

Preparation and Characterization of Metal Complexes of 2,6-Diacetylpyridine Bis(imines). Crystallographic Study of Dinitrato[2,6-diacetylpyridine bis(anil)]nickel(II)

ELMER C. ALYEA,* GEORGE FERGUSON, and RODERIC J. RESTIVO

Received March 27, 1975

AIC50230G

The synthesis and crystal and molecular structure of dinitrato[2,6-diacetylpyridine bis(anil)]nickel(II) ($C_{21}H_{19}N_3Ni(NO_3)_2$) is reported. The compound crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5 , No. 14) with $a = 11.037$ (2) Å, $b = 14.662$ (4) Å, $c = 16.039$ (3) Å, $\beta = 122.66$ (1)°, $V = 2185.0$ Å³, and $Z = 4$. Observed and calculated densities are 1.51 (1) and 1.508 g cm⁻³, respectively. All atoms, including hydrogen atoms, have been located from a single-crystal X-ray structural analysis based on counter data collected with a Hilger and Watts Y290 automated diffractometer. The structure was refined anisotropically to final discrepancy indices of $R_F = 0.040$ and $R_{wF} = 0.050$ for 2148 independent reflections (with $I > 3\sigma(I)$ representing data complete to $2\theta = 50^\circ$ (Mo $K\alpha$ radiation)). The $LNi(NO_3)_2$ complex contains a planar terdentate NNN donor set and both monodentate [Ni-O = 2.027 (5) Å] and near symmetrically bidentate [Ni-O = 2.070 (4), 2.138 (5) Å] nitrate groups. The nickel coordination is distorted octahedral with cis N-Ni-N angles, 77.85 (14) and 78.52 (15)°, distorted from 90° by the bite of the planar terdentate ligand. The Ni-N lengths are 1.958 (4) Å (equatorial) and 2.090 (4) Å (mean axial). Physical measurements indicate that similar structures are found for $LM(NO_3)_2$ ($M = Ni^{II}, Zn^{II}, Cu^{II}$); in particular, infrared bands which arise from the monodentate and bidentate nitrate groups are assigned.

Introduction

A new series of terdentate NNN donor ligands have been synthesized recently by the Schiff base condensation of 2,6-diacetylpyridine and some aromatic amines.^{1,2} Characterization of several first-row transition metal complexes of these 2,6-diacetylpyridine bis(imines) indicates that their coordinating ability is comparable with the well-known terpyridine ligand. We have now isolated some divalent metal nitrate complexes of the 2,6-diacetylpyridine bis(anil) ligand ($L = C_{21}H_{19}N_3$) that display a variety of nitrate bonding types.³ Of special interest are the complexes $LM(NO_3)_2$ ($M = Ni^{II}, Zn^{II}, Cu^{II}$) since six-coordination might be attained by the presence of both monodentate and bidentate nitrate groups. The existence of a few nickel species of this type has been suggested on the basis of infrared data.⁴ We report here the single-crystal X-ray analysis of the structure of $LNi(NO_3)_2$ as well as some physical measurements on related nitrate complexes. A preliminary account of this research has been presented.⁵

Experimental Section

Preparation of the Ni, Cu, and Zn Complexes. Only the details for $LCu(NO_3)_2$ are presented here, as the divalent Ni and Zn nitrate complexes of 2,6-diacetylpyridine bis(anil) were prepared in an analogous fashion.

Dinitrato[2,6-diacetylpyridine bis(anil)]copper(II). The Schiff base ligand (0.31 g, 1.0 mmol) was added to an anhydrous ethanol (ca. 50 ml) solution of copper(II) nitrate trihydrate (0.24 g, 1.0 mmol) previously dehydrated by refluxing with 2.5 ml of dimethoxypropane. The green solution was refluxed briefly, filtered, evaporated to ca. 15 ml, and then cooled to give the product as a green powder; yield 0.37 g (74%). Anal. Calcd for $C_{21}H_{19}N_3O_6Cu$: C, 50.4; H, 3.83; N, 14.0. Found: C, 50.5; H, 3.86; N, 14.1. The complex is readily soluble in dichloromethane and nitromethane.

Dinitrato[2,6-diacetylpyridine bis(anil)]nickel(II). This complex was prepared similarly in 59% yield as a dark red-brown crystalline solid. Anal. Calcd for $C_{21}H_{19}N_3O_6Ni$: C, 50.8; H, 3.87; N, 14.1. Found: C, 51.4; H, 3.92; N, 13.6.

Dinitrato[2,6-diacetylpyridine bis(anil)]zinc(II) Monohydrate. This complex was prepared in a similar manner except that zinc(II) nitrate hexahydrate was not dehydrated. A pale yellow crystalline solid was obtained in 65% yield. The product was recrystallized from ethanol-nitromethane, collected on a frit, washed with ethanol and hexane, and air-dried. Anal. Calcd for $C_{21}H_{21}N_3O_7Zn$: C, 48.4, H, 4.07; N, 13.4. Found: C, 48.3; H, 3.94, N, 13.4.

