$a = 8.410\,(2)$ Å
$b = 11.116\,(2)$ Å
$c = 12.122\,(2)$ Å
$\alpha = 95.24\,(3)^\circ$
$\beta = 108.29\,(3)^\circ$
$\gamma = 93.24\,(3)^\circ$
$V = 1067.1\,(4)$ Å^3
$Z = 1$
$D_x = 1.426$ Mg m^{-3}
D_m not measured

$\theta = 14$–15°
$\mu = 0.836$ mm^{-1}
$T = 293\,(2)$ K
Trigonal prism
$0.20 \times 0.15 \times 0.15$ mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4482 measured reflections
4181 independent reflections
3637 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 26^\circ$
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.116$
$S = 1.084$
4181 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.2407P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.61$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Co—O1	2.047 (2)	Co—O4$^{\rm i}$	2.010 (2)
Co—O2$^{\rm i}$	2.014 (2)	Co—N	2.084 (2)
Co—O3	2.045 (2)	Co···Co$^{\rm i}$	2.8130 (10)
O1—Co—N	94.00 (9)	O2$^{\rm i}$—Co—O3	89.85 (10)
O2$^{\rm i}$—Co—N	102.66 (9)	O3—Co—O1	85.52 (10)
O3—Co—N	93.06 (9)	O4$^{\rm i}$—Co—O1	88.74 (10)
O4$^{\rm i}$—Co—N	103.44 (9)	O4$^{\rm i}$—Co—O2$^{\rm i}$	90.97 (10)
O2$^{\rm i}$—Co—O1	162.93 (8)	O4$^{\rm i}$—Co—O3	162.87 (9)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1324). Services for accessing these data are described at the back of the journal.

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Charge-transfer salt of bis(*cis*-1,2-diphenylethene-1,2-dithiolato)palladate(1−) with cobaltocenium, and neutral bis(*cis*-1,2-diphenylethene-1,2-dithiolato)palladium

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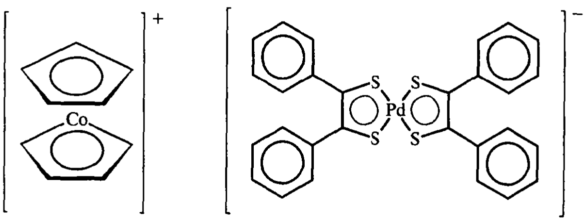
Abstract

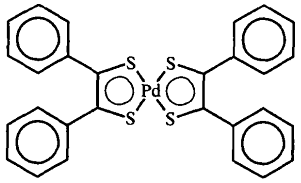
The crystal structure of the charge-transfer salt cobaltocenium bis(*cis*-1,2-diphenylethene-1,2-dithiolato)palladate(1−), $[\mathrm{Co(C_5H_5)_2}][\mathrm{Pd\{S_2C_2(C_6H_5)_2\}_2}]$, consists of linear $-D^+A^-D^+A^-D^+A^--$ chains. The $[\mathrm{Co(C_5H_5)_2}]^+$ cation adopts an approximately eclipsed D_{5h} configuration. The stereochemistry of the $[\mathrm{Pd\{S_2C_2(C_6H_5)_2\}_2}]^-$ anion is largely similar to that of the neutral molecule, bis(*cis*-1,2-diphenylethene-1,2-dithiolato)palladium, $[\mathrm{Pd\{S_2C_2(C_6H_5)_2\}_2}]$, the structure of which has also been determined; however, the Pd atom of the former has a distorted square-planar environment, while the $\mathrm{PdS_4}$ chromophore of the latter is strictly planar. Furthermore, the former has longer Pd—S and S—C distances, and shorter C—C distances (in the chelate rings) than the latter.

