0.01839 (35)	0.00083 (2)	0.00349 (34)	0.00031 (7)	−0.00118 (7)
C(10)	0.25194 (36)	−0.16237 (29)	0.18786 (7)	0.02739 (62)	0.01762 (51)	0.00108 (3)	0.00714 (58)	−0.00058 (13)	−0.00007 (11)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{33}kl)]$. [b] Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant digits.

$b = 7.745$ (3) Å, $c = 30.510$ (16) Å; $Z = 4$; $V = 1830.2$ (3) Å^3; $d_x = 1.600$ g/cm^3; $d_m = 1.59$ (2) g/cm^3.

A crystal cleaved to an irregular wedge shape of approximate dimensions 0.050 at the wide end by 0.100 by 0.525 mm was selected for X-ray examination. The crystal was mounted on a small glass fiber and then on a Picker X-ray four-circle diffractometer so that the Φ axis of the instrument was approximately 3.5° from [001]. Using a few general, strong reflections, the pulse height analyzer was set to include about 95% of the detected intensity, and the takeoff angle was set at 1.20°. An ω scan on several reflections showed half-widths at half-height of 0.18°, indicating that the mosaicity of the crystal was sufficiently small for intensity data collection. The lattice constants were determined by the least-squares fit of the $(\sin^2 \theta)/\lambda^2$ values of 12 reflections. A full sphere of X-ray data was collected using eight orientation matrices obtained from the angular settings of three reflections carefully centered by hand for each octant. The collimators used were 1.0 mm in diameter and the scan rate was 1°/min with a scan width of 1.20°, not including the dispersion correction automatically made at higher angles to account for the increase in spread between $K\alpha_1$ and $K\alpha_2$ characteristic intensity peaks. The intensities were measured, using the 2θ scan technique, to an angle of $2\theta = 45°$ [$(\sin \theta)/\lambda = 0.539$] with Mo $K\alpha$ radiation. Three standard reflections were monitored for every 100 reflections; no individual integrated intensity differed by more than 2% from the average value of that standard reflection. A total of 8371 reflections were collected including the standards. Data were corrected for Lorentz and polarization effects, for attenuation by the copper attenuators, and for absorption, using the dimensions given above. The linear absorption coefficient is 10.9 cm^{-1} and the transmission coefficients varied between 0.93 and 0.89. The data were then averaged and standard deviations were assigned as the larger of modified counting statistics ($p = 0.05$)[23] and population statistics (p/c weights). This produced a total of 702 reflections of which 648 were observed with F_o greater than 2σ.

Table II. Positional and Thermal Parameters for Hydrogen Atoms in $Ni(DAPD)_2$ Using p/c Weights

Atom	x	y	z	β
HC(3)	0.1289 (22)	0.0251 (22)	0.2644 (6)	2.42 (47)
HC(4)	0	0.25	0.3019 (8)	2.66 (70)
H(1)	0.2875[a]	−0.2191	0.1630	4.20[b]
H(2)	0.3469	−0.1314	0.2042	4.20
H(3)	0.1821	−0.2337	0.2041	4.20
H(4)	0.2565	−0.1706	0.2179	4.20
H(5)	0.1976	−0.2580	0.1766	4.20
H(6)	0.3623	−0.1555	0.1768	4.20

[a] Positional parameters were calculated for a disordered methyl group. See text. [b] Thermal parameters for disordered methyl hydrogen atoms are taken as the approximate isotropic thermal parameter of the methyl carbon atom.

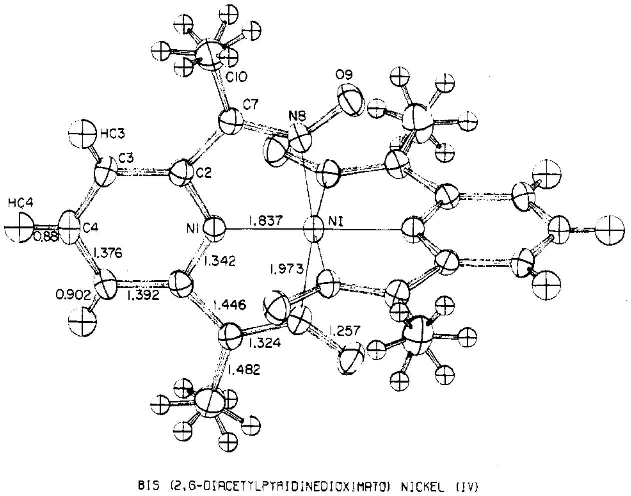

Figure 1. Molecular structure of bis(2,6-diacetylpyridine dioximato)nickel(IV).

