(CO-*n*-Pr)(PPh_3)(C_5H_5N)(mnt), 70728-78-8; Rh($COCH_2Ph$)(PPh_3)(C_5H_5N)(mnt), 70728-79-9; Rh($COCH_2Ph$)(PPh_3)($C_6H_{11}NH_2$)(mnt), 70728-80-2; Rh(COMe)(PEt_3)(C_5H_5N)(mnt), 70728-81-3; Rh(COEt)(PEt_3)(CH_3CN)(mnt), 70728-82-4; [(*n*-Bu)$_4$N][Rh(CO)(PPh_3)(mnt)], 29985-52-2; [(*n*-Bu)$_4$N][Rh(CO)(PEt_3)(mnt)], 70728-83-5.

Supplementary Material Available: A listing of observed and calculated structure factors for Rh(CO)(PPh_3)(Et-mnt) (20 pages). Ordering information is given on any current masthead page.

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Pentagonal-Bipyramidal Complexes. Synthesis and Characterization of Aqua(nitrato)[2,6-diacetylpyridinebis(benzoic acid hydrazone)]cobalt(II) Nitrate and Diaqua[2,6-diacetylpyridinebis(benzoic acid hydrazone)]nickel(II) Nitrate Dihydrate

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The reaction of 2,6-diacetylpyridinebis(benzoic acid hydrazone), DAPBH, with $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ yields the pentagonal-bipyramidal complexes $[Co(DAPBH)(H_2O)(NO_3)]^+NO_3^-$ (I) and $[Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$ (II), respectively. The infrared spectra suggested differences in the interaction of the metal with DAPBH and also the presence of a coordinated nitrate in I but not in II. Complex I crystallizes in the monoclinic space group $P2_1/n$, with four molecules per cell. The unit cell dimensions are $a = 7.361$ (2), $b = 17.423$ (5), and $c = 19.876$ (5) Å with $\beta = 97.86$ (2)°. Complex II crystallizes in the orthorhombic space group *Pbca*, with eight molecules per cell. The cell dimensions are $a = 24.624$ (3), $b = 15.942$ (7), and $c = 14.589$ (3) Å. Intensity data for both complexes were measured by using Mo Kα radiation. The structures were determined by the heavy-atom method and refined by least-squares techniques to an unweighted residual of 0.035 for I and 0.059 for II. The cations in both complexes are pentagonal bipyramids. The DAPBH ligand is in the equatorial plane and one monodentate nitrate and one water molecule are in the axial positions of I, with two water molecules axially coordinated in II. The equatorial plane distances are as follows: Co–N of 2.194, 2.203, and 2.190 Å; Co–O of 2.150 and 2.229 Å; Ni–N of 2.018, 2.090, and 2.178 Å; Ni–O of 2.282 and 2.477 Å. The large difference in the Ni–O bond lengths is attributed to Jahn–Teller distortions in the Ni^{2+} case and explains the differences in the infrared spectra of I and II.

Introduction

The role that seven-coordinate intermediates play in the substitution reactions of six- and eight-coordinate complexes and in the oxidative-addition reactions of five-coordinate species has stimulated interest in complexes with high coordination numbers.[1,2] A further impetus came from our early reports that the then relatively rare pentagonal-bipyramidal (PB) complex could be stabilized by planar pentadentate ligands such as DAPSC (2,6-diacetylpyridinebis(semicarbazone)) or DAPPH (2,6-diacetylpyridinebis(2′-pyridylhydrazone)).[3–7] A number of other seven-coordinate complexes have now been synthesized by utilizing either planar[8] or macrocyclic pentadentate ligands[9] and their structures have been determined by X-ray diffraction techniques.

Although the majority of the PB complexes of DAPSC and DAPPH are relatively regular, large distortions were observed in the high-spin $Cr(DAPSC)(H_2O)_2^{3+}$ and $Ni(DAPSC)(H_2O)_2^{2+}$ cations.[3,6] These distortions could be explained on the basis of the Jahn–Teller[10] theorem, the observed spin state, and the expected splitting of the d orbitals in a PB field.[11] Since the Cr(III) and Ni(II) complexes represented the first examples of Jahn–Teller distortions in a PB field, we decided to synthesize other seven-coordinate Ni(II) complexes to explore in greater detail these distortions. Furthermore, to investigate the general utility of planar pentadentate ligands in stabilizing PB complexes, we prepared a series of ligands derived from the reaction of 2,6-diacetylpyridine with various acid hydrazides. The donor properties of these planar pentadentate hydrazone ligands should be dependent upon the nature of the parent acid hydrazide. Our present study demonstrates that PB Co(II) and Ni(II) complexes of 2,6-diacetylpyridinebis(benzoic acid hydrazone), DAPBH, can be prepared. In addition, the Ni(II) complex was found to be distorted in a manner which is very similar to that found in

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Table I. Crystal Data for Aqua(nitrato)[2,6-diacetylpyridinebis(benzoic acid hydrazone)]cobalt(II) Nitrate (I) and Diaqua[2,6-diacetylpyridinebis(benzoic acid hydrazone)]nickel(II) Nitrate Dihydrate (II)