Comment

Bis(dithiolato)metal complexes, $[M(S_2C_2R_2)_2]^{n-}$ (R = H, CN, CF_3, C_6H_5 *etc.*; M = Ni, Cu, Pd *etc.*), are an interesting class of compounds which exhibit widely different electrical, magnetic and optical properties associated with crystallographic packing and highly delocalized electronic structures (Alcàcer & Novais, 1982; Clemenson, 1990). These complexes are remarkable in the variety of oxidation states they can present, commonly with n = 0, 1 and 2, and the fact that they can easily be converted into each other. Some bis(dithiolato)metalate salts of metalloceniums have been prepared and characterized in order to provide insight into structure–property relationships (Miller & Epstein, 1995). For example, $[Mn(C_5Me_5)_2-M(tfd)_2]$ [tfd is bis(trifluoromethyl)ethylenedithiolate; M = Ni, Pd, Pt] complexes have a one-dimensional $-D^+A^-D^+A^-D^+A^--$ chain structure and exhibit metamagnetic behavior (Broderick *et al.*, 1991). To extend these studies, we have synthesized a series of metallocenium salts, $[M(C_5R_5)_2]^+$ (R = H and Me; M = Co and Fe), of the $[M(dpt)]^-$ anion (dpt is *cis*-1,2-diphenylethene-1,2-dithiolate; M = Ni, Pd and Pt). We report here the crystal structure of $[Co(C_5H_5)_2][Pd(dpt)_2]$, (I), together with the structure of neutral $Pd(dpt)_2$, (II), to compare the molecular geometries of the $[Pd(dpt)_2]^-$ anion and $Pd(dpt)_2$ molecule.



(I)



(II)

A displacement ellipsoid drawing of $[Co(C_5H_5)_2]$-$[Pd(dpt)_2]$ with the atom-labeling scheme is shown in Fig. 1. The Pd atom of the anion is located on a twofold rotation axis and has a distorted square-planar environment, with a twist angle of 5.7 (1)° between the two PdS_2C_2 rings. The mean Pd—S bond distance is 2.264 (1) Å and the S—Pd—S bite angle is 88.79 (3)°. The $[Co(C_5H_5)_2]^+$ cation adopts an approximately eclipsed D_{5h} configuration, with the Co atom also residing on a twofold rotation axis, which is orthogonal to the local C_5 axis of the cation. The average Co—C bond distance [2.011 (15) Å] is similar to that found in $[Co(C_5H_5)_2][Ni(dmit)_2]$ [2.037 (16) Å; dmit is 4,5-dimercapto-1,3-dithiole-2-thionate], where the cation is in a partially oxidized state with its charge less than +1 (Fang *et al.*, 1993), and is significantly shorter than the value observed in neutral $Co(C_5H_5)_2$ [2.096 (15) Å; Bünder & Weiss, 1975]. The crystal structure consists of one-dimensional $-D^+A^-D^+A^-D^+A^--$ chains along the b axis, with the local C_5 axes of the cations parallel to the best PdS_4 planes of the anions (Fig. 2). The linear chain is almost equally spaced, with alternating distances of 4.703 (1) and 4.740 (1) Å between adjacent Pd and Co atoms. The closest interchain distance is 7.208 (1) Å between Pd and Co($1-x$, $1-y$, $-z$) atoms, and 8.037 (1) Å between Pd and Pd($1-x$, $-y$, $-z$) paramagnetic centers.

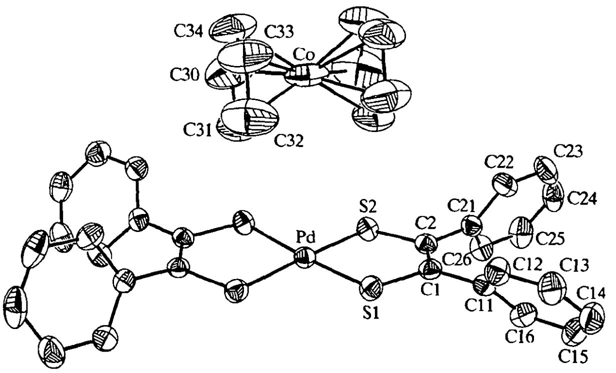


Fig. 1. A view of $[Co(C_5H_5)_2][Pd(dpt)_2]$, with displacement ellipsoids at the 30% probability level (*XP*; Siemens, 1994*b*).