Structural Solution and Refinement. The structural solution was carried out using the heavy atom method. The nickel atom lies on one of the two fourfold inversion centers, $\bar{4}a$ or $\bar{4}b$. At this special position, it contributes intensity to only those reflections which satisfy the condition $2k + l = 2n + 1$ or $4n$. Therefore, only these reflections were used for calculating the initial Fourier map. In this map, all nonhydrogen atoms appeared with electron densities for the carbon atoms varying between 3.0 and 4.5 e/Å^3 up to 6.5 e/Å^3 for the oxime nitrogen atoms. These positions were refined by isotropic least squares on $|F|$.[24] A difference Fourier revealed the pyridine hydrogen atoms at electron densities of 0.65 e/Å^3 with background appearing at a maximum of ±0.4 e/Å^3 in the proximity of the nonhydrogen atoms, except at the nickel atom where there was a +0.50 e/Å^3 peak. The methyl hydrogen atoms appeared as a disordered doughnut around C(10) (see Figure 1 for atom labels) at a density of 0.45–0.55 e/Å^3. Since it was not possible to locate the three methyl hydrogen atoms from the difference Fourier map through the plane of the methyl hydrogen atoms, their positions were calculated by assuming sp^3 hybridized carbon orbitals and a carbon–hydrogen bond distance of 0.92 Å. Two positions for the methyl group were calculated, the first with the hydrogen atom staggered around the C(10)–C(7) axis with respect to C(2) and the second group staggered around the same axis with respect to N(8). These six disordered half-hydrogen atoms were included in the structure factor refinement, but their positional and thermal parameters were not varied in the least-squares calculations. After each cycle of least squares, the atomic coordinates of these six disordered hydrogen atoms were recalculated for the next cycle.

Anisotropic refinement of the nonhydrogen atom parameters and refinement of the pyridine hydrogen atom positional parameters converged using both observed and unobserved data at $R = 0.031$ and $R_w = 0.022$. With the above (p/c) weighting scheme, the estimated standard deviation of an observation of unit weight was $S = 3.18$. A check on the linearity of the weighting scheme as a function of various parameters indicated that the 50 highest intensity reflections were not sufficiently downweighted and that the weights were nonlinear as a function of $(\sin \theta)/\lambda$. The final parameters and their standard devia-

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Table III. Positional and Thermal Parameters for Nonhydrogen Atoms in $Ni(DAPD)_2$ Using Unit Weights

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0.25	0.125	0.01213 (7)	0.01213 (7)	0.00046 (1)	0	0	0
N(1)	0	0.25	0.18517 (8)	0.01262 (54)	0.01205 (55)	0.00056 (3)	0.00058 (49)	0	0
C(2)	0.07835 (31)	0.11769 (32)	0.20545 (7)	0.01152 (44)	0.01285 (46)	0.00068 (3)	−0.00064 (40)	−0.00016 (9)	0.00013 (10)
C(3)	0.07866 (35)	0.11613 (35)	0.25114 (8)	0.01457 (51)	0.01597 (51)	0.00061 (3)	0.00085 (46)	−0.00023 (10)	0.00062 (12)
C(4)	0	0.25	0.27314 (12)	0.01405 (72)	0.02011 (86)	0.00052 (4)	−0.00055 (70)	0	0
C(7)	0.15469 (33)	−0.00548 (33)	0.17544 (8)	0.01438 (49)	0.01234 (46)	0.00070 (3)	0.00077 (44)	−0.00037 (10)	−0.00002 (10)
N(8)	0.13073 (27)	0.03378 (27)	0.13363 (6)	0.01332 (39)	0.01428 (40)	0.00066 (3)	0.00026 (35)	0.00004 (8)	−0.00052 (8)
O(9)	0.18760 (25)	−0.05702 (25)	0.10256 (5)	0.01974 (41)	0.01871 (39)	0.00082 (2)	0.00338 (34)	0.00018 (8)	−0.00122 (8)
C(10)	0.25178 (45)	−0.16222 (40)	0.18787 (9)	0.02726 (75)	0.01777 (60)	0.00107 (4)	0.00726 (60)	−0.00058 (14)	−0.00012 (12)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

tions as calculated using this p/c weighting scheme are listed in Tables I and II. Refinement was also carried out using unit weights and gave convergence at $R = 0.028$, $R_W = 0.025$; the estimated standard deviation for an observation of unit weight was $S = 0.93$. The final difference Fourier map showed electron densities of 0.28 e/Å^3 near the nickel atom and none larger than 0.20 e/Å^3 elsewhere. Tables III and IV list final parameters and their standard deviations for unit weight refinement.[25] The refinement using p/c weights produced positional and thermal parameters that generally differed less than 2σ from the parameters obtained using the unit weights. The only exceptions to this were in the thermal parameters β_{11} for the nickel atom which differed by 5σ and β_{11} for N(8) which differed by 3.5σ.

