rangement following the isomerization will be given in a subsequent article describing the isomerization of $[Co(NH_3)_5ONO]Cl_2$.[4]

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Supplementary Material Available: Listings of structure factor amplitudes for products I–IV (25 pages). Ordering information is given on any current masthead page.

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A Short Intramolecular Hydrogen Bond: Crystal Structure of a Tetradentate α-Amine Oxime Complex of Palladium(II)

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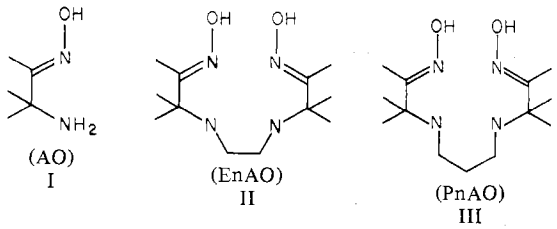
The crystal structure of [*N,N'*-(1,3-propanediyl)bis(2-amino-2-methyl-3-butanone oximato)]palladium(II) nitrate, $[Pd(PnAO\text{-}H)](NO_3)$, $[Pd(C_{13}H_{27}N_4O_2)]NO_3$, has been determined from three-dimensional X-ray diffraction counter data. Unit cell dimensions are a = 11.0424 (5), b = 12.9114 (5), and c = 12.5871 (7) Å. The density of 1.65 g/cm^3 calculated for four formula units per unit cell agrees with the flotation density of 1.66 g/cm^3. The space group is $P2_12_12_1$. A full-matrix least-squares refinement with 2838 independent reflections gave a final $R(F^2)$ value of 0.050. The structure consists of discrete, nearly square-planar palladium(II) complex cations and nitrate ions. A network of hydrogen bonding between amine nitrogens of the cation and oxygens of nitrate stabilizes the crystal structure. The steric requirements of the tetradentate PnAO are quite similar to two-coordinated bidentate AO ligands ($C_5H_{12}N_2O$), and a propylene bridge does not impose any significant constraint on the coordination geometry. Similarly, the size of the metal ion in going from palladium(II) to platinum(II) does not change the molecular parameters because of lanthanide contraction in the case of platinum(II). The average Pd–N(amine) and Pd–N(oxime) distances are 2.040 (4) and 1.969 (4) Å, respectively. These distances are quite similar to the comparable distances in related platinum(II) complexes. The short intramolecular O(1)···O(2) hydrogen bond (2.474 (5) Å) is apparently quite asymmetric and is equal to the corresponding bond in platinum(II) complexes, but significantly (0.05 Å) longer than that observed in the case of nickel(II) complexes. Other important average bond distances are N–O = 1.352 (5), C–N(oxime) = 1.278 (6), and C–N(amine) = 1.512 (6) Å.

Introduction

Several metal complexes of α-amine oxime ligands (I–III)



have been studied by X-ray and neutron diffraction to understand the effects of O···O distance and of crystallographic environment on the hydrogen atom position and the associated potential function. In these complexes it is possible to obtain a wide variation in O···O distance by changing the size of the metal ion and by varying the steric requirements of the ligand in the square plane about the metal from least constrained AO to the most constrained EnAO. The relatively small nickel(II) and cobalt(III) ions exhibit the shortest distances of 2.40–2.42 Å with the unconstrained AO ligand,[1-3] while the same ligand gives a longer (2.47 Å) distance with platinum(II).[4,5] Introduction of an ethylene bridge (EnAO) opposite the hydrogen bond increases the O···O distance from 2.42 Å in $[Ni(AO)_2\text{-}H]^{+2}$ to 2.47 Å in $[Ni(EnAO\text{-}H)]^+$.[6,7] A still longer distance (2.69 Å) is found with relatively larger copper(II) ions in the dimeric copper–EnAO complex.[8] A propylene bridge (PnAO) instead of an ethylene bridge does not impose too much constraint relative to AO, and only intermediate distances of 2.46 and 2.43 Å are found in square-pyramidal $[Cu(PnAO\text{-}H)ReO_4]$[9] and near-octahedral $[Co(PnAO\text{-}H)(NO_2)_2]$.[10] Thus, it is clear that a range of O···O distances from 2.40 to 2.70 Å could be obtained either by changing the steric requirements of the ligand or by changing the size of

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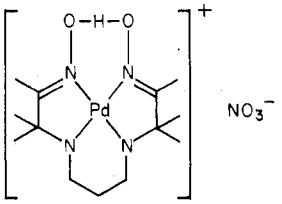
the metal ion. The variation of the potential function for the hydrogen bond in this range should be quite large.

So far the structural studies have been done either on the first-row transition-metal complexes or on platinum(II) complexes, and no second-row transition-metal complex has been investigated. The present study reports the structure of IV in order to examine the effect of the Pd(II) ion on the O···O



IV

distance. The results would indicate a link between smaller first-row transition-metal complexes and larger platinum(II) complexes particularly when variation in O···O distance is considered a function of the metal ion size. A comparison of the bond distances and angles with those of the platinum(II) complexes also provides for an examination of the lanthanide contraction effect.

