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Structures of Five-Coordinate Dinitrosyls of Manganese. 2. The Triclinic Form of Dinitrosylbis(dimethyl phenylphosphonite)manganese(I) Chloride, $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$

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The crystal structure of the second polymorph of dinitrosylbis(dimethyl phenylphosphonite)manganese(I) chloride, $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$, has been determined by X-ray diffraction. This form crystallizes from C_2H_5OH/CH_2Cl_2 in the triclinic space group $P\bar{1}$, with $a = 15.727$ (5) Å, $b = 15.198$ (5) Å, $c = 9.405$ (5) Å, $\alpha = 90.97$ (5)°, $\beta = 89.04$ (5)°, $\gamma = 97.21$ (5)°, $V = 2229.6$ Å^3, $\rho_{obsd} = 1.45$ g cm^{-3}, and $Z = 4$ (two molecules per asymmetric unit). The structure was solved by direct methods and refined by block-diagonal least squares to a conventional R of 0.040 for 3711 reflections with $I > 1.65\sigma(I)$. The coordination about the manganese is trigonal bipyramidal in both molecules; however, the relative conformation of phosphonite ligands in the two molecules is not the same. One molecule has symmetry 2, while the other has symmetry m. In both isomers the NO groups are ordered, and the atoms of the $\{Mn(NO)_2Cl\}$ groups are coplanar with the two NO groups bent in toward each other. Bond lengths and angles of interest are as follows. Molecule "2": Mn–P = 2.285, 2.295 (5) Å; Mn–Cl = 2.360 (5) Å; Mn–N = 1.657, 1.644 (10) Å; N–O = 1.19, 1.18 (1) Å; P–Mn–P = 163.9 (5)°; N–Mn–N = 113.5 (5)°; O–Mn–O = 101.9 (5)°; Cl–Mn–P = 82.3, 82.4 (5)°; Cl–Mn–N = 129.2, 117.3 (5)°; Mn–N–O = 167, 165 (1)°. Molecule "M": Mn–P = 2.298, 2.297 (5) Å; Mn–Cl = 2.352 (5) Å; Mn–N = 1.633, 1.642 (10) Å; N–O = 1.19, 1.19 (1) Å; P–Mn–P = 167.6 (5)°; N–Mn–N = 112.1 (5)°; O–Mn–O = 99.8 (5)°; Cl–Mn–P = 83.4, 84.5 (5)°; Cl–Mn–N = 123.0, 124.9 (5)°; Mn–N–O = 166, 165 (1)°.

Introduction

A large number of solvents were tried before crystals of $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$ of quality suitable for X-ray analysis could be obtained.[1] The combination of ethanol/methylene dichloride was found to yield a second polymorph, triclinic with two molecules per asymmetric unit. The first structure determination had shown that the two Mn–N–O groups were nonlinear, in contrast to the results reported[2] for the series $[Mn(NO)(CO)_{4-x}\{P(C_6H_5)_3\}_x]$ (x = 0, 1, 2). The two molecules per asymmetric unit in this second form offered the chance of getting four independent measures of the Mn–N–O angle and the Mn–N and N–O bond lengths, and for this reason the crystal structure was determined. Preliminary results have been published.[3]

Experimental Section

The compound was prepared as described previously,[4] and crystals were obtained from C_2H_5OH/CH_2Cl_2. Preliminary oscillation and Weissenberg photographs showed that the crystals were triclinic; satisfactory elucidation of the structure confirmed that the space group was centrosymmetric, $P\bar{1}$.

Crystal data: $C_{16}H_{22}MnClN_2O_6P_2$, mol wt 490.4, triclinic space group $P\bar{1}$, $a = 15.727$ (5) Å, $b = 15.198$ (5) Å, $c = 9.405$ (5) Å, $\alpha = 90.97$ (5)°, $\beta = 89.04$ (5)°, $\gamma = 97.21$ (5)°, $V = 2229.6$ Å^3, $\rho_{obsd} = 1.45$ (3) g cm^{-3}, $Z = 4$, μ(Mo Kα) = 9.2 cm^{-1}; two independent molecules per asymmetric unit.

Accurate unit cell dimensions were determined from least-squares refinement of the 2θ, χ, and ϕ angles of 25 reflections measured on a Philips PW 1100 four-circle diffractometer (C.S.I.R., Pretoria) with graphite-monochromated Mo Kα radiation (λ 0.7107 Å). Intensity data were collected for θ between 3 and 20°. Three reflections were used as intensity standards and remeasured after every 60 reflections; no decomposition of the crystal was detectable. The diffractometer was operated in the standard mode; the ω–2θ scan technique was used; the scan width was 1.2°, each peak was scanned over 40 s, and the background was counted for 40 s. Of the 4135 reflections measured, 3711 were classed as observed: $I > 1.65\sigma(I)$. Only Lorentz–polarization corrections were applied.

