C(32)	0.9245 (3)	0.1095 (4)	0.1192 (3)	7.9 (4)
C(33)	0.9936 (3)	0.1394 (4)	0.1452 (3)	6.4 (3)
C(34)	1.0037 (3)	0.2339 (5)	0.1656 (4)	10.1 (5)
C(35)	0.9494 (3)	0.2980 (5)	0.1622 (4)	10.2 (5)
C(36)	1.0533 (3)	0.0697 (5)	0.1489 (3)	7.8 (4)
C(37)	1.0410 (4)	−0.0332 (6)	0.1660 (5)	12.8 (7)
C(38)	1.1233 (4)	0.1055 (6)	0.1979 (5)	12.3 (6)
C(39)	1.0595 (6)	0.0698 (9)	0.0849 (5)	16.8 (9)

Table 2. *Selected geometric parameters* (Å, °)

Sn—Cl	2.349 (2)	Sn—C(20)	2.119 (5)
Sn—C(10)	2.098 (6)	Sn—C(30)	2.106 (5)
		Sn—C (average)	2.108 (5)
Cl—Sn—C(10)	105.30 (16)	C(10)—Sn—C(20)	112.3 (2)
Cl—Sn—C(20)	107.29 (14)	C(10)—Sn—C(30)	111.2 (2)
Cl—Sn—C(30)	106.31 (16)	C(20)—Sn—C(30)	113.80 (19)
Cl—Sn—C (average)	106.30 (15)	C—Sn—C (average)	112.4 (2)

The full-matrix least-squares refinement was based on *F*, with all non-H atoms anisotropic and H atoms isotropic. H atoms were initially calculated at idealized positions (C—H = 0.95 Å, sp^2 or sp^3 hybridization), with $U_{\rm iso}$ initially refined then fixed in the last cycles [$U_{\rm iso}$ = 0.10 (phenyl), 0.36 (*tert*-butyl, 1×) and 0.18 Å^2 (*tert*-butyl, 2× and 3×). The final Fourier map showed eight peaks of 0.56–0.36 e Å^{-3} at 0.58–1.48 Å from tin or chlorine, and three peaks of 0.43–0.36 e Å^{-3} corresponding to local disorder at *tert*-butyl (1×), not introduced in the refined model.

The structure was solved by direct methods using *SHELX*86 (Sheldrick, 1985) and difference Fourier synthesis using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The graphics were produced using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinitrato(diphenylphenanthroline)palladium(II) Complex

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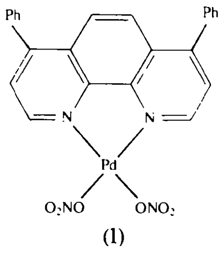
Abstract

The crystal structure of di(nitrato-*O*)(4,7-diphenyl-1,10-phenanthroline-*N*,*N*′)palladium(II) dimethyl sulfoxide solvate, $[Pd(NO_3)_2(C_{24}H_{16}N_2)].C_2H_6OS$, contains two unidentate O-bonded nitrato groups, and the bidentate 4,7-diphenyl-1,10-phenanthroline molecule in almost square-planar coordination around the Pd atom. The phenanthroline ring system is non-planar, exhibiting a bow-shaped deformation likely originating from the metal coordination. The coordinated ligand, as a consequence, exhibits geometrical deformations compared with the free ligand molecule. The crystals have channels which host the disordered solvate molecules. The geometrical results are compared with those for related compounds.

Comment

This paper reports the structure of a mixed-ligand complex, (I), of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline = Bphen) and nitrate ions, with palladium(II) as the coordinating metal (Fig. 1). The low affinity of Pd^{II} for oxygen ligands is well known, and in addition to this, the reactivity of the nitrate groups and susceptibility to substitution by water molecules renders such complexes rather unstable.



