Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.088$
$S = 1.053$
3602 reflections
326 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 1.0044P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.283$ e Å^{-3}
$\Delta\rho_{\min} = -0.242$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0009 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—O*W*3	2.053 (2)	Ni1—N2	2.070 (2)
Ni1—O*W*2	2.059 (2)	Ni1—O*W*4	2.103 (2)
Ni1—N1	2.068 (2)	Ni1—O*W*1	2.105 (2)
O*W*3—Ni1—O*W*2	90.11 (9)	N1—Ni1—O*W*4	92.12 (9)
O*W*3—Ni1—N1	173.99 (9)	N2—Ni1—O*W*4	92.81 (9)
O*W*2—Ni1—N1	95.81 (8)	O*W*3—Ni1—O*W*1	87.3 (1)
O*W*3—Ni1—N2	93.25 (9)	O*W*2—Ni1—O*W*1	85.04 (9)
O*W*2—Ni1—N2	176.58 (8)	N1—Ni1—O*W*1	92.19 (9)
N1—Ni1—N2	80.83 (8)	N2—Ni1—O*W*1	94.48 (8)
O*W*3—Ni1—O*W*4	89.1 (1)	O*W*4—Ni1—O*W*1	172.04 (9)
O*W*2—Ni1—O*W*4	87.9 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···O5	0.80 (3)	2.03 (3)	2.822 (3)	171 (3)
O*W*1—H2*W*1···O2^{i}	0.76 (4)	2.15 (4)	2.896 (3)	166 (4)
O*W*2—H1*W*2···O4	0.82 (3)	1.96 (4)	2.785 (3)	177 (3)
O*W*2—H2*W*2···O3^{ii}	0.88 (4)	1.95 (4)	2.799 (3)	160 (4)
O*W*3—H1*W*3···O1	0.76 (4)	2.00 (4)	2.764 (3)	173 (4)
O*W*3—H2*W*3···O*W*5	0.87 (4)	1.82 (4)	2.684 (4)	176 (4)
O*W*4—H1*W*4···O6^{iii}	0.84 (4)	2.01 (4)	2.847 (4)	175 (3)
O*W*4—H2*W*4···O3	0.78 (3)	2.08 (3)	2.833 (3)	164 (3)
O*W*5—H1*W*5···O4^{iv}	0.86 (4)	1.97 (4)	2.830 (4)	179 (3)
O*W*5—H2*W*5···O*W*4^{v}	0.81 (5)	2.28 (5)	3.062 (4)	161 (4)

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

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992; Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1300). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1250–1253

A selenium-bridged mixed-metal cluster, $(CO)_5(PPh_3)_2FePt_2(\mu_3\text{-}Se)$

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(*Received 7 December 1998; accepted 30 March 1999*)

Abstract

Stirring at room temperature of $[(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(CH_2OH)Se\}]$ with $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$ in dichloromethane affords the μ_3-Se-bridged mixed-metal cluster pentacarbonyl-1κ^3C,2κC,3κC-μ_3-selenido-1:2:3κ^3Se-bis(triphenylphosphine)-2κP,3κP-irondiplatinum(2 *Fe*—*Pt*), $[FePt_2(\mu_3\text{-}Se)(C_{18}H_{15}P)_2(CO)_5]$. The structure can be described as an $FePt_2Se$ butterfly; each Pt atom is coordinated by one CO and one PPh_3 group,

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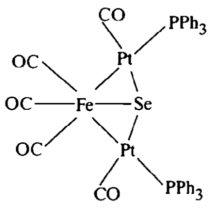
whereas the Fe atom is bonded to three CO groups. The Fe atom is in a distorted octahedral environment. The bridging Se atom is bonded to the open triangular array of $FePt_2$ in a μ_3 coordination mode. The geometry around the Pt atoms is distorted square planar.