Table I

	triclinic $[Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl]$	ideal centrosymmetric distribution
$\lvert E \rvert$	0.805	0.798
$\lvert E^2 - 1 \rvert$	0.973	0.968
$\lvert E^2 \rvert$	1.014	1.00
%$E > 3.0$	0.3	0.3
%$E > 2.0$	4.6	4.6
%$E > 1.0$	26.6	31.7
Probk	0.0973	

Starting Set of Reflections

hkl	E	cor soln	hkl	E	cor soln
623	2.83^a	+	522	2.96^b	–
332	3.50^a	+	5$\bar{8}$0	3.40^b	–
1$\bar{4}$3	3.02^a	+	$\bar{4}\bar{3}$8	3.09^b	–
$\bar{1}\bar{3}$3	3.21^b	–	$\bar{6}\bar{5}$7	2.95^b	+

^{a} Origin definers. ^{b} Variables.

A three-dimensional Patterson map showed that the two molecules, A and B, in the asymmetric unit were aligned so that the Mn–Cl vector

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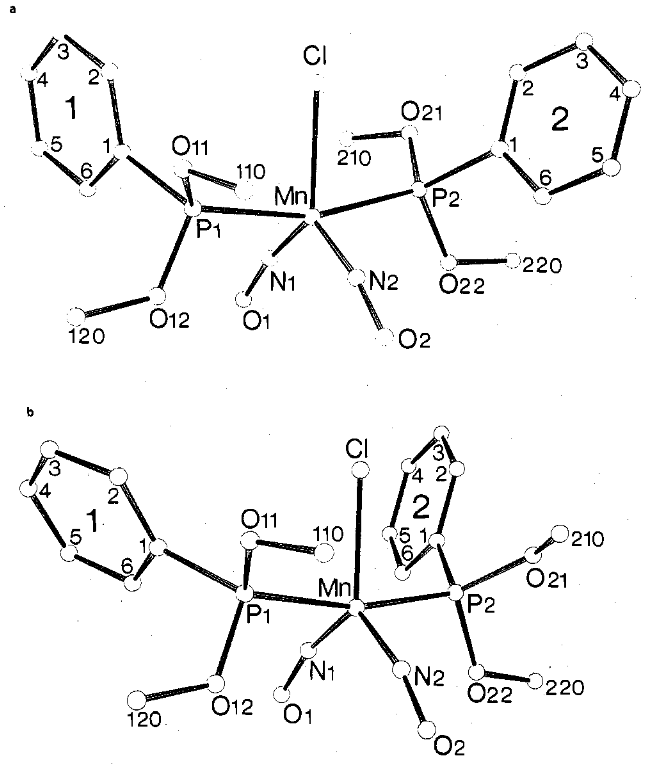

Figure 1. Projections of molecules "2" and "M" showing the numbering system. C atoms are identified by numbers only, viz., atom 2 in phenyl ring 1 is C(12); parentheses have been omitted to improve clarity. The near coplanarity of the atoms Mn, Cl, P(1), P(2), O(12), O(22), C(120), and C(220) is clearly seen: (a) molecule "2", phenyl rings staggered, trans or anti; (b) molecule "M", phenyl rings eclipsed, cis or syn.

in one was approximately parallel to the Mn–P vector in the other. The overlap of the vector patterns of the (MnP_2Cl) moieties for the combinations A–Ā, B–B̄, and A–B complicated the analysis of the map. For this reason, the structure was solved by direct methods. The origin-defining reflections were chosen so that they included planes parallel to the two P–Mn–P vectors.[5] (See Table I.) The program SAYRE[6] was used with 354 E's > 1.75; NBACK = 0, NVAR = 5. The correct solution had 182 "+" signs and 172 "–" signs, the highest consistency index (0.9782), and required three cycles to converge. The E map clearly showed all Mn, P, and Cl atoms, and the Fourier map phased on these eight atoms yielded the coordinates of all the light atoms. The structure was refined by block-diagonal least squares, first isotropically and then anisotropically, to yield a final conventional R of 0.040 for 3711 observed data. Weighting was proportional to $1/\sigma(F)$; scattering factors were taken from ref 7, and that of manganese was corrected for the real part of anomalous dispersion. All calculations were done with the local set of programs[8] on a Burroughs 5700 computer. A list of observed and calculated structure factors is available.[9]

The fractional atomic coordinates are given in Table II and the anisotropic thermal parameters are in Table III; estimated standard deviations in the last significant figure are given in parentheses.

