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Bis(triphenylphosphine)iminium Nitrito(phthalocyaninato)zincate Hydrate

Barbara Assmann, Svend Sievertsen and Heiner Homborg

Institut für Anorganische Chemie, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany. E-mail: nac74@rz.uni-kiel.d400.de

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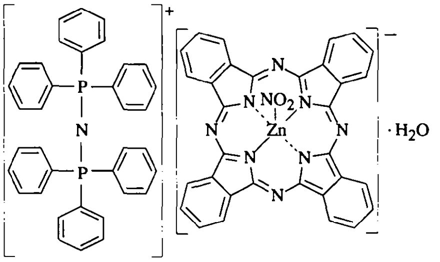
Abstract

^{b}(PNP)[Zn(ONO)Pc^{2-}].H_2O [Pc^{2-} = $(C_{32}H_{16}N_8)^{2-}$] has been prepared from zinc phthalocyanine and bis(triphenylphosphine)iminium nitrite [(PNP)NO_2] in acetone. The Zn atom has tetragonal pyramidal coordination geometry with the Zn atom displaced out of the center (Ct) of the four inner N atoms (N_{iso}) of the non-planar Pc ligand toward the nitrite ligand [Zn—Ct = 0.469 (3) Å]. The nitrite ion is monodentate O-coordinated [Zn—O = 2.059 (3) Å]. The average Zn—N_{iso} distance is 2.032 Å. Pairs of weakly overlapping anions are present. The cation adopts a bent conformation [^{b}(PNP): P1—N(*K*) = 1.576 (2), P2—N(*K*) = 1.582 (2) Å; P1—N(*K*)—P2 = 141.12 (13)°].

Comment

The nitrite ion is a very versatile ligand with rich chemistry and bonding characteristics. These properties derive from the fact that it can function as a ligand in up to nine different crystallographically confirmed ways (Hitchman & Rowbottom, 1982; Burmeister, 1990). Of great interest are the widespread reactions of the nitrite ion with hemoproteins in assimilatory and dissimilatory nitrite reductases reducing the nitrite ion to ammonia (Coleman, Cornish-Bowden & Cole, 1978) and nitrous oxide, nitric oxide or dinitrogen (Johnson, Thomson, Walsh, Barber & Greenwood, 1980). Furthermore, the nitrite–nitrosyl conversions have become important processes in mild nitrosyl-assisted oxidations of organic substrates (Ercolani, Paoletti, Pennesi & Rossi, 1991; Hubbard, Zoch & Elcesser, 1993). As part of our systematic investigation of the mode of ligand binding and catalytical reactivity of the nitrite ion with structurally related metallophthalocyanines, we report an X-ray study of a five-coordinate zinc complex salt, (I).

Only a few examples of metallophthalocyanines with this coordination geometry have been reported (Fischer, Templeton, Zalkin & Calvin, 1970; Palmer *et al.*, 1985; Assmann, Ostendorp & Homborg, 1995).

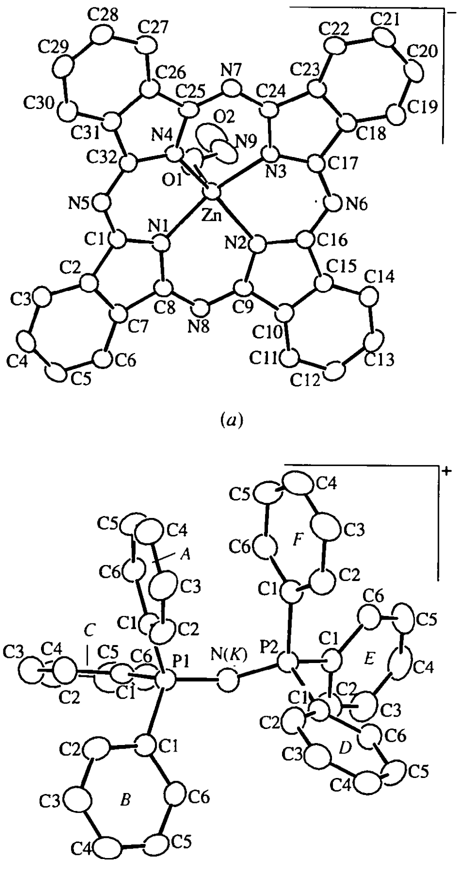


(I)