Comment

The chemistry of metal clusters continues to be of interest because of the potential application of such clusters in catalysis, directly in homogeneous or heterogeneous form or as catalytic precursors (Shriver *et al.*, 1990). The use of certain main-group elements as bridging or capping ligands serves to prevent degradative fragmentation resulting from forcing reaction conditions. This method has demonstrated the remarkable utility of such ligands to facilitate stabilization of some unusual cluster geometries (Linford & Raubenheimer, 1991). There has been continued interest in chalcogen-stabilized transition metal carbonyl clusters and several synthetic approaches have been developed for the incorporation of chalcogen atoms in metal complexes (Roof & Kolis, 1993; Whitmire, 1988; Kolis, 1990). The classes of compounds $(CO)_9Fe_3(\mu_3\text{-}EE')$ and $(CO)_6Fe_2(\mu\text{-}EE')$ (EE' = S, Se or Te) have been shown to be good and convenient starting materials for the facile synthesis of chalcogen-bridged metal clusters, and the addition of small organic moieties at the bridging chalcogen atoms has been demonstrated (Mathur, 1997). We have reported previously the facile addition of acetylenes across the $E—E'$ bonds of $(CO)_6Fe_2(\mu\text{-}EE')$, and several complexes of the form $(CO)_6Fe_2\{\mu\text{-}EC(H){=}C(R)E'\}$ have been prepared and characterized (Mathur *et al.*, 1995; Mathur, Dash *et al.*, 1996). In $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(Ph)Se\}$, the facile addition of $(CO)_6Fe_2(\mu\text{-}Se_2)$ and $Pt(PPh_3)_2$ occurs readily, and a corresponding reduction of the acetylenic C≡C bond is observed (Mathur & Hossain, 1993; Mathur, Hossain, Das & Sinhua, 1993). The addition of phenylacetylene to $(CO)_6Fe_2(\mu\text{-}Se_2)$ blocks the reactive Se sites and stabilizes the Fe_2Se_2 framework, thus enabling cluster growth to occur across the Fe—Fe bond, as in the formation of the triselenide Fe–Mo mixed-metal cluster $Cp_2Mo_2(CO)_6Fe(\mu_4\text{-}Se)(\mu_3\text{-}Se)_2$ (Mathur, Hossain & Rheingold, 1993). We wish to report here the structural characterization of a platinum-containing mixed-metal chalcogenide butterfly cluster, $(CO)_5(PPh_3)_2FePt_2(\mu_3\text{-}Se)$, (I).



(I)

The structure consists of an $FePt_2Se$ core with a non-bonding distance of 3.178 (1) Å between the two Pt atoms. Each Pt atom possesses one CO and one PPh_3 group, while the Fe atom is coordinated by three CO groups. The three CO groups, the μ_3-Se atom and the Fe—Pt bonds define a distorted octahedral environment around the Fe center. The Pt atoms are in a distorted square-planar environment. The Pt1 and Pt2 atoms are 0.018 and 0.113 Å away from their respective coordination planes defined by atoms P1/C40/Fe1/Se1 and P2/C41/Fe1/Se1. The average Pt—Fe and Pt—Se bond distances are 2.560 (1) and 2.418 (1) Å, respectively. The Pt—Se distance is comparable to that in $(CO)_6Fe_2(\mu\text{-}Se)_2Pt(PPh_3)_2$ (Day *et al.*, 1982). The Fe—Se bond distance of 2.343 (1) Å is comparable to the corresponding bond distance of 2.320 (2) Å observed in $Cp_2Mo_2(CO)_7Fe(\mu\text{-}Se)$ (Mathur *et al.*, 1994) and of 2.401 (1) Å in $(CO)_6Fe_2(\mu\text{-}Se)_2Pt(PPh_3)_2$ (Day *et al.*, 1982). The average C—O bond length bonded to Pt is 1.137 (9) Å and that bonded to Fe is 1.144 (9) Å. The Pt—Se—Pt bond angle of 82.14 (3)° is greater than the Mo—Se—Mo bond angle of 76.2 (1)° observed in $Cp_2Mo_2(CO)_7Fe(\mu\text{-}Se)$, consistent with an opening of the tetrahedron as a result of the non-bonding interactions between the Pt atoms. The Pt—P—C angles range from 110.3 (2) to 118.6 (2)°, larger than the ideal value of 109.5°, while all C—P—C bond angles, ranging from 102.7 (3) to 104.9 (3)°, are smaller than the ideal tetrahedral angle.

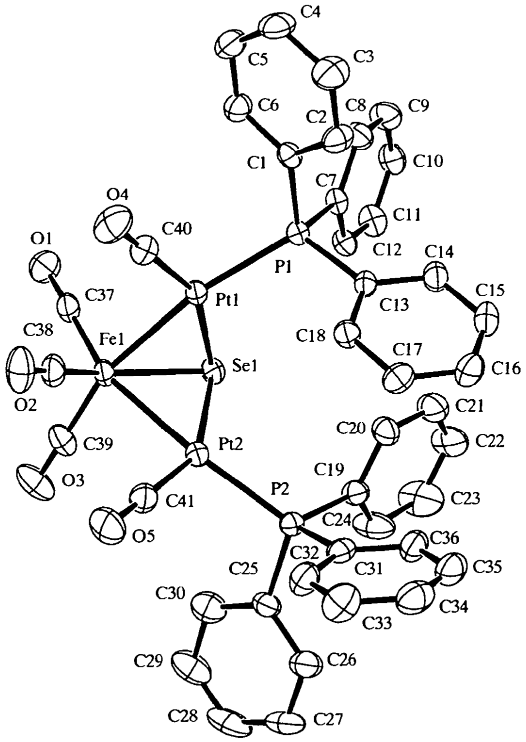


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

The deviation from normal tetrahedral angles was observed previously in free and coordinated phosphine ligands of this type and was explained on the basis of valence-shell electron-pair repulsion (VSEPR) energy (Houlton *et al.*, 1990).

