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Linear vs. Bent Nitrosyl Ligands in Pseudotetrahedral Nitrosyl Complexes. Low-Temperature Structure of $CoI(NO)_2(P(C_6H_5)_3)$

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The structure of $CoI(NO)_2(P(C_6H_5)_3)$ has been determined at low temperature (−170 °C) and is compared with the structure of a similar disordered complex, $CoI(NO)_2(P(C_6H_5)_2R')$ ($R' = CH_2CH_2P(O)(C_6H_5)_2$), which was claimed to possess strongly bent nitrosyl ligands. The title complex has two nearly linear NO groups with Co–N(1)–O(2) = 165.2 (2)° and Co–N(2)–O(2) = 163.3 (2)°. The compound crystallized in space group C_{2h}^3-$C2/m$ with $a = 17.356$ (8) Å, $b = 10.677$ (3) Å, $c = 20.998$ (10) Å, $\beta = 96.93$ (1)°, and $Z = 8$. On the basis of 4020 unique reflections with $F_o^2 > \sigma(F_o^2)$, the structure was refined with use of full-matrix, least-squares methods to $R(F) = 0.031$ and $R_w(F) = 0.025$.

Introduction

The structures of a number of four-coordinate dinitrosyl complexes are known such as $M(NO)_2(PPh_3)_2$ (M = Fe, Ru, Os) and $M'(NO)_2(PPh_3)_2^+$ (M′ = Co, Rh, Ir). All have distorted-tetrahedral geometries with nearly linear NO ligands and formal d^{10} configurations (the linear nitrosyl ligand is considered to be NO^+). The greatest distortion about the metal and the greatest bending at the nitrosyl ligand occurs in $Rh(NO)_2(PPh_3)_2^+$ (Rh–N–O = 158.9 (4)°).[1] Similar mononitrosyl complexes, $M''X(NO)(PPh_3)_2$ (M″ = Ni, Pt; X = Cl, Br, NO_3, N_3, etc.),[2] are also known, and the Ni complexes have similar pseudotetrahedral geometries.[3]

One structural report indicated that strongly bent nitrosyl ligands were found in the pseudotetrahedral molecule $CoI(NO)_2(PPh_2R')$ ($R' = CH_2CH_2P(O)Ph_2$).[4] This result stands apart from the other structural results; simple molecular orbital considerations suggest that strongly bent nitrosyl ligands should only be found in square-planar complexes.[5] Because the presence of disorder obscured some of the structural results in $CoI(NO)_2(PPh_2R')$, we decided to reinvestigate the $CoI(NO)_2(PR_3)$ complexes. We now report the structural results for $CoI(NO)_2(PPh_3)$.

Experimental Section

Iododinitrosyl(triphenylphosphine)cobalt. This compound was prepared with use of a modification of the published method.[6] With 100 mL of freshly distilled acetone under an N_2 atmosphere, 2.46 g of $Co(NO)_2I$[7] and 2.62 g of triphenylphosphine were refluxed for 1 h. The cooled solution was filtered, and 100 mL of absolute ethanol was added. The volume was reduced to about 40 mL with use of a rotary evaporator, and the reaction mixture was allowed to stand for about 1 h to allow for complete crystallization. The mixture was filtered to yield 3.7 g of large, shiny, black crystals. Hexane (15 mL) was added to the mother liquor, and the resulting mixture was cooled to 0 °C. An additional 0.9 g of product was obtained, giving a total yield of 91%; ν(NO) = 1830, 1771 cm^{-1}. Anal. Calcd for $C_{18}H_{15}CoIN_2O_2P$: C, 42.55; H, 2.98; N, 5.51. Found: C, 42.75; H, 3.05; N, 5.39. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Iododinitrosyl(diphenylethylphosphine)cobalt. This complex was prepared according to the above procedure using 2.14 g of Ph_2PEt. The total yield was 3.2 g (70%) of black crystals; ν(NO) = 1825, 1762 cm^{-1}.