*ORTEP*II (Johnson, 1976) diagrams with labeling schemes for the [Zn(ONO)Pc^{2-}]$^-$ anion (*a*) and the ^{b}(PNP)$^+$ cation (*b*) are shown in Fig. 1. The geometric data for the cation and the Pc ligand are close to usual values (Safarpour Haghighi, Franken & Homborg, 1994; Assmann, Franken & Homborg, 1995; Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985). The cation adopts the bent conformation: the P1/P2—N(*K*) distances are 1.576 (2)/1.582 (2) Å, the P1—N(*K*)—P2 angle is 141.12 (13)°. The average values for the unique chemical classes of distances and angles in the ZnPc core and the perpendicular displacements of each atom from the 'best' N_{iso} plane (N_{iso}: N1-N4) are given in Fig. 2. The Pc ligand has a non-planar 'saucer-like' conformation. However, the pyrrole and benzene rings are essentially planar.

The Zn atom is displaced 0.469 (3) Å out of the N_{iso} plane toward the nitrite ligand. The average Zn—N_{iso} distance is 2.032 Å. The nitrite ligand is coordinated *via* the O atom to zinc in the monodentate nitrito arrangement (type II), which is the preferred method of nitrite coordination to this metal ion (Hitchman & Rowbottom, 1982). The Zn—O distance is 2.059 (3) Å. The Zn—O vector is essentially collinear with the Zn—Ct vector, where Ct is the center of the N_{iso} plane. The distortion is <1° for the O—Ct vector. The non-bonded O atom is *trans* to the Zn atom.

The anions are close together forming partially overlapping 'dimers' related by an inversion center. The closest atomic approach between the anions is 3.294 (5) Å for the distance between C8 of one



(*a*)

(*b*)

Fig. 1. *ORTEP*II (Johnson, 1976) diagrams of (*a*) the [Zn(ONO)Pc^{2-}]$^-$ anion, and (*b*) the ^{b}(PNP)$^+$ cation with their labeling schemes. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

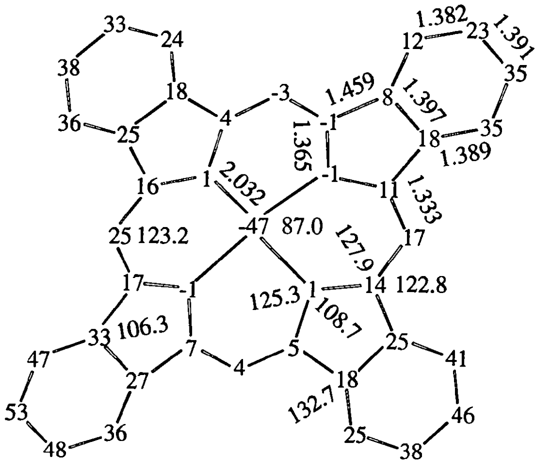


Fig. 2. Formal diagram of the zinc phthalocyanine core displaying average values for selected bond parameters and the perpendicular displacements (in units of 0.01 Å) of each atom from the 'best' N_{iso} plane.

anion and C20 of the other. The Zn···Zn distance is 6.530 (5) Å and the N_{iso} planes are separated by 3.482 (6) Å. The lateral shift of the 'slipped' arrangement of the two rings is 4.81 (1) Å and the 'slip angle' between the zinc centers is 42.6 (5)°. Similar geometries are found for other five-coordinate metallophthalocyanines and for complex salts containing *cis*-[MX_yPc^{2-}]$^-$ anions (y = 2, 3) (Gorsch, Franken, Sievertsen & Homborg, 1995; Assmann, Ostendorp & Homborg, 1995). The geometric data are characteristic for very weak π–π interactions between the macrocyclic rings (Scheidt & Lee, 1987; Scheidt & Turowska-Tyrk, 1994; Cheng *et al.*, 1994).