(1)

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The O-bonded unidentate nitrate groups and the bidentate Bphen ligand form an approximately square-planar coordination geometry around the Pd atom, which lies 0.065 (2) Å out of the least-squares ligand plane defined by the atoms N(1), N(10), O(1) and O(4). This plane is essentially coplanar with the least-squares plane through the phenanthroline molecule [dihedral angle 1.7 (1)°]. The N(1)—Pd—N(10) bite angle of the five-membered chelate ring is 81.84 (16)°, the average bond length of Pd—N is 1.993 (4) Å, and that of Pd—O is 2.028 (3) Å. The two nitrate groups are planar within the range of error and are in a mutual *cis* orientation, *i.e.* they lie on the same side of the ligand plane. However, their least-squares planes are non-parallel, as may be perceived from the differing torsion angles: Pd—O(1)—N(1*n*)—O(2) 16.9 (5)° and Pd—O(4)—N(2*n*)—O(6) 6.0 (6)°. Furthermore, the O(4)—Pd—N(10) angle [90.25 (15)°] is significantly smaller than the opposite angle O(1)—Pd—N(1) [96.34 (15)°], and O(4) lies at a distance of 2.843 (5) Å from N(10) in the phenanthroline molecule, the corresponding distance O(1)—N(1) being 3.003 (5) Å. These distortions, which destroy the approximate C_2 symmetry of the complex (excluding the phenyl groups), may most certainly be attributed to the steric influence of neighbouring molecules in the crystal on, in particular, the N(2*n*) nitrate group. The short distances of O(2) and O(6) from the Pd atom [2.913 (4) and 2.939 (4) Å, respectively] are characteristic for this type of nitrato compound (Addison, Logan, Wallwork & Gartner, 1971) due to the geometry of the nitrate group itself. However, the distances are still too long to be considered as bonding, and the O-atom orientations do not correspond with any probable coordination sites.

The ring system of the phenanthroline molecule, which is planar in its free state (Ceolin, Mariaud, Levillain & Rodier, 1979), deviates significantly from planarity. It is curved since the outermost points of the molecule exhibit the largest departures from the mean plane [C(2) −0.050 (4), C(3) −0.100 (4), C(7) −0.119 (4) and C(8) −0.058 (4) Å], while the middle-ring atoms lie above the plane [*e.g.* N(1) 0.035 (4), N(10) 0.073 (4), C(5) 0.060 (4) and C(6) 0.027 (4) Å]. The deformation seems to be a direct result of the bidentate coordination to the relatively small Pd atom, which brings the two N atoms closer to each other: 2.610 (6) Å in the title compound, 2.690 (4) Å in the free ligand. A comparison between the coordinated and free phenanthroline ligand reveals significant differences in the geometry, which are consistent with the observed bending of the complexed molecule. The statistically most significant deviations are seen for the angles. Thus, C(4*a*)—C(1*a*)—C(10*a*) and C(6*a*)—C(10*a*)—C(1*a*) increase on average by 2.0 (4)°, with a corresponding decrease of N(1)—C(1*a*)—C(10*a*) and N(10)—C(10*a*)—C(1*a*) by 1.4 (4)°, and C(1*a*)—C(4*a*)—C(5) and C(10*a*)—C(6*a*)—C(6) by 2.1 (4)°. Differences in distances are most significant for C(1*a*)—C(10*a*), −0.024 (7) Å, C(1*a*)—C(4*a*) and C(6*a*)—C(10*a*), −0.023 (7) Å, while the distances C(1*a*)—N(1) and C(10*a*)—N(10) increase by 0.023 (7) Å, on average. The two phenyl substituents are oriented differently in both cases, the interplanar angles between the mean phenanthroline plane and the phenyl rings are 61.5 (1)° for the C(11)–C(16) ring and 42.6 (1)° for the C(21)–C(26) ring.

The bite angle and average Pd—N bond lengths deviate from those of other palladium–phenanthroline complexes (which do not coordinate O atoms), as in $Pd(Bphen)Cl_2$ [80.8 (2)°, 2.036 (6) Å (Anbei, Krüger & Pfeil, 1987)] and Pd{2,9-bis[2,2-bis(methoxycarbonyl)-ethyl]-1,10-phenanthroline}Cl_2 [80.51 (6)°, 2.059 (2) Å (Fronczek *et al.*, 1988)]. However, they are in fair agreement with those of related compounds that coordinate O atoms *trans* to a phenanthroline ligand, *e.g.* Pd(1,10-phenanthroline)NCO_2 and Pd-(Bphen)tetrachloroorthoquinone [81.5 (3)°, 2.009 (6) Å and 81.5 (2)°, 2.010 (6) Å, respectively (Zagorodnikov, Khodashova, Vargaftik, Moiseev & Porai-Koshita, 1985)]. These two molecules show shorter Pd—O distances [1.966 (6)–1.990 (6) Å] than $Pd^{II}Bphen(NO_3)_2$ [2.028 (3) Å]. The latter distance, however, agrees well with the mean Pd—O distance of 2.031 (8) Å found in the crystal structure of the *trans*-dinitrato complex $Pd(NO_3)_2(OPPh_3)(PPh_3)$, displaying unidentate coordination (Jones, McCleverty, Rothin, Adams & Bailey, 1986). Other compounds (that do not coordinate N atoms) with Pd—O distances deviating from these values, are *cis*-$Pd(NO_3)_2(DMSO)_2$ [2.066 Å (Langs, Hare & Little, 1967)], Pd[(*i*-$C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$ [1.992 (6) Å (Jessup, Duesler & Paine, 1983)] and Pd(1,10-dithia-18-