	I	II
formula	$C_{23}H_{23}N_7O_9Co$	$C_{23}H_{29}N_7O_{12}Ni$
mol wt	600.41	654.23
space group	$P2_1/n$	$Pbca$
a, Å	7.361 (2)	24.624 (3)
b, Å	17.423 (5)	15.942 (7)
c, Å	19.876 (5)	14.589 (3)
β, deg	97.86 (2)	
volume, Å^3	2525 (1)	5727
Z	4	8
D_m, g cm^{-3}	1.63	1.51
D_c, g cm^{-3}	1.579	1.517
crystal size, mm	0.10 × 0.18 × 0.39	0.25 × 0.34 × 0.48
μ, cm^{-1}	7.80	7.56
radiation used	Mo	Mo
2θ range	0–45	0–60
no. of measd reflcns	3313	5062
no. of reliable reflcns	2613	3261
K (in $I \leq k\sigma(I)$)	2.0	2.0
F(low)	21.5	40.0
F(high)	57.0	160.0
goodness of fit	1.08	2.8

Table II. Final Positional Parameters for Aqua(nitrato)[2,6-diacetylpyridinebis(benzoic acid hydrazone)]cobalt(II) Nitrate[a]

atom	x	y	z
Co	6142 (6)	21064 (2)	21663 (2)
O(1)	1201 (3)	1395 (1)	1339 (1)
O(2)	418 (3)	937 (1)	2606 (1)
O(4)	3499 (3)	2115 (1)	2495 (1)
O(31)	−2302 (3)	2005 (1)	1924 (1)
O(32)	−2602 (4)	1780 (2)	837 (1)
O(33)	−4863 (4)	1615 (2)	1391 (1)
O(41)	5118 (5)	1204 (2)	3570 (1)
O(42)	3809 (4)	1622 (2)	4407 (2)
O(43)	6709 (4)	1754 (1)	4417 (1)
N(1)	612 (4)	3313 (1)	2483 (1)
N(2)	990 (3)	2861 (2)	1307 (1)
N(3)	1163 (4)	2477 (2)	720 (1)
N(5)	−64 (4)	2199 (1)	3202 (1)
N(6)	−474 (4)	1526 (1)	3511 (1)
N(30)	−3248 (4)	1791 (2)	1376 (1)
N(40)	5185 (4)	1524 (2)	4132 (1)
C(1)	910 (4)	3873 (2)	2044 (2)
C(2)	986 (5)	4639 (2)	2235 (2)
C(3)	776 (6)	4820 (2)	2895 (2)
C(4)	457 (5)	4252 (2)	3348 (2)
C(5)	403 (4)	3496 (2)	3120 (2)
C(6)	1115 (4)	3595 (2)	1355 (2)
C(7)	1439 (5)	4140 (2)	803 (2)
C(8)	1195 (4)	1700 (2)	780 (2)
C(9)	66 (4)	2827 (2)	3542 (2)
C(10)	−53 (5)	2908 (2)	4284 (2)
C(11)	−249 (4)	889 (2)	3139 (2)
C(14)	−729 (4)	140 (2)	3424 (2)
C(15)	−1181 (5)	62 (2)	4078 (2)
C(16)	−1557 (5)	−651 (2)	4325 (2)
C(17)	−1504 (5)	−1291 (2)	3919 (2)
C(18)	−1058 (6)	−1224 (2)	3269 (2)
C(19)	−677 (5)	−507 (2)	3023 (2)
C(24)	1251 (4)	1245 (2)	151 (2)
C(25)	2241 (5)	570 (2)	194 (2)
C(26)	2247 (6)	108 (2)	−371 (2)
C(27)	1269 (6)	322 (2)	−980 (2)
C(28)	290 (6)	998 (2)	−1032 (2)
C(29)	273 (5)	1461 (2)	−468 (2)

[a] The values are ×10^{+4} except those for the Co atoms which are ×10^{+5}.

the DAPSC complex, confirming the presence of Jahn–Teller distortions in PB complexes.

Experimental Section

Materials. Benzoic acid hydrazide and 2,6-diacetylpyridine, obtained from Pfaltz and Bauer, were used as supplied. All other solvents and chemicals were reagent grade.

Physical Measurements. Infrared spectra were obtained with a Beckman IR-10. Mass spectra were recorded on an AEI MS-30. All C, H, and N analyses were carried out by Atlantic Microlabs, Atlanta, Ga.

Preparation of the Ligand DAPBH. 2,6-Diacetylpyridine (0.8160 g, 5.0 mmol) and benzoic acid hydrazide (1.3615 g, 10.0 mmol) were dissolved in 75 mL of 95% ethanol, and 1 drop of hydrochloric acid was added. The solution was heated and stirred, and after about 15 min a solid began forming. Heating was continued for about 1 h, and the mixture was cooled overnight. The solid was filtered and dried. The melting point was 236–237 °C. The infrared and mass spectra were in agreement with the formulation as the bis(hydrazone).