Experimental

The title compound was prepared by the reaction of ZnPc^{2-} with an excess of (PNP)NO$_2$ in hot acetone. Single crystals were obtained by slow dilution of the filtered acetone solution with *n*-hexane at ambient temperature.

Crystal data

$(C_{36}H_{30}NP_2)[Zn(NO_2)(C_{32}H_{16}N_8)].H_2O$
M_r = 1180.47
Triclinic
$P\overline{1}$
a = 12.6439 (15) Å
b = 13.677 (2) Å
c = 17.107 (3) Å
α = 67.357 (10)°
β = 85.069 (12)°
γ = 86.429 (10)°
V = 2718.9 (6) Å^3
Z = 2
D_x = 1.442 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 4.2–16.1°
μ = 0.573 mm^{-1}
T = 208 (2) K
Prismatic
0.7 × 0.6 × 0.6 mm
Red–violet

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7941 measured reflections
7540 independent reflections
6404 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0179
θ_{max} = 23.02°
h = −13 → 13
k = −14 → 15
l = 0 → 18
3 standard reflections frequency: 240 min intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0295
$wR(F^2)$ = 0.0776
S = 1.040
7540 reflections
766 parameters
Coordinates and U_{iso} of the H atoms of the hydrate refined; H atoms of the phthalocyanine and (PNP)$^+$ cation idealized (riding model)