Spectra. Infrared spectra were recorded in the range 1700–1200 cm⁻¹ using a Beckman IR-12 and mulls in Nujol and halocarbon between KBr plates. The NMR spectrum for the zinc complex was recorded in nitromethane at room temperature using TMS as internal

reference and a Varian A-60A spectrometer.

Crystal Structure Analysis. Dark red-brown parallelepiped crystals of the $LNi(NO_3)_2$ compound, suitable for X-ray analysis, were obtained by slow evaporation from ethanol-nitromethane. Precession and Weissenberg photographs indicated a monoclinic space group with systematic absences of $h0l$ when l is odd and of $0k0$ when k is odd; these conditions define the space group as $P2_1/c$ (C_{2h}^5 , No. 14). The unit cell parameters $a = 11.037$ (2) Å, $b = 14.662$ (4) Å, $c = 16.039$ (3) Å, and $\beta = 122.66$ (1)° were obtained by a least-squares fit of the θ values of 12 reflections measured on a Hilger and Watts diffractometer using a crystal elongated along the b axis with approximate dimensions $0.13 \times 0.20 \times 0.11$ mm. The unit cell volume V , based on these dimensions, is 2185 Å³. A density of 1.508 g cm⁻³ was calculated for $Z = 4$ and this agreed with that of 1.51 (1) g cm⁻³ measured by flotation of several crystals in chlorobenzene-carbon tetrachloride.

Data were collected at room temperature (22°) with a Hilger and Watts Y290 computer-controlled diffractometer equipped with a scintillation counter and a pulse height analyzer, with graphite-monochromated Mo $K\alpha$ radiation (λ 0.71069 Å). A θ - 2θ scanning technique was used to collect a unique data set to a maximum of $\theta = 25^\circ$; a rate of 60 steps of 0.01° with a 1-sec count at each step was used. Zirconium foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded 10,000 counts/sec. Background measurements (b_1, b_2) of 15-sec duration were made at the beginning and end of each scan with the counter stationary. The intensity of two standard reflections, measured at 100-reflection intervals, dropped by approximately 5% over the period of data collection and this was corrected for by application of linear scale factors.

A total of 3839 intensity maxima were collected and corrected for Lorentz and polarization effects [$1/Lp = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_s$ and $2\theta_m$ are the angles at the sample crystal and monochromator, respectively]. The absorption corrections were not considered necessary for a crystal of the size used to collect data. With an absorption coefficient $\mu = 9.39$ cm⁻¹ for Mo $K\alpha$ radiation, transmission coefficients of the order 88–90% would arise. Standard deviations were assigned to intensity values according to $\sigma(I) = (S + B)^{1/2}$ where S is scan count and $B = 4(b_1 + b_2)$. Of the 3839 measured reflections, 2148 with $I > 3\sigma(I)$ were used throughout the structural solution and refinement.

An estimate of the overall scale factor was obtained using Wilson's method. Approximate coordinates for the unique nickel atom were readily obtained from a sharpened Patterson map.⁶ A Fourier synthesis based on the nickel phases revealed the positions of all carbon, nitrogen, and oxygen atoms.

Isotropic refinement by full-matrix least squares with unit weights was initiated using the atomic scattering functions of Cromer and Mann⁷ for nickel, carbon, nitrogen, and oxygen. All atoms were treated as neutral species, and both real and imaginary parts of the anomalous dispersion correction were applied to nickel.⁸ Three cycles

