Table 1. *Selected geometric parameters (Å, °)*

Sn1—C18	2.110 (6)	S1—C3	1.713 (6)
Sn1—C19	2.113 (7)	S1—C1	1.730 (5)
Sn1—C20	2.120 (8)	O1—C17	1.272 (6)
Sn1—O1	2.167 (4)	O2—C17	1.220 (6)
Sn1—O3	2.490 (4)	N1—C1	1.290 (7)
Cl1—C13	1.730 (6)	N1—C2	1.383 (6)
C18—Sn1—C19	123.2 (4)	C19—Sn1—O3	84.9 (2)
C18—Sn1—C20	117.3 (4)	C20—Sn1—O3	87.9 (2)
C19—Sn1—C20	117.6 (4)	O1—Sn1—O3	178.30 (14)
C18—Sn1—O1	96.0 (2)	C3—S1—C1	90.3 (3)
C19—Sn1—O1	96.6 (2)	C17—O1—Sn1	119.4 (3)
C20—Sn1—O1	90.8 (2)	C1—N1—C2	111.4 (4)
C18—Sn1—O3	83.7 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O2^{i}	0.82	1.91	2.713 (6)	168
O3—H32···N1^{ii}	0.82	2.13	2.928 (6)	163

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*97.

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A trinuclear Pd_2Ni complex, $[(C_6H_5)_4P]_2$-$[(PdCl_3)_2\{Ni(C_{12}H_{18}N_2O_2)\}]$

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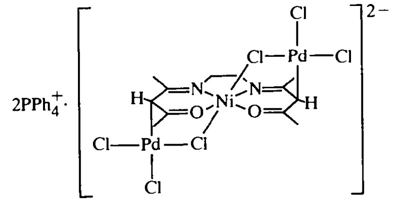
Abstract

In the title complex, bis(tetraphenylphosphonium) di-μ-chloro-1:3κ^2*Cl*,2:3κ^2*Cl*-tetrachloro-1κ^2*Cl*,2κ^2*Cl*-μ_3-[4,4′-(1,2-ethanediyldinitrilo)bis(pentan-2-onato)]-1κC^3:-2κ^4*O*,*N*,*N*′,*O*′:3$\kappa C^{3'}$-dipalladium(II)nickel(II), $(C_{24}H_{20}P)_2[Pd_2NiCl_6(C_{12}H_{18}N_2O_2)]$, the trinuclear complex anion, $[(PdCl_3)_2\{Ni(acen)\}]^{2-}$, has twofold crystallographic symmetry and consists of a central {Ni(acen)} unit and two terminal $\{PdCl_3\}$ moieties. These are connected through Pd—C [2.120 (2) Å] and Cl—Ni bonds [2.4919 (5) Å], giving an elongated octahedral coordination geometry around the central Ni^{II} ion. The $\{PdCl_3\}$ moiety acts as a pendant arm attached to the {Ni(acen)} unit, and the geometry around the Pd atom is of the square-planar type.

Comment

Schiff base complexes derived from the metal-template reaction of acetylacetone and polyamines have a chargedelocalized β-ketoiminate six-membered chelate ring. It has been shown that the central C atom of the chelate ring has nucleophilic character, and some unique coordinated ligand reactions originating as a result of this have been reported, *e.g.* acid–base reaction (Mochizuki *et al.*, 1996) and C—C bond formation (Kajiwara *et al.*, 1993). This suggests that a chelate ring of this type may undergo metal–carbon bond formation under appropriate conditions. In fact, we reported recently that Hg—C bonds are formed in a reaction between [Ni(tmtaa)] (H_2tmtaa is 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) and $HgBr_2$, and that the C—Hg bond formation is caused by the nucleophilic attack of the anionic carbon on a mercury ion (Kajiwara *et al.*, 1997). The study demonstrated also that this type of reaction can be a useful method of constructing multimetal complexes. We wish to report here Pd—C bond formation and a new trinuclear Pd_2Ni complex, (1), formed by this bond using [Ni(acen)], which has two nucleophilic centers within a molecule [H_2acen is *N*,*N*′-bis(1-methyl-3-oxobutylidene)ethylenediamine].