Experimental

When a dichloromethane solution (20 ml) of [$(CO)_6Fe_2$-{μ-SeC(H)=C(CH_2OH)Se}] (0.6 g, 0.121 mmol) was stirred with $Pt(PPh_3)_4$ (0.2 g, 0.16 mmol) at room temperature under an N_2 atmosphere for 24 h, a dark-yellow band of $(CO)_5(PPh_3)_2FePt_2(\mu_3\text{-Se})$ was obtained in 12% yield after chromatographic work-up on silica-gel thin-layer chromatography plates using a 2:3 CH_2Cl_2/hexane mixture as eluent, along with the phosphine adduct [$(CO)_5(PPh_3)Fe_2$-{μ-SeC(H)=C(CH_2OH)Se}] (Mathur, Hossain *et al.*, 1996). It was observed that when the more labile coordinatively unsaturated $Pt(C_2H_4)(PPh_3)_2$ compound (0.12 g, 0.16 mmol) was used, the yield of $(CO)_5(PPh_3)_2FePt_2(\mu_3\text{-Se})$ could be increased up to 16%. Rectangular air-stable crystals of $(CO)_5$-$(PPh_3)_2FePt_2(\mu_3\text{-Se})$ were obtained by slow evaporation from a mixture of CH_2Cl_2/hexane at 263 K.

Crystal data

[$FePt_2Se(C_{18}H_{15}P)_2(CO)_5$]
$M_r = 1189.58$
Triclinic
$P\bar{1}$
$a = 10.598\ (2)$ Å
$b = 10.880\ (3)$ Å
$c = 18.824\ (1)$ Å
$\alpha = 75.17\ (1)^\circ$
$\beta = 80.87\ (1)^\circ$
$\gamma = 73.72\ (2)^\circ$
$V = 2005.3\ (7)$ Å^3
$Z = 2$
$D_x = 1.970$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.04$–15.61°
$\mu = 8.345$ mm^{-1}
$T = 293\ (2)$ K
Rectangular
$0.219 \times 0.188 \times 0.156$ mm
Dark yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.220$, $T_{\max} = 0.272$
12 211 measured reflections
11 625 independent reflections

7492 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 29.98^\circ$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 15$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.110$
$S = 0.920$
11 625 reflections
469 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.615$ e Å^{-3}
$\Delta\rho_{\min} = -0.729$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pt1—C40	1.859 (8)	Fe1—C37	1.765 (8)
Pt1—P1	2.302 (2)	Fe1—C38	1.768 (9)
Pt1—Se1	2.422 (1)	Fe1—C39	1.770 (8)
Pt1—Fe1	2.558 (1)	P1—C7	1.804 (6)
Pt1—Pt2	3.178 (1)	P1—C13	1.812 (6)
Pt2—C41	1.835 (8)	P1—C1	1.817 (6)
Pt2—P2	2.312 (2)	P2—C25	1.799 (7)
Pt2—Se1	2.415 (1)	P2—C19	1.805 (7)
Pt2—Fe1	2.563 (1)	P2—C31	1.822 (8)
Se1—Fe1	2.343 (1)		
C40—Pt1—P1	98.3 (2)	C37—Fe1—C38	100.6 (3)
C40—Pt1—Se1	154.1 (2)	C37—Fe1—C39	98.7 (4)
P1—Pt1—Se1	107.5 (1)	C38—Fe1—C39	96.8 (4)
C40—Pt1—Fe1	98.1 (2)	C37—Fe1—Se1	100.2 (2)
P1—Pt1—Fe1	163.5 (1)	C38—Fe1—Se1	145.6 (2)
Se1—Pt1—Fe1	56.0 (1)	C39—Fe1—Se1	106.7 (3)
C40—Pt1—Pt2	116.5 (2)	C37—Fe1—Pt1	91.6 (2)
P1—Pt1—Pt2	120.13 (4)	C38—Fe1—Pt1	93.3 (3)
Se1—Pt1—Pt2	48.83 (2)	C39—Fe1—Pt1	164.0 (3)
Fe1—Pt1—Pt2	51.72 (2)	Se1—Fe1—Pt1	59.05 (3)
C41—Pt2—P2	103.5 (2)	C37—Fe1—Pt2	159.0 (2)
C41—Pt2—Se1	151.7 (2)	C38—Fe1—Pt2	97.5 (2)
P2—Pt2—Se1	104.5 (1)	C39—Fe1—Pt2	89.6 (3)
C41—Pt2—Fe1	95.8 (2)	Se1—Fe1—Pt2	58.77 (3)
P2—Pt2—Fe1	157.4 (1)	C7—P1—Pt1	118.6 (2)
Se1—Pt2—Fe1	56.0 (1)	C13—P1—Pt1	111.8 (2)
C41—Pt2—Pt1	113.9 (3)	C1—P1—Pt1	112.5 (2)
P2—Pt2—Pt1	127.00 (5)	C25—P2—C19	104.7 (3)
Se1—Pt2—Pt1	49.03 (2)	C25—P2—C31	102.7 (3)
Fe1—Pt2—Pt1	51.56 (2)	C19—P2—C31	104.0 (3)
Fe1—Se1—Pt2	65.18 (3)	C25—P2—Pt2	110.3 (3)
Fe1—Se1—Pt1	64.90 (3)	C19—P2—Pt2	115.9 (2)
Pt2—Se1—Pt1	82.14 (3)	C31—P2—Pt2	117.7 (2)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*97.