There are at least two sources of systematic error in the data which can be noted. First, as indirect evidence indicates, the Ni^0 form factor is undoubtedly inaccurate but was used in the absence of any experimental information about the actual electron density at the nickel atom. Another source of error is the treatment of the methyl group which was approximated by two disordered sets of methyl hydrogen atoms. A scattering factor treatment for a rotating methyl group would be more realistic.

A representation of the chelate complex is depicted in Figure 1 along with the calculated anisotropic thermal motion and selected bond distances as found using p/c statistics. The interatomic distances and angles along with their standard deviations based on the inverse matrix may be found in Table V. A stereoscopic view of the packing of the molecules in the unit cell is shown in Figure 2.

Discussion

Coordination Sphere and Ligand Geometry. There is a very noticeable closing of the several chelate angles in $Ni(DAPD)_2$ from the "expected value" of 120° for sp^2 hybridization: Ni-N(1)-C(2), 111.3 (2)°; N(1)-C(2)-C(7), 113.3 (3)°; C(2)-C(7)-N(8), 113.8 (3)°; C(7)-N(8)-Ni, 113.2 (3)°. The ligand $(DAPD)^{2-}$ does not naturally provide a geometry suitable for the small nickel(IV) ion and an interesting feature is the severe distortion that occurs on complexation in order to accommodate the nickel ion; the chelating oxime groups are pulled toward the nickel atom. Even the normally stable delocalized pyridine molecule appears significantly distorted; for example, the C(2)-N-C(2′) angle is open from 116.8[26] to 125.3 (4)°. An additional feature is that the oxime nitrogen atoms lie 0.262 (3) Å above the basal plane through the nickel atom and perpendicular to the nickel atom-pyridine nitrogen atom bond, while the nickel atom-oxime nitrogen atom bond makes an angle of 7.6 (1)° with this plane. The three nitrogen atoms from one ligand thus lie on one side of the basal plane. In summary, the geometry about nickel is octahedral, with the basal plane distorted into D_{2d} (toward tetrahedral) symmetry. Angular distortions of the chelating oxime groups [dilute C(2)-C(7)-N(8) angles] enable N(8) to approach more closely the ideal octahedral position; further distortion is presumably inhibited by angular strain in the chelating groups.

Table IV. Positional and Thermal Parameters for Hydrogen Atoms in $Ni(DAPD)_2$ Using Unit Weights

Atom	x	y	z	β
HC(3)	0.1320 (33)	0.0269 (34)	0.2654 (8)	3.36 (61)
HC(4)	0	0.25	0.3037 (12)	3.63 (85)
H(1)	0.2871[a]	−0.2192	0.1630	4.20[b]
H(2)	0.3468	−0.1315	0.2042	4.20
H(3)	0.1819	−0.2336	0.2042	4.20
H(4)	0.2566	−0.1704	0.2179	4.20
H(5)	0.1972	−0.2580	0.1767	4.20
H(6)	0.3620	−0.1558	0.1768	4.20

[a] Positional parameters were calculated for a disordered methyl group. See text. [b] Thermal parameters for disordered methyl hydrogen atoms are taken as the approximate isotropic thermal parameter of the methyl carbon atom.