Preparation of $[Co(DAPBH)(NO_3)(H_2O)]^+NO_3^-$ (I) and $[Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$ (II). Both complexes were prepared in the same manner. DAPBH (0.4994 g, 1.25 mmol) was suspended in 25 mL of water and the temperature was raised to 55 °C. The hydrated metal nitrate (1.25 mmol) was dissolved in 25 mL of 95% ethanol and was added to the ligand suspension. A clear solution resulted (orange in the cobalt case and brown for the nickel) which was filtered and cooled. Slow evaporation of the filtrate gave orange-brown crystals of the cobalt complex and green crystals of the nickel complex. Anal. Calcd for $C_{23}H_{23}N_7O_9Co$: C, 46.01; H, 3.86; N, 16.33. Found: C, 46.39; H, 3.90; N, 16.30. Calcd for $C_{23}H_{29}N_7O_{12}Ni$: C, 42.22; H, 4.47; N, 14.99. Found: C, 42.32; H, 4.45; N, 14.90.

The following IR bands (cm^{-1}) were observed in a Nujol mull: for the ligand DAPBH 3195 (m), 3070 (w, bd), 1665 (s), 1605 (w), 1570 (s), 1495 (w), 1330 (m), 1300 (s), 1260 (w), 1170 (s), 1150 (m, sh), 820 (m), 725 (s), 690 (s); for $[Co(DAPBH)(H_2O)(NO_3)]^+NO_3^-$ 3410 (m, bd), 3205 (m, bd), 1650 (m, sh), 1640 (s), 1625 (m, sh), 1610 (m), 1585 (w), 1550 (m, sh), 1540 (s), 1500 (m), 1310 (s, bd), 1220 (w), 1195 (s), 1170 (m), 1140 (w), 1080 (w), 1040 (m), 1020 (w, bd), 900 (s), 820 (m, sh), 810 (s), 790 (w), 740 (s), 710 (s), 685 (s), 670 (w); for $[Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$ 3500 (m, bd), 3200 (m, bd), 1670 (s), 1640 (s), 1610 (m), 1590 (m), 1540 (s, bd), 1500 (w), 1340 (s, bd), 1295 (s), 1280 (s), 1220 (w), 1190 (m), 1170 (w), 1135 (w), 1080 (w), 1050 (w), 1030 (w), 1000 (w), 940 (w), 900 (m), 825 (m), 810 (s), 800 (m), 745 (w), 710 (s), 690 (w).

Data Collection and Reduction. Preliminary photographs taken of both complexes were used to determine the space groups and approximate unit cell dimensions. The unit cell dimensions reported in Table I and the intensity data were measured by using a Syntex P$\bar{1}$ diffractometer. The pertinent crystal data, together with some details of the intensity measurements are given in Table I. A variable speed (1–24°/min) θ–2θ scan technique was used for measuring the intensity. Four standard reflections were measured after every 96 measurements and were used to correct for the small variations (±2% for the Co and ±7% for the Ni complex) of intensity during the experiment. Only those reflections with an intensity greater than or equal to twice the estimated σ (intensity) were considered reliable and were used in the determination. Graphite-monochromatized molybdenum radiation was used for the measurements of the data for the Co complex while zirconium-filtered molybdenum radiation was used in the Ni case. The crystals were mounted so that the long dimension was approximately parallel to ϕ in order to minimize absorption effects. Absorption corrections were not made because of the small value of μ and an estimation that the transmission coefficients would only vary from about 0.8 to 0.9. Furthermore, any absorption errors will mainly affect the thermal parameters and not significantly change the bond distances and angles.

Structure Determination and Refinement. Both structures were solved by the heavy-atom method and refined by least-squares techniques. The heavy-atom position was determined from a Patterson function and the remaining nonhydrogen atoms were determined in successive Fourier synthesis. The R value ($=\sum||F_o| - |F_c||/\sum|F_o|$) was 0.19 for the Co complex and 0.22 for the Ni complex at the start of the least-squares refinement. After three least-squares cycles using isotropic thermal parameters and then three cycles using anisotropic thermal parameters, the R values were 0.082 and 0.083 for Co and Ni, respectively. A difference Fourier synthesis was used to locate the hydrogen atoms and their contributions were included in the subsequent refinement, but their parameters were not varied. An

Table III. Final Positional Parameters for Diaqua[2,6-diacetylpyridinebis(benzoic acid hydrazone)]nickel(II) Nitrate Dihydrate[a]

