K salt

K(1)—O(11)	2.871 (5)	K(1)—O(11^{iii})	2.772 (5)
K(1)—O(12^{i})	2.688 (4)	K(1)—O(12^{ii})	2.730 (4)
K(1)—O(2^{iv})	2.775 (5)	K(1)—O(3^{v})	2.833 (4)
C(1)—C(2)	1.532 (9)	C(2)—C(3)	1.535 (9)
C(1)—O(11)	1.248 (7)	C(3)—C(3′)	1.525 (8)
C(1)—O(12)	1.239 (7)		
C(2)—C(1)—O(11)	118.9 (5)	C(3)—C(2)—O(2)	112.0 (5)
C(2)—C(1)—O(12)	116.1 (5)	C(2)—C(3)—O(3)	109.9 (5)
O(11)—C(1)—O(12)	125.0 (6)	C(2)—C(3)—C(3′)	111.9 (5)
C(1)—C(2)—C(3)	108.1 (5)	O(3)—C(3)—C(3′)	108.9 (5)
C(1)—C(2)—O(2)	114.8 (5)		

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O(2)—H(O2)···O(12^{i})	1.87 (5)	2.770 (6)	160 (5)
O(2)—H(O2)···O(11)	2.38 (5)	2.741 (6)	103 (4)
O(3)—H(O3)···O(11^{ii})	1.78 (6)	2.756 (6)	164 (5)
O(3)—H(O3)···O(12^{ii})	2.25 (5)	2.978 (6)	129 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $-x, 1-y, -z$; (vii) $1-x, 1-y, 1-z$; (viii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $-x, -y, -z$.

Data were collected using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). The structures were solved using *MULTAN*88 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1988). Structure refinement, geometric calculations and preparation of the figures were performed using *KPPXRAY* (Taga, Masuda, Higashi & Iizuka, 1991) on a FACOM M1900 computer at the Data Processing Center, Kyoto University, Japan. *EDCIF-J* (Osaki & Taga, 1993) was used to prepare the material for publication.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AS1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two 4-Nitropyridine *N*-Oxide Adducts: $(C_5H_4N_2O_3)_2.AgNO_3$ and $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$

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(*Received* 8 *July* 1993; *accepted* 1 *November* 1993)

Abstract

Two new addition compounds of the optically non-linear molecule 4-nitropyridine *N*-oxide (NPO) have been synthesized and characterized: bis(4-nitropyridine *N*-oxide)silver nitrate and bis(4-nitropyridine *N*-oxide)cobalt nitrate tetrahydrate. Their structural features are described and compared, in particular the arrangement of the NPO molecules, the type of linkage in the inorganic entities (the cationic polyhedra and the nitrate anions) which make up the host matrice for the organic molecules and the hydrogen-bonding scheme contributing to the packing cohesion. Certain characteristics of both these centrosymmetric structures are also discussed with respect to some non-linear optical NPO derivatives.

Comment

It has been shown in previous studies (Nicoud & Twieg, 1987) that aromatic molecules, characterized by a strong charge transfer occurring between a donor and an acceptor substituent and by a small ground-state dipole moment, can lead to non-linear optical materials if, of course, the non-centrosymmetry of the crystal structure is assured. Effectively, these molecular features give a high molecular first-order hyperpolarizability. Besides, a small dipole almost cancels the electrostatic interactions between molecules and consequently may prevent centrosymmetric arrangement of the molecules while facilitating the growth of good quality crystals (chemical feasibility).

4-Nitropyridine *N*-oxide (NPO) displays both the required properties: an important electronic charge transfer from the *N*-oxide group to the nitro group and a quasi-cancelled total dipole moment. Nevertheless, its crystal structure is centrosymmetric. So, the aim of the molecular engineering of efficient non-linear optically related compounds is to find either supplementary substituents for the aromatic ring, or other entities which do not disturb the charge-transfer mechanism and remove the centrosymmetry from the NPO structure. The former possibility has already been investigated in depth by Zyss, Chemla & Nicoud (1981), who, among various substituted NPO molecules, found an attractive candidate for non-linear optical applications, namely 3-methyl-4-nitropyridine *N*-oxide (POM) (Shiro, Yamakawa & Kubota, 1977). The latter possibility, using other entities, is found to have a different effect on the intermolecular bonds, in particular by association of organic molecules (or cations) with inorganic molecules (or anions). The resulting ionic bonds have to be strong enough to orient the organic entities in a favourable direction, not only for non-centrosymmetric final crystal packing, but also for increased efficiency of the non-linear properties (phase matching). This type of approach has recently been employed with organic cations such as 2-amino-5-nitropyridinium (2A5NP) associated to inorganic anions of various geometries and charges (Masse, Bagieu-Beucher, Pécaut, Levy & Zyss, 1993).

