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Dinitrosylbis(trimethyl phosphite)cobalt(−I) Tetraphenylborate, $[Co(NO)_2\{P(OMe)_3\}_2][BPh_4]$

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Abstract. $M_r = 686{\cdot}33$, triclinic, $P\bar{1}$, $a = 11{\cdot}584\ (9)$, $b = 11{\cdot}123\ (9)$, $c = 14{\cdot}990\ (13)$ Å, $\alpha = 117{\cdot}1\ (1)$, $\beta = 91{\cdot}5\ (1)$, $\gamma = 100{\cdot}1\ (1)°$, $V = 1680\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}356$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}49$ cm^{-1}, $F(000) = 716$, 298 K, $R = 0{\cdot}051$ for 2017 independent observed reflections. The structure consists of well separated BPh_4^- anions and complex cations, the tetrahedral distorted coordination of the cobalt in the cation involving two nitrogen atoms from linearly bonded nitrosyl groups and two phosphorus atoms from trimethyl phosphite ligands.

Introduction. Several tetracoordinated dinitrosyl complexes of the Group VIII metals, $M(NO)_2L_2$ (L is frequently PPh_3), have been studied extensively in order to clarify their chemical and catalytic properties. New penta- and tetracoordinated dinitrosyl cobalt complexes have been obtained from the reaction, in mild conditions, of NO with $[CoXL_4]^+$ cations (X = Cl, Br, I; L = phosphite) (Albertin, Bordignon, Canovese & Orio, 1980). The structure of the tetracoordinated $[Co(NO)_2\{P(OMe)_3\}][BPh_4]$ complex has been determined by X-ray methods to confirm the tetrahedral environment of the cobalt and to ascertain the modifications in the geometry of the complex induced by the presence of a better π-acceptor phosphite ligand.

Experimental. Red-brown crystals, prepared as reported by Albertin, Bordignon, Canovese & Orio (1980), small irregularly shaped crystal used for data collection ($0{\cdot}13 \times 0{\cdot}19 \times 0{\cdot}25$ mm), Siemens AED diffractometer, Nb-filtered Mo $K\alpha$ radiation, unit-cell parameters determined by a least-squares procedure applied to 16 reflections, with θ 9–13°; 3616 independent reflections, h $-11 \to 11$, k $-10 \to 9$, l $0 \to 15$, $2\theta \leq 42°$, 2017 reflections with $I \geq 2\sigma(I)$; one standard reflection ($4\bar{3}2$) showed no significant intensity decay; Lp correction, absorption ignored; Patterson and Fourier methods for structure determination, full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms (*SHELX*, Sheldrick, 1976), hydrogen atoms localized in a ΔF map and refined isotropically; $\sum w|\Delta F|^2$ minimized, $R = 0{\cdot}051$, $wR = 0{\cdot}062$, unit weights in each stage of refinement; atomic scattering factors including anomalous-dispersion corrections for Co and P from *International Tables for X-ray Crystallography* (1974). Final coordinates for the non-hydrogen atoms are given in Table 1.* All the calculations were performed on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Discussion. The crystal structure consists of well separated $[Co(NO)_2\{P(OMe)_3\}_2]^+$ cations and tetraphenylborate anions. Selected bond distances and angles are given in Table 2. In the cationic complex, depicted in Fig. 1, the cobalt atom is in a distorted tetrahedral arrangement involving two nitrogen atoms from two nearly linear nitrosyl groups and two phosphorus atoms from two trimethyl phosphite ligands. The short Co—N bond distances [1·594 (13) and 1·613 (12) Å] and the almost linear bonding of the nitrosyl ligands [Co—N—O angles 177·0 (13) and 179·7 (13)°] lead to the formulation of the compound as a NO^+ complex of Co^{-I}.