Table I. Final Positional and Thermal^a Parameters for LNi(NO₃)₂

Atom	x	y	z
Ni	0.38979 (6)	0.17873 (4)	0.05919 (4)
O(41)	0.5267 (4)	0.1574 (2)	0.0047 (3)
O(42)	0.5686 (4)	0.2615 (2)	0.1116 (2)
O(43)	0.7094 (4)	0.2496 (4)	0.0552 (3)
O(51)	0.3331 (4)	0.2431 (3)	0.1451 (3)
O(52)	0.1838 (5)	0.3112 (3)	0.1692 (4)
O(53)	0.1057 (5)	0.2092 (3)	0.0580 (4)
N(1)	0.2420 (4)	0.0854 (3)	-0.0128 (3)
N(2)	0.4783 (4)	0.0660 (3)	0.1535 (3)
N(3)	0.2412 (4)	0.2488 (3)	-0.0694 (3)
N(4)	0.6056 (5)	0.2235 (3)	0.0571 (3)
N(5)	0.2044 (5)	0.2547 (3)	0.1236 (3)
C(2)	0.2597 (5)	0.0036 (3)	0.0281 (3)
C(3)	0.1534 (6)	-0.0622 (4)	-0.0190 (4)
C(4)	0.0305 (6)	-0.0399 (4)	-0.1103 (4)
C(5)	0.0152 (6)	0.0457 (4)	-0.1510 (4)
C(6)	0.1240 (5)	0.1089 (4)	-0.0996 (4)
C(7)	0.4001 (6)	-0.0062 (3)	0.1256 (4)
C(8)	0.4336 (7)	-0.0941 (3)	0.1804 (4)
C(9)	0.1266 (5)	0.2047 (3)	-0.1300 (4)
C(10)	0.0012 (6)	0.2398 (4)	-0.2241 (4)
C(21)	0.6201 (5)	0.0708 (3)	0.2424 (3)
C(22)	0.6456 (6)	0.1402 (4)	0.3083 (4)
C(23)	0.7829 (6)	0.1498 (4)	0.3925 (4)
C(24)	0.8918 (7)	0.0939 (4)	0.4086 (4)
C(25)	0.8657 (7)	0.0267 (4)	0.3412 (5)
C(26)	0.7296 (6)	0.0144 (4)	0.2568 (4)
C(31)	0.2669 (5)	0.3403 (3)	-0.0893 (3)
C(32)	0.3113 (6)	0.3527 (4)	-0.1537 (4)
C(33)	0.3452 (7)	0.4413 (4)	-0.1677 (4)
C(34)	0.3332 (6)	0.5139 (4)	-0.1194 (4)
C(35)	0.2897 (6)	0.4995 (4)	-0.0553 (4)
C(36)	0.2589 (6)	0.4129 (4)	-0.0372 (4)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni	4.26 (3)	3.82 (3)	4.18 (3)	-0.44 (3)	1.76 (2)	0.03 (3)
O(41)	6.06 (23)	5.80 (23)	6.12 (21)	-0.74 (18)	3.18 (19)	-0.51 (18)
O(42)	5.31 (21)	4.62 (20)	5.48 (19)	-0.73 (17)	2.63 (17)	-0.25 (16)
O(43)	6.04 (27)	9.73 (32)	10.37 (33)	-1.07 (24)	4.98 (26)	0.50 (27)
O(51)	5.51 (23)	6.75 (24)	5.51 (21)	0.48 (19)	2.68 (10)	-0.79 (19)
O(52)	10.43 (35)	7.97 (30)	13.13 (40)	1.11 (28)	7.59 (33)	-2.75 (30)
O(53)	7.04 (27)	10.28 (34)	11.32 (35)	-2.31 (26)	5.78 (27)	-2.75 (29)
N(1)	4.81 (23)	4.30 (24)	4.71 (23)	-0.66 (20)	2.25 (20)	-0.22 (19)
N(2)	5.20 (24)	3.75 (22)	4.76 (22)	0.15 (19)	2.65 (20)	-0.27 (18)
N(3)	4.63 (23)	4.34 (22)	4.20 (21)	-0.51 (19)	1.98 (18)	0.31 (18)
N(4)	4.46 (24)	5.89 (27)	5.76 (26)	0.09 (21)	2.21 (22)	0.98 (22)
N(5)	6.93 (30)	4.63 (25)	6.56 (27)	0.21 (22)	4.22 (25)	0.64 (21)
C(2)	5.26 (30)	3.99 (27)	5.15 (29)	-0.35 (23)	2.97 (25)	-0.59 (23)
C(3)	7.87 (40)	4.72 (33)	7.05 (36)	-2.09 (29)	4.02 (33)	-1.56 (29)
C(4)	6.99 (38)	5.73 (36)	7.27 (38)	-2.55 (30)	3.45 (33)	-1.87 (30)
C(5)	5.33 (33)	6.47 (37)	5.56 (32)	-1.50 (29)	2.14 (28)	-1.58 (29)
C(6)	4.75 (30)	5.62 (32)	4.90 (29)	-0.89 (26)	2.34 (25)	-0.92 (25)
C(7)	6.65 (34)	3.82 (27)	5.23 (29)	-0.01 (25)	3.76 (27)	-0.29 (23)
C(8)	8.88 (43)	3.72 (29)	6.78 (36)	0.56 (29)	4.36 (34)	0.94 (27)
C(9)	4.46 (28)	5.65 (32)	4.61 (28)	-0.21 (24)	2.30 (24)	0.06 (24)
C(10)	5.00 (31)	7.91 (41)	4.58 (29)	0.16 (30)	1.19 (25)	0.67 (29)
C(21)	5.30 (29)	4.10 (28)	4.46 (27)	0.18 (23)	2.24 (24)	1.25 (22)
C(22)	6.11 (34)	5.51 (31)	5.09 (29)	0.17 (28)	2.87 (27)	-0.03 (26)
C(23)	6.34 (36)	7.62 (40)	5.26 (31)	-1.20 (31)	2.56 (29)	-0.18 (29)
C(24)	6.21 (37)	7.52 (41)	6.37 (41)	0.24 (33)	1.94 (31)	0.73 (32)
C(25)	6.32 (41)	7.43 (42)	8.83 (46)	2.01 (34)	2.38 (37)	1.15 (36)
C(26)	6.76 (38)	5.75 (35)	6.41 (34)	1.06 (30)	2.99 (31)	-0.34 (29)
C(31)	3.66 (25)	4.72 (31)	4.01 (24)	0.36 (22)	1.20 (21)	0.93 (21)
C(32)	7.70 (38)	5.43 (33)	5.96 (34)	0.23 (29)	3.95 (31)	0.23 (27)
C(33)	8.26 (42)	6.75 (38)	7.53 (39)	0.60 (33)	4.89 (35)	2.36 (32)
C(34)	5.21 (32)	5.58 (34)	6.58 (35)	0.07 (27)	1.84 (28)	1.83 (28)
C(35)	6.66 (37)	5.24 (33)	7.06 (37)	0.25 (29)	2.59 (32)	-0.30 (29)
C(36)	6.83 (37)	5.94 (36)	6.47 (35)	-0.27 (29)	4.23 (31)	-0.29 (28)