Table I. Positional Parameters for Atoms in $CoI(NO)_2(P(C_6H_5)_3)$

atom	$10^4x/a$[a]	$10^4y/b$	$10^4z/c$	$10B$[b]
Co	2613.2 (2)	988.4 (3)	−2028.9 (2)	14
I	1582.1 (1)	−719.5 (2)	−1957.8 (1)	18
N(1)	3172.2 (13)	772.0 (20)	−2608.9 (11)	18
N(2)	2308.9 (12)	2407.3 (21)	−1844.9 (11)	18
O(1)	3677.8 (13)	748.5 (21)	−2198.5 (11)	30
O(2)	2289.6 (13)	3444.8 (19)	−1694.5 (11)	29
P	3435.0 (4)	479.0 (6)	−1163.1 (3)	13
C(1)	4082.7 (15)	9225.7 (24)	8657.3 (12)	15
C(2)	4881.1 (17)	−598.9 (28)	−1299.7 (15)	23
C(3)	5353.3 (19)	−1568.6 (32)	−1462.6 (18)	30
C(4)	5034.1 (20)	−2705.5 (30)	−1669.4 (15)	27
C(5)	4242.6 (20)	−2878.0 (29)	−1715.8 (15)	26
C(6)	3766.5 (17)	−1918.2 (27)	−1558.2 (14)	21
C(7)	4068.1 (14)	1787.8 (24)	−910.2 (13)	15
C(8)	4246.4 (16)	2646.2 (26)	−1370.1 (15)	19
C(9)	4755.1 (17)	3616.2 (28)	−1202.5 (16)	23
C(10)	5090.0 (16)	3742.1 (29)	−574.5 (16)	24
C(11)	4905.7 (17)	2920.1 (29)	−115.2 (15)	24
C(12)	4394.9 (16)	1939.3 (27)	−279.2 (14)	19
C(13)	3018.2 (14)	0.1 (24)	−449.8 (12)	15
C(14)	2387.9 (16)	666.2 (28)	−277.9 (14)	22
C(15)	2073.5 (19)	355.1 (32)	276.4 (15)	27
C(16)	2381.8 (19)	−624.8 (30)	653.5 (15)	26
C(17)	3002.0 (21)	−1287.5 (30)	486.8 (15)	28
C(18)	3328.7 (18)	−974.4 (27)	−63.6 (14)	22
H(26)	5095 (15)	217.8 (28)	8831 (13)	18 (6)
H(27)	5827 (18)	−1480 (30)	−1470 (15)	28 (7)
H(28)	5290 (17)	−3307 (30)	−1786 (14)	25 (7)
H(29)	4054 (17)	−3586 (31)	−1870 (14)	25 (7)
H(30)	3217 (16)	7939 (25)	8421 (12)	16 (6)
H(31)	4047 (19)	2585 (31)	−1770 (16)	33 (8)
H(32)	4864 (15)	4122 (25)	−1509 (13)	12 (6)
H(33)	5437 (17)	4422 (28)	−458 (15)	26 (7)
H(34)	5091 (17)	3008 (29)	307 (15)	26 (7)
H(35)	4247 (14)	1422 (25)	15 (12)	9 (5)
H(36)	2152 (18)	1322 (30)	9461 (15)	30 (7)
H(37)	1665 (19)	810 (29)	393 (15)	30 (7)
H(38)	2195 (18)	−844 (28)	1021 (16)	29 (7)
H(39)	3223 (18)	−1951 (32)	723 (15)	33 (8)
H(40)	3763 (16)	−1431 (27)	−178 (13)	17 (6)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.
[b] Isotropic thermal parameters ($Å^2$) or their equivalents for anisotropic atoms.

Crystallographic Data and Structure Refinement. Table S-I[10] contains a summary of pertinent information about data acquisition,

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(1) Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3070 and references therein. Abbreviation: Ph = C_6H_5.

(2) Feltham, R. D. *Inorg. Chem.* **1964**, *3*, 116. Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A.; Benn-Taarit, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 694.

(3) Enemark, J. H. *Inorg. Chem.* **1971**, *10*, 1952.

(4) Field, J. S.; Wheatley, P. J.; Bhaduri, S. *J. Chem. Soc., Dalton Trans.* **1974**, 74.

(5) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(6) Hieber, W.; Heinecke, K. *Z. Anorg. Allg. Chem.* **1962**, *316*, 305.

(7) Haymore, B. L.; Fletham, R. D. *Inorg. Synth.* **1973**, *14*, 81.

