the conformers indicate that in one of the ligands (with donors N(3), N(4), O(2)) the rings have inverted conformations, while in the other ligand (with donors N(1), N(2), O(1)) the chiralities are alike.

Hydrogen Bonding and Nonbonded Contacts. Table VI gives pertinent data relevant to the hydrogen bonding. Nonbonded contacts less than 3.5 Å are listed in Table VII. Figure 2 shows a projection of the unit cell along the *b* axis.

Each complex cation is involved in five N-H- - -O hydrogen bonds with three neighboring perchlorate groups. Two of the bonds appear to be weak. Their N-O distances (3.259 (5) and 3.269 (5) Å) are longer than the upper limit listed by Pimentel and McClellan[25] for such bonds. However, the H-O distances for these bonds (2.46 (3) and 2.44 (3) Å) are significantly shorter than the sum of the van der Waals radii for an oxygen atom and a hydrogen atom (2.6 Å).[26] The N-H- - -O angles each deviate from linearity and range from 151 (3) to 165 (3)°.

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Registry No. $[Cu(C_4H_{12}N_2O)_2](ClO_4)_2$, 36539-67-0.

Supplementary Material Available. Table I, 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, 20× 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 $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2621.

[25] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., and London, 1960, p 287.

[26] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

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An Unsymmetrical *trans*-Dinitrocobalt(III) Complex. A Crystal Structure Determination

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The crystal structure of *trans*-dinitro-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone)dioximatocobalt(III), $[Co(PnAO\text{-}H)(NO_2)_2]^0$, $C_{13}H_{27}N_6O_6Co$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 8.563 \pm 0.008$ Å, $b = 16.62 \pm 0.02$ Å, $c = 17.54 \pm 0.02$ Å, and $\beta = 133.4 \pm 0.1°$; the space group is $P2_1/c$. The density by flotation is 1.55 g/cm³; four formula units in the unit cell give a calculated density of 1.547 g/cm³. The basic structure was obtained from film data. The final parameters were obtained by refinement using the intensities of 2963 independent reflections measured with a Picker diffractometer using a scintillation counter. Three-dimensional Patterson and Fourier methods, followed by full-matrix least-squares refinement, gave a conventional R factor of 3.5%. The structure consists of discrete neutral molecules with near-octahedral coordination about the cobalt atom. The nitro groups are nitrogen bound and are in the trans configuration. The nitro nitrogens are different distances from the cobalt atom (1.984 ± 0.003 and 1.937 ± 0.003 Å) with the cobalt slightly out of the plane of the amine and oxime nitrogens toward the nitro nitrogen with the short Co-N distance. Weak intramolecular hydrogen bonding may occur between one set of the nitro oxygens and the amine hydrogens. The O- - -O distance for the characteristic intramolecular hydrogen bond formed between the oxime groups is 2.432 ± 0.003 Å.

Introduction

The molecule described in this paper is of special interest from two points of view. First, it contains a short intramolecular hydrogen bond which may be nearly symmetrical.[1] Structures of similar planar complexes of α-amine oxime ligands[2,3] with Ni(II) and Pt(II) have been determined and compared with the dimethylglyoximates[4] and glyoximates[5,6] of these metals. Modifications in the hydrogen bond due to a small metal ion such as Co(III) and to an octahedral geometry could lead to a better understanding of the nature of all hydrogen bonds. Second, this complex is related to vitamin B_{12} in having a strongly planar inducing ligand and apical positions containing more labile groups. Numerous chemical studies have been made on the cobalt(II)-cobalt(III)-bis(dimethylglyoxime) system which has been called a model system[7] for the B_{12} moiety. Of consequence is the possibility that the apical positions are not equivalent and that one may have considerably more π-bonding capability than the other. If a difference exists, then the cause, steric or electronic, becomes important. This paper summarizes a structure determination on a complex with a strong tetradentate ligand PnAO (Figure 1) in the planar positions and nitro groups in the trans positions. Before and during this structural study, chemical experiments were being conducted investigating the kinetic behavior toward substitution of the trans nitro groups. A substantial difference in lability for the two nitro groups was observed.

[1] R. K. Murmann, *J. Amer. Chem. Soc.*, 79, 521 (1957); 80, 4174 (1958); E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, 6, 2043 (1967).

[2] E. O. Schlemper, *Inorg. Chem.*, 7, 1130 (1968).

[3] E. O. Schlemper, *Inorg. Chem.*, 8, 2740 (1969).

[4] (a) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, 6, 487 (1953); (b) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, 81, 755 (1959); (c) E. Frasson, C. Panattoni, and R. Zannetti, *Acta Crystallogr.*, 12, 1027 (1959).

[5] (a) M. Calleri, G. Ferraris, and D. Viterbo, *Acta Crystallogr.*, 22, 468 (1967); (b) R. K. Murmann and E. O. Schlemper, *ibid.*, 23, 667 (1967).

[6] G. Ferraris and D. Viterbo, *Acta Crystallogr.*, 25, 2066 (1969).

[7] G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 97, 3056 (1964).

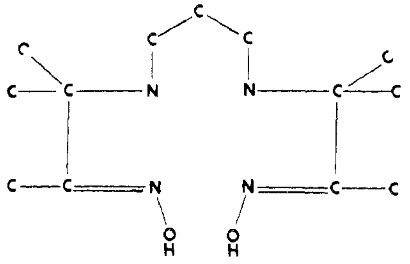

Figure 1. Structural formula of the 2,2′-(1,3-diaminopropane)-bis(2-methyl-3-butanone)dioxime (PnAO) neutral ligand.

Experimental Section

Crystal Preparation. The complex $[Co(PnAO\text{-}H)(NO_2)_2]^0$ was prepared as described in a parallel paper.[8] Its final crystallization was carried out by slow evaporation of a acetone–water solution. Previous studies indicated that no chemical change occurs with these crystallization conditions.