Table II. Fractional Atomic Coordinates

atom	x	y	z
		Molecule "2"	
Mn	0.33354 (5)	0.22352 (5)	0.17931 (9)
Cl	0.3888 (1)	0.3077 (1)	−0.0174 (2)
P(1)	0.4181 (1)	0.3311 (1)	0.3023 (2)
P(2)	0.2529 (1)	0.1452 (1)	0.0072 (2)
N(1)	0.2518 (3)	0.2386 (3)	0.2865 (5)
N(2)	0.3835 (3)	0.1394 (3)	0.2235 (5)
O(1)	0.1993 (3)	0.2375 (3)	0.3792 (4)
O(2)	0.4050 (3)	0.0767 (3)	0.2791 (5)
O(11)	0.5170 (2)	0.3538 (3)	0.2611 (5)
O(12)	0.4146 (2)	0.3042 (2)	0.4651 (4)
O(21)	0.1900 (3)	0.1972 (3)	−0.0826 (4)
O(22)	0.1943 (2)	0.0638 (2)	0.0779 (4)
C(11)	0.3847 (3)	0.4393 (3)	0.2970 (6)
C(12)	0.4178 (4)	0.5021 (4)	0.1957 (6)
C(13)	0.3832 (5)	0.5822 (4)	0.1889 (7)
C(14)	0.3184 (4)	0.5989 (4)	0.2803 (8)
C(15)	0.2856 (4)	0.5384 (4)	0.3807 (8)
C(16)	0.3189 (4)	0.4581 (4)	0.3872 (7)
C(21)	0.3107 (4)	0.0977 (4)	−0.1336 (6)
C(22)	0.3176 (4)	0.1314 (5)	−0.2690 (7)
C(23)	0.3674 (5)	0.0936 (6)	−0.3699 (8)
C(24)	0.4088 (5)	0.0225 (5)	−0.3344 (8)
C(25)	0.4033 (5)	−0.0101 (5)	−0.2002 (9)
C(26)	0.3549 (4)	0.0277 (4)	−0.0988 (7)
C(110)	0.5693 (4)	0.2819 (5)	0.2318 (9)
C(120)	0.4646 (4)	0.3563 (5)	0.5749 (7)
C(210)	0.1385 (4)	0.2589 (5)	−0.0075 (7)
C(220)	0.1349 (4)	0.0014 (4)	−0.0083 (8)
		Molecule "M"	
Mn	0.89342 (5)	0.24329 (5)	0.36079 (8)
Cl	0.9168 (1)	0.3525 (1)	0.5410 (2)
P(1)	0.8607 (1)	0.1502 (1)	0.5493 (2)
P(2)	0.9253 (1)	0.3600 (1)	0.2091 (2)
N(1)	0.8005 (3)	0.2163 (3)	0.2866 (5)
N(2)	0.9665 (3)	0.1849 (3)	0.2959 (5)
O(1)	0.7428 (3)	0.1848 (3)	0.2146 (5)
O(2)	1.0041 (3)	0.1329 (3)	0.2328 (5)
O(11)	0.9282 (3)	0.1510 (3)	0.6740 (4)
O(12)	0.8477 (2)	0.0517 (2)	0.4856 (4)
O(21)	1.0167 (2)	0.4174 (3)	0.2157 (4)
O(22)	0.9162 (2)	0.3211 (2)	0.0506 (4)
C(11)	0.7647 (4)	0.1611 (3)	0.6534 (6)
C(12)	0.7642 (4)	0.1767 (4)	0.7991 (6)
C(13)	0.6856 (5)	0.1800 (4)	0.8709 (7)
C(14)	0.6112 (5)	0.1706 (4)	0.7991 (8)
C(15)	0.6115 (4)	0.1569 (4)	0.6546 (8)
C(16)	0.6874 (4)	0.1517 (4)	0.5810 (6)
C(21)	0.8572 (3)	0.4469 (3)	0.2187 (5)
C(22)	0.8814 (4)	0.5230 (4)	0.2976 (6)
C(23)	0.8276 (4)	0.5888 (4)	0.3064 (7)
C(24)	0.7518 (4)	0.5799 (4)	0.2396 (7)
C(25)	0.7275 (4)	0.5039 (5)	0.1604 (8)
C(26)	0.7798 (4)	0.4371 (4)	0.1509 (7)
C(110)	1.0194 (4)	0.1501 (6)	0.6405 (8)
C(120)	0.8242 (5)	−0.0257 (4)	0.5789 (7)
C(210)	1.0897 (4)	0.3992 (4)	0.2946 (7)
C(220)	0.9345 (5)	0.3781 (5)	−0.0754 (6)

Results and Discussion

As was found previously,[1] the coordination about the manganese is trigonal bipyramidal. However, the two molecules in the asymmetric unit are not identical and are best described as "conformational or rotational isomers". Comparison of parts a and b of Figure 1 shows that one molecule ("2") approximates symmetry 2 with the twofold axis coincident with the Mn–Cl bond, while the other ("M") approximates symmetry m with the atoms of the $\{Mn(NO)_2Cl\}$ group defining the mirror plane. Molecule "2" can be transformed into "M" by a 120° rotation of the phosphonite ligand P(2)—effectively interchanging phenyl ring 2 for the OCH_3 group O(21)–C(210). In both "2" and "M" (and in the monoclinic form[1]) the $\{PO_2C\}$ groups of the phosphonite ligands are staggered relative to the $\{MnN_2Cl\}$ groups, with one OCH_3 group trans to the Cl atom. (Table VIII). A comparable form of isomerism in compounds containing PX_2Y ligands has been found before.[10]

In both isomers, the P atoms are bent toward the Cl atom and away from the NO groups. This distortion maximizes the P···N distances, thus reducing the van der Waals repulsions between these atoms (see Table VI; P···N ~ 2.9 Å, P···Cl ~ 3.1 Å as was also found previously[1]).

There are no significant differences between analogous bond lengths in the two isomers.