$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 1.6713P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.138
$\Delta\rho_{max}$ = 0.345 e Å^{-3}
$\Delta\rho_{min}$ = −0.251 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Zn	0.54228 (2)	0.30468 (2)	0.93504 (2)	0.02546 (9)
O1	0.53721 (15)	0.28829 (15)	0.82070 (12)	0.0430 (5)
O2	0.5624 (2)	0.3533 (2)	0.68999 (13)	0.0691 (7)
N(*L*)	0.5538 (2)	0.3661 (2)	0.7578 (2)	0.0497 (6)
N1	0.62214 (14)	0.16826 (14)	1.00074 (12)	0.0258 (4)
N2	0.68061 (14)	0.38059 (14)	0.91805 (12)	0.0258 (4)
N3	0.46766 (14)	0.44581 (14)	0.92043 (12)	0.0263 (4)
N4	0.40965 (14)	0.23472 (15)	1.00583 (12)	0.0261 (4)
N5	0.47645 (14)	0.05426 (15)	1.07612 (12)	0.0265 (4)
N6	0.61621 (15)	0.56318 (14)	0.86942 (12)	0.0263 (4)
N7	0.28765 (15)	0.3869 (2)	0.96424 (12)	0.0278 (4)
N8	0.80257 (14)	0.22834 (15)	0.95893 (12)	0.0264 (4)
C1	0.5791 (2)	0.0733 (2)	1.05149 (14)	0.0257 (5)
C2	0.6639 (2)	−0.0075 (2)	1.07923 (14)	0.0261 (5)
C3	0.6651 (2)	−0.1161 (2)	1.12613 (14)	0.0299 (6)
C4	0.7626 (2)	−0.1695 (2)	1.1365 (2)	0.0339 (6)
C5	0.8572 (2)	−0.1173 (2)	1.1027 (2)	0.0327 (6)
C6	0.8567 (2)	−0.0093 (2)	1.05651 (15)	0.0291 (5)
C7	0.7589 (2)	0.0446 (2)	1.04435 (14)	0.0259 (5)
C8	0.7302 (2)	0.1550 (2)	0.99625 (14)	0.0255 (5)
C9	0.7787 (2)	0.3319 (2)	0.92511 (14)	0.0255 (5)
C10	0.8594 (2)	0.4116 (2)	0.89367 (14)	0.0260 (5)
C11	0.9700 (2)	0.4043 (2)	0.8859 (2)	0.0314 (6)
C12	1.0243 (2)	0.4973 (2)	0.8527 (2)	0.0380 (6)
C13	0.9705 (2)	0.5954 (2)	0.8293 (2)	0.0410 (7)
C14	0.8608 (2)	0.6031 (2)	0.8374 (2)	0.0348 (6)
C15	0.8057 (2)	0.5098 (2)	0.86933 (14)	0.0275 (5)
C16	0.6925 (2)	0.4876 (2)	0.88513 (14)	0.0255 (5)
C17	0.5132 (2)	0.5424 (2)	0.88691 (14)	0.0253 (5)
C18	0.4302 (2)	0.6253 (2)	0.87168 (14)	0.0263 (5)
C19	0.4331 (2)	0.7349 (2)	0.84162 (15)	0.0310 (6)
C20	0.3371 (2)	0.7915 (2)	0.8337 (2)	0.0344 (6)
C21	0.2412 (2)	0.7403 (2)	0.8578 (2)	0.0360 (6)
C22	0.2379 (2)	0.6309 (2)	0.8914 (2)	0.0326 (6)
C23	0.3337 (2)	0.5740 (2)	0.89702 (14)	0.0268 (5)
C24	0.3603 (2)	0.4606 (2)	0.92937 (14)	0.0260 (5)
C25	0.3117 (2)	0.2842 (2)	1.00212 (14)	0.0265 (5)
C26	0.2329 (2)	0.2060 (2)	1.04879 (14)	0.0267 (5)
C27	0.1231 (2)	0.2148 (2)	1.06319 (15)	0.0308 (6)
C28	0.0701 (2)	0.1224 (2)	1.1087 (2)	0.0333 (6)
C29	0.1240 (2)	0.0250 (2)	1.1399 (2)	0.0358 (6)
C30	0.2333 (2)	0.0163 (2)	1.12780 (15)	0.0320 (6)
C31	0.2874 (2)	0.1081 (2)	1.08132 (14)	0.0268 (5)
C32	0.3995 (2)	0.1295 (2)	1.05404 (14)	0.0254 (5)
P1	0.75357 (5)	0.13819 (5)	0.47463 (4)	0.02516 (15)
C1*A*	0.6380 (2)	0.2242 (2)	0.45126 (14)	0.0267 (5)
C2*A*	0.5892 (2)	0.2532 (2)	0.5153 (2)	0.0349 (6)
C3*A*	0.5165 (2)	0.3373 (2)	0.4962 (2)	0.0416 (7)
C4*A*	0.4910 (2)	0.3911 (2)	0.4133 (2)	0.0430 (7)
C5*A*	0.5354 (2)	0.3603 (2)	0.3500 (2)	0.0403 (7)
C6*A*	0.6101 (2)	0.2776 (2)	0.3681 (2)	0.0325 (6)
C1*B*	0.7260 (2)	0.0347 (2)	0.57665 (15)	0.0281 (5)
C2*B*	0.6261 (2)	−0.0078 (2)	0.5992 (2)	0.0389 (6)
C3*B*	0.6076 (2)	−0.0943 (2)	0.6736 (2)	0.0438 (7)
C4*B*	0.6889 (2)	−0.1394 (2)	0.7261 (2)	0.0411 (7)
C5*B*	0.7881 (2)	−0.0969 (2)	0.7046 (2)	0.0391 (6)
C6*B*	0.8074 (2)	−0.0100 (2)	0.6302 (2)	0.0336 (6)
C1*C*	0.7721 (2)	0.0715 (2)	0.40172 (15)	0.0294 (5)
C2*C*	0.6903 (2)	0.0161 (2)	0.3906 (2)	0.0395 (6)
C3*C*	0.7061 (3)	−0.0415 (2)	0.3400 (2)	0.0510 (8)
C4*C*	0.8043 (3)	−0.0458 (2)	0.3003 (2)	0.0542 (8)
C5*C*	0.8867 (3)	0.0084 (2)	0.3110 (2)	0.0529 (8)
C6*C*	0.8710 (2)	0.0677 (2)	0.3611 (2)	0.0391 (6)
P2	0.89980 (5)	0.29772 (5)	0.47986 (4)	0.02624 (15)
C1*D*	0.9066 (2)	0.2824 (2)	0.58861 (15)	0.0283 (5)
C2*D*	0.8146 (2)	0.2627 (2)	0.6425 (2)	0.0380 (6)
C3*D*	0.8177 (2)	0.2536 (2)	0.7254 (2)	0.0380 (6)
C4*D*	0.9122 (2)	0.2631 (2)	0.7555 (2)	0.0377 (6)
C5*D*	1.0036 (2)	0.2831 (2)	0.7026 (2)	0.0398 (6)
C6*D*	1.0011 (2)	0.2930 (2)	0.6198 (2)	0.0335 (6)
C1*E*	1.0325 (2)	0.3197 (2)	0.43179 (15)	0.0276 (5)
C2*E*	1.1040 (2)	0.2337 (2)	0.4494 (2)	0.0378 (6)
C3*E*	1.2073 (2)	0.2492 (2)	0.4158 (2)	0.0451 (7)
C4*E*	1.2394 (2)	0.3489 (2)	0.3637 (2)	0.0454 (7)
C5*E*	1.1694 (2)	0.4346 (2)	0.3463 (2)	0.0429 (7)
C6*E*	1.0658 (2)	0.4205 (2)	0.3805 (2)	0.0344 (6)
C1*F*	0.8226 (2)	0.4176 (2)	0.42880 (15)	0.0289 (5)
C2*F*	0.7940 (2)	0.4878 (2)	0.4686 (2)	0.0370 (6)
C3*F*	0.7378 (2)	0.5809 (2)	0.4268 (2)	0.0446 (7)
C4*F*	0.7088 (2)	0.6035 (2)	0.3457 (2)	0.0474 (7)
C5*F*	0.7376 (2)	0.5354 (2)	0.3055 (2)	0.0470 (7)
C6*F*	0.7951 (2)	0.4427 (2)	0.3466 (2)	0.0373 (6)
N(*K*)	0.85914 (15)	0.1963 (2)	0.46996 (13)	0.0308 (5)
O(*S*)	0.5500 (2)	0.1213 (2)	0.7309 (2)	0.0785 (8)