atom	*x*	*y*	*z*
Ni	1659 (3)	11867 (4)	13305 (5)
O(1)	688 (1)	69 (2)	909 (3)
O(2)	−406 (2)	−91 (2)	1371 (3)
O(3)	−85 (2)	1254 (2)	15 (2)
O(4)	433 (2)	943 (2)	2607 (3)
O(W1)	1424 (2)	306 (5)	3002 (4)
O(W2)	3572 (3)	4399 (6)	4623 (6)
O(31)	4364 (2)	2182 (3)	269 (4)
O(32)	4544 (2)	991 (3)	829 (4)
O(33)	5066 (3)	2025 (4)	1084 (4)
O(41)	2465 (2)	1418 (3)	763 (4)
O(42)	3166 (2)	1028 (3)	1471 (3)
O(43)	2404 (2)	1000 (4)	2148 (4)
N(1)	107 (2)	2444 (2)	1462 (3)
N(2)	928 (2)	1629 (2)	922 (3)
N(3)	1317 (2)	1064 (3)	663 (3)
N(5)	−647 (2)	1418 (3)	1860 (3)
N(6)	−1010 (2)	784 (3)	2003 (3)
N(30)	4651 (2)	1736 (3)	732 (3)
N(40)	2671 (2)	1151 (3)	1475 (4)
C(1)	527 (2)	2914 (3)	1181 (3)
C(2)	492 (3)	3780 (3)	1197 (4)
C(3)	31 (3)	4154 (3)	1529 (4)
C(4)	−396 (3)	3661 (3)	1832 (4)
C(5)	−348 (2)	2792 (3)	1766 (4)
C(6)	1002 (2)	2423 (3)	870 (4)
C(7)	1503 (3)	2860 (4)	508 (5)
C(8)	1154 (2)	252 (3)	685 (3)
C(9)	−790 (2)	2186 (3)	1980 (4)
C(10)	−1354 (3)	2480 (4)	2248 (6)
C(11)	−846 (2)	4 (3)	1731 (4)
C(14)	−1227 (2)	−706 (3)	1883 (4)
C(15)	−1754 (3)	−597 (4)	2178 (5)
C(16)	−2094 (3)	−1292 (5)	2283 (6)
C(17)	−1882 (3)	−2088 (4)	2105 (5)
C(18)	−1371 (3)	−2185 (4)	1826 (5)
C(19)	−1035 (2)	−1507 (4)	1703 (4)
C(24)	1545 (2)	−391 (3)	393 (4)
C(25)	1422 (2)	−1218 (4)	597 (4)
C(26)	1762 (3)	−1868 (4)	287 (5)
C(27)	2199 (3)	−1676 (4)	−226 (5)
C(28)	2337 (3)	−858 (5)	−412 (5)
C(29)	2005 (2)	−217 (4)	−115 (5)

[a] The values are $\times 10^{+4}$ except those for the Ni atoms which are $\times 10^{+5}$.

Table IV. Intramolecular Distances (Å) in $[Co(DAPBH)(H_2O)(NO_3)]^+NO_3^-$ (I) and $[Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$ (II)

bond	I, M = Co	II, M = Ni
	In the Cation	
M–N(1)	2.194 (3)	2.018 (4)
M–N(2)	2.203 (2)	2.090 (4)
M–N(5)	2.190 (2)	2.178 (4)
M–O(1)	2.150 (2)	2.282 (3)
M–O(2)	2.229 (2)	2.477 (4)
M–O(3)		2.019 (4)
M–O(4)	2.135 (2)	2.012 (4)
M–O(31)	2.142 (2)	
N(1)–C(1)	1.346 (4)	1.343 (6)
N(1)–C(5)	1.335 (4)	1.327 (7)
C(1)–C(2)	1.387 (4)	1.383 (7)
C(4)–C(5)	1.390 (5)	1.393 (8)
C(2)–C(3)	1.378 (6)	1.371 (9)
C(3)–C(4)	1.379 (5)	1.385 (9)
C(1)–C(6)	1.479 (4)	1.478 (7)
C(5)–C(9)	1.478 (4)	1.489 (8)
C(6)–C(7)	1.495 (5)	1.513 (8)
C(9)–C(10)	1.496 (4)	1.517 (9)
N(2)–C(6)	1.285 (4)	1.282 (6)
N(5)–C(9)	1.283 (4)	1.286 (7)
N(2)–N(3)	1.365 (4)	1.369 (6)
N(5)–N(6)	1.376 (4)	1.366 (6)
N(3)–C(8)	1.358 (4)	1.355 (6)
N(6)–C(11)	1.355 (4)	1.367 (7)
C(8)–O(1)	1.231 (4)	1.227 (6)
C(11)–O(2)	1.231 (4)	1.214 (6)
C(8)–C(24)	1.486 (4)	1.470 (7)
C(11)–C(14)	1.485 (4)	1.487 (8)
C(14)–C(15)	1.391 (5)	1.379 (8)
C(14)–C(19)	1.384 (5)	1.386 (8)
C(15)–C(16)	1.379 (5)	1.397 (10)
C(18)–C(19)	1.383 (5)	1.372 (9)
C(16)–C(17)	1.380 (5)	1.398 (10)
C(17)–C(18)	1.381 (6)	1.333 (11)
C(24)–C(25)	1.380 (5)	1.385 (8)
C(24)–C(29)	1.390 (4)	1.383 (8)
C(25)–C(26)	1.383 (5)	1.406 (9)
C(28)–C(29)	1.383 (5)	1.377 (9)
C(26)–C(27)	1.373 (5)	1.346 (9)
C(27)–C(28)	1.376 (6)	1.374 (10)
	In the Nitrate Ions	
N(30)–O(31)	1.265 (4)	1.210 (7)
N(30)–O(32)	1.231 (4)	1.224 (6)
N(30)–O(33)	1.232 (4)	1.232 (8)
N(40)–O(41)	1.243 (4)	1.233 (7)
N(40)–O(42)	1.226 (5)	1.235 (6)
N(40)–O(43)	1.252 (4)	1.205 (7)

additional six cycles of block-diagonal refinement reduced *R* to 0.039 for Co and 0.065 for the Ni complex. Three additional cycles were calculated in which the hydrogen atom parameters were also varied and the final *R* values were 0.035 for Co and 0.059 for the Ni case.