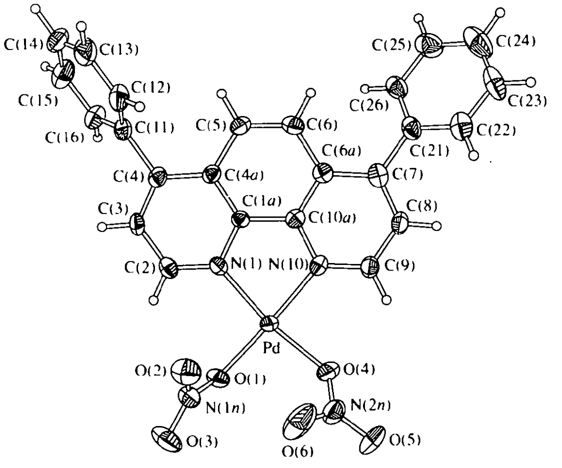

Fig. 1. Structure of the title compound displaying 90% probability displacement ellipsoids and atomic labelling.

crown-6)$(NO_3)_2$ [2.046 (9) Å (Izatt, Wu, Jiang & Dalley, 1990)].

The O—Pd—O angle [91.3 (1)°] in $Pd^{II}Bphen(NO_3)_2$ is significantly larger than in any of the *cis*-dinitrato coordinating compounds mentioned above, which have a corresponding angle in the range 83.0–89.0°. The geometries of the nitrate groups are basically equal in all the dinitrato(Pd) structures discussed so far. In the title compound there is an elongated N—O bond to the coordinating O atom, with a mean value of 1.312 (6) Å, and a mean uncoordinated N—O distance of 1.223 (6) Å. The corresponding averages are 1.31–1.32 and 1.21–1.22 Å in the literature structures cited.

The DMSO solvate molecule is disordered, but could be resolved into two orientations; one major with an occupation factor of 0.768 (6), and a minor orientation with an occupation of 0.232 (6). The minor orientation is approximately a mirror image of the major molecule in the plane of its C and O atoms. The geometries of the two orientations are relatively reasonable as refined without any geometrical restraints. Fig. 2 shows the packing of the complex normal to the (100) plane in the crystal. It reveals channels approximately parallel to the *a* axis, in which the disordered DMSO molecules are located. The metal complex molecules stack into columns also coinciding with the *a* axis. The shortest intermetallic Pd···Pd distance is 4.800 (1) Å. Interplanar distances between phenanthroline rings reach a minimum value of 3.26 (1) Å for C(2)···C(9)(−*x*, −*y*, 1 − *z*), but the shortest intermolecular contacts are found between the nitrate O atoms and the phenanthroline plane, the shortest distance being 3.09 (1) Å for O(5)···C(8)(−*x*, 1 − *y*, 1 − *z*).

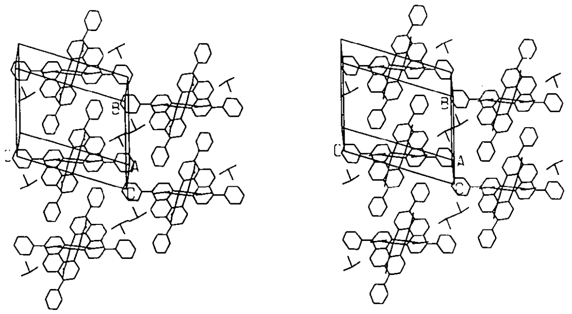

Fig. 2. Crystal packing viewed normal to the (100) plane with H atoms omitted. Only the major orientation of the disordered DMSO molecule is displayed.