Experimental Section

A. Crystal Preparation. Colorless crystals of $[Pd(PNAO\text{-}H)]NO_3$ were obtained by refluxing equimolar methanol solutions of $Pd(NO_3)_2 \cdot H_2O$ (Apache Chemicals) and PnAO at about 40 °C for 2–3 h and then cooling them to room temperature. Some of the crystals were fairly large in size. It was difficult to obtain good crystals if the solvent was nearly completely removed. The most prominent faces were {110} and {$\bar{1}\bar{1}0$}, and the others were {001}, {00$\bar{1}$}, {$\bar{1}$10}, and {1$\bar{1}$0}. Most crystals were relatively equidimensional.

B. X-ray Data. [*N,N'*-(1,3-Propanediyl)bis(2-amino-2-methyl-3-butanone oximato)]palladium(II) nitrate, $[Pd(C_{13}H_{27}N_4O_2)]NO_3$, crystallizes in the orthorhombic crystal system with four formula units in a unit cell with a = 11.0424 (5), b = 12.9114 (5), and c = 12.5871 (7) Å. These cell dimensions and their standard deviations were determined from a least-squares refinement[10] of the setting angles of 21 reflections that had been carefully centered with a narrow vertical slit in front of the detector and a low takeoff angle on a Picker four-circle X-ray diffractometer using Mo Kα_1 radiation. A measurement of density by flotation in carbon tetrachloride–1,2-dibromoethane solution gave 1.66 g/cm^3. A calculated density of 1.65 g/cm^3 is obtained on the assumption of four molecules per unit cell. The precession photographs show orthorhombic symmetry, and the systematic extinctions for $h00$, h odd, for $0k0$, k odd, and for $00l$, l odd, indicate that the space group is $P2_12_12_1$.

C. Collection and Reduction of Intensity Data. For the collection of intensity data, a crystal of approximate dimensions 0.13 × 0.18 × 0.17 mm bounded by six faces was mounted with c^* about 5° from the ϕ axis. The crystal was aligned, and with the orientation matrix and cell dimensions from the above-mentioned cell refinement, the setting angles for all intensity measurements were calculated. Intensity data were collected at a takeoff angle of 2.4° by use of Mo Kα radiation filtered through a niobium β filter. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min, monitoring the crystal and instrument stability by remeasuring a group of three standard reflections periodically. The scan width was variable to account for the α_1–α_2 splitting and was from 0.45° below to 0.45° above the Kα_1 and Kα_2 settings, respectively. Backgrounds at either end of the scan range were collected for 20 s. The pulse-height analyzer was set for about 95% window, centered on the Mo Kα peak. The intensities of 4870 reflections were measured. For the 0–40° 2θ region, hkl, $\bar{h}\bar{k}\bar{l}$, and $\bar{h}kl$ reflections were measured; for the 40–45° 2θ region, hkl and $\bar{h}kl$ reflections were measured; for the 45–55° 2θ region, only hkl reflections were measured. When the data were averaged, the agreement factor ($=\sum|F^2 - F^2_{av}|/\sum F^2$) was 4.5%. The total number of the unique data obtained was 3295, the nonequivalence of Friedel pairs being taken into account. Of these, 2838 which had $F_o^2 > 2\sigma(F_o^2)$, where $\sigma = [\sigma^2_{counting} + (0.035F_o^2)^2]^{1/2}$, were used in structure solution and least-squares refinement.

During the data collection, all standard reflections dropped in intensity by about 12%. The data were corrected for this decrease on the basis of two straight lines obtained by plotting the sum of the intensities of the standards vs. time. Background and Lorentz–polarization corrections were made with the usual equations. Absorption corrections were made before averaging (μ = 10.7 cm^{-1}) with the transmission factor ranging from 0.850 to 0.889.

Table I. Final Fractional Atom Coordinates for Nonhydrogen Atoms in $Pd(PnAO\text{-}H)NO_3$

atom	x	y	z
Pd	0.13559 (2)	−0.00051 (3)	0.16464 (2)
O(1)	0.0041 (3)	−0.1411 (3)	0.0284 (3)
O(2)	0.2121 (3)	−0.1967 (3)	0.0739 (3)
O(3)	0.4621 (6)	0.0546 (5)	0.0204 (5)
O(4)	0.5493 (5)	0.1878 (4)	−0.0451 (4)
O(5)	0.4339 (5)	0.2022 (5)	0.0898 (5)
N(1)	0.2888 (4)	0.0543 (3)	0.2361 (3)
N(2)	0.2435 (4)	−0.1200 (3)	0.1425 (3)
N(3)	−0.0066 (4)	−0.0562 (3)	0.0896 (3)
N(4)	0.0215 (4)	0.1225 (3)	0.1806 (3)
N(5)	0.4837 (5)	0.1498 (5)	0.0220 (5)
C(1)	0.3652 (4)	−0.0362 (4)	0.2715 (4)
C(2)	0.3458 (4)	−0.1214 (4)	0.1901 (4)
C(3)	−0.1069 (4)	−0.0074 (4)	0.0960 (3)
C(4)	−0.1075 (4)	0.0832 (4)	0.1738 (4)
C(5)	−0.2184 (5)	−0.0389 (5)	0.0374 (5)
C(6)	−0.1911 (5)	0.1698 (5)	0.1385 (6)
C(7)	−0.1479 (5)	0.0416 (5)	0.2823 (5)
C(8)	0.4377 (5)	−0.2021 (5)	0.1718 (5)
C(9)	0.4963 (4)	−0.0043 (5)	0.2825 (4)
C(10)	0.3191 (6)	−0.0767 (4)	0.3783 (4)
C(11)	0.0503 (5)	0.1935 (5)	0.2688 (5)
C(12)	0.1843 (6)	0.2208 (4)	0.2712 (5)
C(13)	0.2662 (5)	0.1369 (4)	0.3155 (5)