^a The thermal parameters U_{ij} ($\text{Å}^2 \times 10^2$) are terms in the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

of refinement reduced $R_F = \sum |F_o| - |F_c| / \sum |F_o|$ to 0.081.

A weighting scheme was then chosen such that $w^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$ with $p = 10^{-3}$, and an analysis of variance indicated that $\sum w\Delta^2$ was independent of $|F_o|$ and $(\sin \theta)/\lambda$. Two cycles of refinement by block-diagonal least squares with anisotropic thermal parameters

for all atoms reduced R_F to 0.055 and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$, the function minimized, to 0.063. A difference Fourier map, computed at this stage, revealed electron density maxima in chemically reasonable positions for all the hydrogen atoms; these were then allowed for (in chemically expected positions with isotropic U

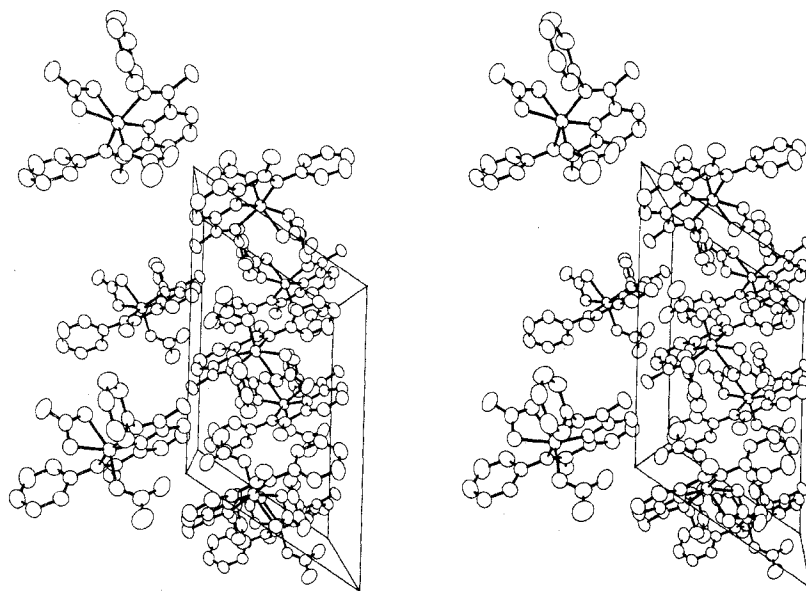


Figure 1. Stereoview of the molecular packing diagram of dinitrato[2,6-diacetylpyridine bis(anil)]nickel(II). The hydrogen atoms have been omitted for clarity.

Table II. Positional Parameters for the Hydrogen Atoms of $\text{LNi}(\text{NO}_3)_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(3)	0.166	-0.128	0.014
H(4)	-0.053	-0.090	-0.148
H(5)	-0.081	0.064	-0.220
H(22)	0.560	0.185	0.294
H(23)	0.804	0.202	0.445
H(24)	0.996	0.101	0.474
H(25)	0.956	-0.014	0.354
H(26)	0.708	-0.038	0.204
H(32)	0.319	0.297	-0.194
H(33)	0.383	0.453	-0.216
H(34)	0.358	0.581	-0.131
H(35)	0.281	0.557	-0.018
H(36)	0.228	0.403	0.015
H(81)	0.352	-0.108	0.195
H(82)	0.432	-0.147	0.135
H(83)	0.532	-0.102	0.250
H(101)	-0.016	0.197	-0.283
H(102)	-0.092	0.234	-0.220
H(103)	0.000	0.307	-0.247

values of 0.063 \AA^2 and scattering factors from ref 9) but not refined in subsequent calculations. Two additional refinement cycles converged to $R_F = 0.040$ and $R_{wF} = 0.050$ for 2148 observed reflections; the overall R_F for the entire set of 3839 reflections is 0.075. The standard deviation of an observation of unit weight is 0.99 and a final difference Fourier showed no significant features. A list of observed and calculated structure factors is available.¹⁰

Final positional and thermal parameters for the nonhydrogen atoms are in Table I; the calculated positions of the hydrogen atoms are in Table II.