Molecule "2". This molecule is superficially the same as that found in the monoclinic form,[1] yet closer examination

Table III. Anisotropic Thermal Parameters[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule “2”						
Mn	346 (4)	255 (4)	633 (12)	103 (7)	5 (11)	0 (11)
Cl	641 (10)	391 (9)	723 (22)	−125 (15)	36 (23)	246 (22)
P(1)	286 (8)	294 (8)	762 (22)	54 (13)	−41 (20)	59 (21)
P(2)	362 (8)	315 (8)	614 (21)	38 (13)	24 (21)	23 (21)
N(1)	36 (2)	29 (2)	97 (7)	10 (4)	2 (7)	2 (7)
N(2)	48 (3)	36 (3)	84 (7)	37 (4)	−1 (7)	3 (7)
O(1)	45 (2)	46 (2)	143 (7)	20 (4)	62 (6)	14 (6)
O(2)	80 (3)	58 (3)	141 (7)	74 (5)	20 (7)	38 (7)
O(11)	28 (2)	51 (2)	158 (7)	3 (4)	8 (6)	16 (7)
O(12)	47 (2)	40 (2)	78 (6)	0 (4)	25 (5)	16 (5)
O(21)	48 (2)	55 (2)	92 (6)	12 (4)	−27 (6)	29 (6)
O(22)	42 (2)	44 (2)	88 (6)	−2 (3)	17 (5)	14 (6)
C(11)	30 (3)	29 (3)	80 (8)	2 (5)	−14 (8)	−13 (8)
C(12)	59 (4)	36 (3)	86 (9)	−1 (6)	−15 (9)	−7 (8)
C(13)	83 (5)	28 (3)	124 (10)	−2 (6)	−54 (11)	17 (9)
C(14)	60 (4)	34 (4)	224 (13)	21 (6)	−86 (12)	−28 (11)
C(15)	39 (3)	35 (4)	238 (14)	10 (6)	−1 (11)	−32 (11)
C(16)	37 (3)	29 (3)	171 (11)	−4 (5)	7 (9)	−13 (9)
C(21)	39 (3)	35 (3)	78 (8)	−14 (5)	12 (8)	−26 (8)
C(22)	60 (4)	76 (5)	79 (10)	−1 (7)	35 (10)	−36 (10)
C(23)	76 (5)	108 (6)	116 (11)	−52 (9)	59 (12)	−49 (13)
C(24)	67 (5)	76 (5)	222 (14)	−55 (8)	120 (13)	−173 (14)
C(25)	66 (5)	48 (4)	275 (16)	−3 (7)	106 (13)	−77 (13)
C(26)	56 (4)	42 (4)	158 (11)	4 (6)	70 (10)	−47 (10)
C(110)	41 (4)	68 (5)	323 (18)	65 (7)	62 (13)	22 (14)
C(120)	60 (4)	73 (5)	96 (10)	−17 (7)	−90 (10)	−40 (11)
C(210)	61 (4)	69 (5)	150 (11)	86 (7)	30 (11)	8 (11)
C(220)	53 (4)	51 (4)	176 (12)	−49 (6)	−46 (11)	−24 (11)
Molecule “M”						
Mn	289 (4)	249 (4)	543 (11)	−29 (7)	−18 (11)	186 (11)
Cl	549 (9)	330 (8)	620 (21)	−51 (14)	−90 (21)	−96 (20)
P(1)	351 (8)	268 (8)	588 (21)	−10 (13)	−38 (20)	234 (20)
P(2)	276 (7)	271 (8)	573 (20)	−61 (12)	−17 (19)	246 (20)
N(1)	36 (3)	40 (3)	89 (7)	−22 (4)	−37 (7)	22 (7)
N(2)	45 (3)	32 (3)	95 (7)	11 (4)	25 (7)	28 (7)
O(1)	54 (3)	74 (3)	160 (8)	−32 (4)	−70 (7)	41 (8)
O(2)	68 (3)	55 (3)	190 (8)	39 (5)	75 (8)	−3 (7)
O(11)	50 (2)	56 (3)	75 (6)	5 (4)	−40 (6)	46 (6)
O(12)	50 (2)	28 (2)	91 (6)	7 (3)	23 (6)	14 (5)
O(21)	33 (2)	49 (2)	154 (7)	−23 (3)	−16 (6)	83 (7)
O(22)	57 (2)	36 (2)	56 (5)	0 (4)	8 (6)	12 (5)
C(11)	46 (3)	22 (3)	67 (8)	−5 (5)	21 (8)	21 (7)
C(12)	67 (4)	39 (3)	79 (9)	26 (6)	1 (9)	11 (9)
C(13)	84 (5)	56 (4)	85 (10)	41 (7)	65 (11)	23 (10)
C(14)	70 (4)	45 (4)	169 (12)	1 (7)	109 (12)	11 (11)
C(15)	42 (4)	59 (4)	179 (12)	−21 (6)	35 (10)	−29 (11)
C(16)	37 (3)	54 (4)	107 (10)	−18 (6)	28 (9)	−21 (10)
C(21)	30 (3)	31 (3)	60 (8)	−10 (5)	−2 (7)	28 (8)
C(22)	42 (3)	30 (3)	83 (9)	8 (5)	−1 (8)	23 (8)
C(23)	65 (4)	37 (3)	102 (10)	2 (6)	9 (10)	15 (9)
C(24)	60 (4)	54 (4)	147 (11)	42 (6)	−4 (11)	41 (11)
C(25)	43 (4)	78 (5)	178 (13)	24 (7)	−61 (11)	39 (12)
C(26)	38 (3)	38 (3)	146 (10)	10 (5)	−37 (9)	11 (9)
C(110)	34 (4)	118 (6)	196 (14)	27 (8)	−43 (11)	50 (15)
C(120)	82 (4)	25 (3)	152 (11)	8 (6)	50 (11)	105 (10)
C(210)	26 (3)	61 (4)	155 (11)	18 (6)	−50 (9)	8 (10)
C(220)	89 (5)	64 (4)	56 (9)	6 (7)	30 (10)	91 (10)