The scattering factors were taken from the usual sources.[12] All calculations were carried out on an IBM-370/165 using local programs written or modified by G.J.P. The final positional parameters for the nonhydrogen atoms are given in Tables II and III, with the bond distances and angles given in Tables IV and V. Tables of thermal parameters for the nonhydrogen atoms, the hydrogen atom parameters and distances, and the observed and calculated structure amplitudes are available.[13]

Results and Discussion

A comparison of the infrared spectrum of the ligand with the spectra of the cobalt and nickel complexes reveals several interesting features. The N–H frequencies at 3195 and 3070 cm^{-1} in DAPBH shift and become broad in both the cobalt (3410 and 3205 cm^{-1}) and the nickel (3500 and 3200 cm^{-1}) complexes. The strong C=O absorption at 1665 cm^{-1} in DAPBH is shifted to 1640 cm^{-1} in the cobalt complex, I, and is shifted and split, 1670 and 1640 cm^{-1}, in the nickel complex, II. Therefore, the DAPBH ligand is coordinated to the metal in both I and II, but there appears to be a difference in the interaction of the metal ion with the C=O in the two complexes. The broad bands at 1310 cm^{-1} in I and 1340 cm^{-1} in II were assigned to ionic nitrates, but the additional band at 1040 cm^{-1}, present in I but absent in II, is indicative of a coordinated nitrate.[14] X-ray crystal structure studies of I and II were undertaken to confirm the infrared assignments and to establish whether pentagonal-bipyramidal cations were indeed present in both I and II.

The X-ray studies confirmed that a pentagonal-bipyramidal cation exists in both I and II and that one nitrate is coordinated only in the cobalt complex. The cations are shown in Figures 1 and 2, together with the atomic numbering and the thermal ellipsoids. The two Ni–O (ligand) bonds differ by 0.195 Å (see Table IV) which is considerably larger than the difference of 0.079 Å in the cobalt complex. The difference in the Ni–O bonds is slightly smaller than the difference of 0.262 Å found in the $Ni(DAPSC)(H_2O)_2^{2+}$ cation[6] but is similar to the distortion (difference of 0.195 Å) found in the $Cr(DAPSC)(H_2O)_2^{3+}$ cation.[3] The large difference in the Ni—O bond lengths also explains the splitting of the C=O frequency observed for II. The Ni—N(2) and Ni—N(5) distances differ by 0.088 Å which is similar to the difference of 0.104 Å in the $Ni(DAPSC)(H_2O)_2^{2+}$ cation[6] but significantly smaller than the 0.374 Å found in the $Cr(DAPSC)(H_2O)_2^{3+}$ cation.[3] Nevertheless, the results in all three cases are consistent with

Table V. Bond Angles (deg) in [Co(DAPBH)(H_2O)(NO_3)]$^+NO_3^-$ (I) and [Ni(DAPBH)($H_2O)_2]^{2+}(NO_3^-)_2\cdot 2H_2O$ (II)