D. Solution and Refinement of the Structure. The scattering factors used in subsequent calculations for C, N, and O were taken from Ibers,[12a] those for H from Stewart,[12b] and those for Pd from Cromer and Waber.[12c] By use of the tabulated values[12d] of $\Delta f'$ and $\Delta f''$ for Pd, the effects of anomalous dispersion were included in F_c.[12e] The palladium atom was located by the Patterson method, and all other atoms were located from successive Fourier and difference Fourier syntheses. Refinement of positional and isotropic thermal parameters for all atoms except hydrogens converged with $R = \sum|F_o^2 - kF_c^2|/\sum F_o^2 = 0.089$ and $r = [\sum w(F_o^2 - kF_c^2)^2/\sum wF_o^4]^{1/2} = 0.163$ where $w = 1/\sigma^2(F_o^2)$. Refinement with all atoms anisotropic increased the number of variables from 97 to 218 (including extinction parameter) and reduced R to 0.074 and r to 0.123. At this stage, a difference Fourier map revealed almost all hydrogen atoms. Inclusion of hydrogen atoms, in keeping with difference Fourier observations and in chemically reasonable positions with fixed isotropic temperature factors of 6.0 Å and fixed positional parameters except that of the hydrogen-bonded hydrogen atom, gave R = 0.055 and r = 0.093. In order to ensure the correct indexing since Friedel's law is not applicable, the signs of hkl were reversed.[13] Two cycles of least-sqaures refinement further reduced R to 0.050 and r to 0.085, and this choice was then taken as correct. The final value for the extinction parameter was 1.470×10^{-5}. Except for a peak of 0.52 e/Å^3 at 0.35 Å from the Pd atom, a final difference Fourier synthesis had no peaks greater than 0.41 e/Å^3. The maximum shift in any parameter after the final least-squares cycle was much less than one-tenth of the estimated standard deviation of that parameter. The observed and calculated structure factors are available.[14] The final positional and thermal parameters of all nonhydrogen atoms are given in Tables I and II. The hydrogen atom positions are included in Table III. In these tables and other portions of the manuscript, least-squares estimated standard deviations of the least significant figure are given in parentheses.

Results and Discussion

A. Nature of the Structure. A stereoscopic view of the packing in the unit cell is shown in Figure 1. The structure consists of discrete square-planar $[Pd(PnAO\text{-}H)]^+$ complex ions and nitrate anions. Unlike most of the α-amine oxime complexes reported so far, no water of hydration was found, probably because the complex was prepared and crystallized from nearly anhydrous methanol. There are no unusually short intermolecular contacts as can be seen in Table IV in which all interionic distances (ignoring hydrogens) under 3.9 Å are

Table II. Anisotropic Thermal Parameters for Pd(PnAO-H)NO_3[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.03206 (2)	0.03579 (2)	0.03909 (2)	0.00040 (2)	−0.00012 (1)	−0.00567 (2)
O(1)	0.0488 (21)	0.0502 (20)	0.0567 (24)	0.0013 (17)	−0.0107 (17)	−0.0163 (18)
O(2)	0.0596 (21)	0.0444 (19)	0.0477 (20)	0.0049 (19)	−0.0058 (18)	−0.0159 (17)
O(3)	0.1170 (44)	0.1066 (41)	0.1194 (48)	−0.0274 (38)	−0.0130 (38)	0.0269 (39)
O(4)	0.0932 (37)	0.1254 (43)	0.1105 (41)	0.0083 (35)	0.0309 (34)	0.0565 (37)
O(5)	0.1050 (46)	0.1472 (53)	0.0809 (37)	0.0032 (45)	0.0159 (35)	0.0011 (39)
N(1)	0.0449 (22)	0.0426 (21)	0.0518 (23)	0.0014 (19)	0.0018 (20)	−0.0072 (20)
N(2)	0.0473 (23)	0.0435 (22)	0.0471 (23)	−0.0031 (19)	0.0001 (18)	−0.0088 (20)
N(3)	0.0490 (24)	0.0441 (20)	0.0392 (21)	0.0000 (20)	0.0013 (17)	−0.0030 (18)
N(4)	0.0434 (23)	0.0474 (22)	0.0545 (25)	0.0020 (19)	0.0027 (19)	−0.0088 (20)
N(5)	0.0592 (33)	0.1064 (47)	0.0909 (46)	−0.0038 (34)	−0.0080 (31)	0.0295 (41)
C(1)	0.0353 (25)	0.0428 (24)	0.0521 (28)	−0.0037 (20)	−0.0009 (22)	−0.0047 (21)
C(2)	0.0411 (27)	0.0391 (25)	0.0501 (28)	0.0025 (21)	0.0032 (22)	−0.0019 (23)
C(3)	0.0381 (22)	0.0552 (27)	0.0420 (22)	−0.0023 (33)	−0.0021 (17)	0.0065 (30)
C(4)	0.0406 (26)	0.0506 (27)	0.0547 (30)	0.0054 (22)	0.0010 (24)	−0.0068 (25)
C(5)	0.0486 (29)	0.0755 (39)	0.0710 (38)	0.0005 (27)	−0.0143 (27)	0.0008 (30)
C(6)	0.0498 (34)	0.0633 (36)	0.1026 (49)	0.0109 (28)	−0.0128 (34)	−0.0028 (36)
C(7)	0.0646 (37)	0.0856 (43)	0.0622 (35)	−0.0037 (31)	0.0196 (29)	−0.0029 (32)
C(8)	0.0536 (34)	0.0736 (38)	0.0834 (45)	0.0248 (31)	−0.0112 (34)	−0.0213 (37)
C(9)	0.0413 (24)	0.0637 (30)	0.0853 (36)	0.0051 (38)	−0.0094 (24)	−0.0013 (43)
C(10)	0.0769 (38)	0.0552 (31)	0.0382 (26)	−0.0069 (29)	−0.0074 (28)	0.0003 (25)
C(11)	0.0556 (32)	0.0654 (35)	0.0770 (39)	0.0121 (29)	−0.0073 (30)	−0.0209 (32)
C(12)	0.0705 (38)	0.0456 (29)	0.0811 (40)	−0.0032 (28)	−0.0113 (34)	−0.0191 (30)
C(13)	0.0500 (30)	0.0570 (31)	0.0710 (37)	0.0027 (26)	−0.0131 (28)	−0.0188 (30)