[a] $\times 10^5$ for Mn, Cl, and P atoms; $\times 10^4$ for N, O, and C atoms. The form of the equation is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$.

shows that there are large differences between some of the bond angles. Although the N–Mn–N angles are similar, 113.5 vs. 111.5°, the Cl–Mn–N angles are not: 129.2, 117.3° vs. 123.9, 124.6°. There is no obvious reason why the two Cl–Mn–N angles in molecule “2” should differ by 12° or why they should not be the same as was found previously. However, this distortion gives rise to (or results from?) several other changes in coordination geometry around the Mn atom. The parameters associated with N(1)— the atom with the large Cl–Mn–N angle—show considerable distortions from regularity. For example: P(1)–Mn–N(1) = 89.7°, P(1)–Mn–N(2) = 97.3°; P(2)–Mn–N(1) = 95.9°, P(2)–Mn–N(2) = 94.4°. The analogous values in the monoclinic form were between 91.3 and 95.6°. N(1)···O(12) is 3.13 Å, significantly shorter than the other N···O distances (see Table VI) and the analogous nonbonded contacts found before.[1]

The NO group with the large Cl–Mn–N angle and close N···O contact has the smaller thermal vibrational ellipsoids (see Table IX). The other NO group, the two groups in molecule “M” and the two in the monoclinic form[1] have ellipsoids which are similar in size.

The geometry of the phosphonite groups are the same as found in the monoclinic form.[1] The Mn–P–O angles for the OCH_3 groups in the $\{MnP_2Cl\}$ plane are small (~108°)

Table IV. Bond Lengths (Å)

	molecule "2"	molecule "M"
Mn-Cl	2.360 (5)	2.352 (5)
Mn-P(1)	2.285 (5)	2.298 (5)
Mn-P(2)	2.295 (5)	2.297 (5)
Mn-N(1)	1.657 (10)	1.633 (10)
Mn-N(2)	1.644 (10)	1.642 (10)
N(1)-O(1)	1.19 (1)	1.19 (1)
N(2)-O(2)	1.18 (1)	1.19 (1)
P(1)-O(11)	1.59 (1)	1.59 (1)
P(1)-O(12)	1.59 (1)	1.59 (1)
P(2)-O(21)	1.60 (1)	1.59 (1)
P(2)-O(22)	1.59 (1)	1.60 (1)
P(1)-C(11)	1.79 (1)	1.81 (1)
P(2)-C(21)	1.79 (1)	1.80 (1)
O(11)-C(110)	1.47 (2)	1.47 (2)
O(12)-C(120)	1.47 (2)	1.49 (2)
O(21)-C(210)	1.48 (2)	1.43 (2)
O(22)-C(220)	1.48 (2)	1.48 (2)
C-C	1.36-1.41	1.35-1.40
C-C(mean)	1.38	1.38

Table V. Bond Angles (deg)

	molecule "2"	molecule "M"
P(1)-Mn-P(2)	163.9 (5)	167.6 (5)
N(1)-Mn-N(2)	113.5 (5)	112.1 (5)
O(1)-Mn-O(2)	101.9 (5)	99.8 (5)
P(1)-Mn-Cl	82.3 (5)	83.4 (5)
P(2)-Mn-Cl	82.4 (5)	84.5 (5)
P(1)-Mn-N(1)	89.7 (5)	93.5 (5)
P(1)-Mn-N(2)	97.3 (5)	93.4 (5)
P(2)-Mn-N(1)	95.9 (5)	91.1 (5)
P(2)-Mn-N(2)	94.4 (5)	95.5 (5)
Cl-Mn-N(1)	129.2 (5)	123.0 (5)
Cl-Mn-N(2)	117.3 (5)	124.9 (5)
Mn-N(1)-O(1)	167 (1)	166 (1)
Mn-N(2)-O(2)	165 (1)	165 (1)
Mn-P(1)-O(11)	120 (1)	119 (1)
Mn-P(1)-O(12)	108 (1)	107 (1)
Mn-P(1)-C(11)	115 (1)	119 (1)
Mn-P(2)-O(21)	118 (1)	119 (1)
Mn-P(2)-O(22)	109 (1)	107 (1)
Mn-P(2)-C(21)	116 (1)	117 (1)
O(11)-P(1)-O(12)	106 (1)	106 (1)
O(11)-P(1)-C(11)	100 (1)	100 (1)
O(12)-P(1)-C(11)	106 (1)	105 (1)
O(21)-P(2)-O(22)	106 (1)	106 (1)
O(21)-P(2)-C(21)	100 (1)	100 (1)
O(22)-P(2)-C(21)	105 (1)	105 (1)
P(1)-O(11)-C(110)	120 (1)	120 (1)
P(1)-O(12)-C(120)	123 (1)	121 (1)
P(2)-O(21)-C(210)	119 (1)	128 (1)
P(2)-O(22)-C(220)	121 (1)	122 (1)