X-Ray Data. *trans*-Dinitro-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butane)dioximatocobalt(III) crystallizes in the monoclinic crystal system with four molecules in a unit cell with $a = 8.563 \pm 0.008$ Å, $b = 16.62 \pm 0.02$ Å, $c = 17.54 \pm 0.02$ Å, and $\beta = 133.4 \pm 0.1°$. These cell constants and their standard deviations were determined from a least-squares refinement of the setting angles of 27 reflections that had been left-right centered on a Picker four-circle X-ray diffractometer with Mo Kα radiation. These values agree well with those determined from Mo Kα precession photographs which gave $a = 8.57 \pm 0.01$ Å, $b = 16.59 \pm 0.02$ Å, $c = 17.56 \pm 0.02$ Å, and $\beta = 133.4 \pm 0.1°$. A measurement of the density by flotation in a benzene-carbon tetrachloride solution gave 1.55 g/cm^3. A calculated density of 1.547 g/cm^3 is obtained, assuming four molecules per unit cell. The systematic extinctions were for $h0l$, l odd, and for $0k0$, k odd, indicating that the space group is $P2_1/c$.

Two sets of intensity data were collected. The first set was collected using a crystal of near-octahedral shape with dimensions approximately 0.2 × 0.2 × 0.3 mm, mounted with the a axis as the rotation axis. From this crystal, using a Zr filter and brass attenuating sheets, multiple-film Mo Kα Weissenberg photographs were taken of the $0kl$–$8kl$ levels. Multiple exposures were taken of the $hk0$–$hk4$ and $h0l$–$h3l$ levels by the precession method. The relative intensities were estimated by visual comparison with a series of timed exposures of a selected reflection. There were 1477 reflections of measurable intensity. The usual Lorentz and polarization corrections were applied. The data were placed on a common scale using the interlayer scaling program of Hamilton, Rollett, and Sparks.[9] These data were used to solve the basic structure.

The second data set which was used in the final refinement was collected on a Picker Four-Angle Programmer System.[10] The crystal used for this data set had approximate dimensions of 0.3 × 0.4 × 0.5 mm. The crystal was mounted about the b axis. The data were collected using Mo Kα radiation with a niobium β filter. Twenty-seven manually centered reflections were used to refine the orientation and cell constants. Intensity data were collected at a takeoff angle of 3.0°. At this takeoff angle there was essentially no loss of integrated intensity. The receiving aperture was 3 × 3 mm and was positioned 27 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min. The scan was variable to account for the α_1–α_2 splitting and ranged from 0.74 to 1.04° in 2θ in the 0–50° 2θ region collected. Stationary-counter backgrounds were taken for 20 sec on each side of the scan. Automatic attenuation was used to prevent exceeding about 8000 cps during the scan. One-mil brass foils were used as attenuators to give attenuator factors of about 3. The pulse height analyzer was set for about a 95% window, centered on the Mo Kα peak. Two standard reflections were measured about every 50 reflections as a check on crystal and instrument stability. No systematic drift was observed.

Background and Lorentz-polarization corrections were made with a local program which uses the same approach as that of Corfield, Doedens, and Ibers.[11] The value of p in $\sigma = [\sigma^2{}_{\text{counting}} + (pF_o{}^2)^2]^{1/2}$ was chosen as 0.05 in keeping with the findings of other workers. Absorption corrections were made ($\mu = 10.3$ cm^{-1}) with the transmission factor ranging from 0.69 to 0.77. Equivalent and duplicate reflections were then averaged, reducing the number of reflections from about 4500 to 3144 independent reflections. Of these, 2963 which had $F_o{}^2 > 2\sigma(F_o{}^2)$ were used in the final stages of refinement of the structure.

Determination of the Structure. The basic structure was solved from the film data as follows. The position of the cobalt atom was found from a three-dimensional Patterson synthesis and was used to phase the F_o values for a three-dimensional Fourier synthesis. From these maps all atoms except hydrogens were located. Refinement of positional and isotropic thermal parameters by full-matrix least squares with the film data set converged with $R = \Sigma|F_o{}^2 - kF_c{}^2|/\Sigma F_o{}^2 = 0.186$ and $r = [\Sigma w(F_o{}^2 - kF_c{}^2)^2/\Sigma wF_o{}^4]^{1/2} = 0.271$ where $w = 1/\sigma^2(F_o{}^2)$. In this and all refinements, the quantity $\Sigma w(F_o{}^2 - kF_c{}^2)^2$ was minimized. In the final refinement of the film data $\sigma(F_o{}^2)$ was selected[12] to make $(F_o{}^2 - F_c{}^2)/\sigma$ nearly independent of $F_o{}^2$. In this and subsequent calculations, scattering factors[13a] for neutral atoms were used. Using the tabulated values[13b] of f' and f'' for Co, the effects of anomalous dispersion were included in F_c.[13c] Refinement with the cobalt atom anisotropic reduced R to 0.181 and r to 0.259, corresponding to a conventional agreement factor ($r^* = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.108. The standard deviation of an observation of unit weight was 1.30.

Since the standard deviations were too large to clearly establish a difference in Co–N(NO$_2$) distances and since a Picker automated diffractometer had become available, a new set of data was collected and used for the final refinement of the structure (see X-ray data section). Refinement of the counter data set began using the final parameters from the film data refinement. Full-matrix least-squares refinement with all 26 nonhydrogen atoms anisotropic reduced R to 0.133 and r to 0.200. At this stage a difference Fourier was prepared from which all 27 hydrogen atoms were located. Some of the methyl hydrogens were not well resolved, probably due to hindered methyl groups rotation; but chemically reasonable positions could be selected with electron densities from 0.5 to 0.9 e/Å^3. These hydrogens (Table I) were included in subsequent refinement at fixed positions with fixed isotropic temperature factors. All anisotropic refinement then resulted in $R = 0.054$ and $r = 0.113$. Since the weighted r was much higher than the unweighted R and the standard deviation of an observation of unit weight was 1.91, the weighting scheme was modified to make $(F_o{}^2 - F_c{}^2)/\sigma$ nearly independent of $F_o{}^2$. The final weighting scheme which had $\sigma = -0.0213F_o{}^4 + 0.62F_o{}^2$ for $F_o{}^2 < 15.0$, $\sigma = -0.00846F_o{}^4 + 0.237F_o{}^2$ for $28.0 \leqslant F_o{}^2 < 76.0$, $\sigma = -0.000345F_o{}^4 + 0.136F_o{}^2$ for $76.0 \leqslant F_o{}^2 < 270.0$, and $\sigma = 0.040F_o{}^2$ for $F_o{}^2 \geqslant 270.0$ gave $R = 0.052$ and $r = 0.084$. The conventional agreement factor was 0.035.[14] The standard deviation of an observation of unit weight was 1.50. The hydrogen atom positions were not refined.