Discussion of the Structure

Interatomic distances and angles with their estimated standard deviations included in the parentheses are shown in Table III. The crystal structure consists of monomeric units of the $\text{LNi}(\text{NO}_3)_2$ complex separated by normal van der Waals distances (Figure 1); there are no abnormally close contacts.

A view of the molecule is given in Figure 2; the central nickel atom is hexacoordinated to the NNN terdentate ligand and two nitrate groups. The geometry about the nickel atom is best described as distorted octahedral with the $\text{N}(1)\text{-Ni-N}(2)$ and $\text{N}(1)\text{-Ni-N}(3)$ angles, $77.84(12)$ and $78.52(15)^\circ$, respectively, distorted from 90° by the bite of the terdentate ligand. The plane (Table IV) formed by atoms $\text{N}(1)$, Ni ,

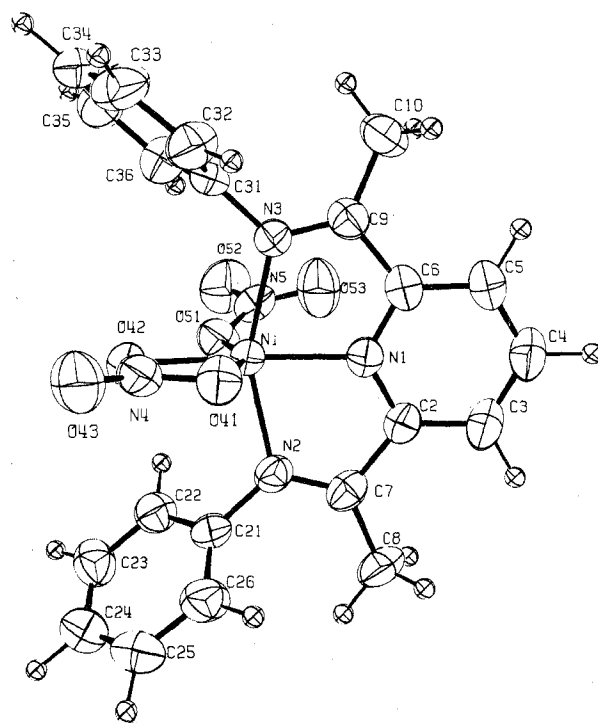


Figure 2. Perspective view with 50% probability ellipsoids of dinitrato[2,6-diacetylpyridine bis(anil)]nickel(II) showing the molecular geometry and atomic numbering.

$\text{O}(41)$, and $\text{O}(42)$ makes a dihedral angle of 89.9° with the terdentate NNN donor set. The terminal nickel-nitrogen bond distances of the NNN terdentate donor (mean of $\text{Ni-N}(2)$ and $\text{Ni-N}(3)$, $2.090(4) \text{ \AA}$) are somewhat longer than the central $\text{Ni-N}(1)$ bond length ($1.958(4) \text{ \AA}$); an exactly analogous situation is found in metal terpyridine complexes (e.g., M-N differences of 0.078 \AA for Ga ,^{12a} 0.08 \AA for Sn ,^{12b} 0.12 \AA for Zn ,^{12c} and $0.123, 0.262 \text{ \AA}$ for Cu^{12d} complexes of terpyridine have been reported).

In this nickel complex, with one nitrate group monodentate and the other bidentate, the nickel-oxygen distances to the bidentate nitrate group ($\text{Ni-O}(41) = 2.138(5) \text{ \AA}$ and $\text{Ni-O}(42) = 2.070(4) \text{ \AA}$), although significantly different, indicate that this group is nearly symmetrically coordinated.

Table III. Interatomic Distances (Å) and Angles (deg) for $\text{LNi}(\text{NO}_3)_2$