Table VI. Intramolecular Nonbonded Separations (Å)

	molecule "2"	molecule "M"
N(1)···N(2)	2.76	2.72
O(1)···O(2)	4.37	4.29
N(1)···P(1)	2.82	2.90
N(2)···P(1)	2.98	2.90
N(1)···P(2)	2.97	2.84
N(2)···P(2)	2.92	2.95
Cl···P(1)	3.06	3.09
Cl···P(2)	3.07	3.13
Cl···N(1)	3.64	3.52
Cl···N(2)	3.44	3.56
N(1)···O(12)	3.13	3.32
N(1)···O(22)	3.32	3.17
N(2)···O(12)	3.35	3.14
N(2)···O(22)	3.36	3.30

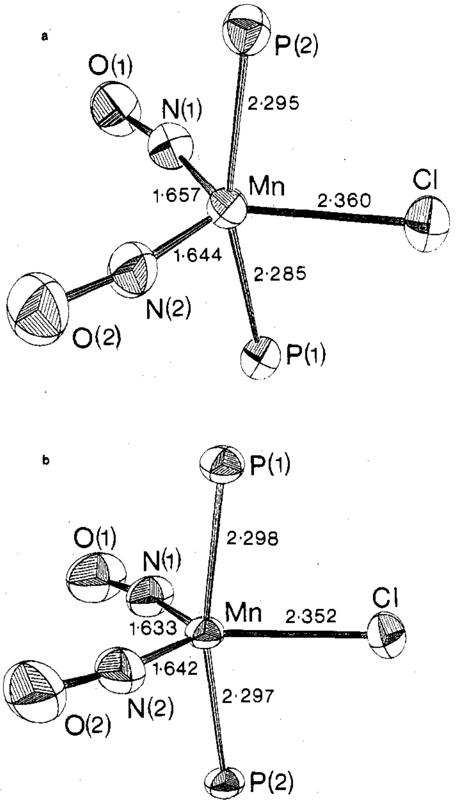

Figure 2. $\{MnClP_2(NO)_2\}$ units, oriented to show the relative size and shape of the thermal ellipsoids. The maximum amplitude of vibration of the Cl atom is approximately in the plane $\{Mn(NO)_2Cl\}$: (a) molecule "2"; (b) molecule "M".

because the O atoms suffer minimal compression, while the Mn–P–O angles for the other OCH_3 groups are very much larger (~119°). The C–P–O angles are large for the OCH_3 groups with the CH_3 group bent away from the $\{Mn(NO)_2Cl\}$ plane (106°) and small for the OCH_3 groups with the CH_3 group turned away from the phenyl ring (100°).

Molecule "M". Although the environments of N(1) and N(2) are necessarily different, the bond angles about the Mn atoms show no deviations from regularity: Cl–Mn–N = 123.0, 124.9°; the P–Mn–N angles are between 91.1 and 95.5°. Both N atoms are involved in close contacts (N(1)···O(22) = 3.17 Å, N(2)···O(12) = 3.14 Å), with the result that both suffer similar stresses and there is negligible angular distortion in the $\{Mn(NO)_2P_2Cl\}$ system. The one relatively large difference is the increased P–Mn–P angle of 167.6° vs. 163.9° in "2": the angle in the monoclinic form[1] was 166.9°.

The internal geometry of the phosphonite ligands follows the same pattern as observed in "2" and as was found before.[1] Where the OCH_3 group is bent away from the $\{Mn(NO)_2Cl\}$ place, the Mn–P–O angle is small (107°); the other Mn–P–O angle is large (119°). Similarly the C–P–O angles come in pairs; 100 and 105° (see Table V).

General Comparisons

The average volume per molecule in the monoclinic form[1] is 558.4 Å^3 (average volume per nonhydrogen atom 19.94 Å^3). In the triclinic form, the volume of the pair of molecules in the asymmetric unit is 1114.8 Å^3 (average volume per nonhydrogen atom 19.91 Å^3). If one assumes that the molecule of symmetry 2 has the same volume as it has in the monoclinic form, then molecule "M" has a volume of 556.4 Å^3—2 Å^3

Table VII. Least-Squares Planes[a] and Deviations Therefrom (A)

(i) The $\{Mn(NO)_2Cl\}$ Group

Molecule "2"

$L = -0.554, M = -0.586, N = -0.591, D = -5.668$

Mn 0.03	N(2) 0.00	P(1) −2.23
Cl −0.02	O(1) −0.03	P(2) 2.30
N(1) 0.02	O(2) −0.01	

Molecule "M"