Several metal dinitrosyl $M(NO)_2L_2$ complexes have been studied by X-ray methods and all have been found with the metal tetrahedrally coordinated with M—N—O angles nearly linear rather than fully bent, in agreement with the nitrosyl ligands acting as three-electron donors (NO^+) and with the metal in a formal d^{10} configuration and a low oxidation state. In these complexes an interesting feature is the N—M—N angle which varies considerably (in the range 110–158°); this variation appears to be largely independent of the steric requirements of the ligands and is probably attributable to electronic factors (Martin & Taylor, 1976; Reichert, 1976; Kaduk & Ibers, 1977). This angle is in fact smaller with less strongly reducing first-row transition

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* Lists of calculated and observed structure factors, H-atom coordinates and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38793 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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metals (110–124°), larger with more strongly reducing heavier transition metals (139–158°) and the complexes exhibiting the largest angles also show the more pronounced bending of the nitrosyl group. So the contribution of the ligands should be determined by their σ,π-accepting or donating properties and in some instances by their steric hindrance. This trend is consistent with an increase of the N—M—N angle with a decrease of the NO^+ character of the nitrosyl group and therefore with a decrease of the M—N—O angle.

In the present complex, the N—Co—N angle is 128·0 (8)° with a dihedral angle between the N—Co—N

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with equivalent isotropic thermal parameters for the non-hydrogen atoms, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \text{ trace } \tilde{\mathbf{U}}.$$

	x	y	z	B_{eq}(Å^2)
Co	3308 (2)	2560 (2)	2226 (1)	4·3 (1)
P(1)	1951 (3)	1691 (4)	2908 (3)	5·1 (2)
P(2)	2275 (3)	1975 (4)	776 (3)	5·0 (2)
O(1)	4987 (10)	965 (12)	1676 (10)	9·2 (7)
O(2)	3605 (9)	5386 (11)	3372 (8)	6·7 (5)
O(3)	2413 (10)	524 (10)	−15 (8)	8·2 (5)
O(4)	2578 (8)	2935 (10)	288 (7)	6·4 (4)
O(5)	947 (9)	1948 (14)	841 (9)	9·9 (7)
O(6)	1306 (8)	199 (8)	2163 (7)	5·5 (4)
O(7)	2360 (10)	1770 (11)	3930 (8)	7·7 (6)
O(8)	868 (7)	2451 (10)	3258 (7)	6·0 (5)
N(1)	4300 (10)	1662 (12)	1928 (9)	6·0 (6)
N(2)	3483 (9)	4212 (12)	2894 (9)	5·0 (6)
C(1)	2054 (17)	−125 (20)	−1045 (12)	9·5 (9)
C(2)	3716 (13)	3314 (17)	49 (13)	7·3 (8)
C(3)	149 (14)	2321 (18)	477 (16)	8·7 (10)
C(4)	423 (13)	−600 (15)	2475 (12)	6·9 (8)
C(5)	3361 (14)	1217 (18)	4038 (14)	7·7 (10)
C(6)	1040 (12)	3822 (14)	4046 (10)	5·9 (6)
C(7)	7787 (10)	4649 (12)	1407 (9)	3·6 (5)
C(8)	7131 (11)	3300 (13)	962 (11)	4·7 (5)
C(9)	7003 (13)	2451 (14)	−96 (11)	5·9 (7)
C(10)	7536 (13)	2934 (15)	−712 (10)	5·2 (6)
C(11)	8162 (13)	4220 (15)	−305 (10)	5·4 (6)
C(12)	8295 (12)	5073 (14)	718 (10)	4·6 (6)
C(13)	7450 (9)	4795 (11)	3218 (8)	3·1 (5)
C(14)	8074 (11)	3808 (12)	3165 (9)	3·9 (5)
C(15)	7765 (12)	2978 (12)	3627 (9)	4·4 (5)
C(16)	6787 (10)	3086 (13)	4147 (9)	4·2 (5)
C(17)	6167 (11)	4066 (12)	4205 (9)	4·2 (5)
C(18)	6502 (10)	4911 (12)	3763 (8)	3·5 (5)
C(19)	7062 (10)	6794 (11)	2717 (8)	3·3 (5)
C(20)	5885 (10)	6331 (14)	2363 (10)	4·5 (6)
C(21)	5135 (13)	7157 (18)	2363 (12)	6·2 (8)
C(22)	5568 (16)	8519 (19)	2751 (13)	7·1 (8)
C(23)	6732 (17)	9053 (16)	3106 (12)	6·6 (8)
C(24)	7444 (13)	8194 (13)	3086 (10)	4·9 (6)
C(25)	9270 (9)	6480 (11)	3129 (9)	3·5 (5)
C(26)	9524 (12)	7503 (13)	4121 (9)	4·7 (5)
C(27)	10672 (15)	8163 (16)	4589 (13)	5·9 (7)
C(28)	11587 (14)	7790 (18)	4060 (13)	6·2 (8)
C(29)	11381 (12)	6782 (17)	3094 (14)	5·9 (7)
C(30)	10251 (11)	6128 (14)	2634 (11)	4·5 (6)
B	7896 (11)	5691 (13)	2618 (10)	3·0 (5)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Co—P(1)	2·214 (5)	N(2)—O(2)	1·15 (2)
Co—P(2)	2·209 (4)	O(3)—C(1)	1·39 (2)
Co—N(1)	1·594 (13)	O(4)—C(2)	1·42 (2)
Co—N(2)	1·613 (12)	O(5)—C(3)	1·28 (3)
P(1)—O(6)	1·547 (8)	O(6)—C(4)	1·46 (2)
P(1)—O(7)	1·550 (14)	O(7)—C(5)	1·44 (2)
P(1)—O(8)	1·602 (10)	O(8)—C(6)	1·41 (1)
P(2)—O(3)	1·547 (10)	B—C(7)	1·64 (2)
P(2)—O(4)	1·547 (14)	B—C(13)	1·65 (2)
P(2)—O(5)	1·540 (11)	B—C(19)	1·65 (2)
N(1)—O(1)	1·16 (2)	B—C(25)	1·65 (2)
P(1)—Co—P(2)	99·5 (3)	O(3)—P(2)—O(5)	108·1 (8)
P(1)—Co—N(1)	109·2 (6)	O(4)—P(2)—O(5)	100·7 (8)
P(1)—Co—N(2)	104·7 (5)	Co—N(1)—O(1)	177·0 (13)
P(2)—Co—N(1)	104·8 (5)	Co—N(2)—O(2)	179·7 (13)
P(2)—Co—N(2)	107·1 (5)	P(2)—O(3)—C(1)	127·3 (13)
N(1)—Co—N(2)	128·0 (8)	P(2)—O(4)—C(2)	124·6 (11)
Co—P(1)—O(6)	112·4 (5)	P(2)—O(5)—C(3)	136·0 (14)
Co—P(1)—O(7)	116·4 (6)	P(1)—O(6)—C(4)	121·5 (9)
Co—P(1)—O(8)	116·9 (6)	P(1)—O(7)—C(5)	121·0 (11)
O(6)—P(1)—O(7)	109·9 (7)	P(1)—O(8)—C(6)	121·4 (9)
O(6)—P(1)—O(8)	101·8 (6)	C(7)—B—C(13)	109·7 (11)
O(7)—P(1)—O(8)	97·7 (6)	C(7)—B—C(19)	104·9 (10)
Co—P(2)—O(3)	109·4 (6)	C(7)—B—C(25)	113·1 (10)
Co—P(2)—O(4)	117·5 (5)	C(13)—B—C(19)	112·9 (11)
Co—P(2)—O(5)	114·0 (5)	C(13)—B—C(25)	104·6 (10)
O(3)—P(2)—O(4)	106·4 (6)	C(19)—B—C(25)	111·9 (11)