Table V. Selected Interatomic Distances and Angles in $Ni(DAPD)_2$ Using p/c Weights

	Distances, Å		
Ni-N(1)	1.837 (4)	C(2)-C(7)	1.446 (5)
Ni-N(8)	1.973 (3)	C(7)-N(8)	1.324 (4)
N(1)-C(2)	1.342 (4)	N(8)-O(9)	1.257 (3)
C(2)-C(3)	1.392 (5)	C(7)-C(10)	1.482 (5)
C(3)-C(4)	1.376 (4)	HC(3)-C(3)	0.902 (28)
		HC(3)-C(4)	0.881 (41)
	Angles, degrees		
N(1)-Ni-N(8)	82.4 (1)	N(1)-C(2)-C(7)	113.3 (3)
Ni-N(1)-C(2)	117.3 (2)	C(2)-C(7)-N(8)	113.8 (3)
C(2)-N(1)-C(2′)	125.3 (4)	C(7)-N(8)-Ni	113.2 (3)
N(1)-C(2)-C(3)	117.8 (4)	C(2)-C(7)-C(10)	125.8 (3)
C(2)-C(3)-C(4)	118.7 (4)	C(10)-C(7)-N(8)	120.4 (3)
C(3)-C(4)-C(3′)	121.8 (5)	C(7)-N(8)-O(9)	123.2 (3)
		O(9)-N(8)-Ni	123.7 (2)

Table VI. Comparison of Planarity[a] of Ligand Atoms for p/c and Unit (u) Weight Refinements

Atom	$P(p/c)$,[b] Å	$P(u)$,[c] Å
Ni	0.0023 (0)	0.0006 (0)
N(1)	−0.0023 (0)	−0.0028 (0)
C(2)	0.0126 (18)	0.0099 (24)
C(3)	0.0121 (21)	0.0116 (27)
C(4)	−0.0091 (0)	−0.0078 (0)
C(7)	0.0022 (20)	0.0021 (25)
N(8)	0.0035 (16)	0.0051 (20)
O(9)	−0.0025 (15)	−0.0040 (19)
C(10)	−0.0111 (26)	−0.0103 (33)
HC(3)	0.0429 (169)	0.0170 (255)
HC(4)	−0.0114 (0)	−0.0096 (0)

[a] Plane is defined by all nonhydrogen atoms. [b] $P(p/c)$ is the perpendicular distance of the atom from the plane defined by $0.8545x + 0.5193y + 0.0025z - 1.0177 = 0$ found for $Ni(DAPD)_2$ refined with p/c weights. [c] $P(u)$ is the perpendicular distance of the atom from the plane defined by $0.8544x + 0.5195y + 0.0018z - 1.0138 = 0$ found for $Ni(DAPD)_2$ refined with unit weights.

All ligand atoms of one tridentate ligand except the methyl hydrogen atoms lie very nearly in a plane. Deviations from planarity vary up to about 0.01 Å for nonhydrogen atoms, using both methods of refinement. (See Table VI for a listing of both sets of parameters and their standard deviations.)

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(25) See paragraph at end of paper regarding supplementary material.

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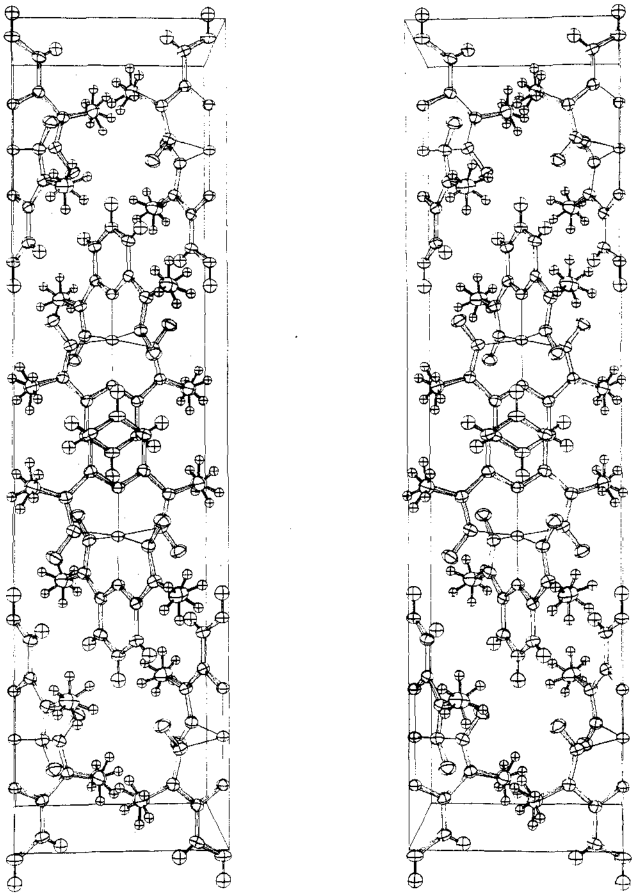

Figure 2. Stereoscopic view of crystal packing and molecular structure of bis(2,6-diacetylpyridine dioximato)nickel(IV).