(a) Distances			
Ni-O(41)	2.138 (5)	C(2)-C(7)	1.501 (6)
Ni-O(42)	2.070 (4)	C(6)-C(9)	1.492 (8)
Ni-O(51)	2.027 (5)	C(7)-C(8)	1.490 (7)
Ni-N(1)	1.958 (4)	C(9)-C(10)	1.484 (6)
Ni-N(2)	2.093 (4)	C(2)-C(3)	1.387 (7)
Ni-N(3)	2.086 (3)	C(3)-C(4)	1.395 (7)
N(4)-O(41)	1.271 (5)	C(4)-C(5)	1.382 (9)
N(4)-O(42)	1.276 (8)	C(5)-C(6)	1.383 (7)
N(5)-O(51)	1.279 (7)	C(21)-C(22)	1.382 (8)
N(4)-O(43)	1.223 (8)	C(22)-C(23)	1.389 (6)
N(5)-O(52)	1.205 (8)	C(23)-C(24)	1.360 (10)
N(5)-O(53)	1.225 (6)	C(24)-C(25)	1.373 (10)
N(1)-C(2)	1.329 (5)	C(25)-C(26)	1.387 (7)
N(1)-C(6)	1.340 (5)	C(21)-C(26)	1.378 (9)
N(2)-C(7)	1.283 (6)	C(31)-C(32)	1.374 (10)
N(3)-C(9)	1.279 (6)	C(32)-C(33)	1.402 (9)
N(2)-C(21)	1.442 (5)	C(33)-C(34)	1.364 (10)
N(3)-C(31)	1.442 (7)	C(34)-C(35)	1.364 (12)
		C(35)-C(36)	1.385 (9)
		C(31)-C(36)	1.385 (9)
(b) Angles			
N(1)-Ni-N(2)	77.84 (14)	N(1)-Ni-O(41)	101.78 (19)
N(1)-Ni-N(3)	78.52 (15)	N(2)-Ni-O(41)	91.27 (18)
N(3)-Ni-O(41)	91.14 (18)	N(2)-Ni-O(42)	101.46 (14)
O(41)-Ni-O(42)	61.48 (15)	N(3)-Ni-O(42)	100.45 (15)
O(42)-Ni-O(51)	91.58 (16)	N(1)-Ni-O(51)	105.16 (20)
N(2)-Ni-O(51)	94.10 (18)	N(3)-Ni-O(51)	94.10 (18)
O(41)-N(4)-O(43)	122.6 (6)	C(6)-N(1)-C(2)	123.1 (4)
O(41)-N(4)-O(42)	115.3 (5)	N(1)-C(2)-C(3)	120.2 (4)
O(42)-N(4)-O(43)	122.0 (4)	C(2)-C(3)-C(4)	117.8 (5)
O(51)-N(5)-O(52)	118.3 (4)	C(3)-C(4)-C(5)	120.7 (5)
O(51)-N(5)-O(53)	120.1 (6)	C(4)-C(5)-C(6)	118.8 (4)
O(52)-N(5)-O(53)	121.6 (6)	C(5)-C(6)-N(1)	119.4 (5)
Ni-O(41)-N(4)	90.1 (4)	C(21)-C(22)-C(23)	118.9 (6)
Ni-O(42)-N(4)	93.1 (3)	C(22)-C(23)-C(24)	120.8 (6)
Ni-O(51)-N(5)	125.7 (3)	C(23)-C(24)-C(25)	119.7 (5)
Ni-N(2)-C(7)	115.8 (3)	C(24)-C(25)-C(26)	121.2 (7)
Ni-N(3)-C(9)	115.4 (3)	C(25)-C(26)-C(21)	118.3 (6)
Ni-N(2)-C(21)	120.7 (3)	C(26)-C(21)-C(22)	121.0 (4)
Ni-N(3)-C(31)	122.3 (2)	C(31)-C(32)-C(33)	118.5 (6)
C(7)-N(2)-C(21)	123.5 (4)	C(32)-C(33)-C(34)	121.1 (8)
C(9)-N(3)-C(31)	122.3 (4)	C(33)-C(34)-C(35)	119.2 (6)
Ni-N(1)-C(2)	119.0 (3)	C(34)-C(35)-C(36)	121.7 (6)
Ni-N(1)-C(6)	117.8 (3)	C(35)-C(36)-C(31)	118.4 (7)
N(2)-C(7)-C(2)	114.0 (4)	C(36)-C(31)-C(32)	121.1 (5)
C(2)-C(7)-C(8)	119.0 (4)	N(3)-C(9)-C(6)	114.4 (4)
N(2)-C(7)-C(8)	127.0 (4)	N(3)-C(9)-C(10)	126.4 (5)
		C(6)-C(9)-C(10)	119.1 (4)

The monodentate nitrate group possesses a coordinated Ni-O(51) bond length, 2.027 (5) Å, which is substantially shorter than the Ni-O distances of the more weakly bonded bidentate nitrate group. The complex $\text{VO}(\text{NO}_3)_3\text{CH}_3\text{CN}^{11}$ is the only other complex which has been characterized structurally as containing both monodentate and almost symmetrically bidentate (V-O bond lengths of 2.04, 2.06 (2) and 2.02, 2.07 (2) Å) nitrate groups.