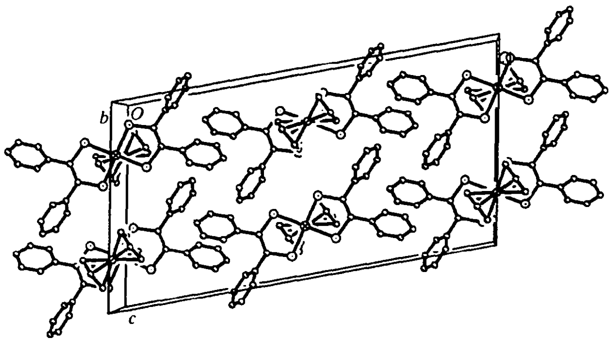


Fig. 2. A view of the packing of $[Co(C_5H_5)_2][Pd(dpt)_2]$ along the b axis.

The neutral $Pd(dpt)_2$ compound crystallizes in the monoclinic $P2_1/n$ space group and is isostructural with the α-modification of $Ni(dpt)_2$ (Sartain & Truter, 1967). Although the geometry of the neutral $Pd(dpt)_2$ molecule (Fig. 3) is largely similar to that of the $[Pd(dpt)_2]^-$ anion, there are significant differences. The Pd atom occupies an inversion center so that the PdS_4 motif is strictly planar and nearly square planar, with a bite angle of 87.92 (2)°. The mean Pd—S bond distance [2.250 (1) Å] is slightly shorter than the corresponding value in the anion of $[Co(C_5H_5)_2][Pd(dpt)_2]$ [2.264 (1) Å]. It has been shown that the lowest unoccupied molecular orbital of neutral $M(S_2C_2R_2)_2$ is an antibonding metal–ligand orbital (Schrauzer & Mayweg, 1965; Schläpfer & Nakamoto, 1975). Consequently, the *M*—S bonds will lengthen upon addition of an electron to form an anion. The reduction of the neutral compound to a monoanion is also expected to lead to an increase of the S—C and a decrease of the C—C bond distances in the chelate rings. The observed values of the S—C and C—C bond distances are 1.704 (12) and 1.400 (3) Å for $Pd(dpt)_2$, and 1.735 (10) and 1.371 (5) Å for $[Co(C_5H_5)_2][Pd(dpt)_2]$, respectively.

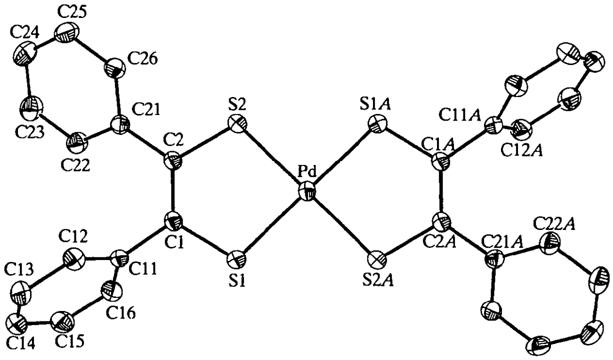


Fig. 3. A view of the neutral $Pd(dpt)_2$ molecule, with displacement ellipsoids at the 30% probability level (*XP*; Siemens, 1994*b*).

All displacement ellipsoids of the $[Co(C_5H_5)_2]^+$ ion show a longitudinal displacement approximately along the local C_5 axis (Fig. 1), indicating that the cation, which resides in a large cavity surrounded by six anions, is slightly disordered.

Experimental

$Pd(dpt)_2$ and $(Et_4N)[Pd(dpt)_2]$ were prepared according to literature methods (Schrauzer & Mayweg, 1965; Davison *et al.*, 1963). Crystals of $Pd(dpt)_2$ were grown from toluene. $[Co(C_5H_5)_2][Pd(dpt)_2]$ was obtained by mixing an equimolar ratio of $[Co(C_5H_5)_2](PF_6)$ (Strem Chemicals) and $(Et_4N)[Pd(dpt)_2]$ in hot acetonitrile. After the filtrate was stored at room temperature for several days, dark-brown chunky crystals formed and were collected *via* vacuum filtration.