[a] Anisotropic temperature factors are of the form: $\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table III. Positional Parameters for the Hydrogen Atoms in Pd(PnAO-H)NO_3

atom[a]	x	y	z
OHO	0.0746 (55)	−0.1628 (44)	0.0498 (49)
HN1	0.3365	0.0845	0.1821
HN4	0.0262	0.1632	0.1162
1H5	−0.2286	−0.0007	−0.0274
2H5	−0.2911	−0.0244	0.0799
3H5	−0.2200	−0.1250	0.0180
1H6	−0.2752	0.1502	0.1497
2H6	−0.1816	0.1860	0.0660
3H6	−0.1760	0.2200	0.1763
1H7	−0.1612	0.1011	0.3266
2H7	−0.0827	0.0030	0.3106
3H7	−0.2181	0.0006	0.2881
1H8	0.3974	−0.2655	0.1621
2H8	0.4814	−0.2070	0.2400
3H8	0.5000	−0.2000	0.1220
1H9	0.5011	0.0558	0.3263
2H9	0.5278	0.0118	0.2145
3H9	0.5479	−0.0486	0.3106
1H10	0.2312	−0.0861	0.3784
2H10	0.3383	−0.0323	0.4352
3H10	0.3534	−0.1459	0.3936
1H11	−0.0007	0.2553	0.2649
2H11	0.0260	0.1604	0.3361
1H12	0.2112	0.2529	0.2066
2H12	0.1789	0.2711	0.3275
1H13	0.3394	0.1627	0.3447
2H13	0.2235	0.1044	0.3793

[a] The last number in the label corresponds to the carbon to which the hydrogen is attached.

given. The shortest contacts (~3.0 Å) are hydrogen bonds among amine nitrogens and the nitrate oxygens. The crystal structure is, presumably, stabilized through this hydrogen-bonding network. Large portions of the complex cation are related by mirror symmetry across a plane passing through the palladium and C(12) atoms. The four nitrogens surrounding the palladium atom define a weighted least-squares plane (Table V, plane 2). The maximum deviation of any nitrogen atom is 0.003 (4) Å indicating no significant deviation from planarity. The palladium atom is slightly out of the plane defined by the four nitrogens and the palladium atom (plane 1, Table V). The distances of all other atoms in the cation

Table IV. Intermolecular Contact Distances (Å)

O(3)-N(1)	3.322 (8)	O(4)-C(12)[b]	3.423 (8)
O(3)-C(2)	3.374 (8)	O(4)-C(6)[b]	3.437 (8)
O(3)-C(9)	3.407 (9)	O(4)-C(6)	3.689 (8)
O(3)-C(1)	3.538 (8)	O(4)-C(4)[b]	3.789 (7)
O(3)-C(10)[c]	3.594 (9)	O(4)-C(7)	3.831 (9)
O(3)-N(2)	3.643 (7)	O(5)-N(1)[a]	3.099 (7)
O(3)-C(5)	3.735 (9)	O(5)-C(13)	3.495 (8)
O(3)-C(8)	3.833 (9)	O(5)-C(8)	3.541 (9)
O(3)-C(7)[c]	3.838 (10)	O(5)-C(12)	3.587 (9)
O(4)-N(4)[a,b]	3.000 (6)	O(5)-C(6)[b]	3.591 (9)
O(4)-C(11)[b]	3.206 (9)	O(5)-C(9)	3.670 (9)
		O(5)-C(1)	3.909 (8)