$L = 0.156, M = 0.702, N = -0.695, D = 2.300$

Mn 0.01	N(2) 0.01	P(1) −2.28
Cl 0.00	O(1) 0.00	P(2) 2.29
N(1) −0.01	O(2) −0.01	

(ii) The $\{Mn(P)_2Cl\}$ Group

Molecule "2"

$L = 0.806, M = -0.586, N = -0.083, D = 1.738$

Mn 0.07	P(2) −0.04	C(120) 0.13
Cl 0.01	O(12) 0.10	C(220) −0.04
P(1) −0.04	O(22) 0.02	

Molecule "M"

$L = -0.988, M = 0.153, N = -0.020, D = -12.966$

Mn −0.03	P(2) 0.02	C(120) −0.16
Cl 0.00	O(12) −0.17	C(220) 0.06
P(1) 0.02	O(22) 0.05	

[a] The equation of the plane is of the form $Lx + My^* + Nz^{**} = D$, where L, M, and N are direction cosines, x, y^*, and z^{**} are orthogonalized coordinates, and D is in Å.

Table VIII. Torsion Angles (deg)

	molecule "2"	molecule "M"
Cl-Mn-P(1)-O(12)	−175	−173
Cl-Mn-P(2)-O(22)	178	−178
O(12)-P(1)-P(2)-O(22)	3	9
C(11)-P(1)-P(2)-C(21)	119	7
P(2)-P(1)-O(12)-C(120)	179	−178
P(1)-P(2)-O(22)-C(220)	177	180

Table IX. Amplitudes of Vibration (Å) for Thermal Ellipsoids

	molecule "2"			molecule "M"		
	min	intermed	max	min	intermed	max
Mn	0.15	0.16	0.22	0.13	0.17	0.20
Cl	0.17	0.21	0.29	0.16	0.20	0.27
P(1)	0.18	0.18	0.19	0.15	0.18	0.22
P(2)	0.16	0.19	0.21	0.14	0.17	0.21
N(1)	0.19	0.20	0.23	0.17	0.19	0.27
N(2)	0.17	0.20	0.27	0.18	0.20	0.26
O(1)	0.19	0.22	0.28	0.21	0.25	0.33
O(2)	0.20	0.24	0.33	0.21	0.26	0.32

Table X. Shortest Intermolecular Nonbonded Contacts Involving the Cl and Nitrosyl O atoms (Å)[a]

atom	molecule	atom	molecule	equiv position[b]	dist
O(1)	M	C(110)	2	1	3.26
O(1)	M	C(25)	2	2(100)	3.29
O(1)	2	C(210)	M	1($\bar{1}$00)	3.29
O(1)	2	C(120)	M	2(101)	3.22
Cl	2	C(24)	M	2(110)	3.66
Cl	M	C(220)	M	1(001)	3.63
Cl	M	C(210)	M	intramolecular	3.56

[a] Atom in molecule to atom in molecule in equivalent position. [b] Equivalent positions: (1) x, y, z; (2) $-x, -y, -z$. Numbers in parentheses indicate translations parallel to the cell edges.

smaller. This implies that molecule "M" is more compact and, presumably, more tighly packed in the crystal.[11] If this is true, then the thermal motion of molecule "M" should be smaller than that of molecule "2". This supposition is borne out by the relatively smaller amplitudes of vibration of the Mn, P and Cl atoms in molecule "M" (see Table IX).

It is certainly not clear why there is no angular distortion about the Mn atom in isomer "M" nor, conversely, is it clear why isomer "2" should be so distorted from the regularity of the molecule in the monoclinic form.[1]

Neither the Cl atoms nor the nitrosyl O atoms are involved in short intermolecular contacts (Table X). One conclusion *can* be drawn: the force constant for distortion of the Cl–Mn–N angles must be remarkably small. If this were not true, it would be difficult to understand how differences in environment can possibly cause such a large change in the Cl–Mn–N angles. In both "2" and "M" (and in the monoclinic form[1]) the largest amplitude of vibration of the Cl atom is approximately in the plane $\{Mn(NO)_2Cl\}$, in accordance with this conclusion (Figure 2).

In spite of the differences in conformation of the phosphonite ligands in isomers "2" and "M" and in spite of the distortions in the $\{Mn(NO)_2Cl\}$ plane of "2", the geometry of the $\{Mn(NO)_2\}$ system is essentially the same in "2", "M", and the monoclinic form.[1] One can only conclude that the $\{Mn(NO)_2\}$ system is very robust and that this particular deviation from linearity of the Mn–N–O group is not caused by either intramolecular or intermolecular packing forces. Quite clearly, the NO groups are *not* bent out of the equatorial plane, and both are bent away from the electronegative Cl atom. This appears to contradict the prediction of Hoffmann and co-workers,[12] who deduced for a complex of trigonal-bipyramidal geometry with *one* equatorial nitrosyl group that the NO would prefer to bend in the axial plane. It is interesting to see that the geometry of this $\{Mn(NO)_2\}$ system falls nicely on the line drawn by Martin and Taylor[13] for tetrahedral $[ML_2(NO)_2]$ compounds.

It is not clear why both isomers should occur together in the triclinic crystals. However, one can say with some degree of confidence that the two isomers must be present in the solution and that they cannot differ greatly in energy. It should, in principle, be possible to isolate pure isomer "M" in the solid state.