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

Zn—N1	2.027 (2)	P1—C1*A*	1.790 (2)
Zn—N3	2.030 (2)	P1—C1*B*	1.796 (3)
Zn—N2	2.032 (2)	P1—C1*C*	1.801 (3)
Zn—N4	2.038 (2)	P2—N(*K*)	1.582 (2)
Zn—O1	2.059 (3)	P2—C1*E*	1.794 (2)
O1—N(*L*)	1.200 (3)	P2—C1*D*	1.799 (4)
O2—N(*L*)	1.234 (3)	P2—C1*F*	1.803 (2)
P1—N(*K*)	1.576 (2)		
N1—Zn—N3	154.11 (8)	N(*K*)—P1—C1*B*	112.50 (12)
N1—Zn—N2	87.69 (7)	C1*A*—P1—C1*B*	107.19 (11)
N3—Zn—N2	86.59 (7)	N(*K*)—P1—C1*C*	107.98 (11)
N1—Zn—N4	86.57 (8)	C1*A*—P1—C1*C*	109.83 (12)
N3—Zn—N4	86.99 (7)	C1*B*—P1—C1*C*	104.85 (14)
N2—Zn—N4	152.61 (8)	N(*K*)—P2—C1*E*	107.70 (11)
N1—Zn—O1	99.92 (9)	N(*K*)—P2—C1*D*	113.46 (11)
N3—Zn—O1	105.97 (8)	C1*E*—P2—C1*D*	106.66 (12)
N2—Zn—O1	101.78 (8)	N(*K*)—P2—C1*F*	114.46 (11)
N4—Zn—O1	105.59 (9)	C1*E*—P2—C1*F*	107.13 (11)
N(*L*)—O1—Zn	116.6 (2)	C1*D*—P2—C1*F*	106.99 (11)
O1—N(*L*)—O2	116.2 (3)	P1—N(*K*)—P2	141.12 (13)
N(*K*)—P1—C1*A*	114.10 (11)		