angle	I	II	angle	I	II
		Angles in the Cation			
O(ax)-M-O(4)	173.6 (1)	171.8 (2)	M-N(1)-C(1)	120.1 (2)	118.0 (3)
O(ax)-M-O(1)	94.6 (1)	87.6 (1)	M-N(1)-C(5)	120.4 (2)	120.6 (3)
O(ax)-M-O(2)	84.0 (1)	83.8 (1)	N(1)-C(1)-C(2)	121.6 (3)	120.2 (5)
O(ax)-M-N(1)	96.0 (1)	90.9 (2)	C(1)-C(2)-C(3)	118.3 (3)	119.5 (5)
O(ax)-M-N(2)	95.9 (1)	89.2 (2)	C(2)-C(3)-C(4)	120.5 (4)	119.6 (6)
O(ax)-M-N(5)	82.4 (1)	92.7 (2)	C(3)-C(4)-C(5)	117.8 (3)	118.6 (6)
O(4)-M-O(1)	86.7 (1)	86.1 (1)	C(4)-C(5)-N(1)	122.2 (3)	120.7 (5)
O(4)-M-O(2)	90.1 (1)	90.3 (1)	C(5)-N(1)-C(1)	119.4 (3)	121.2 (4)
O(4)-M-N(1)	86.9 (1)	97.3 (2)	N(1)-C(1)-C(6)	114.1 (3)	114.0 (4)
O(4)-M-N(2)	90.5 (1)	92.0 (2)	N(1)-C(5)-C(9)	113.6 (3)	114.6 (5)
O(4)-M-N(5)	93.2 (1)	90.3 (2)	C(2)-C(1)-C(6)	124.3 (3)	125.7 (5)
O(1)-M-O(2)	78.7 (1)	71.6 (1)	C(4)-C(5)-C(9)	124.1 (3)	124.7 (5)
O(1)-M-N(2)	72.0 (1)	71.4 (1)	C(1)-C(6)-C(7)	121.2 (3)	120.6 (5)
O(2)-M-N(5)	70.3 (1)	67.0 (1)	C(5)-C(9)-C(10)	121.5 (3)	121.6 (5)
N(1)-M-N(2)	69.9 (1)	76.0 (2)	C(1)-C(6)-N(2)	112.4 (3)	113.1 (5)
N(1)-M-N(5)	69.6 (1)	74.4 (2)	C(5)-C(9)-N(5)	112.4 (3)	112.9 (5)
M-O(1)-C(8)	117.7 (2)	114.4 (3)	N(2)-C(6)-C(7)	126.4 (3)	126.2 (5)
M-O(2)-C(11)	117.1 (2)	114.5 (3)	N(5)-C(9)-C(10)	126.1 (3)	125.4 (5)
M-N(2)-N(3)	114.0 (2)	119.0 (3)	C(6)-N(2)-N(3)	122.5 (3)	122.3 (4)
M-N(5)-N(6)	116.6 (2)	122.0 (3)	C(9)-N(5)-N(6)	119.9 (3)	120.3 (4)
M-N(2)-C(6)	123.4 (2)	118.5 (3)	N(2)-N(3)-C(8)	114.5 (3)	114.4 (4)
M-N(5)-C(9)	123.2 (2)	117.5 (4)	N(5)-N(6)-C(11)	113.8 (2)	115.8 (4)
N(3)-C(8)-O(1)	120.5 (3)	120.7 (5)	N(3)-C(8)-C(24)	117.3 (3)	117.7 (4)
N(6)-C(11)-O(2)	120.4 (3)	120.3 (5)	N(6)-C(11)-C(14)	117.3 (3)	117.5 (5)
O(1)-C(8)-C(24)	122.2 (3)	121.5 (5)	O(2)-C(11)-C(14)	122.2 (3)	122.2 (5)
C(8)-C(24)-C(25)	118.5 (3)	117.4 (5)	C(11)-C(14)-C(15)	122.7 (3)	123.0 (5)
C(8)-C(24)-C(29)	122.0 (5)	123.5 (5)	C(11)-C(14)-C(19)	118.1 (3)	117.2 (5)
C(24)-C(25)-C(26)	120.4 (3)	120.1 (6)	C(14)-C(15)-C(16)	120.4 (3)	120.0 (6)
C(25)-C(26)-C(27)	119.9 (4)	119.2 (6)	C(15)-C(16)-C(17)	119.7 (4)	118.4 (7)
C(26)-C(27)-C(28)	120.3 (4)	121.5 (6)	C(16)-C(17)-C(18)	120.6 (4)	121.0 (7)
C(27)-C(28)-C(29)	120.1 (4)	119.7 (6)	C(17)-C(18)-C(19)	119.5 (4)	121.2 (6)
C(28)-C(29)-C(24)	119.9 (3)	120.4 (6)	C(18)-C(19)-C(14)	120.7 (3)	119.7 (6)
C(29)-C(24)-C(25)	119.4 (3)	119.0 (5)	C(19)-C(14)-C(15)	119.2 (3)	119.7 (5)
		Angles in the Nitrate Ions			
O(31)-N(30)-O(32)	121.5 (3)	120.6 (6)	O(31)-N(40)-O(32)	122.0 (3)	117.2 (5)
O(31)-N(30)-O(33)	118.2 (3)	119.8 (6)	O(31)-N(40)-O(33)	118.2 (3)	122.1 (5)
O(32)-N(30)-O(33)	120.3 (3)	119.6 (6)	O(32)-N(40)-O(33)	119.8 (3)	120.7 (5)

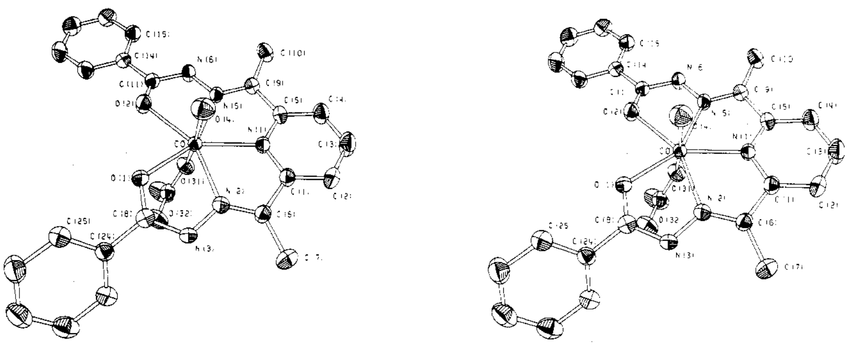

Figure 1. A stereoscopic view of the [Co(DAPBH)(H_2O)(NO_3)]$^+$ cation showing the atomic numbering and thermal ellipsoids. The numbering of N(30) and O(33) of the coordinated nitrate ion was not included for clarity.