A Fourier synthesis using the observed structure factor magnitudes and phases from the last cycle of calculated structure factors showed the weakest carbon atoms to have peak densities of 5.4 e/Å^3. A final difference Fourier revealed no electron density greater than 0.6 e/Å^3. The final positional and thermal parameters are included in Tables II and III.

Continued refinement of the film data set with the hydrogen atoms from the counter data set and with the cobalt anisotropic reduced R to 0.157 and r to 0.222. The other atoms were held with fixed thermal parameters from the counter data refinement. The results of this refinement are in Table IV.

Discussion

Nature of the Structure. The crystal structure consists of discrete neutral octahedral molecules (Figure 2). The octa-

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(8) H. Goff, S. Kidwell, J. Lauher, and R. K. Murmann, *Inorg. Chem.*, 12, 2631 (1973).

(9) This and all other calculations were done on the IBM 360/65 computer of the University of Missouri Computer Research Center using the following programs: W. Hamilton and J. Ibers' NUPIK Picker input program, W. Hamilton's HORSE general absorption correction program, A. Zalkin's FORDAP Fourier program, modified versions of W. Busing and H. Levy's full-matrix least-squares program and ORFFE function and error program, C. Johnson's ORTEP ellipsoid plot program, and local data processing programs.

(10) The diffractometer was aligned with the aid of a basic beryllium acetate crystal using conventional techniques which included an examination of the uniformity of both source and counter.

(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(12) R. A. Lalancette, M. Cefola, W. C. Hamilton, and S. J. LaPlaca, *Inorg. Chem.*, 6, 2127 (1967).

(13) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 216; (c) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

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

Table I. Hydrogen Atom Parameters[a]

Atom	x	y	z
H1	−0.360	0.078	0.370
H2	0.070	0.158	0.045
H3	−0.070	0.024	0.104
H4	−0.410	0.177	−0.035
H5	−0.290	0.118	−0.045
H6	−0.125	0.258	0.085
H7	−0.182	0.252	−0.025
H8	−0.368	0.075	0.063
H9	−0.230	0.148	0.137
H10	0.285	0.305	0.025
H11	0.080	0.262	−0.040
H12	0.235	0.210	0.005
H13	0.065	0.357	0.088
H14	0.315	0.375	0.165
H15	0.220	0.330	0.205
H16	0.300	−0.065	0.440
H17	0.470	−0.085	0.435
H18	0.265	−0.120	0.370
H19	−0.115	−0.108	0.220
H20	−0.265	−0.058	0.125
H21	−0.120	−0.095	0.140
H22	0.010	0.100	0.315
H23	−0.045	0.018	0.330
H24	−0.234	0.050	0.224
H25	−0.360	0.265	0.195
H26	−0.300	0.305	0.280
H27	−0.200	0.230	0.300

[a] H1 is in the intramolecular hydrogen bond ($B = 6$). H2 and H3 are on the amine nitrogens ($B = 5$). H4–H9 are on the methylene carbons ($B = 6$). H10–H27 are the methyl hydrogens ($B = 7$). These positions are directly from a difference Fourier and were not refined.

Table II. Atom Positional Parameters[a]

Atom	x	y	z
Co	0.22347 (5)	0.11313 (2)	0.20633 (2)
N1	0.4788 (3)	0.1625 (1)	0.2557 (1)
N2	0.3508 (3)	0.0320 (1)	0.3109 (1)
N3	−0.0438 (3)	0.0597 (1)	0.1504 (2)
N4	0.0876 (3)	0.1917 (1)	0.0910 (2)
N5	0.2381 (4)	0.0363 (1)	0.1248 (2)
N6	0.2351 (3)	0.1849 (1)	0.2971 (2)
O1	0.6738 (3)	0.1332 (1)	0.3399 (1)
O2	0.5666 (3)	0.0191 (1)	0.3819 (1)
O3	0.1880 (6)	−0.0356 (1)	0.1190 (2)
O4	0.2864 (5)	0.0571 (2)	0.0767 (2)
O5	0.0845 (4)	0.2294 (1)	0.2641 (2)
O6	0.3998 (3)	0.1851 (1)	0.3916 (1)
C1	0.4661 (4)	0.2246 (2)	0.2090 (2)
C2	0.2443 (4)	0.2562 (2)	0.1171 (2)
C3	0.2331 (4)	−0.0119 (1)	0.3141 (2)
C4	−0.0061 (5)	0.0049 (2)	0.2314 (2)
C5	0.6615 (5)	0.2669 (2)	0.2451 (3)
C6	0.2135 (6)	0.2678 (3)	0.0207 (2)
C7	0.2130 (6)	0.3361 (2)	0.1480 (3)
C8	0.3220 (6)	−0.0746 (2)	0.3963 (2)
C9	−0.1317 (6)	−0.0730 (2)	0.1754 (3)
C10	−0.0718 (6)	0.0445 (2)	0.2851 (3)
C11	−0.2435 (4)	0.1091 (2)	0.0883 (2)
C12	−0.1327 (4)	0.2218 (2)	0.0355 (2)
C13	−0.2862 (4)	0.1530 (2)	0.0002 (2)

[a] In this and subsequent tables values in parentheses are standard deviations from the least-squares refinement.

hedron about the cobalt atom consists of the four nitrogens of the amine oxime ligand in a square plane and two nitro groups in trans positions. There are no unusually short intramolecular contacts as can be seen from Table V where all intermolecular distances (ignoring hydrogens) under 4.0 Å are given. The shortest contact distance, 3.04 Å from O3 to O4, is longer than the sum of the van der Waals radii (2.80 Å).[15]

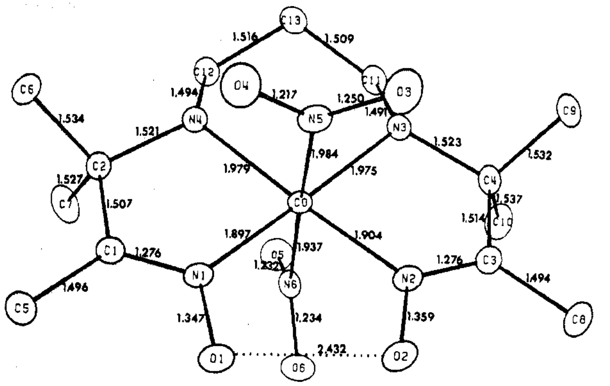

Figure 2. Bond distances in $[Co(PnAO\text{-}H)(NO_2)_2]^0$. The standard deviations are given in Table V.