(8) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

(9) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

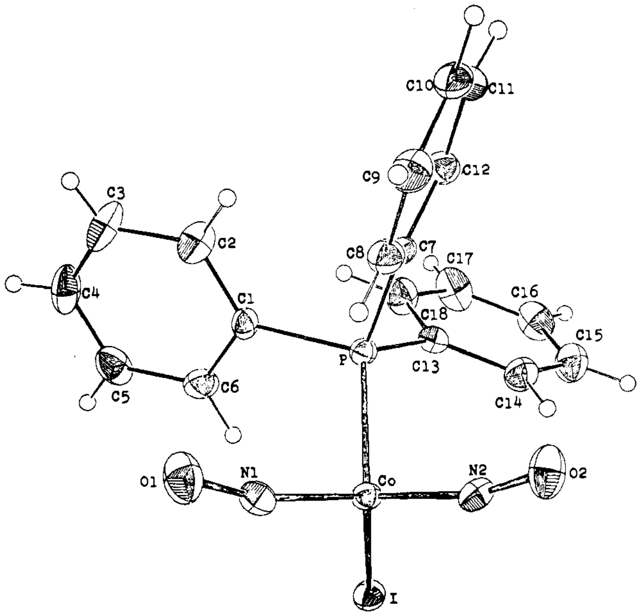

Figure 1. Drawing of a complete molecule of $CoI(NO)_2(P(C_6H_5)_3)$. Vibrational ellipsoids are drawn at the 50% probability level; H atoms are drawn artificially small.

Table II. Selected Bond Distances in $CoI(NO)_2(P(C_6H_5)_3)$

atoms		dist, A	av
Co	P	2.238 (1)	
Co	I	2.572 (1)	
Co	N(1)	1.662 (2)	1.664
Co	N(2)	1.665 (2)	
P	C(1)	1.816 (3)	1.816
P	C(7)	1.817 (3)	
P	C(13)	1.814 (3)	
N(1)	O(1)	1.154 (3)	
N(2)	O(2)	1.153 (3)	

structure refinements and crystal characteristics; the techniques and procedures used are the same as those reported previously.[8] Errors for F_0 were estimated with use of a value of 0.05 for p. There was no observable deterioration of crystal quality during data acquisition. A comparison of F_0 and F_c showed no need for an isotropic extinction correction. An absorption correction was applied to the data.[9]

The structure was solved with use of standard Patterson techniques. *All* hydrogen and non-hydrogen atoms were located and refined with use of full-matrix, least-squares techniques; non-hydrogen atoms had anisotropic thermal parameters and hydrogen atoms had isotropic thermal parameters. Anomalous dispersion terms for Co, P, and I were included in F_c, and weights were taken as $4F_0^2/\sigma^2(F_0^2)$. All data with $F_0^2 > \sigma(F_0^2)$ were used in least-squares calculations. Final difference Fourier syntheses were featureless. Tables I and S-II[10] contain all final positional and thermal parameters. A listing of the observed and calculated structure amplitudes is available.[10]

Results and Discussion

The unit cell of $CoI(NO)_2(PPh_3)$ contains well-separated complex molecules. A perspective view of the complex with the N(1)–Co–N(2) plane normal to the drawing is shown in Figure 1. Tables II, III, S-III,[10] and S-IV[10] contain selected bond distances and angles.

Although the geometry about the cobalt atom is pseudotetrahedral, it has noticeable distortions. The angle between the Co–N(1)–N(2) and Co–I–P planes is 88.8 (1)°. The smallest interligand angle about the cobalt is the P–Co–I angle at 99.22 (3)°, and the largest is the N(1)–Co–N(2) angle at 121.7 (1)°. The atoms N(1) and N(2) are symmetrically displaced toward the P atom away from the I atom by about 12°. This is presumably caused by the larger effective size of the large iodine atom. Table IV gives some structural parameters of cobalt dinitrosyl complexes, and the present one compares favorably with the other two neutral complexes. There seems to be an interesting trend. The cationic complexes have larger N–Co–N angles and nitrosyl ligands that are less bent with the oxygen atoms moving away from each other. The neutral complexes have smaller N–Co–N angles, and the nitrosyl ligands are more bent in a direction toward each other.

Table III. Selected Bond Angles in $CoI(NO)_2(P(C_6H_5)_3)$

atoms			angle, deg	av
P	Co	I	99.22 (3)	
P	Co	N(1)	100.96 (9)	101.88
P	Co	N(2)	102.80 (8)	
I	Co	N(1)	114.57 (8)	113.74
I	Co	N(2)	112.91 (8)	
N(1)	Co	N(2)	121.73 (11)	
O(1)	Co	O(2)[a]	115.09 (7)	
C(1)	P	C(7)	105.05 (12)	105.6
C(1)	P	C(13)	106.38 (12)	
C(7)	P	C(13)	105.24 (12)	
Co	N(1)	O(1)	165.20 (22)	164.2
Co	N(2)	O(2)	163.29 (22)	
P	C(1)	C(2)	121.62 (21)	
P	C(1)	C(6)	118.97 (20)	
P	C(7)	C(8)	118.72 (20)	
P	C(7)	C(12)	122.17 (21)	
P	C(13)	C(14)	118.39 (21)	
P	C(13)	C(18)	121.91 (21)	

[a] Co and O(1) and O(2) are not in bonding distance.