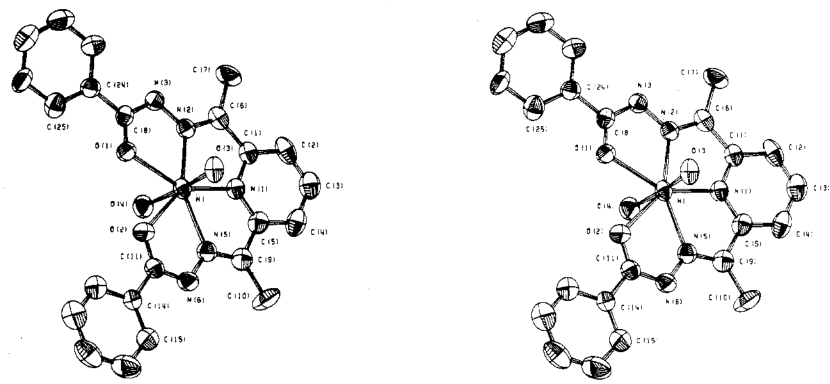

Figure 2. A stereoscopic view of the [Ni(DAPBH)($H_2O)_2]^{2+}$ cation showing the atomic numbering and thermal ellipsoids.

Table VI. Least-Squares Planes[a] and Parameters

	planes			
	1	2	3	4
M	90	−100	−21	42
N(1)	−1*	4*	111*	−56
C(1)	2*	11*	145	−207
C(2)	−4*	−12*	279	−373
C(3)	7*	−1*	398	−340
C(4)	−6*	15*	355	−160
C(5)	4*	−17*	222	−53
C(6)	−6	43	11	−179
C(7)	−14	17	17	−373
N(2)	1	54	−100*	−17*
N(3)	15	78	−216	31
C(8)	169	−34	−175	87
O(1)	376	−164	52*	73*
C(24)	99	−52	−390	106
C(9)	−16	−133	154	15
C(10)	97	−303	368	−104*
N(5)	−110	−150	−76*	103*
N(6)	−213	−288	−241	139
C(11)	−64	−489	−237	37
O(2)	248	−563	13*	−104
C(14)	−212	−632	−460	84
l	9576	3800	9428	3120
m	−0851	−0090	0031	−1167
n	2752	9249	3334	9429
p	0.641	2.034	1.325	1.694
$\Sigma(\mathrm{DEV})^2 \times 10^{+5}$	12	84	3096	3009

[a] The deviations from the plane (Å × 10^3) are given for the specified atom. Equation of the plane: deviation (Å) = $lX + mY + nZ - p$ where X, Y, and Z are the orthogonal coordinates (in Å) relative to a, b, and $c \sin\beta$, and p is the distance of the plane from the origin. The $\Sigma(\mathrm{DEV})^2$ is the sum of the squares of the deviations of the atoms used to define the plane × 10^{+5}. The atoms used to define the planes are noted by an asterisk following the deviations. Planes 1 and 3 are for the cobalt complex, I, and 2 and 4 are for the nickel complex, II.

a Jahn–Teller distortion[10] in high-spin Ni^{2+} and Cr^{3+} ions in a PB crystal field. However, if low-spin PB Ni^{2+} complexes could be prepared, one anticipates that the complexes would be reasonably symmetrical. Consequently, if seven-coordinate intermediates are postulated in any reaction mechanism involving Ni^{2+}, the nature of the complex will be dependent upon the spin state of the Ni(II) ion.

The pyridine ring and the two phenyl groups are planar as expected (see Table VI). However, there is a surprising amount of distortion from the idealized equatorial plane of the PB. The hydrazone side arms [C(6) to O(1) and C(9) to O(2)] are not planar in either I or II, but the distortions are greater in the cobalt complex. The gross deviations from planarity are related to steric interactions involving the phenyl rings since the related DAPSC complexes were much less distorted. The distances from the appropriate phenyl ring hydrogen atom to the hydrogen atom on N(3) or N(6) are 2.48 and 2.15 Å in I and 2.21 and 2.15 Å in II, slightly smaller in most cases than the expected van der Waals contact of 2.4 Å. Obviously, any attempt to make the phenyl rings coplanar with the side arms would require intolerably close H···H contacts. The somewhat longer Ni–ligand distances must relieve some of the steric strain since the sum of the squares of the deviations from planarity of the side chains is about half those found in the cobalt case. In the various DAPSC complexes (where the phenyl ring is replaced by an NH_2 group), the side chains are nearly planar. In summary the distortions from planarity in two DAPBH complexes I and II appear to be related to steric constraints within the DAPBH ligand.

The two axial Co–O bonds in I of 2.135 (2) Å to OH_2 and 2.142 (2) Å to ONO_2^- are possibly significantly different and are slightly shorter than the average axial Co–OH_2 distances found in related PB Co complexes: 2.165 Å in Co(DAPSC)(Cl)$(H_2O)^+$,[5] 2.146 Å in Co(DAPSC)$(H_2O)_2^{2+}$,[15] and 2.150 Å in Co(DAPPH)$(H_2O)_2^{2+}$.[7] The slight lengthening of the Co–OH_2 bond in the Co(DAPSC)(Cl)$(H_2O)^+$ ion could be either a steric effect or a trans effect. However, lack of data on PB Co(II) complexes precludes a definitive conclusion at this time.