The planes of the nitro groups are nearly perpendicular to each other, the dihedral angle being 84.3 (2)°. The tetradentate amine oxime ligand sterically affects one nitro group due to the puckering of the -C-C-C- ring. Two methylene groups (C11 and C12) come in close contact with one nitro group (N6). In particular, O5 of that nitro group is only 3.08 Å from C11 and 3.05 Å from C12. These close contacts are probably responsible for the bending of that nitro group away from the -C-C-C- ring as evidenced by the angles N6-Co-N4, 95.5°, and N6-Co-N3, 94.1°. Because of this bending the cobalt is on the N6 side of the plane of the amine oxime nitrogens. Deviations from weighted least-squares planes through four nitrogens and the cobalt are summarized in Table VI. In no case are the cobalt and four nitrogens coplanar. The deviations are largely due to the steric requirements of the N6 nitro group. It is interesting to note that the puckering about C2 and C4 is considerably less than that observed[2] for bis(2-amino-2-methyl-3-butanoneoximato)nickel(II) chloride monohydrate. In the nickel compound the C7 and C10 methyl groups were 2.09 and 2.12 Å from the square plane whereas they are only 1.63 and 1.76 Å from the square plane in this complex. This difference is most probably brought about by the steric requirements of the -C-C-C- bridge.

The orientation of the N6 nitro group is the most symmetrical possibility that also minimizes the interaction between the N6 oxygens and C7, C10, C11, and C12. The other nitro group, N5, is in a position which places its oxygens in the best possible position for intramolecular hydrogen bonds to amine nitrogen hydrogens on N3 and N4. The O3-N3 distance (2.87 Å) and O4-N4 distance (2.93 Å) are suggestive of hydrogen bonding, but the angles O3-H3-N3 (124.4°) and O4-H2-N4 (129.2°) are far from typical. It is possible that this weak interaction accounts for the orientation of this nitro group.

The short intramolecular O1- - -O2 hydrogen bond (2.432 (3) Å) is typical of complexes of this type. A neutron diffraction study of bis(2-amino-2-methyl-butanoneoximato)nickel(II) chloride monohydrate[16] has revealed an O- - -O distance of 2.420 (3) Å while an X-ray study of dichlorobis(2-amino-2-methylbutanoneoximato)cobalt(III)[17] has revealed an O- - -O distance of 2.421 (3) Å. These latter compounds do not have the propylene ring opposite the hydrogen bond as does the present compound. In the present compound the hydrogen appears to be nearly symmetrically

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(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(16) E. O. Schlemper, S. J. LaPlaca, and W. C. Hamilton, *J. Chem. Phys.*, 54, 3990 (1971).

(17) E. O. Schlemper, S. J. LaPlaca, and W. C. Hamilton, to be submitted for publication.

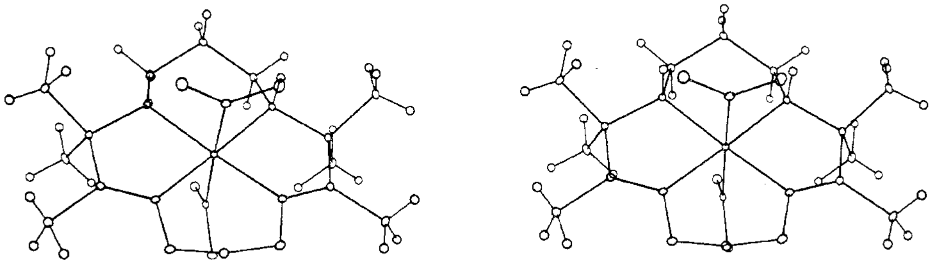

Figure 3. Stereoscopic pair showing the structure of $[Co(PnAO\text{-}H)(NO_2)_2]^0$ including the hydrogen atoms. The atom designations can be found in Figure 2.

Table III. Atomic Thermal Parameters

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.01562 (9)[b]	0.00216 (1)	0.00344 (2)	0.00037 (2)	0.00496 (4)	−0.00015 (1)
N1	0.0152 (5)	0.0036 (1)	0.0035 (1)	0.0004 (2)	0.0050 (2)	−0.00015 (8)
N2	0.0209 (6)	0.0026 (1)	0.0039 (1)	0.0016 (2)	0.0059 (2)	0.00004 (7)
N3	0.0191 (5)	0.0024 (1)	0.0049 (1)	−0.0004 (2)	0.0060 (2)	0.00008 (8)
N4	0.0162 (5)	0.0029 (1)	0.0044 (1)	0.0003 (2)	0.0052 (2)	0.00044 (8)
N5	0.0276 (7)	0.0034 (1)	0.0044 (1)	0.0010 (2)	0.0075 (3)	−0.00041 (9)
N6	0.0235 (6)	0.0022 (1)	0.0059 (1)	−0.0006 (2)	0.0094 (3)	−0.00036 (8)
O1	0.0145 (4)	0.0052 (1)	0.0047 (1)	0.0016 (2)	0.0047 (2)	0.00065 (8)
O2	0.0225 (5)	0.0043 (1)	0.0051 (1)	0.0033 (2)	0.0063 (2)	0.00127 (8)
O3	0.0836 (14)	0.0034 (1)	0.0114 (2)	0.0009 (3)	0.0256 (5)	−0.0008 (1)
O4	0.0633 (12)	0.0056 (1)	0.0114 (2)	−0.0028 (3)	0.0236 (5)	−0.0022 (1)
O5	0.0363 (7)	0.0036 (1)	0.0089 (2)	0.0024 (2)	0.0132 (3)	−0.0005 (1)
O6	0.0303 (6)	0.0047 (1)	0.0051 (1)	−0.0012 (1)	0.0081 (3)	−0.0016 (1)
C1	0.0177 (6)	0.0042 (1)	0.0045 (2)	−0.0009 (2)	0.0064 (3)	−0.0003 (1)
C2	0.0190 (7)	0.0037 (1)	0.0049 (2)	−0.0009 (2)	0.0063 (3)	0.0005 (1)
C3	0.0296 (8)	0.0022 (1)	0.0048 (2)	0.0006 (2)	0.0089 (3)	−0.0002 (1)
C4	0.0281 (8)	0.0025 (1)	0.0064 (2)	−0.0010 (2)	0.0095 (3)	0.0002 (1)
C5	0.0225 (8)	0.0073 (2)	0.0070 (2)	−0.0035 (3)	0.0079 (4)	0.0007 (2)
C6	0.0309 (9)	0.0085 (2)	0.0052 (2)	−0.0045 (4)	0.0080 (4)	0.0011 (2)
C7	0.0346 (10)	0.0028 (1)	0.0120 (3)	−0.0014 (3)	0.0140 (5)	0.0000 (1)
C8	0.0458 (11)	0.0030 (1)	0.0063 (2)	0.0018 (3)	0.0128 (4)	0.0008 (1)
C9	0.0459 (13)	0.0033 (1)	0.0082 (3)	−0.0050 (3)	0.0108 (5)	0.0000 (1)
C10	0.0407 (12)	0.0049 (1)	0.0100 (3)	0.0013 (3)	0.0170 (5)	0.0012 (2)
C11	0.0177 (6)	0.0034 (1)	0.0071 (2)	−0.0002 (2)	0.0071 (3)	0.0005 (1)
C12	0.0171 (6)	0.0032 (1)	0.0060 (2)	0.0010 (2)	0.0060 (3)	0.0010 (1)
C13	0.0147 (6)	0.0033 (1)	0.0057 (2)	0.0004 (2)	0.0045 (3)	0.0004 (1)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses given here and in other tables are estimated standard deviations.