Extending this to 4-nitropyridine *N*-oxide, we shall try to understand the role assumed by the inorganic entity in building the centrosymmetric or non-centrosymmetric framework. Two NPO derivative salts have been studied in the present work: bis(4-nitropyridine *N*-oxide)silver nitrate and bis(4-nitropyridine *N*-oxide)cobalt nitrate tetrahydrate.

Bis(4-*nitropyridine N-oxide*)*silver nitrate*

The crystal structure may be described as a three-dimensional network of NPO molecules oriented almost perpendicularly to each other (Fig. 1). The AgO_6 coordination polyhedra linked to the NO_3 groups connect the organic entities.

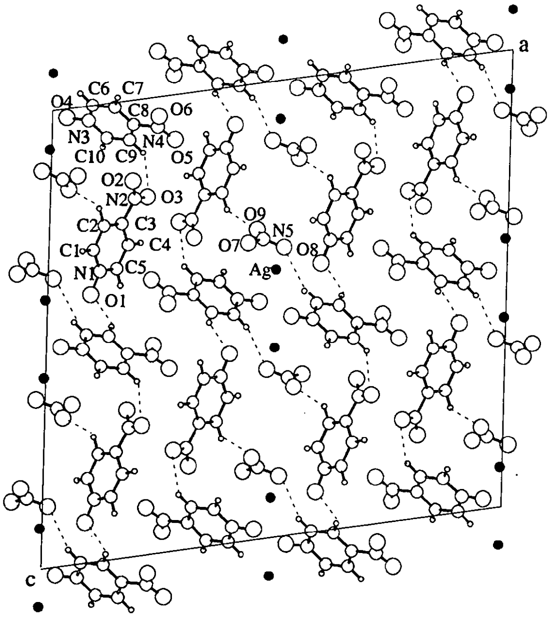

Fig. 1. Projection along the *b* axis of the $(C_5H_4N_2O_3)_2.AgNO_3$ atomic arrangement. C—H···O bonds (long hydrogen bonds) are represented by dashed lines

The organic molecules. Both independent pyridine *N*-oxide rings are approximately planar [maximum deviation 0.020 (6) Å] with an angle of 79° between the two planes. The nitro groups are displaced from the aromatic planes with dihedral angles of 11.7 (8) and 11 (1)°. These values are intermediate between those found in NPO (0°) and POM (16.7°), which should mean that the intramolecular charge transfer (ICT) is slightly stronger than in POM (Yamakawa, Kubota, Ezumi & Mizumo, 1974).

With regard to the interatomic distances and angles in the organic molecules, the values are similar to those observed in NPO (Wang, Blessing, Ross & Coppens, 1976) and its derivatives (Shiro *et al.*, 1977; Pécaut, Le Fur, Levy & Masse, 1993). The C—C bonds in the rings do not differ significantly in length (average 1.372 Å). On the contrary, the C—N bonds inside the ring (average 1.350 Å) are somewhat shorter than the C—N bond of the nitro group (average 1.466 Å). The coordination bond of the *N*-oxide group is highly polarized, with the N atom acting as an electron acceptor; the withdrawal of π-electrons from the ring by this atom, will result in an enhancement of the conjugation of the ring C—N bonds and consequently lead to a shortening of these bonds (Eichhorn, 1956; Zyss *et al.*, 1981).