(1)

The reaction of $[PdCl_2(MeCN)_2]$ and Ph_4PCl followed by addition of [Ni(acen)] in $MeNO_2$ in a 2:2:1 molar ratio afforded red crystals of the trinuclear title complex, $(Ph_4P)_2[(PdCl_3)_2\{Ni(acen)\}]$. Complex (1) has a crystallographic twofold axis passing through the Ni atom and the center of the ethylenic C—C bond. The anionic unit of (1) consists of two $\{PdCl_3\}$ moieties and an {Ni(acen)} unit, which are connected through Pd—C bonds [2.120 (2) Å]. The central Ni^{II} ion is surrounded in a planar fashion by N_2O_2 from the acen ligand [Ni—N 2.001 (2) and Ni—O 2.028 (2) Å] and the axial positions are occupied by two Cl atoms from $PdCl_3$ moieties [Ni—Cl1 2.4919 (5) Å], giving the elongated octahedral coordination geometry. The two $PdCl_3$ moieties act as pendant arms.

The C—N, C—O and two C—C bond lengths of the chelate rings are 1.288 (3), 1.250 (3) and 1.458 (3)/1.466 (3) Å, respectively, which are clearly different from those in the parent [Ni(acen)] compound [C—N 1.310 (6)/1.317 (6), C—O 1.289 (6)/1.276 (5) and average C—C 1.387 Å; Cariati *et al.*, 1976]. The reduction of the C—N and C—O bond lengths, and the elongation of the C—C bond suggest that, upon Pd—C bond formation, the delocalized ketoiminate chelate rings are transformed into the isolated keto–imine form, with the central C atom of the sp^3 type. The two C—C distances are close to C—C single bonds found in $[Ni(H_2O)_2(Hacac)_2](ClO_4)_2$, in which acacH (*i.e.* acetylacetone) is reported to take a completely keto form, and the C—C separations are 1.474 (4) and 1.498 (4) Å (Cramer *et al.*, 1977).

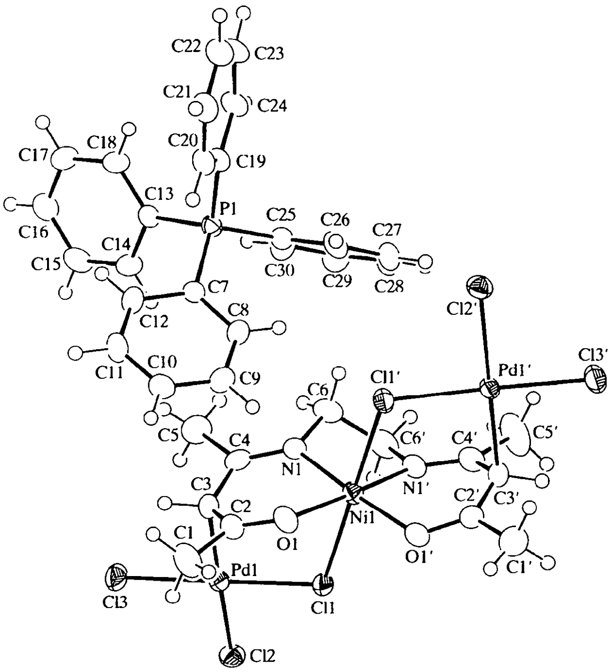


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids.

Experimental

To a yellow solution of *trans*-$[PdCl_2(MeCN)_2]$ (26 mg, 0.1 mmol) in $MeNO_2$ (5 ml) was added Ph_4PCl (37 mg, 0.1 mmol) in $MeNO_2$ (3 ml). The solution was stirred for 5 min and to the resulting orange solution was added [Ni(acen)] (14 mg, 0.05 mmol) in $MeNO_2$ (3 ml). Red crystals were obtained by slow evaporation at room temperature.