Table IV. Comparison of Counter and Film Bond Distances (Å)

Bond	Counter	Film	Bond	Counter	Film
Co-N1	1.897 (3)	1.91 (1)	N4–C2	1.521 (3)	1.50 (2)
Co-N2	1.904 (3)	1.92 (1)	N3–C4	1.523 (3)	1.51 (2)
Co-N3	1.975 (3)	1.99 (1)	N3–C11	1.491 (4)	1.50 (2)
Co-N4	1.979 (3)	1.99 (1)	N4–C12	1.494 (4)	1.51 (2)
Co-N5	1.984 (3)	1.97 (2) (1.95[a])	C1–C5	1.496 (4)	1.47 (2)
Co-N6	1.937 (3)	2.00 (2) (2.01[a])	C3–C8	1.494 (4)	1.45 (2)
N1-O1	1.347 (3)	1.32 (2)	C1–C2	1.507 (4)	1.51 (2)
N2-O2	1.359 (3)	1.37 (2)	C3–C4	1.514 (4)	1.54 (2)
N5-O3	1.250 (3)	1.25 (2)	C2–C6	1.534 (4)	1.50 (3)
N5-O4	1.217 (3)	1.22 (2)	C2–C7	1.527 (5)	1.58 (3)
N6-O5	1.232 (3)	1.15 (2) (1.14[a])	C4–C9	1.532 (4)	1.55 (3)
N6-O6	1.234 (3)	1.23 (2) (1.21[a])	C4–C10	1.537 (4)	1.57 (3)
N1-C1	1.276 (3)	1.28 (2)	C12–C13	1.516 (4)	1.51 (3)
N2-C3	1.276 (3)	1.27 (2)	C11–C13	1.509 (4)	1.52 (3)

[a] Before addition of hydrogens.

Table V. Intermolecular Distances

Dist	Value, Å	Dist	Value, Å
O3–O4	3.04	C8–C8	3.66
O3–N5	3.19	C5–C8	3.69
O3–O3	3.27	O3–C5	3.73
O6–C8	3.27	O3–N4	3.73
O6–C12	3.30	O1–C6	3.74
O6–C13	3.32	O4–C13	3.74
O3–C13	3.36	O2–C7	3.80
O5–C9	3.39	C5–C6	3.82
O2–C8	3.43	O4–C11	3.83
O1–C12	3.54	O5–C6	3.83
O4–N3	3.55	C9–C13	3.87
N5–N5	3.55	C7–C9	3.92
O4–N5	3.64	O3–C12	3.92
O6–C6	3.64	C3–C8	3.97
O4–C9	3.65		

disposed between the oxygens with O1-H1 = 1.19 Å, O2-H1 = 1.26 Å, and an O2-H1-O2 angle of 168°. It should be emphasized that distances and angles involving hydrogens are very approximate and based solely on difference Fourier hydrogen positions. The two O-H distances may then be equal or as much as 0.2-0.3 Å different.

The shapes and orientations of the thermal ellipsoids are shown in Figures 2 and 3. The root-mean-square displacements along the principal axes are in Table VII. The cobalt atom vibration is nearly isotropic with the minimum vibration approximately toward the nitro nitrogens. The orientations of the ellipsoids of the atoms show the expected trend toward reduced vibration along bonds. The oxygens of the least sterically crowded nitro group (N5) are vibrating considerably more than those on N6 with the maximum vibration in the direction expected for hindered rotation.

Distances and Angles Involving the Amine Oxime Ligand. The molecule has approximate $C_s(m)$ symmetry with the near mirror plane passing through the cobalt atom and the nitro groups. The bond distances derived from the counter data are included in Figure 2 and are compared with those from the film data in Table IV. The ligand distances are

Table VI. Deviations from Least-Squares Planes

N2, N4, N5, N5, Co Plane
$7.21x + 5.46y - 4.70z - 12.60 = 0$

Atom	Dist, Å	Atom	Dist, Å
Co	−0.0011 (3)	N5	0.068 (2)
N2	−0.018 (2)	N6	0.048 (2)
N4	−0.010 (2)		

N1, N3, N5, N6, Co Plane
$0.252x - 10.84y + 9.29z - 0.749 = 0$

Atom	Dist, Å	Atom	Dist, Å
Co	−0.0016 (3)	N5	0.078 (2)
N1	−0.013 (2)	N6	0.067 (2)
N3	−0.010 (2)		

N1, N2, N3, N4, Co Plane
$4.80x - 10.59y - 13.50z + 2.907 = 0$

Atom	Dist, Å	Atom	Dist, Å
Co	−0.0028 (3)	C4	−0.298
N1	0.034 (2)	C5	−0.051
N2	0.057 (2)	C8	−0.106
N3	0.034 (2)	C7	−1.627
N4	0.069 (2)	C10	−1.758
O1	0.143	C6	0.820
O2	0.270	C9	0.679
C1	−0.055	C11	−0.610
C3	−0.087	C12	−0.558
C2	0.214	C13	−0.090

Table VII. Root-Mean-Square Components of Thermal Displacement along the Principal Axis (Å)