The environments around the O atoms of both *N*-oxide groups are of the same type as that described for the structure of $(NPO)CdCl_2$ (Pécaut *et al.*, 1993), *i.e.* σ and π bonds between the ligand O atoms and the other three atoms form sp^2-hybridized orbitals. The characteristic bond angles are: $N1—O1—Ag^{i}$ = 117.9 (3), $N1—O1—HC7^{ii}$ = 126 (1), $Ag^{i}—O1—HC7^{ii}$ = 112 (1)° around O1 (sum of angles = 356.2°) and $N3^{iii}—O4^{iii}—Ag^{i}$ = 124.2 (3), $N3^{iii}—O4^{iii}—Ag^{iv}$ = 120.1 (3), $Ag^{i}—O4^{iii}—Ag^{iv}$ = 110.4 (2)° around O4 (sum of angles = 354.7°) [symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x, 1 - y, z + \frac{1}{2}$; (iii) $-x, y + 1, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$]. This geometry would permit an extension of the π molecular orbital of the NPO molecule towards the metal, again leading to a lengthening of the conjugation path.

The Ag *coordination*. Each Ag atom is surrounded by five O atoms with Ag—O distances ranging from 2.320 (4) to 2.612 (4) Å and by a sixth O atom located at 2.919 (7) Å. Three are the O atoms of three *N*-oxide groups, and the remaining three atoms belong to NO_3 groups with two of them issued from the same group [O7···O8 = 2.061 (8) Å]. Thus, the AgO_6 polyhedron is quite irregular. Such an environment is not rare around Ag atoms: a similar example can be found in the phosphate domain (Averbuch-Pouchot & Durif, 1992). A noteworthy feature in this structure is the grouping of two inversely related AgO_6 polyhedra [with Ag···Ag = 4.0544 (8) Å] through the common edge O4···O4. Four NPO molecules are anchored to the resulting centrosymmetric Ag_2O_{10} aggregate oriented along the *c* axis (Fig. 2).

The NO_3 *group*. Like the organic entities, this inorganic substituent is not perfectly planar since the central atom

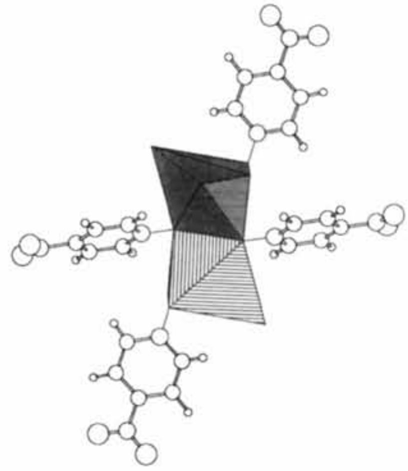

Fig. 2. Perspective view of a centrosymmetric entity formed by four NPO molecules anchored to an Ag_2O_{10} aggregate.

N5 is 0.030 (5) Å out of the mean plane. The N—O distances and O—N—O bond angles reflect a certain deviation from the usual quasi-ternary symmetry observed in NO_3^- anions: 1.183 (7)–1.249 (8) Å for the distances and 115.9 (6)–125.2 (6)° for the angles. This dissymmetry is probably a result of the strong polarizing character of the Ag atom which tends to distort its whole environment.

Other structural features characterize the inorganic framework, in particular the one-dimensional nature of the linkage between the inorganic entities: NO_3 groups alternate with Ag_2O_{10} aggregates by O7···O8 edge and O9 corner sharing, in order to form centrosymmetric double chains along the b axis [b = 5.299 (6) Å].

The packing cohesion. Besides the ionic interaction between NO_3^- and Ag^+, the cohesion of the structure is maintained by the dipole–dipole interaction between the NPO molecules, mainly through the centrosymmetric O4···O4 bond [2.824 (6) Å]. Other short contacts occur in this structure between the C—H bonds of the pyridine rings and the O atoms of NO, NO_2 or NO_3^-. In Table 2 we report the C—H···O bonds corresponding to H···O distances within the sum of van der Waals radii, *i.e.* 2.54 Å, according the values given by Nyburg & Faerman (1985) for the radius of the O atom (1.54 Å) and by Baur (1992) for the radius of the H atom (1 Å). As explained by Cady (1967) and later by Jensen & Jerslev (1969), this type of contact is not exactly a conventional hydrogen bond (large deviations of the H atoms from the linear C···O bond can be seen in Table 2), but it reveals a certain ionic attraction between a weakly charged H atom (shielded by π ring electrons) and a more strongly charged O atom bonded to an N atom. Fig. 1 depicts such C—H···O bonds in the structure. This three-dimensional hydrogen-bonding scheme is stretches between the organic molecules *via* the C7—HC7···O1 and C9—HC9···O3 bonds on the one hand, and between the organic molecules and the inorganic groups *via* the C2—HC2···O9 and C6—HC6···O8 bonds on the other. Finally, some of the intermolecular distances, for example, O6···O6 = 3.044 (6), N1···O5 = 3.016 (6), N2···O3 = 3.040 (6), N4···O6 = 2.965 (6) Å, may indicate van der Waals interactions.