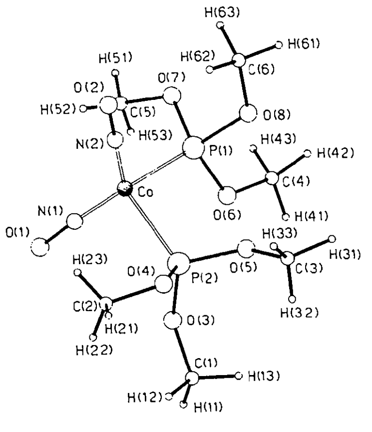

Fig. 1. View of the tetrahedrally coordinated cobalt complex.

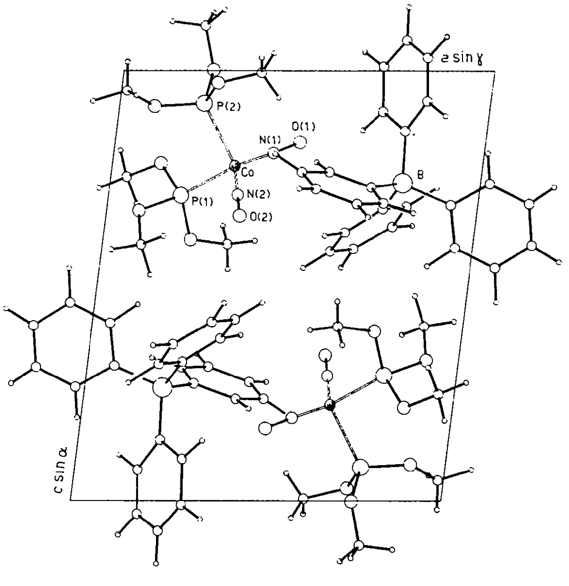

Fig. 2. Projection of the structure along [010].