Experimental

The title compound resulted from a synthesis in which Pd metal was dissolved in warm HNO_3. The Bphen ligand was added in a 4:1 ratio and the resulting pale brown solution was kept warm to allow evaporation. When a quarter of its initial volume remained, the solution was cooled, yielding a yellow–brown precipitate. The dried precipitate was dissolved in a 1:1 mixture of dimethylformamide and dimethyl sulfoxide. Crystals grew upon evaporation in a stream of dry nitrogen gas, and were sensitive light-brown rhombic prisms. A similar procedure, using $Pd(NO_3)_2$ in HNO_3, reacting *L* = 1,10-phenanthroline or 2,2′-bipyridine with Pd or Pt, has been reported by Anderegg & Wanner (1986) and by Wimmer, Castan, Wimmer & Johnson (1989) using Pd(*L*)Cl_2 and Pt(*L*)I_2 as precursors. Nevertheless, none of these reports recorded X-ray crystal structures.

Crystal data

$[Pd(NO_3)_2(C_{24}H_{16}N_2)].$-
C_2H_6OS
$M_r = 640.94$
Triclinic
$P\bar{1}$
$a = 8.785$ (2) Å
$b = 11.233$ (2) Å
$c = 14.555$ (3) Å
$\alpha = 72.47$ (1)°
$\beta = 84.54$ (1)°
$\gamma = 69.54$ (1)°
$V = 1283.1$ (5) Å^3
$Z = 2$
$D_x = 1.659$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 10.1$–13.6°
$\mu = 0.859$ mm^{-1}
$T = 153$ (1) K
Rhombic prism
0.150 × 0.125 × 0.075 mm
Light brown

Data collection

Stoe AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4673 measured reflections
4481 independent reflections
2994 observed reflections
[$I > 3\sigma(I)$]

$R_{\rm int} = 0.0359$
$\theta_{\rm max} = 25.04°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.0329$ [$I > 2\sigma(I)$]
$wR(F^2) = 0.0757$
$S = 1.165$
2994 reflections
365 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + 2.09P + (0.0254P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.87$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.94$ e Å^{-3}
Extinction correction: *SHELXL*92 (Sheldrick, 1992)
Extinction coefficient: 0.0003 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for C and O atoms of DMSO, which was refined in two orientations.
$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all other non-H atoms.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Pd	0.18948 (5)	0.11692 (4)	0.44776 (3)	0.0153 (1)
N(1*n*)	0.4422 (5)	0.0774 (4)	0.3095 (3)	0.024 (1)
N(2*n*)	0.2177 (6)	0.3763 (4)	0.3879 (3)	0.028 (1)
O(1)	0.2820 (4)	0.1158 (3)	0.3144 (2)	0.021 (1)
O(2)	0.5223 (4)	0.0175 (4)	0.3838 (3)	0.031 (1)
O(3)	0.4983 (5)	0.1042 (4)	0.2291 (3)	0.041 (1)
O(4)	0.1096 (5)	0.3174 (3)	0.4093 (3)	0.028 (1)
O(5)	0.1680 (6)	0.4973 (4)	0.3718 (3)	0.043 (1)