The Co–P distance of 2.238 (1) Å compares favorably with similar distances in $Co(CO)_2(NO)(PPh_3)$[11] and $[Co(NO)_2(PPh_3)_2][ClO_4]$.[12] The cobalt–iodine distance appears to be normal (see Table IV). The Co–N distances at 1.664 (2) Å are essentially the same as others in Table IV within the confines of the error limits. The N–O distances at 1.154 (3) Å compare favorably with those in $[Co(NO)_2(PPh_3)_2][ClO_4]$, which is the only other low-temperature structure in which librational shortening has been minimized. The triphenylphosphine ligand was refined as individual anisotropic atoms and isotropic hydrogen atoms. All of the phenyl groups were perfectly planar within one standard deviation. The C–C distances and C–C–C angles were well-behaved. Even at low temperature, the structure shows librational shortening of the C–C bonds farthest from the phosphorus atom.

Our structural results for $CoI(NO)_2(PPh_3)$ clearly show a pseudotetrahedral geometry at cobalt and the absence of strongly bent NO ligands. Our structure is well-behaved and quite accurate. With the exception of the "strongly bent" NO ligands, the structural results of Field, Wheatley, and Bhaduri[4] are basically the same as ours within the confines of their larger error limits. Other than poor crystal quality and/or artifacts of disorder, we do not know how to explain the unusual, bent NO ligands in $CoI(NO)_2(PPh_2R')$. We do believe, however, that the small difference in phosphine substituents would cause only very small differences in Co–N–O angles; furthermore, we do not believe that lattice effects could cause such a large change in Co–N–O angles. We conclude, then, that $CoI(NO)_2(PR_3)$ obeys the generalization that only linear or slightly bent nitrosyl ligands are found in pseudotetrahedral d^{10} nitrosyl complexes and that the bent NO groups in $CoI(NO)_2(PPh_2R')$ are not real.

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

(11) Albano, V. G.; Bellon, P. L.; Ciani, G. *J. Organomet. Chem.* **1972**, *38*, 155.

(12) Huffman, J. C., unpublished results.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in Cobalt Dinitrosyl Complexes

compd	Co-N	N-O	Co-N-O	N-Co-N	Co-L	L-Co-L
$CoI(NO)_2(PPh_2R)$[a,f] (L = I, P)	1.68 (2)[e]	1.05 (2)[e]	121 (2), 149 (6) 155 (4), 166 (3)	120 (1)	2.545 (4) (Co-I) 2.260 (4) (Co-P)	97.1 (2)
$CoI(NO)_2(PPh_3)$[b,g] (L = I, P)	1.662 (2) 1.665 (2)	1.154 (2) 1.153 (3)	165.2 (2) 163.3 (2)	121.7 (1)	2.572 (1) (Co-I) 2.238 (1) (Co-P)	99.22 (3)
$[Co(NO)_2(Ph_2PCH_2CH_2PPh_2)][PF_6]$[m] (L = P, P)	1.656 (10) 1.671 (11)	1.130 (14) 1.142 (13)	176.6 (14) 172.3 (11)	131.7 (5)	2.249 (3) 2.244 (3)	87.87 (9)
$[Co(NO)_2(PPh_3)_2][PF_6]$[h] (L = P, P)	1.645 (6)	1.174 (6)	171.0 (5)	136.7 (4)	2.266 (3)	113.5 (2)
$[Co(NO)_2(PPh_3)_2][ClO_4]$[b,i] (L = P, P)	1.663 (3) 1.665 (3)	1.155 (4) 1.155 (4)	171.2 (3) 171.1 (3)	132.4 (1)	2.282 (1) 2.274 (1)	106.68 (4)
$[Co(NO)_2I]_n$[j] (L = I, I)	1.61 (4) 1.60 (4)	1.16 (5) 1.19 (5)	168 (4) 173 (4)	118 (2)	2.593 (3)	96.2 (1)
$[Co(NO)_2(NO_2)]_n$[c,k] (L = O, N)	1.67 1.67	1.13 1.11	*n*	112	2.15 (Co-O) 1.98 (Co-N)	*n*
$Co(NO)_2(Sacsac)$[d,l] (L = S, S)	1.650 (6)	1.120 (5)	168.9 (5)	115.5 (3)	2.217 (2) 2.224 (2)	100.0 (1)