Bis(4-nitropyridine N-oxide)cobalt nitrate tetrahydrate

In contrast to the previous structure, the NPO molecules appear almost aligned in layers parallel to the (101) planes, with an interplanar spacing of 3.15 Å, and are interconnected by CoO_6 octahedra (Fig. 3). Moreover, the inorganic framework here is two-dimensional, CoO_6 octahedra being hydrogen bonded to NO_3^- anions in the (001) planes separated by c = 8.408 Å (Fig. 4).

The NPO *molecule*. The C atoms and the N atom of the pyridine ring show small deviations [maximum value 0.007 (2) Å] from the expected coplanarity. The nitrogroup plane forms an angle of 5.7 (7)° with the pyridine plane revealing a stronger ICT in the organic molecule. However, the environment of O1, the O atom of the *N*-oxide group, does not display an sp^2 hybridization state. Thus, the N—O distance is slightly lengthened compared to the equivalent distances in the silver nitrate compound [1.309 (6) and 1.314 (5) Å].

The Co *coordination*. The Co atom has quite a regular centrosymmetrical octahedral environment consisting of the atom O1 of the NPO ligand and atoms O7 and O8 of both water molecules, with Co—O distances varying from 2.062 (2) to 2.101 (2) Å. O atoms of the nitrate group do not participate in the metal coordination as in the previous structure. Another characteristic is the absence of

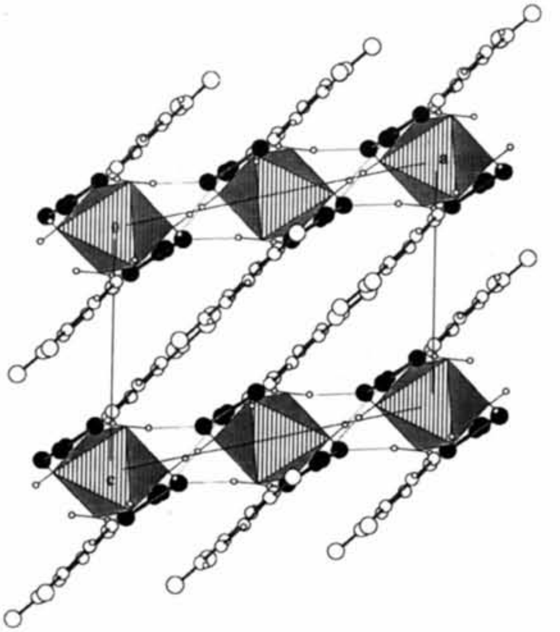

Fig. 3. Projection along the b axis of the $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$ atomic arrangement. The organic layers of NPO molecules are interconnected through the mixed inorganic chains of CoO_6 octahedra linked to the NO_3^- anions *via* short hydrogen bonds.

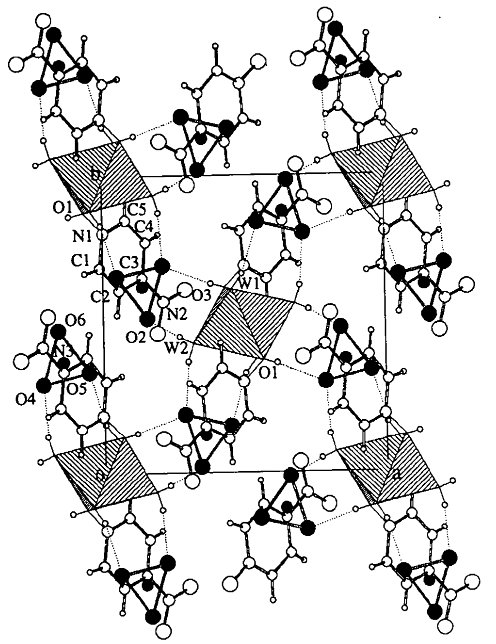

Fig. 4. Projection along the *c* axis of the $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$ atomic arrangement. O*W*—H···O bonds (short hydrogen bonds) are represented by dotted lines.