The degree of symmetrical coordination of the bidentate nitrate group is reflected in the Ni-O(41)-N(4) and Ni-O(42)-N(4) angles, 90.1 (4) and 93.1 (4)°, respectively, as well as the N(4)-O(41) and N(4)-O(42) bond lengths of 1.271 (5) and 1.276 (8) Å which are not significantly different. The Ni-O(41) and Ni-O(42) bond length difference (0.068 Å) is small in comparison to the Co-O bond length differences (0.104 Å) found in $(\text{C}_5\text{H}_5\text{N})_3\text{Co}(\text{NO}_3)_2$ whose bidentate nitrate group exhibits the least amount of asymmetry in the series of related complexes $(\text{C}_5\text{H}_5\text{N})_3\text{M}(\text{NO}_3)_2$ (M = Co^{II}, Cu^{II}, Zn^{II}).¹³

The effect of coordination is discernible in the nitrate groups with the mean noncoordinated N-O bond length, 1.218 (11) Å, shorter than the mean coordinated N-O length, 1.275 (4)

Å. In the monodentate NO₃ group the uncoordinated N-O distances differ by 2-3σ; such variation is not uncommon.³ There is no clear correlation between the Ni-O distances and the relevant O-N distances, although one would, a priori, expect it. Thus our results would appear to be typical of what has appeared in the literature.^{3,13} The O-N-O angle is contracted on bidentate coordination¹¹ [O(41)-N(4)-O(42) = 115.3 (5)°] while the monodentate nitrate group has less distortion from 120° (Table III).

Deviations from a weighted least-squares plane (Table IV) indicate that the NNN terdentate donor set is essentially planar; the two phenyl rings, C(21)---C(26) and C(31)---C(36), of the ligand are asymmetrically twisted out of this plane and make dihedral angles of 58.6 and 103.0°, respectively, with it. This is effectively to minimize steric interactions between phenyl ortho C-H groups and the remainder of the complex. The mean N-C distance in the pyridine ring is 1.335 (8) Å whereas the N(2)-C(7) and N(3)-C(9) distances, mean 1.281 (3) Å, are much shorter, consistent with the double-bond character of these azomethine bonds. The other distances within the molecule are in accord with expected values, e.g., mean C-C aromatic 1.379 (13) Å, C-C(pyridine) 1.387 (6)

Table IV. Weighted Least-Squares Planes^{a, b}

(1) Plane Defined by N(1), N(2), N(3), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)
Equation: $0.820X - 0.320Y - 0.475Z - 1.949 = 0$

Distance to Plane, Å					
N(1)	0.014 (5)	C(4)	0.003 (7)	C(9)	0.005 (6)
N(2)	-0.003 (5)	C(5)	0.014 (7)	C(10)	-0.034 (7)
N(3)	0.006 (5)	C(6)	0.009 (6)	C(21)	0.055 (6)
C(2)	0.004 (6)	C(7)	0.004 (6)	C(31)	0.078 (6)
C(3)	-0.013 (7)	C(8)	-0.021 (7)		

(2) Plane Defined by C(21), C(22), C(23), C(24), C(25), C(26)
Equation: $0.590X + 0.632Y - 0.503Z - 1.822 = 0$

Distance to Plane, Å					
C(21)	-0.012 (5)	C(23)	-0.005 (7)	C(25)	0.004 (7)
C(22)	0.014 (6)	C(24)	-0.005 (7)	C(26)	0.008 (7)

(3) Plane Defined by C(31), C(32), C(33), C(34), C(35), C(36)
Equation: $-0.653X + 0.134Y - 0.745Z + 0.873 = 0$

Distance to Plane, Å					
C(31)	0.011 (5)	C(33)	-0.011 (7)	C(35)	0.009 (7)
C(32)	-0.002 (7)	C(34)	0.006 (6)	C(36)	-0.019 (7)

(4) Plane Defined by Ni, O(41), O(42), N(1)
Equation: $-0.172X + 0.650Y - 0.740Z - 0.459 = 0$

Distance to Plane, Å					
Ni	-0.0001 (6)	O(42)	0.003 (3)	O(51)	-0.010 (4)
O(41)	-0.001 (4)	N(1)	0.004 (4)		

^a The orthogonal vectors X , Y , and Z are related to the unit cell vectors a , b , and c as follows: X is along a , Y is along b , and Z is along c^* . ^b Dihedral angle between planes 1 and 2 is 58.6° , that between planes 1 and 3 is 103.0° , and that between planes 1 and 4 is 89.9° .

Å , C(sp²)-C(methyl) 1.487 (6) Å, and C(sp²)(aromatic)-C(sp²) 1.497 (7) Å.

Structures of LM(NO₃)₂ Complexes. The present X-ray structural determination of the LNi(NO₃)₂ complex verifies the expectation of a distorted octahedral geometry involving both unidentate and bidentate nitrate groups based on magnetic moment, conductivity, and infrared and electronic spectral measurements.⁵ Discussion of criteria to confirm the terdentate behavior of 2,6-diacetylpyridine bis(anil) and the existence of two types of nitrate groups in the same complex is now worthwhile.