Atom	Axis 1	Axis 2	Axis 3
Co	0.160 (1)	0.171 (3)	0.188 (1)
N1	0.169 (3)	0.172 (3)	0.226 (3)
N2	0.170 (3)	0.179 (4)	0.231 (3)
N3	0.179 (3)	0.193 (3)	0.221 (3)
N4	0.176 (3)	0.192 (3)	0.214 (3)
N5	0.172 (3)	0.213 (3)	0.255 (3)
N6	0.172 (4)	0.177 (3)	0.227 (3)
O1	0.164 (3)	0.223 (2)	0.272 (2)
O2	0.175 (3)	0.234 (2)	0.267 (3)
O3	0.188 (3)	0.260 (3)	0.407 (4)
O4	0.183 (3)	0.281 (3)	0.363 (3)
O5	0.180 (3)	0.273 (3)	0.284 (3)
O6	0.177 (3)	0.256 (3)	0.278 (3)
C1	0.176 (3)	0.190 (3)	0.244 (3)
C2	0.183 (4)	0.196 (3)	0.245 (3)
C3	0.161 (4)	0.191 (3)	0.245 (3)
C4	0.173 (4)	0.227 (3)	0.238 (4)
C5	0.187 (4)	0.240 (4)	0.346 (4)
C6	0.181 (4)	0.228 (4)	0.381 (5)
C7	0.190 (4)	0.257 (4)	0.325 (4)
C8	0.185 (4)	0.216 (4)	0.309 (4)
C9	0.177 (4)	0.260 (4)	0.366 (5)
C10	0.195 (4)	0.256 (4)	0.306 (4)
C11	0.181 (3)	0.212 (4)	0.266 (3)
C12	0.177 (3)	0.205 (4)	0.257 (3)
C13	0.168 (4)	0.213 (4)	0.261 (3)

comparable with those observed[2] for the nickel(II) α-amine oxime complex. The average N-O(oxime) distance 1.353 (3) Å is also in good agreement with those observed[4] for metal dimethylglyoximates. The C-N(oxime) bond distances are close to that expected[18] for a double bond (1.29 Å). The C-C distances show the variations expected in going from sp^3 to sp^2 hybridization. The C-C distances in the six-membered ring are a little shorter than the typical 1.54 Å, and the C2-N4 and C4-N3 distances, a bit longer than the usual 1.47 Å. The angles (Table VIII) around the oxime nitrogens are quite close to 120° ranging from 119.2 (3) to 121.1 (3)°. However, the angles about the sp^2 carbons, C1 and C3, deviate more from 120° ranging from 116.2 (3) to 123.1 (3)° with the smaller angles in the chelate rings. The chelate ring angles for the sp^3 carbons, C2 and C4, are also contracted being 106.2 (3) and 106.5 (3)° with the angles N4-C2-C7 and N3-C4-C10 opening up to 112.7 (3) and 112.6 (3)°. The angles about the amine nitrogens, N3 and N4, differ dramatically from tetrahedral values with Co-N3-C11 and Co-N4-C12 approaching 120° angles at 118.0 (3) and 118.5 (3)°. This is probably brought about by the steric requirements of the chelate ring. The angles at the carbon atoms in the six-membered ring also deviate markedly from tetrahedral, especially the C11-C13-C12 angle of 114.4 (3)°.

Table VIII. Bond Angles

Angle	Value, deg	Angle	Value, deg
N1-Co-N2	98.6 (1)	C3-N2-O2	119.2 (2)
N1-C1-N4	82.2 (1)	Co-N3-C4	112.0 (2)
N2-Co-N3	82.0 (1)	Co-N3-C11	118.0 (2)
N3-Co-N4	97.1 (1)	C4-N3-C11	114.3 (2)
N5-Co-N1	89.0 (1)	Co-N4-C2	112.4 (2)
N5-Co-N2	87.7 (1)	Co-N4-C12	118.5 (2)
N5-Co-N4	88.4 (1)	N1-C1-C5	122.2 (2)
N6-Co-N1	88.0 (1)	N1-C1-C2	117.2 (2)
N6-Co-N2	88.4 (1)	C2-C1-C5	120.6 (3)
N6-C0-N3	94.1 (1)	N2-C3-C8	123.1 (2)
N6-Co-N4	95.5 (1)	N2-C3-C4	116.2 (3)
N5-Co-N6	174.8 (1)	C4-C3-C8	120.7 (2)
N1-Co-N3	177.7 (1)	N4-C2-C1	106.2 (2)
N2-Co-N4	176.0 (1)	N4-C2-C6	108.0 (2)
Co-N5-O3	119.1 (2)	N4-C2-C7	112.7 (2)
Co-N5-O4	122.4 (2)	C1-C2-C6	111.0 (2)
O3-N5-O4	118.4 (2)	C1-C2-C7	108.8 (2)
Co-N6-O5	122.5 (2)	C6-C2-C7	110.1 (3)
Co-N6-O6	118.1 (2)	N3-C4-C3	106.5 (2)
O5-N6-O6	119.4 (2)	N3-C4-C9	107.6 (2)
O1-N1-Co	121.1 (2)	N3-C4-C10	112.6 (2)
C1-N1-Co	119.6 (2)	C3-C4-C9	110.4 (3)
O1-N1-C1	119.3 (2)	C3-C4-C10	108.4 (2)
O2-N2-Co	120.8 (2)	C9-C4-C10	111.3 (3)
C3-N2-Co	120.1 (2)	N4-C12-C13	111.5 (2)
C2-N4-C12	114.1 (2)	N3-C11-C13	111.3 (2)
		C11-C13-C12	114.4 (2)

The Co-N distances are compared with those in related compounds in Table IX. The Co-N(amine) distances are in good agreement with those observed for other nitroammine complexes.[19-24] The Co-N(oxime) distances are shorter than those observed for diamminebis(dimethylglyoximato)-cobalt(III) nitrate.[25] There is of course a large deviation from 90° angles for the N-Co-N angles in the amine oxime plane because of the different ring systems.

The distances and angles involving hydrogen atoms are not reportedly individually because the hydrogen atom positions are not of sufficient accuracy and have not been refined. The C-H distances range from 0.76 to 1.06 Å, the N-H distances are 0.90 and 0.91 Å, and the O-H distances in the hydrogen bond are 1.19 and 1.26 Å. The H-C-X angles range from 84 to 125° with the large deviations from tetrahedral values coming for C5 and C6. The H-N-X angles range from 97 to 106°, and O- - -H- - -O angle for the hydro-

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(18) Reference 15, p 228.