direct bonding between the CoO_6 octahedra. The smallest Co—Co distance is 7.9483 Å. Fig. 4 shows how two NPO molecules are anchored centrosymmetrically to a CoO_6 octahedron through the O atom of the *N*-oxide group.

The NO_3 *group*. The NO_3^- anions are quasi-planar (deviations are shorter than 0.0003 Å) and almost parallel to the NPO molecules (dihedral angle of 12° between the two mean planes). They are linked to the CoO_6 octahedra *via* short hydrogen bonds (Table 4) issued from the water molecules and occurring along the diagonal direction $a \pm b$ [H···O distances from 1.99 (3) to 2.09 (3) Å]. Fig. 4 exhibits this two-dimensional hydrogen-bonding scheme.

The packing cohesion. The cohesion of the molecular packing is mainly assured by the short metal bonds but also by long hydrogen bonds of a similar type as found previously: C4—HC4···O2 connecting two NPO molecules inside a layer and C1—HC1···O6 connecting an NPO molecule to an NO_3 group [H···O distances of 2.42 (3) and 2.46 (3) Å, respectively]. Also in this structure, weak intermolecular bonds between neighbouring NPO layers may characterize van der Waals interactions: $O1\cdots O3^{i}$ = 2.951 (3), $O1\cdots N2^{ii}$ = 2.997 (3), $O3\cdots N1^{i}$ = 3.043 (3) Å [symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (ii) $x + \frac{1}{2}, \frac{3}{2} - y, z$].

In both these structures, the mixed entity consisting of one coordination polyhedron or aggregate and two or four NPO molecules are locally centrosymmetric. In contrast to the $CdCl_2$ group in the structure of $(NPO).2CdCl_2$ (Pécaut *et al.*, 1993), the NO_3^- anion seems to be unfavourable to the distortion of these entities in such a manner that their final packing becomes non-centrosymmetric. This opinion can be supported by the fact that several addition compounds obtained with NPO molecules and other metal nitrates (Fe, Mn, Zn) did not exhibit a second-harmonic generation signal, which implies a centrosymmetric or pseudo-centrosymmetric arrangement of the NPO molecules.

Experimental

To prepare $(C_5H_4N_2O_3)_2.AgNO_3$, $AgNO_3$ (0.006 mol) was added to an aqueous solution of NPO (0.002 mol in 8 cm^3 H_2O) obtained at about 333 K. The mixture was kept at room temperature for one day, then filtrated. During evaporation of the resulting solution the crystallization of elongated yellow prisms (5 × 5 × 10 mm average size) was observed. The same route was applied to prepare $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$ but with different proportions of reagents (0.001 mol NPO for 0.001 mol $Co(NO_3)_2$ in 4 cm^3 water). Orange prisms were obtained after a longer evaporation period. The chemical formulae of both adducts were established from the results of the structural analyses.

$(C_5H_4N_2O_3)_2.AgNO_3$

Crystal data

M_r = 450.07
Monoclinic
$C2/c$
a = 24.066 (11) Å
b = 5.299 (6) Å
c = 23.401 (19) Å
β = 98.73 (6)°
V = 2950 (8) Å^3
Z = 8
D_x = 2.027 Mg m^{-3}

Ag *Kα* radiation
λ = 0.5608 Å
Cell parameters from 25 reflections
θ = 10.1–12.0°
μ = 0.726 mm^{-1}
T = 295 K
Elongated prism
0.24 × 0.16 × 0.13 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
1660 measured reflections
1610 independent reflections
No reflections rejected
R_{int} = 0.010