[a] This is the intermolecular hydrogen bond between amine nitrogens and nitrate oxygens. [b] On position $^1/_2 + x, ^1/_2 - y, -z$. [c] On position $^1/_2 - x, -y, ^1/_2 + z$.

from the PdN_4 plane are given in Table V. All carbon atoms except C(12) are below the plane. Because of puckering in the chelate rings, the pseudo-mirror-related carbon atoms are almost equidistant from this plane; e.g., C(11) and C(13) are about 0.48 Å below and C(1) and C(4) are about 0.054 Å below the plane. Similarly, C(3), C(5), C(6), and C(7) are at about the same distance from the plane as are C(2), C(8), C(9), and C(10), respectively. Both oxime oxygens are above the PdN_4 plane. The oxime nitrogen and oxygen atoms define a very good plane (Table V, plane 3) which nearly includes the hydrogen-bonded hydrogen. The nitrate ion is strictly planar (plane 5, Table V). Each amine nitrogen is involved in a hydrogen bond with nitrate oxygens: N(4) is at hydrogen-bonding distance from O(4), and N(1) is at a similar distance from O(5) (Table IV). The shape and orientations of the thermal ellipsoids are shown in Figures 2 and 3, while the root-mean-square displacements along the principal axes are given in Table VI.[14] The maximum vibrations tend to be perpendicular to the direction of the bond, and the terminal nonhydrogen atoms show higher vibrational amplitude. As expected, the greatest thermal motion is in the nitrate oxygens.

The configuration of the chelate rings in the PnAO is the same as that observed for two AO ligands in $[Ni(AO)_2\text{-}H]^{+2}$ or in $[Pt(AO)_2\text{-}H]^{+5}$ complexes; i.e., all nonhydrogen atoms except C(12) are off to one side of the metal–nitrogens plane. The puckering of the chelate rings in EnAO in [Ni-

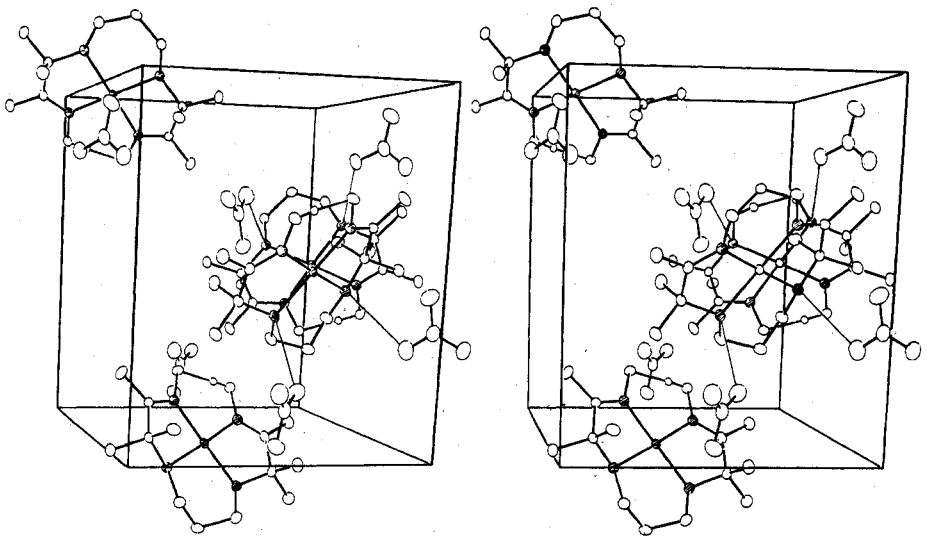


Figure 1. Stereoscopic view of a unit cell showing the packing of the molecules. The crystallographic *a* axis lies along the horizontal direction, the *c* axis is in the vertical direction, and the *b* axis completes a right-handed coordinate system.

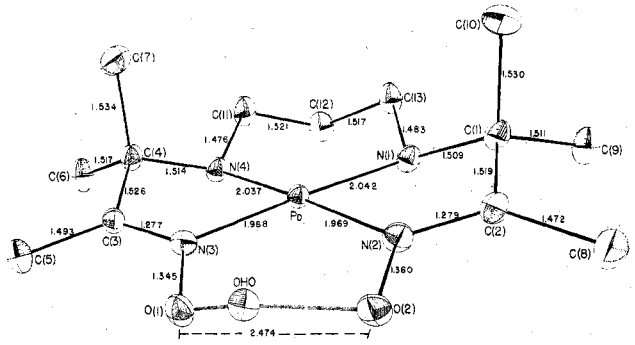


Figure 2. Bond distances for the complex cation. Standard deviations in distances: Pd–N, 0.004 Å; C–N, 0.006 Å; C–C, 0.008 Å; N–O, 0.005 Å.

(EnAO)-H]$^{+}$[7] is quite different with N(oxime)–N(amine) chelate rings in the δ conformation while the N(amine)–N(amine) ring is in the λ configuration. The crystal structures of AO complexes of nickel(II) and platinum(II) are stabilized by a network of hydrogen bonds involving amine nitrogens of the complex cations, chlorides, and oxygens of water of hydration. In the present study, the structure is stabilized through interionic hydrogen bonds (Table IV).