O(6)	0.3611 (5)	0.3099 (4)	0.3840 (4)	0.050 (1)
N(1)	0.2398 (5)	−0.0788 (4)	0.4997 (3)	0.016 (1)
C(2)	0.3098 (6)	−0.1717 (5)	0.4559 (3)	0.018 (1)
C(3)	0.3410 (6)	−0.3069 (5)	0.5032 (3)	0.018 (1)
C(4)	0.3037 (5)	−0.3481 (4)	0.5994 (3)	0.017 (1)
C(4*a*)	0.2257 (5)	−0.2501 (4)	0.6467 (3)	0.016 (1)
C(5)	0.1702 (6)	−0.2755 (5)	0.7451 (4)	0.019 (1)
C(6)	0.0867 (6)	−0.1761 (5)	0.7832 (3)	0.020 (1)
C(6*a*)	0.0483 (5)	−0.0390 (5)	0.7283 (3)	0.017 (1)
C(7)	−0.0459 (6)	0.0719 (5)	0.7618 (4)	0.018 (1)
C(8)	−0.0610 (6)	0.1964 (5)	0.7019 (4)	0.022 (1)
C(9)	0.0064 (6)	0.2143 (5)	0.6106 (3)	0.018 (1)
N(10)	0.0887 (5)	0.1128 (4)	0.5765 (3)	0.017 (1)
C(1*a*)	0.1944 (5)	−0.1174 (4)	0.5936 (3)	0.014 (1)
C(10*a*)	0.1088 (5)	−0.0128 (4)	0.6347 (3)	0.015 (1)
C(11)	0.3456 (6)	−0.4927 (5)	0.6515 (4)	0.020 (1)
C(12)	0.4468 (6)	−0.5475 (5)	0.7321 (4)	0.025 (1)
C(13)	0.4875 (7)	−0.6813 (5)	0.7803 (4)	0.031 (1)
C(14)	0.4278 (7)	−0.7606 (5)	0.7482 (4)	0.031 (1)
C(15)	0.3297 (7)	−0.7076 (5)	0.6677 (5)	0.032 (1)
C(16)	0.2882 (7)	−0.5720 (5)	0.6182 (4)	0.025 (1)
C(21)	−0.1274 (6)	0.0579 (5)	0.8567 (4)	0.021 (1)
C(22)	−0.1267 (6)	0.1390 (5)	0.9129 (4)	0.025 (1)
C(23)	−0.2111 (7)	0.1314 (6)	0.9986 (4)	0.033 (1)
C(24)	−0.2924 (7)	0.0432 (6)	1.0313 (4)	0.039 (1)
C(25)	−0.2940 (7)	−0.0383 (6)	0.9763 (4)	0.032 (1)
C(26)	−0.2125 (6)	−0.0310 (5)	0.8894 (4)	0.024 (1)
S(1)	0.2328 (4)	0.5109 (2)	0.0716 (2)	0.058 (1)
O1(S1)	0.1316 (9)	0.6128 (8)	−0.0105 (6)	0.063 (2)
C1(S1)	0.1074 (14)	0.4492 (12)	0.1541 (9)	0.063 (2)
C2(S1)	0.3221 (16)	0.3693 (12)	0.0304 (8)	0.063 (2)
S(2)	0.2333 (10)	0.4258 (8)	0.0343 (6)	0.050 (3)
O1(S2)	0.179 (3)	0.570 (2)	−0.032 (1)	0.047 (4)
C1(S2)	0.438 (3)	0.402 (3)	0.060 (2)	0.047 (4)
C2(S2)	0.157 (4)	0.416 (3)	0.144 (2)	0.047 (4)

Table 2. *Geometric parameters* (Å, °)

Pd—N(1)	1.996 (4)	C(4)—C(11)	1.498 (6)
Pd—N(10)	1.989 (4)	C(4*a*)—C(5)	1.445 (6)
Pd—O(1)	2.034 (3)	C(5)—C(6)	1.348 (7)
Pd—O(4)	2.022 (3)	C(6)—C(6*a*)	1.439 (6)
N(1*n*)—O(1)	1.321 (5)	C(6*a*)—C(7)	1.430 (7)
N(1*n*)—O(2)	1.222 (5)	C(6*a*)—C(10*a*)	1.398 (6)
N(1*n*)—O(3)	1.218 (5)	C(7)—C(8)	1.375 (7)
N(2*n*)—O(4)	1.302 (6)	C(7)—C(21)	1.484 (7)
N(2*n*)—O(5)	1.227 (6)	C(8)—C(9)	1.388 (7)
N(2*n*)—O(6)	1.225 (6)	C(9)—N(10)	1.329 (6)
N(1)—C(2)	1.323 (6)	N(10)—C(10*a*)	1.369 (6)
N(1)—C(1*a*)	1.369 (6)	S(1)—O1(S1)	1.482 (8)
C(1*a*)—C(10*a*)	1.423 (7)	S(1)—C1(S1)	1.708 (12)
C(1*a*)—C(4*a*)	1.398 (6)	S(1)—C2(S1)	1.766 (12)
C(2)—C(3)	1.403 (7)	S(2)—O1(S2)	1.55 (2)
C(3)—C(4)	1.383 (6)	S(2)—C1(S2)	1.78 (3)
C(4)—C(4*a*)	1.411 (7)	S(2)—C2(S2)	1.66 (3)