The equation of the plane through one tridentate ligand and the nickel atom using the *p/c* weighting scheme refinement is $0.8545x + 0.5193y + 0.0025z - 1.0177 = 0$. The same equation using unit weight refinement is $0.8544x + 0.5195y + 0.0018z - 1.0138 = 0$.

Metal-Nitrogen Atom Coordination. In comparing the nickel-nitrogen distances of this supposedly nickel(IV) complex with those of nickel(II) compounds, we first note that for several square-planar complexes the average nitrogen to nickel(II) interatomic distance is 1.88 (4) Å[27] and the corresponding value for the approximately tetrahedral metal ion is 1.95 (1) Å.[28] Bond distances for octahedral nickel(II) are far more numerous and a perusal of the literature shows a variation of about 0.05 Å from an average value of approximately 2.10 Å. Reported octahedral bond distances with N-bonded ligands include: 2.15 (3) Å for NH_3 and 2.07 (3) Å for NCS in *trans*-diisothiocyanatotetraamminenickel(II);[29] 2.11 (4) Å for CN and 2.10 (4) Å for NH_3 in amminenickel(II) cyanide (hydrated);[30] 2.097 (2) and 2.087 (3) Å in dichlorotetrapyrazolenickel(II);[31] 2.093 (2) Å in bis(perchlorato)tetrakis(3,5-dimethylpyridine)nickel(II);[32] 2.100 (9) Å in diaquobis(L-serinato)nickel(II);[33] 2.129 (6) Å in hexakis(imidazole)nickel(II) nitrate;[34] 2.081 (2) and 2.068 (2) Å for oxime nitrogen atoms and 2.115 (2) Å for the amino atoms in bis[2,2′-iminobis(acetamidoxime)]nickel(II) chloride dihydrate;[35] and 2.124 (6) Å in tris(ethylenediamine)nickel(II) sulfate.[36] An example of one of the shorter nickel(II)-nitrogen bond distances is found in a complex, (tetrafluoroboro)tris[(2-carboxaldimino-6-pyridyl)phosphine]nickel(II) tetrafluoroborate, in which a Ni-N distance of 2.030 (8) Å has been reported.[37] The chelating group in this compound is a rigid hexadentate ligand, and it may be that the short nickel-nitrogen distance is due to the small space available for the nickel atom in the six-atom cage formed by the nitrogen atoms of this ligand. In the octahedral complex reported here, the average metal-ligand bond distance is 1.93 Å, which is 0.17 Å shorter than the value of 2.10 ± 0.05 Å for averaged octahedral distances in d^8 nickel(II) compounds, indicating that this complex does indeed contain a more highly oxidized form of nickel. The Ni(II) compound which is most analogous to $Ni(DAPD)_2$ is bis[2,2′-iminobis(acetamidoxime)]nickel(II) chloride dihydrate,[35] which has a secondary amine fragment replacing the pyridine group, and a proton on each oxime oxygen atom. In this complex, the nickel-amine nitrogen distance of 2.115 (2) Å is 0.28 Å greater than the nickel-pyridine nitrogen distance in $Ni(DAPD)_2$, the nickel-oxime nitrogen distance of 2.075 (8) Å is 0.102 Å greater than the analogous distance in $Ni(DAPD)_2$, and the average chelation bond distance is 2.088 Å, which is 0.16 Å longer than the average distance in $Ni(DAPD)_2$. *It is particularly interesting to note that, despite the difference in formal oxidation states of 2 in the nickel systems and 1 in the two cobalt hexamine complexes,*[38] *there is a similar lengthening of the metal-ligand bonds when two antibonding e_g electrons are added.* The ~0.16-Å difference in the octahedral nickel-nitrogen coordination distances may be compared with the 0.18-Å bond length difference between the d^7 Co(II) $t_{2g}{}^5e_g{}^2$ and low-spin d^6 Co(III) $t_{2g}{}^6$ hexamine systems[38] and again suggests that the antibonding character of (in this case) two e_g electrons results in a bond length increase of 0.15-0.20 Å.

Crystal Packing. The packing of the molecule in the lattice is determined largely by the pyridine-pyridine ring interactions. The two rings of closest approach are parallel and the planes in which they lie are separated by 3.326 ± 0.003 Å with the apical carbon C(4) approximately above the center of the pyridine ring of closest approach.

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Registry No. $Ni(DAPD)_2$, 41699-86-9.

Supplementary Material Available. A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or

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