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Table IX. Comparison of Co-N Distances with Those in Related Compounds

Compd	Dist	Value,[a] Å	Ref
$[Co(PnAO\text{-}H)(NO_2)_2]^0$	Co-N(amine)	1.977 (3)	*b*
$[Co(NO_2)_3NH_3en]^0$	Co-N(amine)	1.950 (7)	*c*
$(-)_{546}$-*cis*-β-$[Co(NO_2)_2$-(L-3,8-dimetrien)$]ClO_4$	Co-N(amine)	1.972 (15)	*d*
$(-)_{546}$-*cis*-β-$[Co(NO_2)_2$-(L-3,8-dimetrien)$]ClO_4$	Co-N(NO_2)	1.932 (17)	*d*
trans-$[Co(NH_3)_4(NO_2)_2]NO_3\cdot H_2O$	Co-N(NH_3)	1.969 (12)	*e*
cis-$[Co(NH_3)_4(NO_2)_2]NO_3$	Co-N(NH_3)	1.997 (12)	*f*
$[Co(NH_3)_5NO_2]Cl_2$	Co-N(NH_3)	1.961 (10)	*g*
$[Co(NH_3)_5NO_2]Br_2$	Co-N(NH_3)	1.978 (15)	*h*
$[Co(PnAO\text{-}H)(NO_2)_2]^0$	Co-N(oxime)	1.900 (3)	*b*
$[Co(DMG\text{-}2H)(NH_3)_2]NO_3$	Co-N(oxime)	1.95 (2)	*i*
$[Co(PnAO\text{-}H)(NO_2)_2]^0$	Co-N6(NO_2)	1.935 (3)	*b*
$[Co(PnAO\text{-}H)(NO_2)_2]^0$	Co-N5(NO_2)	1.982 (3)	*b*
trans-$[Co(NH_3)_4(NO_2)_2]NO_3\cdot H_2O$	Co-N(NO_2)	1.935 (11)	*e*
cis-$[Co(NH_3)_4(NO_2)_2]NO_3$	Co-N(NO_2)	1.924 (24)	*f*
trans-[Co(L-3,8-dimetrien)$(NO_2)_2]ClO_4$	Co-N(NO_2)	1.93 (2) 1.98 (2)	*j*
$[Co(NH_3)_5NO_2]Cl_2$	Co-N(NO_2)	1.912 (14)	*g*
$[Co(NH_3)_5NO_2]Br_2$	Co-N(NO_2)	1.921 (21)	*h*
$[Co(NO_2)_3NH_3en]^0$	Co-N(NO_2)	1.933 (7)	*c*
cis-$[Co(en)_2(NO_2)_2]NO_3$	Co-N(NO_2)	1.90	*k*
trans-$[Co(en)_2(NO_2)_2]NO_3$	Co-N(NO_2)	1.92	*l*

[a] Average values are reported except for the Co-N(NO_2) distances in the present compound. [b] This work. [c] Reference 19. [d] Reference 20. [e] Reference 21. [f] Reference 22. [g] Reference 23. [h] Reference 24. [i] Reference 25. [j] M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 28, 463 (1972). [k] O. Bortin, *Acta Chem. Scand.*, 23, 3273 (1969). [l] O. Bortin, *ibid.*, 23, 3274 (1969).

gen bond is 168°. The positions found for the hydrogens should be considered quite approximate. From Figure 3 it can be seen, however, that the hydrogen positions are nearly mirrored from one side of the molecule to the other.

Nature of the NO_2-Co-NO_2 Linkage. Any orientation of the N6 nitro group plane brought about by rotation around the cobalt-nitrogen bond results in a steric interaction with the PnAO ligand. A minimum in this steric factor is expected when an oxygen is directed toward C13. While this is the position actually taken, the steric factor, although minimized, is still present as evidenced by the movement of N6 from the octahedral position toward the oxime groups. The N5-Co-N6 bond angle is 174.8 (1)°. The N5 nitro group is not sterically involved with the organic ligand and its position, at a dihedral angle of 84.3 (2)° to the N6 nitro group, is probably determined by weak hydrogen bonding to the N3 and N4 hydrogens. No electronic bonding significance can be attached to the perpendicular nature of these nitro groups (note that *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ has the two nitrogens and four oxygens coplanar). It is significant that the thermal vibrations of O3 and O4 are greater than those of O5 and O6, probably because of less steric restrictions on the rotational motion of the O3-O4 nitro group. The average nitro N-O distances (1.233 (9) Å) and O-N-O angles (118.9 (5)°) are comparable to those in ionic nitrites such as $NaNO_2$ (1.236 Å and 115.4°)[26] and to those in other Co(III) complexes such as $[Co(NH_3)en(NO_2)_3]$ (1.223 (10) Å and 118.4 (1.4)°).[19] The source of the difference in N5-O3 and N5-O4 distances is not apparent.

The basic interest in the structure lay in the Co-N5 and Co-N6 bond lengths. The structure from the film data showed the Co-N5 distance to not be significantly (3σ) different from Co-N6. However, the more precise counter data shortened the Co-N6 distance making it significantly shorter (8σ) than Co-N5. A fair comparison between the counter and film data cannot be made, however, without adding the hydrogens to the least-squares refinement of the latter. These comparisons are shown in Table IV and establish that the relative Co-N bond lengths are reversed between the two sets of data. There is little doubt, however, that the most reliable distances are given by the counter data which show the most sterically involved N6 nitro group to have the shortest bond to the cobalt atom. Thus, it is clear that the long Co-N5 bond is not due to steric repulsion and it is likely that electronic factors are of primary importance.

The comparison of Co-N distances with those in other cobalt complexes (Table IX) shows clearly that this Co-N6 distance (1.982 (3) Å) is abnormally long and that the Co-N5 distance (1.935 (3) Å) represents a "normal" Co-N(NO_2) distance; *e.g.*, the average Co-N distance in $[Co(NO_2)_3en(NH_3)]^0$ is 1.933 (7) Å. It should be noted that the entry[26] which contains a structurally similar ligand shows Co-N(NO_2) distances that are dissimilar as was found for the PnAO complex. This may be significant and suggests that it would be of importance to reduce the standard deviations of the distances with a new set of data. In passing it should be noted that with many atoms in the asymmetric unit certain parts of the structure may be relatively sensitive to systematic data errors and the standard deviations calculated by the usual programs are probably too optimistic. It is for that reason that we report the results of both the film and counter studies in some detail.