The infrared bands observed for the NNN donor ligand near 1600 cm⁻¹ that are associated with the -C=N- linkage occur at 1625 cm⁻¹ (medium) and 1590 cm⁻¹ (strong) for LNi(NO₃)₂. This two-band pattern thus appears to be related to the Schiff base ligand acting as a terdentate and is indeed typical of the infrared spectra of all LMX₂ and related (ML₂)(BF₄)₂ complexes that we have studied to date.^{1,2} In the case of LZnX₂ complexes, the occurrence of the resonance due to the methyl hydrogens in the NMR spectra as a singlet (downfield relative to the uncoordinated ligand) is also indicative of terdentate behavior. For LZn(NO₃)₂·H₂O the methyl resonance was observed at 2.63 ppm (δ) as compared to 2.40 ppm (δ) for the free ligand.

Criteria for identifying the mode of coordination of nitrate groups on the basis of vibrational spectra have been discussed.³ While the best means of distinguishing between monodentate and bidentate coordination of the nitrate group appears to be a comparison of the relative intensities of the three highest frequency Raman shifts of the nitrate fundamentals, together with their depolarization ratios, application of this criterion is difficult for a species containing both bonding types. At the same time, attempts to record the Raman spectrum of LNi(NO₃)₂ have failed due to decomposition of the sample by the laser beam. Several workers⁴ have suggested previously the existence of nickel complexes containing both monodentate and bidentate nitrate groups from analysis of infrared bands

Table V. Nitrate Stretching Vibrations for LM(NO₃)₂

LNi(NO ₃) ₂	LZn(NO ₃) ₂ ·H ₂ O	LCu(NO ₃) ₂
1512 sh	1485 vs, br	1490
1502 s	1430 w	1453 w
1455 vs	1305 vs	1418 s, br
1298 vs	1290 vs	1310 sh
1272 vs		1290 vs

in the 1200–1500-cm⁻¹ region attributable to the nitrate ion. These bands arise as a result of splitting of the asymmetric N–O stretching vibration (ν_3 ca. 1370 cm⁻¹ in ionic nitrates of D_{3h} symmetry) into two components by the lower symmetry. The magnitude of this splitting is greater for the bidentate than for the monodentate nitrate group, and peaks observed at ca. 1270 and 1500 cm⁻¹ and ca. 1300 and 1450 cm⁻¹ were assigned to the bidentate and monodentate nitrate groups, respectively, by the earlier workers. The analogous bands in the infrared spectra of LM(NO₃)₂ (M = Ni^{II}, Zn^{II}, Cu^{II}) in the 1200–1500 cm⁻¹ region are given in Table V. The similarity of the infrared spectra of the zinc and copper derivatives and those reported earlier⁴ for other nickel nitrate complexes to the infrared spectrum of LNi(NO₃)₂ gives credence to the assignment of very similar structures to these complexes. The degree of asymmetry of the bidentate nitrate group in these complexes cannot be established from the spectroscopic data but will be ascertained by crystallographic studies being undertaken in our laboratory.^{5b}

Acknowledgment. The assistance of Dr. P. H. Merrell, Bowdoin College, in obtaining crystals and vibrational spectra is gratefully acknowledged. This work was supported primarily by grants from the National Research Council of Canada (to G.F. and E.C.A.).

Registry No. LNi(NO₃)₂, 55853-48-0; LZn(NO₃)₂, 55853-49-1; LCu(NO₃)₂, 55853-50-4.

Supplementary Material Available. A listing of 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 microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50230G-10-75.

References and Notes

- (1) E. C. Alyea and P. H. Merrell, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 535 (1974).
- (2) E. C. Alyea and P. H. Merrell, Abstracts, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 9–13, 1974, No. INOR 103.
- (3) C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev. Chem. Soc.*, **25**, 289 (1971).
- (4) (a) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965); (b) L. M. Vallarino, W. E. Hill, and J. V. Quagliano, *ibid.*, **4**, 1599 (1965); (c) R. V. Biagetti and H. M. Haendler, *ibid.*, **5**, 383 (1966); (d) L. Sacconi, I. Bertini, and R. Morassi, *ibid.*, **6**, 1548 (1967); (e) L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc. A*, 1510 (1968).
- (5) (a) E. C. Alyea, G. Ferguson, R. J. Restivo, and P. H. Merrell, *J. Chem. Soc., Chem. Commun.*, 269 (1975); (b) R. J. Restivo, G. Ferguson, and E. C. Alyea, Abstracts, 25th Anniversary Meeting of the American Crystallographic Association, Charlottesville, Va., March 9–13, 1975, No. J12.
- (6) A locally modified version of DATCOS from the X-ray 72 system was used for data handling on the IBM 370/155 computer. Stewart's X-Ray 72 system and Johnson's ORTEP II thermal ellipsoid plotting program were used for all other calculations.
- (7) D. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (8) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
- (9) R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1964).
- (10) Supplementary material.
- (11) F. W. B. Einstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, **10**, 678 (1971).
- (12) (a) G. Beran A. J. Carty, H. A. Patel, and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 22 (1970); (b) F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968); (c) F. W. B. Einstein and B. R. Penfold,