θ_{max} = 30°
$h = 0 \rightarrow 34$
$k = 0 \rightarrow 6$
$l = -30 \rightarrow 28$
2 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
R = 0.032
wR = 0.033
S = 1.530
1610 reflections
258 parameters
All H-atom parameters refined
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.218 e Å^{-3}
$\Delta\rho_{min}$ = −0.311 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.28)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $(C_5H_4N_2O_3)_2.AgNO_3$

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ag	0.49954 (2)	0.9378 (1)	0.41445 (2)	4.77 (1)
O1	0.0977 (2)	0.445 (1)	0.4147 (2)	4.65 (9)
O2	0.1821 (2)	0.3920 (9)	0.1796 (2)	4.9 (1)
O3	0.2150 (2)	0.041 (1)	0.2179 (2)	5.5 (1)
O4	0.0359 (1)	−0.2986 (8)	0.0206 (2)	4.15 (9)
O5	0.2715 (2)	0.1448 (9)	0.1001 (2)	4.9 (1)
O6	0.2353 (2)	0.4427 (8)	0.0435 (2)	4.44 (9)
O7	0.4370 (2)	0.664 (1)	0.3483 (3)	8.3 (2)
O8	0.5159 (2)	0.507 (1)	0.3688 (3)	9.1 (2)
O9	0.4561 (3)	0.285 (1)	0.3216 (3)	12.6 (2)
N1	0.1163 (2)	0.389 (1)	0.3665 (2)	3.5 (1)
N2	0.1878 (2)	0.236 (1)	0.2186 (2)	3.8 (1)
N3	0.0830 (2)	−0.1705 (9)	0.0326 (2)	2.84 (9)
N4	0.2331 (2)	0.2367 (9)	0.0671 (2)	3.4 (1)
N5	0.4696 (2)	0.484 (1)	0.3441 (2)	5.2 (1)
C1	0.1006 (2)	0.525 (1)	0.3184 (3)	3.9 (1)
C2	0.1232 (2)	0.481 (1)	0.2689 (2)	3.9 (1)
C3	0.1612 (2)	0.285 (1)	0.2696 (2)	3.0 (1)
C4	0.1754 (2)	0.138 (1)	0.3177 (2)	3.6 (1)
C5	0.1525 (2)	0.194 (1)	0.3660 (2)	3.8 (1)
C6	0.0904 (2)	0.035 (1)	0.0004 (2)	3.3 (1)
C7	0.1395 (2)	0.173 (1)	0.0110 (2)	3.1 (1)
C8	0.1803 (2)	0.094 (1)	0.0550 (2)	2.8 (1)
C9	0.1730 (2)	−0.115 (1)	0.0875 (2)	3.1 (1)
C10	0.1234 (2)	−0.244 (1)	0.0761 (2)	3.2 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* $(C_5H_4N_2O_3)_2.AgNO_3$

N1—O1	1.309 (6)	N3—C10	1.355 (6)
N2—O2	1.222 (7)	C6—C7	1.379 (7)
N2—O3	1.224 (7)	C7—C8	1.377 (7)
N2—C3	1.462 (7)	C8—C9	1.369 (8)
O2· · ·O3	2.162 (7)	C9—C10	1.367 (7)
N1—C1	1.341 (7)	Ag—O1^{i}	2.361 (4)
N1—C5	1.354 (8)	Ag—O4^{ii}	2.612 (4)
C1—C2	1.372 (9)	Ag—O4^{iii}	2.320 (4)
C2—C3	1.380 (8)	Ag—O7	2.461 (6)
C3—C4	1.370 (8)	Ag—O8	2.574 (6)
C4—C5	1.363 (8)	Ag—O9^{iv}	2.919 (7)
N3—O4	1.314 (5)	N5—O7	1.249 (8)
N4—O5	1.214 (6)	N5—O8	1.183 (7)
N4—O6	1.228 (7)	N5—O9	1.198 (9)
O5· · ·O6	2.158 (6)	O7· · ·O8	2.061 (8)
N4—C8	1.470 (6)	O8· · ·O9	2.048 (9)
N3—C6	1.351 (7)	O9· · ·O7	2.172 (9)
O1—N1—C1	120.8 (5)	C6—N3—C10	120.8 (4)
O1—N1—C5	119.1 (5)	O5—N4—C8	118.0 (5)
C1—N1—C5	120.1 (5)	O6—N4—C8	117.8 (4)
O2—N2—C3	118.3 (5)	O5—N4—O6	124.2 (4)
O3—N2—C3	117.5 (5)	N3—C6—C7	120.5 (4)
O2—N2—O3	124.2 (5)	C6—C7—C8	117.9 (5)
N1—C1—C2	121.4 (5)	N4—C8—C7	119.1 (5)
C1—C2—C3	117.7 (5)	N4—C8—C9	119.2 (4)
N2—C3—C2	119.8 (5)	C7—C8—C9	121.7 (5)
N2—C3—C4	118.9 (5)	C8—C9—C10	118.5 (4)
C2—C3—C4	121.3 (5)	N3—C10—C9	120.5 (5)
C3—C4—C5	118.3 (5)	O7—N5—O8	115.9 (6)
N1—C5—C4	121.0 (5)	O7—N5—O9	125.2 (6)
O4—N3—C6	118.6 (4)	O8—N5—O9	118.7 (6)
O4—N3—C10	120.6 (4)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{3}{2}+y, \frac{1}{2}-z$; (iv) $x, 1+y, z$.