Summary

This structure shows independent neutral molecules with no significant intermolecular bonding. The coordination around the cobalt atom is a distorted octahedron. The nitro groups are trans to each other and are bound to the metal ion through nitrogen. All C–C, C–N, O–N, and C=N bonds and angles are within the normally expected ranges. The bond angles and distances are internally consistent with respect to a formal mirror symmetry of the tetradentate ligand. The hydrogen bond shows the same distance and OHO angle as observed for other dioxime- and α-amine oxime-metal complexes. Thus the O-H-O distance appears to be nearly independent of the metal ion, its ionic radius and coordination number, and the structure of the ligand.

The planes of the nitro groups are perpendicular to each other, and the Co-N(NO_2) bond lengths are significantly different. The nitro group with the short Co-N bond, because of steric requirements imposed by the tetradentate ligand, is oriented with its plane between the oxime oxygens. The oxygens of the other nitro group are *weakly* hydrogen bonded to the amine hydrogens, and thus the perpendicular nature of the nitro group planes is not due to electronic factors brought about by bonding to the cobalt atom.

The nitro group with the short Co-N bond is to be considered normal from other structural studies. The long Co-N bond cannot be a result of steric factors or of the hydrogen bonding: the H bonding is far too weak. Thus this long bond is probably due to electronic factors and may be viewed as a tendency toward five-coordination.

The presence of a ligand in the equatorial positions which has a great tendency to stabilize the planar configuration (as with Ni^{2+}) is likely to cause a tendency toward the

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(26) M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 28, 463 (1972).

square-pyramidal five-coordinate structured Co(III) complexes. The crystal structure is in agreement with the chemical studies[8] and would predict as is observed a difference in thermodynamic and kinetic stability of the two nitro groups in this compound.

Registry No. [Co(PnAO-H)$(NO_2)_2$], 41444-82-0.

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, 20× 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2625.

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Kinetic and Thermodynamic Studies on a Labile *trans*-Dinitrocobalt(III) Complex

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Cobalt(III) complexes of an α-amine oxime *trans*-[Co(PnAO-H)X_2]^0 have been prepared where X is one of the following ligands: NO_2^-, N_3^-, Cl^-, or OH_2. The trans ligands are relatively labile to substitution even in nearly neutral aqueous media. Replacement of a coordinated NO_2^- group by N_3^- or the reverse follows the path $Co\text{-}NO_2 \rightleftharpoons Co\text{-}OH_2 \rightleftharpoons Co\text{-}N_3$. The forward rate is controlled by the replacement of NO_2^- by H_2O which follows the rate law rate = $k[Co\text{-}NO_2] + k'[Co\text{-}NO_2][OH^-]$. The same law and constants are obtained for the $^{15}NO_2^-$ exchange with the *trans*-dinitro complex. Equilibrium constants are reported for NO_2^--N_3 competition for the trans coordination positions and for NO_2^-, Cl^-, and N_3^- competition with H_2O. Using isotopic rates of exchange studies it is shown that in the trans complexes (dinitro, diazido, dichloro), the axial ligands are not equivalent and substitute with rates differing by factors of 15-50. Isotopic NO_2^- exchange rate studies on other more common *trans*-dinitro complexes are compared in an effort to distinguish between steric and electronic effects as the cause of the nonequivalence of the axial ligands. The solution results are compared with the crystal structure of [Co(PnAO-H)$(NO_2)_2$]^0 concurrently presented.[1]

Introduction

The presence of a tetradentate ligand occupying equatorial positions around a cobalt(III) ion has been known to give remarkable properties to the ligands in the apical positions.[2-4] These complexes have been suggested as model systems for the vitamin B_{12} compounds and considerable effort has been expended (using two hydrogen-bonded dimethylglyoxime ligands) to understand the unusual bonding factors involved.[5,6] The existence of hydride ion and alkyl complexes[7] points up the unusual bonding factors, and in a few cases the excessive lability of an axial ligand has been noted. It appeared that quantitative kinetic studies were needed to help decipher the underlying factors involved in these systems. The properties of the dimethylglyoxime complexes do not lend themselves to precise kinetic studies since they are difficult to prepare and maintain pure, have rather nonspecific absorption spectra in the useful visible region, and often have marginal solubility characteristics. Certain substituted ethylenediamines and α-amine oximes tend toward planar coordination[8] and give cobalt(III) complexes with more suitable properties.[9] The ligand selected for the majority of this work, PnAO,[10] is tetradentate and forms an intramolecular hydrogen bond of the highest stability thus becoming a closed multicyclic ligand. The original purpose was to measure, by isotopic ligand exchange, the magnitude of the steric factor which nmr and X-ray studies had shown to exist[2,11] which would lead to the nonequivalence of structurally identical ligands in the axial positions.

Early in the studies it became apparent that the behavior of the *trans*-[Co(PnAO-H)X_2]^0 compounds[12] (Figure 1) was abnormal when compared to the analogous NH_3, en, or, to a lesser extent, DMG complexes, the major differences being that "strong ligands" such as NO_2^-, SCN^-, and N_3^- could be easily and quickly replaced under mild conditions and that the rates of replacement of identical trans groups were drastically different. Following these observations, the scope of the investigation was extended to include preparation studies, equilibrium studies, kinetics of aquation, anation, and isotopic ligand-exchange studies, and, reported in a concurrently submitted paper, an X-ray structural study of one compound, *trans*-[Co(PnAO-H)$(NO_2)_2$]^0.[1]

Experimental Section

The ligand PnAO was prepared as previously described[10] and gave equivalent C, H, and N analyses. The starting complex (Table I) [Co(PnAO-H)Cl_2]^0 was prepared using several oxidants. The best procedure was with PbO_2.

[Co(PnAO-H)Cl_2]^0. A 16.3-g (0.06-mol) sample of PnAO and 14.3 g (0.06 mol) of $CoCl_2 \cdot 6H_2O$ were dissolved in 250 ml of water and NaOH(s) was added until the pH was 6.3. With rapid stirring ten 1-g portions of PbO_2 were added over equally spaced periods, totaling 10 hr. Concentrated HCl was added at intervals to keep the

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