Crystal data

$(C_{24}H_{20}P)_2[Pd_2NiCl_6(C_{12}H_{18}N_2O_2)]$
$M_r = 1385.23$
Orthorhombic
*Fdd*2
$a = 25.4930 (13)$ Å
$b = 49.577 (3)$ Å
$c = 9.1095 (5)$ Å
$V = 11513.2 (10)$ Å^3
$Z = 8$
$D_x = 1.598$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8088 reflections
$\theta = 1.64$–$27.55°$
$\mu = 1.321$ mm^{-1}
$T = 223 (2)$ K
Prism
0.35 × 0.2 × 0.15 mm
Red

Data collection

Bruker CCD area-detector diffractometer

6284 reflections with $I > 2\sigma(I)$

ω scans
Absorption correction:
multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.690$, $T_{max} = 0.825$
23 653 measured reflections
3521 independent reflections (plus 3071 Friedel-related reflections)

$R_{int} = 0.025$
$\theta_{max} = 27.55°$
$h = -26 \rightarrow 32$
$k = -64 \rightarrow 63$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.047$
$S = 0.959$
6592 reflections
343 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.344$ e Å^{-3}
$\Delta\rho_{min} = -0.361$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.005 (9)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—C3	2.120 (2)	N1—C4	1.288 (3)
Pd1—Cl3	2.3073 (6)	N1—C6	1.465 (3)
Pd1—Cl1	2.3369 (5)	C1—C2	1.508 (3)
Pd1—Cl2	2.3525 (5)	C2—C3	1.458 (3)
Ni1—N1	2.0005 (17)	C3—C4	1.466 (3)
Ni1—O1	2.0277 (15)	C4—C5	1.506 (3)
Ni1—Cl1	2.4919 (5)	C6—C6^i	1.510 (5)
O1—C2	1.250 (3)		
C3—Pd1—Cl3	87.49 (6)	O1—Ni1—Cl1^i	95.53 (4)
C3—Pd1—Cl1	91.24 (6)	N1—Ni1—Cl1	86.13 (5)
Cl3—Pd1—Cl1	178.38 (2)	O1—Ni1—Cl1	83.50 (4)
C3—Pd1—Cl2	173.95 (7)	Cl1^i—Ni1—Cl1	178.63 (3)
Cl3—Pd1—Cl2	92.05 (2)	Pd1—Cl1—Ni1	108.986 (19)
Cl1—Pd1—Cl2	89.317 (19)	C4—N1—Ni1	125.21 (15)
N1—Ni1—N1^i	84.56 (11)	C6—N1—Ni1	109.61 (14)
N1—Ni1—O1	92.04 (7)	C2—C3—C4	124.62 (19)
N1—Ni1—O1^i	176.33 (7)	C2—C3—Pd1	103.88 (14)
O1—Ni1—O1^i	91.40 (9)	C4—C3—Pd1	98.99 (14)
N1—Ni1—Cl1^i	94.89 (5)	N1—C4—C3	121.1 (2)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

The H3 atom was refined isotropically, whereas other H atoms were placed in calculated positions and refined as riding atoms.

Data collection: *SMART* (Bruker, 1998). Cell refinement: *SMART* and *SAINT* (Bruker, 1998). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN* (Molecular Structure Corporation/Rigaku Corporation, 1998). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1087). Services for accessing these data are described at the back of the journal.

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(*meso*-Tetraethylporphyrinato)bis(tetrahydrofuran)iron(III) perchlorate

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Abstract

In the title compound, (5,10,15,20-tetraethylporphyrinato-κ^4N)bis(tetrahydrofuran-O)iron(III) perchlorate, $[Fe(C_{28}H_{28}N_4)(C_4H_8O)_2]ClO_4$, the Fe^{III} atom has a slightly distorted octahedral coordination. The porphyrin ring of the complex cation, which has twofold symmetry, has an S_4-ruffled structure and the maximum deviation of the *meso*-carbon from the least-squares plane of the $FeC_{20}N_4$ core is 0.274 (3) Å. The average Fe—N bond distance is 2.006 (3) Å.

Comment

meso-Tetraalkylporphyrin–iron(III) complexes have attracted much attention because of the difference in their physicochemical properties compared with those of tetraarylporphyrin complexes (Veyrat *et al.*, 1995; Nakamura *et al.*, 1996, 1998; Saitoh *et al.* 1997; Wolowiec *et al.*, 1998; Ikeue *et al.*, 1999); one of the reasons for the difference is the deformed porphyrin core in the former complexes. We reported that the ground-state electron configuration of low-spin ferric porphyrin complexes

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