Table 3. *Hydrogen-bonding geometry* (Å, °) *for* $(C_5H_4N_2O_3)_2.AgNO_3$

D	H	*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
C2	HC2	O9^{i}	1.03 (5)	2.19 (5)	3.083 (9)	144 (4)
C6	HC6	O8^{ii}	0.93 (4)	2.51 (4)	3.326 (7)	147 (4)
C7	HC7	O1^{iii}	0.89 (5)	2.34 (4)	3.084 (7)	141 (4)
C9	HC9	O3	0.96 (4)	2.53 (5)	3.175 (6)	125 (4)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, 1-y, z-\frac{1}{2}$.

$(C_5H_4N_2O_3)_2.CoN_2O_6.4H_2O$

Crystal data

M_r = 535.20
Monoclinic
$P2_1/a$
a = 11.095 (3) Å
b = 11.384 (2) Å
c = 8.408 (2) Å
β = 102.91 (2)°
V = 1035.2 (8) Å^3
Z = 2
D_x = 1.717 Mg m^{-3}

Ag $K\alpha$ radiation
λ = 0.5608 Å
Cell parameters from 25 reflections
θ = 10.4–12.0°
μ = 0.506 mm^{-1}
T = 295 K
Prism
0.25 × 0.23 × 0.23 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
1545 measured reflections
1440 independent reflections
No reflections rejected
R_{int} = 0.011

θ_{max} = 30°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = -12 \rightarrow 9$
2 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
R = 0.024
wR = 0.027
S = 0.630
1440 reflections
183 parameters
All H-atom parameters refined
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.08
$\Delta\rho_{max}$ = 0.178 e Å^{-3}
$\Delta\rho_{min}$ = −0.232 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.28)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	0	0	0	2.524 (7)
O1	−0.0670 (2)	0.8774 (2)	0.8216 (2)	3.86 (4)
O2	0.1931 (2)	0.4682 (2)	0.5584 (3)	7.00 (7)
O3	0.2924 (2)	0.6147 (2)	0.4796 (3)	6.01 (6)
O4	0.2876 (2)	0.1962 (2)	0.8941 (3)	4.83 (5)
O5	0.4496 (2)	0.1580 (2)	0.7992 (3)	4.93 (5)
O6	0.3436 (2)	0.0179 (2)	0.8709 (3)	4.90 (5)
O*W*1	0.0448 (2)	0.1153 (2)	0.8269 (2)	3.59 (4)
O*W*2	0.1799 (2)	−0.0657 (2)	1.0474 (2)	3.90 (4)
N1	0.0031 (2)	0.8063 (2)	0.7563 (3)	2.91 (4)
N2	0.2151 (2)	0.5732 (2)	0.5475 (3)	4.79 (6)
N3	0.3609 (2)	0.1241 (2)	0.8543 (3)	3.53 (5)
C1	−0.0089 (2)	0.6896 (2)	0.7756 (3)	3.27 (5)
C2	0.0595 (3)	0.6117 (2)	0.7088 (3)	3.46 (6)