N(1)—Pd—N(10)	81.84 (16)	C(4*a*)—C(5)—C(6)	121.8 (4)
O(4)—Pd—N(10)	90.25 (15)	C(5)—C(6)—C(6*a*)	121.9 (4)
O(4)—Pd—N(1)	171.21 (16)	C(6)—C(6*a*)—C(10*a*)	117.0 (4)
O(1)—Pd—N(10)	176.22 (17)	C(6)—C(6*a*)—C(7)	125.3 (4)
O(1)—Pd—N(1)	96.34 (15)	C(7)—C(6*a*)—C(10*a*)	117.7 (4)
O(1)—Pd—O(4)	91.33 (14)	C(6*a*)—C(7)—C(21)	123.1 (4)
O(1)—N(1*n*)—O(2)	118.9 (4)	C(6*a*)—C(7)—C(8)	117.3 (4)
O(1)—N(1*n*)—O(3)	116.0 (4)	C(8)—C(7)—C(21)	119.6 (4)
O(2)—N(1*n*)—O(3)	125.1 (4)	C(7)—C(8)—C(9)	121.5 (5)
O(4)—N(2*n*)—O(5)	117.0 (5)	C(8)—C(9)—N(10)	122.1 (5)
O(4)—N(2*n*)—O(6)	119.3 (4)	Pd—N(10)—C(9)	128.5 (3)
O(5)—N(2*n*)—O(6)	123.8 (5)	Pd—N(10)—C(10*a*)	113.4 (3)
Pd—N(1)—C(1*a*)	113.2 (3)	C(9)—N(10)—C(10*a*)	118.2 (4)
Pd—N(1)—C(2)	128.8 (3)	N(1)—C(1*a*)—C(4*a*)	123.3 (4)
C(2)—N(1)—C(1*a*)	118.1 (4)	C(4*a*)—C(1*a*)—C(10*a*)	121.1 (4)
Pd—O(1)—N(1*n*)	115.2 (3)	N(1)—C(1*a*)—C(10*a*)	115.6 (4)
Pd—O(4)—N(2*n*)	117.8 (3)	N(10)—C(10*a*)—C(1*a*)	115.8 (4)
N(1)—C(2)—C(3)	122.1 (4)	C(1*a*)—C(10*a*)—C(6*a*)	121.2 (4)
C(2)—C(3)—C(4)	120.5 (4)	C(6*a*)—C(10*a*)—N(10)	123.1 (4)
C(3)—C(4)—C(11)	120.6 (4)	O1(S1)—S(1)—C1(S1)	108.1 (6)
C(3)—C(4)—C(4*a*)	118.1 (4)	O1(S1)—S(1)—C2(S1)	104.7 (5)
C(4*a*)—C(4)—C(11)	121.3 (4)	C1(S1)—S(1)—C2(S1)	96.8 (6)
C(4)—C(4*a*)—C(1*a*)	117.8 (4)	O1(S2)—S(2)—C1(S2)	100.7 (13)
C(4)—C(4*a*)—C(5)	125.2 (4)	O1(S2)—S(2)—C2(S2)	112.5 (16)
C(5)—C(4*a*)—C(1*a*)	117.0 (4)	C1(S2)—S(2)—C2(S2)	99.3 (15)

The crystal specimen was mounted on a glass capillary and cooled with a custom-made nitrogen cooling device. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined by full-matrix least-squares techniques with *SHELXL*92 (Sheldrick, 1992). Anisotropic displacement parameters were refined for all non-H atoms, except C and O atoms in the DMSO molecule. H-atom positions were geometrically idealized, with isotropic displacement refined in five variables pertaining to the H atoms in each phenyl group, the phenanthroline ring, and one variable each for the H atoms in the two orientations of the disordered DMSO molecule. The two DMSO orientations, with site occupation factors of 0.768 (6) and 0.232 (6), were refined without any restraints on the geometry. However, an isotropic displacement variable was assigned common to the C and O atoms in each of the two orientations. It is around the DMSO molecule that the maximum residual density, $0.87\ \text{Å}^{-3}$, is found. Additional computer programs used: *DIF*4 (Stoe & Cie, 1988*a*) and *REDU*4 (Stoe & Cie, 1988*b*) for data collection, refinement and reduction; *SCHAKAL*92 (Keller, 1992) and *SHELXTL-Plus* (Sheldrick, 1991) for molecular graphics.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(2-chloroethylammonium) Hexachloroplumbate(II) Chloride

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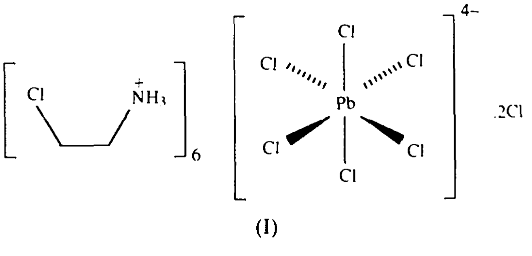
Abstract

The crystal structure of 6(C$_2$H$_7$ClN)[PbCl$_6$]2Cl consists of discrete [PbCl$_6$]$^{4-}$ octahedra and Cl$^-$ anions to which the ClCH$_2$CH$_2$NH$_3^+$ cations are hydrogen bonded. Due to intramolecular hydrogen bonding, the cations adopt conformations with N—C—C—Cl torsion angles ranging from 59.4 (6) to 72.4 (6)°.