Two of the authors (KP and THL) thank the National Science Council for support under grants NSC88-2811-M007-0004 and NSC88-2112-M007-013. The others (AKD and PM) are grateful to the Council of Scientific and Industrial Research, Government of India, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1064). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1253–1255

Bis[bis(triphenylphosphoranylidene)ammonium] μ-tetrathiaoxalato-bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)]

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(*Received 19 November 1998; accepted 30 March 1999*)

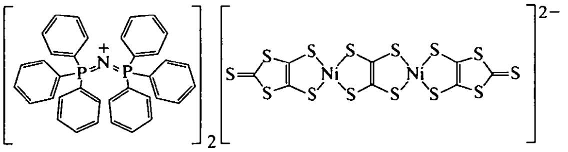
Abstract

The binuclear complex anion in $[(C_6H_5)_6P_2N]_2[(C_3S_5)Ni(C_2S_4)Ni(C_3S_5)]$, conventionally abbreviated $(PPN)_2[(dmit)Ni(tto)Ni(dmit)]$, where PPN is bis(triphenylphosphoranylidene)ammonium, dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate and tto is tetrathiaoxalate, is centrosymmetric and essentially planar, except for a small twist of 2.7 (1)° at the Ni centers. The bond lengths [average Ni—S distance 2.166 (8) Å] and angles are comparable to those reported elsewhere for other salts of the component ions. The crystal packing and the charge state of the complex anion are not favorable for electrical conduction. The binuclear complex anion was synthesized by a simpler method than that published previously.

Comment

In the last decade, considerable effort has been devoted to the synthesis and study of the electrical properties of dmit (2-thioxo-1,3-dithiole-4,5-dithiolate) ligand-based metal–dithiolate complexes, leading to the discovery of several superconducting systems containing the $[M(\text{dmit})_2]^{n-}$ (M = Ni, Pd; $0 \le n \le 2$) ion (Cassoux *et al.*, 1991; Olk *et al.*, 1992). The dmit-based complexes are sulfur-rich, fully conjugated and completely planar, and these structural features play a crucial role in the formation of superconducting organic materials (Cassoux & Valade, 1992; Williams *et al.*, 1992). Recently, a new class of Ni–dithiolenes, $[\text{Ni}(R_2\text{timdt})_2]$ (where R_2timdt is the monoanionic 1,3-dialkylimidazolidine-2,4,5-trithione) has been synthesized (Bigoli *et al.*, 1997).

These materials show a very intense low-energy electronic absorption (ε = 80000 dm^3 mol^{-1} cm^{-1}; λ = 1000 nm) near the emission frequency of neodymium lasers, and therefore are excellent candidates as near-IR dyes. The iodine (1310 nm) and the solid-state erbium (1540 nm) lasers lie beyond the neodymium laser wavelength (1060 nm), and the synthesis of materials that exhibit strong absorption in this range is of particular technological importance. Since both dithiolenes show unique optical and electronic properties, it is of considerable interest to synthesize the unsymmetrical mixed-ligand bis(dithiolene) nickel(II) complexes with the aim of obtaining highly conductive materials which are simultaneously highly absorbing in the near-IR. We have already prepared the unsymmetrical nickel–dithiolate anion by a ligand-exchange reaction between $[M(\text{dmit})_2]$ and $[\text{Ni}(R_2\text{timdt})_2]$ complexes in boiling tetrahydrofuran (THF) (Deplano *et al.*, 1998). In an attempt to improve the synthesis conditions, we obtained instead the bimetallic complex salt bis[bis(triphenylphosphoranylidene)ammonium] μ-tetrathiaoxalato-bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)], $(PPN)_2[(dmit)Ni(tto)Ni(dmit)]$, (I), as the major product of the reaction. The tetra-n-butylammonium salt of this complex anion was synthesized by a different method by Pullen *et al.* (1997).



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