and P—Co—P planes of 87·3 (4)° denoting a small deviation from the tetrahedral geometry. The N—Co—N and the Co—N—O angles are smaller and larger respectively than in the $[Co(NO)_2(PPh_3)_2]^+$ complex [136·7 (4) and 171·0 (5)° (Reichert, 1976)] and are consistent with a more evident NO^+ character of the nitrosyl with the phosphite than phosphine ligands, according to the higher π-acceptor character of the phosphite compared with the phosphine ligand.

Also, the Co—P bond distances in the complex with the phosphite ligand [2·214 (5) and 2·209 (4) Å] shorter than those found in the phosphine cation [2·266 (3) Å] are consistent with a greater π-acceptor character of the phosphite. In the phosphite complex the P—Co—P angle [99·5 (3)°] is smaller than in the phosphine complex [113·5 (2)°] probably because of the smaller steric demand of the $P(OMe)_3$ ligand than that of the bulky PPh_3 ligand.

The projection of the structure along [010] is shown in Fig. 2. The cations and the BPh_4^- anions are linked by normal van der Waals contacts, no non-bonded distances being particularly short.

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Structure of *fac*-(2,2′-Bipyridyl)trichloro(1*H*-1,2,4-triazole-*N*⁴)iron(III), $[Fe(C_2H_3N_3)(C_{10}H_8N_2)Cl_3]$

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Abstract. $M_r = 387·46$, monoclinic, $P2_1/n$, $a = 9·179$ (2), $b = 14·288$ (5), $c = 12·001$ (3) Å, $\beta = 98·01$ (2)°, $V = 1558·6$ (9) Å^3, $Z = 4$, $D_m = 1·64$ (2), $D_x = 1·651$ (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 14·84$ cm^{-1}, $F(000) = 770·8$, 295 K, $R = 0·022$ for 2012 significant $[I > 2\sigma(I)]$ reflexions. The iron(III) ion is coordinated by three chloride ions (in a *fac* arrangement), the two bipyridyl nitrogens, and the N(4) triazole atom in a distorted octahedral geometry. The bipyridyl and triazole molecules are planar. The least-squares planes of these molecules intersect at an angle of 91·05 (8)°.

Introduction. A large number of structures is possible for a species with molecular formula $FeLCl_3$ with L 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen) but little is known about the chemistry of these compounds (Cotton, 1972). $Fe(bpy)Cl_3$ and $Fe(phen)Cl_3$ were first reported by Simon, Morgenstern & Albrecht (1937) and later formulated as $[FeL_2Cl_2]^+[FeCl_4]^-$ (Harris & Lockyer, 1958; Figgis & Lewis, 1964). Indeed, the crystal structure of $[Fe(phen)_2Cl_2]^+[FeCl_4]^-$ has recently been published (Goodwin, McPartlin & Goodwin, 1977). However, Mössbauer experiments pointed to the existence of another species with a dimeric halogen-bridged structure (Berrett, Fitzsimmons & Owusu, 1968). To obtain more information about this type of compound the preparation of $Fe(bpy)Cl_3$ was re-investigated, whereby polymorphism was established (Vos, 1983). Reaction of $Fe(bpy)Cl_3$ with various nitrogen donor ligands resulted in a number of mixed-ligand adduct compounds. We report the crystal structure of one of these complexes, $Fe(bpy)(Htrz)Cl_3$, where Htrz is 1*H*-1,2,4-triazole, the first structure of an iron(III)–bipyridyl compound to be reported.

Experimental. Pale orange-brown needles, grown at room temperature from an acetone/toluene solution containing $Fe(bpy)Cl_3$ and three equivalents of 1*H*-1,2,4-triazole; D_m by flotation in chloroform–dibromoethane; approx. $0·50 \times 0·35 \times 0·10$ mm; Enraf–Nonius CAD-4 four-circle diffractometer,

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