C3	0.1405 (2)	0.6555 (2)	0.6209 (3)	3.23 (5)
C4	0.1519 (3)	0.7747 (3)	0.5990 (3)	3.74 (6)
C5	0.0812 (3)	0.8495 (2)	0.6682 (3)	3.61 (6)

Table 5. *Selected geometric parameters* (Å, °) *for* $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$

N1—O1	1.323 (3)	C4—C5	1.373 (4)
N2—O2	1.227 (4)	Co—O1^{i}	2.062 (2)
N2—O3	1.227 (4)	Co—OW1^{ii}	2.101 (2)
O2···O3	2.182 (4)	Co—OW2^{ii}	2.085 (2)
N1—C1	1.349 (3)	N3—O4	1.252 (3)
N1—C5	1.354 (8)	N3—O5	1.239 (3)
N2—C3	1.473 (4)	N3—O6	1.238 (3)
C1—C2	1.366 (4)	O4···O5	2.168 (3)
C2—C3	1.379 (4)	O4···O6	2.145 (3)
C3—C4	1.379 (4)	O5···O6	2.146 (3)
O1—N1—C1	118.2 (2)	N2—C3—C2	119.3 (2)
O1—N1—C5	120.9 (2)	N2—C3—C4	119.5 (3)
C1—N1—C5	121.1 (2)	C2—C3—C4	121.2 (3)
O2—N2—C3	116.7 (3)	C3—C4—C5	118.4 (3)
O3—N2—C3	117.8 (3)	N1—C5—C4	120.3 (2)
O2—N2—O3	125.5 (3)	O4—N3—O5	120.9 (2)
N1—C1—C2	120.7 (3)	O4—N3—O6	118.9 (2)
C1—C2—C3	118.3 (2)	O5—N3—O6	120.1 (2)

Symmetry codes: (i) $x, y-1, z-1$; (ii) $x, y, z-1$.

Table 6. *Hydrogen-bonding geometry* (Å,°) *for* $(C_5H_4N_2O_3)_2.Co(NO_3)_2.4H_2O$

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1	H1*W*1	O4	0.80 (3)	1.99 (3)	2.783 (3)	172 (3)
O*W*1	H2*W*1	O5^{i}	0.73 (3)	2.09 (3)	2.779 (3)	158 (3)
O*W*2	H1*W*2	O4^{ii}	0.76 (3)	2.03 (3)	2.764 (3)	162 (3)
O*W*2	H2*W*2	O6	0.74 (3)	2.02 (3)	2.758 (3)	170 (3)
C1	HC1	O6^{i}	0.98 (3)	2.42 (3)	3.080 (3)	124 (3)
C4	HC4	O2^{iii}	0.90 (4)	2.46 (3)	3.252 (4)	148 (3)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (Enraf–Nonius, 1977). Program(s) used to solve structure: *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Program(s) used to refine structure: *SDP*. Molecular graphics: *MolView* (Cense, 1989). Software used to prepare material for publication: *SDP*. The same computer programs were used for both analyses.

The X-ray diffraction data collection for both compounds was made possible thanks to the cooperation of Enraf-Nonius, Delft, The Netherlands.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Tetracarbonylbis[tris(*p*-fluorophenyl)phosphine]molybdenum(0)

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(*Received* 11 *August* 1993; *accepted* 14 *December* 1993)

Abstract

The molecule *cis*-tetracarbonylbis[tris(*p*-fluorophenyl)phosphine]molybdenum(0), $[Mo(C_{18}H_{12}F_3P)_2(CO)_4]$, has twofold crystallographic symmetry; the Mo geometry is irregular octahedral, with principal dimensions Mo—P 2.5644 (4), Mo—C (*trans* to P) 1.9869 (16), Mo—C (*trans* to C) 2.0310 (18) Å, P—Mo—P 107.33 (1), *trans*-P—Mo—C 166.76 (5) and *trans*-C—Mo—C 174.31 (8)°. The P geometry is irregular tetrahedral, with enlarged Mo—P—C [average 115.94 (5)°] and reduced C—P—C [average 102.22 (7)°] angles. ^{95}Mo NMR chemical shift data are in accord with the observed structure.

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Acta Crystallographica Section C
ISSN 0108-2701 ©1994