In the Ni complex II, the two axial Ni–OH_2 bond lengths of 2.019 (4) and 2.012 (4) Å are not significantly different but are slightly shorter than the corresponding distances of 2.048 (6) and 2.090 (6) Å found in the Ni(DAPSC)$(H_2O)_2^{2+}$ cation.[6,15] The reason for this difference may be related to different hydrogen-bonding patterns in the two structures. Furthermore, the decrease in the axial M–OH_2 distances in going from Co to Ni is consistent with the orbital splitting pattern and the increase in nuclear charge. In contrast the changes in the equatorial distances in going from Co to Ni are much more complicated because of the Jahn–Teller distortion. Finally, we note that while the DAPSC complexes formed two isomorphous series, the DAPBH system does not appear to be as obliging. Moreover, while Co(II) forms complexes with two different axial groups, the only PB Ni(II) complexes isolated to date always have two axial waters. We cannot rationalize this observation and since only three PB Ni(II) complexes have been reported, further speculation is not warranted.

The bond distances and angles in the DAPBH ligand are not particularly noteworthy, being similar to the DAPSC

Table VII. Hydrogen Bonds in $[Co(DAPBH)(NO_3)(H_2O)]^+(NO_3^-)$ and $[Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$

		dist, Å			angle, deg
bond D–H···A[a]	position of A	D–H	H···A	D···A	D–H–A
		In $[Co(DAPBH)(H_2O)(NO_3^-)]^+(NO_3^-)$			
O(4)–H(1)···O(33)	$1 + x, y, z$	0.91 (4)	1.88 (4)	2.784 (4)	171 (4)
O(4)–H(2)···O(41)	x, y, z	0.80 (4)	2.00 (4)	2.794 (4)	169 (4)
N(6)–H(4)···O(43)	$1 - x, y, z$	0.91 (3)	2.05 (3)	2.954 (4)	172 (3)
		In $Ni(DAPBH)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot 2H_2O$			
O(3)–H(15)···O(31)	$-{}^1/_2 + x, {}^1/_2 - y, -z$	0.68 (5)	2.20 (5)	2.869 (6)	169 (6)
O(3)–H(16)···O(1)	$-x, -y, -z$	0.73 (7)	2.25 (7)	2.911 (5)	152 (7)
O(3)–H(16)···O(2)	$-x, -y, -z$	0.73 (7)	2.44 (7)	2.998 (6)	135 (6)
O(4)–H(17)···O(w1)	x, y, z	0.66 (5)	2.06 (5)	2.706 (7)	166 (6)
O(4)–H(18)···O(32)	$-{}^1/_2 + x, y, {}^1/_2 - z$	0.77 (6)	2.51 (6)	3.163 (7)	144 (5)
O(4)–H(18)···O(33)	$-{}^1/_2 + x, y, {}^1/_2 - z$	0.77 (6)	1.99 (6)	2.728 (7)	161 (6)
N(3)–H(3)···O(41)	x, y, z	0.78 (5)	2.11 (5)	2.886 (6)	172 (5)
N(6)–H(4)···O(42)	$-{}^1/_2 + x, y, {}^1/_2 - z$	0.85 (5)	2.20 (5)	3.036 (7)	166 (4)
O(w1)–H(19)···O(w2)	${}^1/_2 - x, -{}^1/_2 + y, z$	0.69 (7)	2.11 (7)	2.772 (8)	162 (7)
O(w1)–H(20)···O(43)	x, y, z	0.79 (7)	2.17 (7)	2.932 (8)	163 (7)

[a] Donor–hydrogen···acceptor. D–H is at x, y, z and A is at the position given.

ligand where appropriate. However, the C(11)–O(2) distance of 1.214 (6) Å is shorter (although not significantly) than the C(8)–O(1) distance of 1.227 (6) Å. The difference in the C–O bond lengths is consistent with the corresponding Ni–O bond distances and is similar to the difference in the C–O bond lengths found in other distorted PB Ni(II) complexes.

There is a slight lengthening of Ni(30)–O(31) of the coordinated nitrate in I which is reasonable since O(31) is bonded to the Co atom. The average of all six N–O nitrate bonds is 1.242 (15) Å in I and 1.223 (13) Å in II. These averages are not significantly different and are in agreement with the value of 1.22 Å generally accepted for the N–O bond in ionic nitrates.[16]

The ions in both compounds are hydrogen bonded in the solid state. The various hydrogen bonds are summarized in Table VII. In I, three of the four hydrogen atoms capable of hydrogen bonding form hydrogen bonds, while in II, nine of a possible ten hydrogen bonds are formed. The situation in II is somewhat more complicated since there appear to be two bifurcated hydrogen bonds, one involving H(16) and the other H(18) on the coordinated water molecules.

In conclusion we see that planar pentadentate ligands such as DAPSC, DAPBH, and DAPPH consistently yield seven-coordinate complexes with Co(II) and, in some cases, Ni(II). Consequently, seven-coordinate complexes of a variety of metal ions can probably be prepared by using these ligands. Results in our laboratory with other ions support this conclusion. Finally, we note that high-spin PB Ni(II) complexes are always distorted in accordance with the Jahn–Teller theory. Therefore, in considering seven-coordinate complexes as intermediates in various reactions involving Ni(II), one must consider the spin-state of the metal ion.

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Registry No. I, 70659-11-9; II, 70659-14-2.

Supplementary Material Available: Tables of the refined thermal parameters, the hydrogen atom positions, and observed and calculated structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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