B. Bond Distances and Angles. The bond distances for all atoms except hydrogens are given in Figure 2 and Table VII. Table VII also contains the important angles, and in Table VIII the distances and angles are compared with those from the X-ray and neutron diffraction studies of related nickel(II) and platinum(II) complexes.

As in the nickel(II) and platinum(II) complexes, the average Pd–N(amine) distance (2.040 (4) Å) is significantly larger than the average Pd–N(oxime) distance (1.969 (4) Å). The difference (0.07 Å) is similar to that found in the platinum

Table V. Deviations from Least-Squares Planes

atom	dist, Å	atom	dist, Å
Plane 1: N(1), N(2), N(3), N(4), Pd			
$3.564x + 4.978y - 10.88z + 1.310 = 0$			
Pd	−0.0007 (3)	C(4)	−0.550
N(1)	0.040 (4)	C(5)	−0.069
N(2)	0.030 (4)	C(6)	−0.033
N(3)	0.032 (4)	C(7)	−2.081
N(4)	0.031 (4)	C(8)	−0.005
O(1)	0.313	C(9)	−0.016
O(2)	0.283	C(10)	−2.050
C(1)	−0.523	C(11)	−0.472
C(2)	−0.130	C(12)	0.115
C(3)	−0.152	C(13)	−0.492
		OHO	0.217
Plane 2: N(1), N(2), N(3), N(4)			
$3.55x + 4.96y - 10.89z + 1.28 = 0$			
N(1)	0.003 (4)	N(3)	0.003 (4)
N(2)	−0.003 (4)	N(4)	−0.003 (4)
Plane 3: N(2), N(3), O(1), O(2)			
$3.901x + 7.138y - 9.49z + 1.270 = 0$			
N(2)	0.009 (4)	O(2)	−0.009 (4)
N(3)	−0.008 (4)	OHO	−0.074
O(1)	0.010 (4)	Pd	0.233
Plane 4: Pd, O(1), O(2), N(2), N(3)			
$3.734x + 6.057y - 1.027z + 1.188 = 0$			
O(1)	0.058 (4)	N(2)	−0.093 (4)
O(2)	0.030 (4)	N(3)	−0.097 (4)
Pd	0.0008 (3)		
Plane 5: O(3), O(4), O(5), N(5) (Nitrate Ion)			
$8.653x - 1.915y + 7.593z - 4.054 = 0$			
O(3)	−0.006 (6)	O(5)	−0.005 (6)
O(4)	−0.004 (5)	N(5)	0.012 (5)

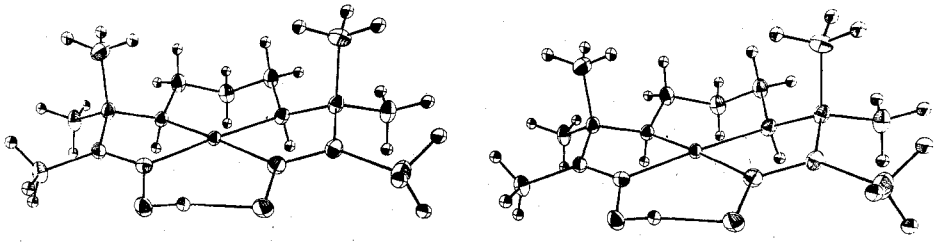


Figure 3. Stereoscopic pair showing the structure of the [Pd(PnAO)]$^{+}$ cation.

Table VII

Intramolecular Bond Angles (deg)

N(1)-Pd-N(2)	80.4 (2)	C(4)-N(4)-C(11)	116.9 (4)
N(3)-Pd-N(4)	80.7 (2)	N(2)-C(2)-C(8)	123.1 (5)
N(2)-Pd-N(3)	97.4 (2)	N(3)-C(3)-C(5)	123.4 (5)
N(1)-Pd-N(4)	101.5 (2)	N(2)-C(2)-C(1)	115.5 (4)
N(1)-Pd-N(3)	177.0 (2)	N(3)-C(3)-C(4)	115.0 (4)
N(2)-Pd-N(4)	177.4 (2)	C(8)-C(2)-C(1)	121.3 (4)
N(3)-O(1)-O(2)	100.7 (3)	C(5)-C(3)-C(4)	121.6 (4)
N(2)-O(2)-O(1)	99.6 (3)	C(2)-C(1)-C(9)	113.3 (4)
C(2)-N(2)-O(2)	120.9 (4)	C(3)-C(4)-C(6)	112.3 (4)
C(3)-N(3)-O(1)	120.9 (4)	C(2)-C(1)-N(1)	106.4 (4)
O(2)-N(2)-Pd	120.4 (3)	C(3)-C(4)-N(4)	106.8 (4)
O(1)-N(3)-Pd	120.2 (3)	N(1)-C(1)-C(10)	109.7 (4)
C(3)-N(3)-Pd	118.8 (3)	N(4)-C(4)-C(7)	110.0 (4)
C(2)-N(2)-Pd	118.6 (3)	C(9)-C(1)-C(10)	109.4 (4)
Pd-N(1)-C(1)	108.9 (3)	C(6)-C(4)-C(7)	110.0 (5)
Pd-N(4)-C(4)	108.4 (3)	N(4)-C(11)-C(12)	111.6 (5)
Pd-N(1)-C(13)	114.0 (3)	N(1)-C(13)-C(12)	111.5 (4)
Pd-N(4)-C(11)	115.2 (3)	C(11)-C(12)-C(13)	115.0 (5)
C(1)-N(1)-C(13)	116.9 (4)		