[a] Nitrosyl groups were partially disordered; R = $CH_2CH_2P(O)Ph_2$; Ph = C_6H_5. [b] Structure determined at low temperature. [c] No errors reported. [d] Sacsac = dithioacetylacetonate. [e] Average value. [f] Reference 4. [g] This work. [h] Reference 17. [i] Reference 12. [j] Dahl, L. F.; deGil, E. R.; Feltham, R. D. *J. Am. Chem. Soc.* 1969, *91*, 1653. For chloro analogue see: Jagner, S.; Vannerberg, N. G. *Acta Chem. Scand.* 1967, *21*, 1183. [k] Strouse, C. E.; Swanson, B. I. *J. Chem. Soc., Chem. Commun.* 1971, 55. [l] Reference 13. [m] Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* 1977, *16*, 3283. [n] Information not given.

The two nitrosyl ligands are bent with Co–N(1)–O(1) = 165.2 (2)° and Co–N(2)–O(2) = 163.3 (2)°. This is the largest bending of all cobalt dinitrosyl complexes (Table IV), and only $[Rh(NO)_2(PPh_3)_2][ClO_4]$[1] has nitrosyls that are bent more. However, careful inspection of the structure shows that most of the bending occurs normal to the N(1)–Co–N(2) plane. Simple calculations show that O(1) and O(2) are bent normal to the N(1)–Co–N(2) plane by 13.9 and 14.1° toward the phosphorus ligand, and they are bent in plane toward each other by 5.0 and 8.8°, respectively. This small in-plane bending, toward each other, seems to be characteristic of the neutral dinitrosyl complexes of cobalt. Recently, Martin and Taylor demonstrated an interesting correlation between the N–M–N angle and the bending of "linear" nitrosyl ligands in pseudotetrahedral dinitrosyl complexes.[13] They found that the complexes that exhibit the greatest N–M–N angles also show the largest bending of the nitrosyl ligands away from each other. They also found that complexes that exhibit the smallest N–M–N angles also show the largest bending of the nitrosyl ligands toward each other. The crossover point comes at about N–M–N = 131°. At first glance it would appear that $CoI(NO)_2(PPh_3)$ is an exception to the rule. The N–Co–N angle is greater by 6.2°, yet the Co–N–O angles are smaller by 4.7° in comparison to those in $Co(NO)_2(CH_3C(S)CHC(S)CH_3)$. As noted, much of the bending is out-of-plane bending (N–Co–N plane), which undoubtedly arises from the unequal effects of the I and PPh_3 ligands on the out-of-plane π-bonding system. If the oxygen atoms are projected onto the N–Co–N plane, the in-plane bending results in an "in-plane" O–Co–O angle of 116.1°, which is in excellent agreement with the Martin and Taylor correlation.[14] Their criterion of comparing N–M–N angles with O–M–O angles is useful if there is no appreciable out-of-plane bending, that is, when C_{2v} symmetry is maintained. It is probably worth noting that some caution is necessary in interpreting structural parameters derived from solid-state structures. The structures of $Ru(NO)_2(PPh_3)_2$[15,16] and $Co(NO)_2(PPh_3)_2^+$[12,17] have both been determined in two different lattices, and there are some small but significant differences. However, lattice effects are not likely to cause such large differences in the Co–N–O angles between the $CoI(NO)_2(PPh_3)$ and $CoI(NO)_2(PPh_2R')$ structures.

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Registry No. $CoI(NO)_2(P(C_6H_5)_3)$, 14318-98-0.

Supplementary Material Available: A summary listing of crystallographic data and tables of anisotropic thermal parameters, C–C and C–H bond distances, C–C–C and C–C–H bond angles, and observed and calculated structure factor amplitudes (47 pages). Ordering information is given on any current masthead page.

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(13) Martin, R. L.; Taylor, D. *Inorg. Chem.* **1976**, *15*, 2970.

(14) The actual O(1)–Co–O(2) angle is 115.1°.

(15) Gaughan, A. P.; Corden, B. J.; Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 786.

(16) Bhaduri, S.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1975**, *B31*, 897.

(17) Reichert, B. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1934.