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Palladium Complexes of 1,4,7-Trithiacyclodecane

GENE-HSIANG LEE* AND BIING-CHIAU TZENG

Department of Chemistry, National Taiwan University, Taipei 10764, Taiwan

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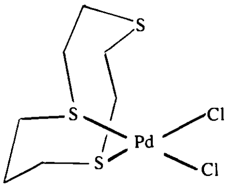
Abstract

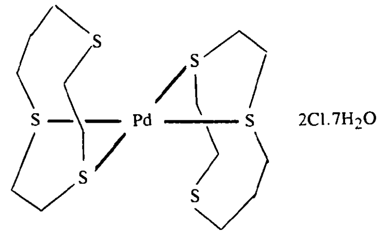
The 10S3 ligand in $[Pd(10S3)Cl_2]$, dichloro(1,4,7-trithiacyclodecane)palladium(II), where 10S3 is 1,4,7-trithiacyclodecane, $C_7H_{14}S_3$, forms a six-membered chelate ring in which the average length of the two equatorial Pd—S bonds is 2.264 (2) Å and the weak axial Pd···S bond is 3.071 (2) Å. The same ligand in bis(1,4,7-trithiacyclodecane)palladium dichloride heptahydrate, $[Pd(10S3)_2]Cl_2.7H_2O$, forms two five-membered chelate rings, in which the average length of the four equatorial Pd—S bonds is 2.310 (1) Å and the length of the two weak axial Pd—S bonds is 3.051 (1) Å.

Comment

The molecular structure of $[Pd(10S3)Cl_2]$ with the atomic labelling scheme is shown in Fig. 1 and that of the cation $[Pd(10S3)_2]^{2+}$ is shown in Fig. 2. In $[Pd(10S3)_2]Cl_2.7H_2O$, the Pd atom lies at a centre of symmetry, while the 10S3 ligand lies on a general position, generating another 10S3 ligand through $\bar{1}$ symmetry. One O atom from a water molecule and a chloride ion are disordered and are labelled as OCl.



$[Pd(10S3)Cl_2]$



$[Pd(10S3)_2]Cl_2.7H_2O$

The central Pd atom in $[Pd(10S3)Cl_2]$ is surrounded by a distorted square-pyramidal array of two Cl atoms and three S atoms; the bond between the Pd atom and the axial S atom is weak [3.071 (2) Å] and is shorter than that in $[Pd(9S3)Cl_2]$, where 9S3 is 1,4,7-trithiacyclononane [3.140 (2) Å; Blake, Holder, Roberts & Schröder, 1988]. The average length of the two equatorial Pd—S bonds is 2.264 (2) Å, close to that in $[Pd(9S3)Cl_2]$ [2.256 (2) Å; Blake *et al.*, 1988].

The Pd atom in $[Pd(10S3)_2]^{2+}$ is in a distorted octahedral environment with four equatorial Pd—S bonds and two weak axial Pd···S interactions. The average length of the four equatorial Pd—S bonds [2.310 (1) Å] and that of the two weak axial Pd···S

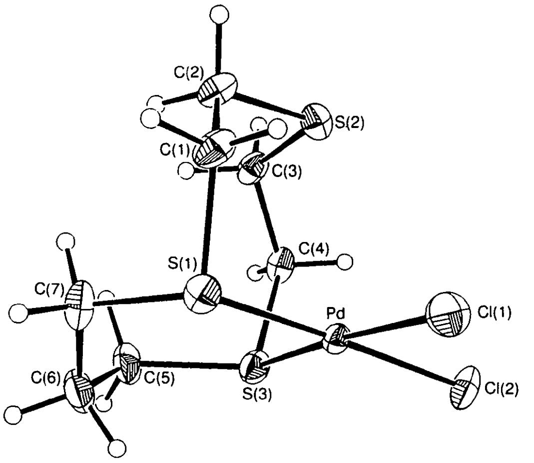


Fig. 1. The molecular structure of $[Pd(10S3)Cl_2]$. Displacement ellipsoids are shown at the 30% probability level.