Nitrate Ion Distances (Å) and Angles (deg)

O(5)-N(5)-O(4)	122.1 (7)	N(5)-O(5)	1.220 (8)
O(5)-N(5)-O(3)	118.0 (7)	N(5)-O(4)	1.216 (7)
O(4)-N(5)-O(3)	119.9 (8)	N(5)-O(3)	1.253 (7)

complex but is more pronounced than that found in the nickel complex (0.04 Å). The average Pd–N(amine) and Pd–N(oxime) distances found in the present study are in good agreement with the corresponding distances in other studies, e.g., 1.965 (4) Å observed for Pd–N(oxime) in $Pd(DMG)_2$[15] and an average of 2.037 Å observed for Pd–N(amine) in $[Pd(en)_2]Cl_2$.[16] All C–C and C–N distances in the ligand moiety are quite normal and agree within experimental error with the corresponding distances observed in the other α-amine oxime complexes of nickel(II) and platinum(II). However, a significant difference (0.014 Å) is observed in chemically equivalent N(3)–O(1) (1.345 (5) Å) and N(2)–O(2) (1.359 (5) Å) distances. Such a difference was also observed earlier in Ni(II) and Pt(II) complexes and has been attributed to the asymmetric nature of the hydrogen bond.

The angles around the palladium(II) atom are of significant interest. Although the palladium atom is coordinated with four nitrogen atoms which are in the same plane, the chelate N–M–N angles are highly distorted from ideal square-planar values (Table VIII). The largest deviation is in the bite angle N(1)–Pd–N(4) of 101.5 (2)°. The three kinds of bite angles, i.e., N(amine)–Pd–N(amine), N(amine)–Pd–N(oxime), and N(oxime)–Pd–N(oxime), in the present study resemble very closely the corresponding angles in the platinum–AO complexes (Figure 4). Also similar to the case of the Pt–AO complexes, the N(amine)–Pd–N(amine) angle is larger than the N(oxime)–Pd–N(oxime) angle, indicating that the steric

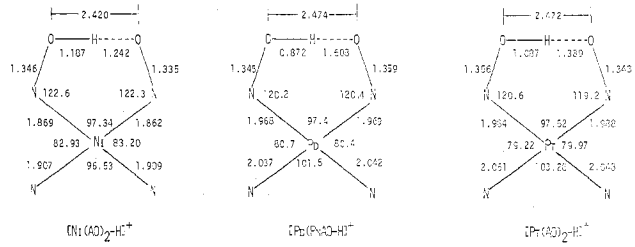


Figure 4. Variation of bond distances and angles as a function of the size of the metal atoms.

requirements of the PnAO ligand are almost the same as that of coordinated AO ligands and that the propylene bridge in the former imposes no significant constraint on the ligand. As a result of a slight constraint in the six-membered chelate ring, the N–M–N angle is squeezed to 101.5° compared with 103.3° in $[Pt(AO)_2\text{-}H]^+$, and the N(oxime)–Pd–N(amine) angles are correspondingly increased by about 1°. This is in contrast to the constrained $[Ni(EnAO)\text{-}H]^+$ complexes[6,7] where N(amine)–Ni–N(amine) angles are invariably smaller than N(oxime)–Ni–N(oxime) angles because of an appreciable constraint imposed by the ethylene bridge. The average bite angle N(amine)–Pd–N(oxime) of 80.6° is much closer to 79.6° observed for the corresponding angle in $[Pt(AO)_2\text{-}H]^+$ than to 85.1 or 83.07° observed in $[Ni(EnAO)\text{-}H]^+$ or $[Ni(AO)_2\text{-}H]^+$, respectively. The absence of any significant difference in molecular parameters, in going from palladium(II) to platinum(II) complexes of AO and PnAO clearly indicates that the steric requirements of the two ligands are similar and also that the changes in the central metal ion do not affect the coordination distances and angles. This is probably to be expected since as a result of lanthanide contraction, platinum(II) should exhibit almost the same ionic size as palladium(II). Similar effects of the lanthanide contraction were observed for dimethylglyoxime complexes of Pd(II) and Pt(II).[15a] The molecular parameters for nickel(II) complexes are significantly different from either those of platinum(II) or those of palladium(II) compounds.

The distances and angles in the nitrate ion are quite distorted from the ideal planar values though the ion is quite planar. The N–O distances are from 1.216 (8) to 1.253 (7) Å, and O–N–O angles are from 118.0 (7) to 122.1 (7)°. A similar but larger range for N–O distances (1.166–1.228 Å) was observed in $[Ni(EnAO)\text{-}H]NO_3\cdot H_2O$,[6] and an even larger range (1.11–1.29 (3) Å) was observed in (nitrato)bis(acetone thiosemicarbazone)nickel(II) nitrate monohydrate[17] for the uncoordinated nitrate ion.