Comment

Alkylammonium haloplumbates(II) form structures which have not been observed for other alkylammonium halometallates(II). The methylammonium trihaloplumbates, for example, are the only alkylammonium trihalometallates(II) known to have an anionic partial structure analogous to the octahedral network of cubic perovskite (Knop, Wasylishen, White, Cameron & van Oort, 1990). The same workers were also the first to report on an alkylammonium hexahaloplumbate(II): they obtained tetrakis(methylammonium) hexaiodoplumbate(II) dihydrate as a byproduct of the synthesis of the corresponding triiodoplumbate(II) (Vincent, Robertson, Cameron & Knop, 1987). The present work is part of a systematic investigation on alkylammonium haloplumbates(II) and is the first report on a hexachloro derivative.



(I)

Hexakis(2-chloroethylammonium) hexachloroplumbate(II) chloride, (I), was prepared by slow evaporation of a concentrated hydrochloric acid solution containing lead(II) chloride and 2-chloroethylamine hydrochloride in stoichiometric quantities. Its crystal structure consists of alternating layers parallel to (010) of discrete centrosymmetric [PbCl$_6$]$^{4-}$ octahedra and Cl ions. Each octahedron forms hydrogen bonds to four cations, two of which are each connected to a Cl ion *via* another hydrogen bond. The units thus built are linked to each other *via* hydrogen bonds between one cation and two Cl ions to yield a network which can be described as hydrogen-bonded ribbons along [010] of alternating tetrakis(2-chloroethylammonium) hexachloroplumbate(II) and dimeric 2-chloroethylammonium chloride units. Cl···H distances are 2.30 (2)–2.45 (3) Å for Cl belonging to [PbCl$_6$]$^{4-}$ and 2.18 (2)–2.46 (3) Å for the Cl ion. N—H···Cl angles are in the range 131 (2)–163 (2)°.

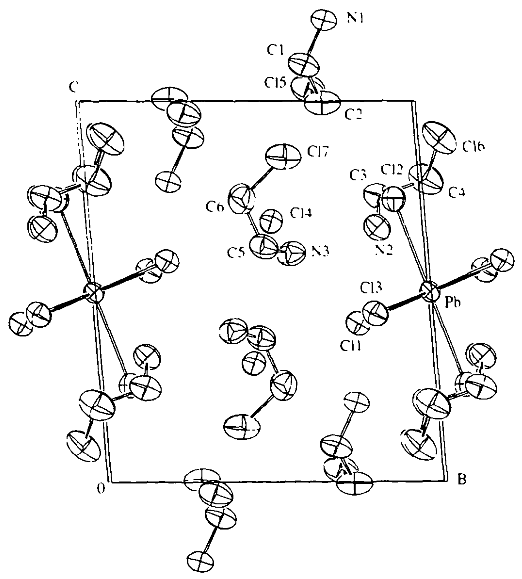


Fig. 1. *ORTEP* view (Johnson, 1965; Hall, Flack & Stewart, 1992) along [100] with H atoms omitted for clarity. The displacement ellipsoids are plotted at the 50% probability level.

In Cs$_4$PbCl$_6$ [the only hexachloroplumbate(II) reported previously], Petrov *et al.* (1987) found almost ideal [PbCl$_6$]$^{4-}$ octahedra with Pb—Cl bond lengths between 2.882 (3) and 2.889 (3) Å and Cl—Pb—Cl bond angles deviating from ideal values by no more than 0.42°. In the title compound the octahedron is slightly distorted. Pb—Cl1 is *ca* 0.05 Å shorter than the other two Pb—Cl bond lengths. The distortion can be accounted for by scrutiny of the hydrogen bonding. Cl1 forms a hydrogen bond with a Cl···H distance of 2.45 (3) Å, whereas for Cl2