Conclusion

With the determination of the crystal structure of the triclinic form, six independent measures of the geometry of the Mn–N–O system in $[Mn(NO_2)\{P(OCH_3)_2C_6H_5\}_2Cl]$ have been made. The Mn–N–O group is undoubtedly nonlinear.

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Registry No. $Mn(NO)_2\{P(OCH_3)_2C_6H_5\}_2Cl$, 68366-07-4.

Supplementary Material Available: A listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Structural Characterization of Spirophosphoranes Existing as Nearly Perfect Trigonal Bipyramids[1]

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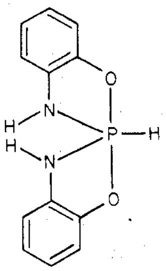
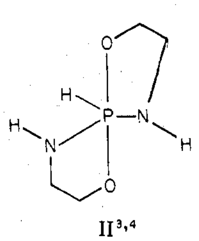
The single-crystal X-ray characterization of 2,3:7,8-dibenzo-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, IV, and 2,3:7,8-dibenzo-9-methyl-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, V, revealed relatively undistorted trigonal bipyramids with the unique proton ligand occupying an equatorial site. The structures lie along the coordinate connecting idealized trigonal-bipyramidal and rectangular-pyramidal geometries. They are displaced from the trigonal bipyramid by 5.5 (IV) and 11.2% (V) as measured by dihedral-angle differences from polytopal faces. Data for both compounds were collected by using Mo K$\bar{\alpha}$ radiation on an Enraf-Nonius CAD4 automated diffractometer. IV crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 5.729$ (2) Å, $b = 11.218$ (5) Å, $c = 17.234$ (7) Å, and $Z = 4$. Full-matrix least-squares refinement gave $R = 0.032$ and $R_w = 0.042$ for the 1393 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 59°$. V crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.142$ (2) Å, $b = 16.491$ (6) Å, $c = 8.133$ (2) Å, $\beta = 95.90$ (2)°, and $Z = 4$. Full-matrix least-squares refinement gave $R = 0.038$ and $R_w = 0.048$ for the 2062 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 55°$. Examination of the structural data on these and related spirophosphoranes suggests that the small size of the phosphorus-bound proton acts as a principal factor in producing conformations of IV and V little distorted from a trigonal bipyramid. The presence of only one equatorial ring nitrogen atom in IV and V also appears to allow the ideal trigonal bipyramid to be closely approached.

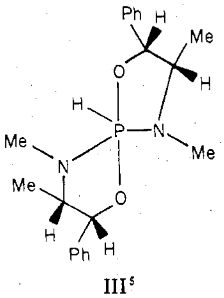
In previous X-ray studies of the structures of spirophosphoranes containing P–H bonds, the basic geometrical arrangement is that of a trigonal bipyramid, I–III.[3-5]



I[3]



II[3,4]

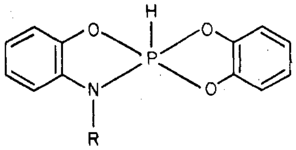


III[5]

For II, the position of the hydrogen atom was sufficiently resolved to allow the determination of the mode of the distortion. As with previous phosphoranes whose structural parameters have been fully established,[6,7] distortion is found to closely adhere to the Berry coordinate[8] governing ligand exchange.[9] In the case of II, the degree of distortion from the idealized trigonal bipyramid to an ideal rectangular pyramid is 22%,[3] measured by the dihedral-angle method based on unit bond lengths.[6] For derivative I, it is estimated[3] that the degree of distortion from the idealized trigonal bipyramid is approximately the same. However, for II, the point at which the structure rests along this low-energy distortion coordinate is strongly influenced by intermolecular hydrogen bonding. In the absence of the latter effect, the structure of II is expected to lie closer to a perfect trigonal bipyramid. The presence of two neighboring equatorial nitrogen atoms is also felt to move the structure away from the idealized trigonal bipyramid by way of P–N π bonding serving to widen the N–P–N equatorial angle. The latter is considered a secondary effect.[3]

Derivative I contains unsaturated rings in the spiro system in contrast to that in II. From observations on trends in related derivatives,[6,7] ring unsaturation, by way of a more constrained ring system,[10] generally causes large structural distortions toward the rectangular-pyramidal geometry,[10,11] again along the Berry coordinate. However, these latter derivatives have rings containing like heteroatoms directly bonded to phosphorus. Thus, the presence of an equatorially positioned nitrogen atom in the dioxadiazaspirophosphorane I appears to act as a structural determinant in maintaining a much more modest perturbation of the ideal trigonal bipyramid. However, the presence of a proton as a ligand in these derivatives has not been adequately explored.

In order to more clearly establish the competing effects of these equatorial ligands as well as the role of ring unsaturation in a spirophosphorane like I, the derivatives IV and V were chosen for X-ray studies. Use of one rather than two ring nitrogen atoms, as in I–III, removes the possible structural complication associated with π p–d effects in the equatorial bonding arrangement, N–P–N. Further, the influence of possible intermolecular hydrogen bonding in IV relative to its



IV, R = H
V, R = CH_3

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