Although most of the hydrogen atom positions are in agreement with peaks in difference Fourier maps, the positions of all hydrogen atoms, except that involved in the intramolecular hydrogen bond, have not been refined. The positions

Table VIII. Comparison of Average Bond Distances and Angles with Those from Structural Studies of Similar Nickel(II) and Platinum(II) Complexes

complex	O···O	M–N(oxime)	M–N(amine)	N(oxime)–M–N(amine)	N(oxime)–M–N(oxime)	N(amine)–M–N(amine)	method	ref
$[Ni(AO)_2\text{-}H]Cl\cdot H_2O$	2.420 (3)	1.866 (1)	1.908 (1)	83.20 (6) 82.93 (6)	97.34 (6)	96.53 (6)	neutron diffraction	2
$[Ni(AO)_2\text{-}H]Cl\cdot H_2O$	2.38 (2)	1.86 (1)	1.91 (1)	83.4 (4) 83.1 (4)	97.7 (5)	95.8 (4)	X-ray diffraction	1
$[Ni(EnAO\text{-}H)]NO_3\cdot H_2O$	2.474 (6)	1.838 (5)	1.872 (5)	85.4 (2) 84.9 (2)	100.4 (2)	90.2 (2)	X-ray diffraction	6
$[Ni(EnAO\text{-}H)]ClO_4$	2.478 (5)	1.841 (3)	1.877 (2)	85.3 (2) 84.9 (2)	100.4 (2)	90.2 (2)	neutron diffraction	7
$[Pt(AO)_2\text{-}H]Cl\cdot 3.5H_2O$	2.472 (5)	1.986 (2)	2.054 (6)	79.97 (2) 79.22 (2)	97.5 (1)	103.3 (1)	neutron diffraction	5
$[Pt(AO)_2\text{-}H]Cl\cdot H_2O$	2.48 (4)	1.99 (3)	2.03 (3)	81.9 (1) 79.2 (1)	98 (1)	101 (1)	X-ray diffraction	4
$[Pd(PnAO)\text{-}H]NO_3$	2.474 (5)	1.969 (4)	2.040 (4)	80.4 (2) 80.7 (2)	97.4 (2)	101.5 (2)	X-ray diffraction	this work

reported for the hydrogens should be considered quite approximate. The distances and angles involving hydrogen atoms are not reported individually. The C–H distances range from 0.82 to 1.14 Å; the N–H distances are 0.95 and 0.97 Å. The H–C–H angles range from 103 to 111°.

C. Intramolecular Hydrogen Bond. The effects of the metal-ion size on the hydrogen bond and the metal coordination geometry for the nickel(II), palladium(II), and platinum(II) complexes of unconstrained α-amine oxime complexes are illustrated in Figure 4. The short intramolecular hydrogen bond O···O (2.474 (5) Å) is equal to that observed (2.472 (5) Å) for $[Pt(AO)_2\text{-}H]^{+}$ [5] but is considerably longer than 2.420 (3) Å in $[Ni(AO)_2\text{-}H]^{+}$.[2] The elongation of 0.05 Å in the O···O distance in going from nickel(II) to palladium(II) can be associated with the larger size of palladium(II), whereas similarity in this distance for palladium(II) and platinum(II) complexes is a consequence of lanthanide contraction in the latter case. The Pd–N–O and Pt–N–O angles are close to 120°, further indicating identical effects of the two metals. This angle is approximately 2° larger in the case of nickel(II) complexes.

Similar to several recent studies of cobalt(III)[18-20] and platinum(II) complexes having O···O distances greater than 2.46 Å, the hydrogen atom in the present work appears to be nearly covalently bonded to one oxime oxygen and weakly bonded to the other. The position of the hydrogen atom (OHO) in the intramolecular hydrogen bond was obtained from the least-squares refinement of the coordinates from a difference Fourier synthesis. These coordinates give the O(1)–(OHO) distance of 0.86 (6) Å and the O(2)–(OHO) distance of 1.63 (6) Å, indicating appreciable asymmetry in the O–H–O bond. Almost exactly similar asymmetry was observed in an X-ray study of $[Ni(EnAO)\text{-}H]NO_3 \cdot H_2O$,[6] while a neutron diffraction study[7] of $[Ni(EnAO)\text{-}H]ClO_4$ gave the corresponding distances of 1.171 (8) and 1.316 (8) Å. The O(1) and O(2) atoms have nearly identical environments and neighboring contacts, and neither is involved in any other hydrogen bonding. Because of the near-equivalence of these oxygen atoms, a double-well potential with equal occupancy might be expected with a resulting disorder of hydrogen atom OHO on either side of the center of the O(1)–O(2) hydrogen bond. The asymmetry in the hydrogen bond is clearly related to O···O distance: the larger the distance the more asymmetric is the intramolecular hydrogen bond. The O–H–O angle of 172° is nearly the same as that observed (173.8°) in the $[Pt(AO)_2\text{-}H]Cl$ complex.[5]

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Registry No. $[Pd(PnAO\text{-}H)](NO_3)$, 69155-25-5.

Supplementary Material Available: Root-mean-square components of thermal displacement (Table VI) and listings of observed and calculated structure factors for Pd(PnAO-H)NO (19 pages). Ordering information is given on any current masthead page.

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