Compound (I)

Crystal data

$[Co(C_5H_5)_2][Pd(C_{14}H_{10}S_2)_2]$
$M_r = 780.19$
Monoclinic
$C2/c$
$a = 26.413 (4)$ Å
$b = 9.4429 (8)$ Å
$c = 14.2752 (12)$ Å
$\beta = 100.703 (9)°$
$V = 3498.5 (6)$ Å^3
$Z = 4$
$D_x = 1.481$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.92–13.47°$
$\mu = 1.252$ mm^{-1}
$T = 293 (2)$ K
Block
0.78 × 0.38 × 0.10 mm
Black

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ scans (*SHELXL*93; Sheldrick, 1993)
$T_{min} = 0.790$, $T_{max} = 0.988$
3155 measured reflections
3084 independent reflections

2422 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 24.99°$
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: 8.94%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.098$
$S = 1.072$
3084 reflections
200 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 3.1958P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.263$ e Å^{-3}
$\Delta\rho_{min} = -0.599$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd—S1	2.2643 (10)	Co—C30	1.994 (9)
Pd—S2	2.2644 (10)	Co—C31	2.006 (8)
S1—C1	1.742 (4)	Co—C32	2.005 (9)
S2—C2	1.728 (4)	Co—C33	2.017 (9)
C1—C2	1.371 (5)	Co—C34	2.033 (8)
S1^i—Pd—S1	175.36 (5)	C1—S1—Pd	104.44 (13)
S1—Pd—S2^i	91.29 (3)	C2—S2—Pd	104.33 (12)
S1—Pd—S2	88.79 (3)	C2—C1—S1	120.6 (3)
S2^i—Pd—S2	178.02 (5)	C1—C2—S2	121.8 (3)

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

Compound (II)

Crystal data

$[Pd(C_{14}H_{10}S_2)_2]$
$M_r = 591.08$
Monoclinic
$P2_1/n$
$a = 5.9472 (6)$ Å
$b = 11.2387 (10)$ Å
$c = 18.6239 (13)$ Å
$\beta = 91.659 (7)°$
$V = 1244.3 (2)$ Å^3
$Z = 2$
$D_x = 1.578$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.88–12.98°$
$\mu = 1.097$ mm^{-1}
$T = 293 (2)$ K
Needle
0.40 × 0.38 × 0.25 mm
Black

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction:
 empirical *via* ψ scans (*SHELXL*93; Sheldrick, 1993)
 $T_{\min} = 0.666$, $T_{\max} = 0.760$
2409 measured reflections
2183 independent reflections
1933 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 24.99°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -22 \rightarrow 22$
3 standard reflections
 every 97 reflections
 intensity decay: 3.19%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.064$
$S = 1.052$
2182 reflections
191 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.4364P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.253$ e Å^{-3}
$\Delta\rho_{\min} = -0.278$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd—S2	2.2496 (6)	S2—C2	1.712 (2)
Pd—S1	2.2501 (6)	C1—C2	1.400 (3)
S1—C1	1.695 (2)		
S2$^{\rm i}$—Pd—S1	92.08 (2)	C2—S2—Pd	105.93 (8)
S2—Pd—S1	87.92 (2)	C2—C1—S1	121.6 (2)
C1—S1—Pd	105.32 (8)	C1—C2—S2	119.2 (2)

Symmetry code: (i) $-x, -y, -z$.

For both compounds, data collection: *XSCANS* (Siemens, 1994*a*); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1234). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1072–1075

A linear trinuclear Cd$^{\rm II}$–Cd$^{\rm II}$–Cd$^{\rm II}$ complex with a μ-acetato bridge: bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]cadmium(II)}cadmium(II)

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Abstract

The title complex, bis(μ-acetato)-1:2κ^2O:O';2:3κ^2O:O'-bis{μ-2,2′-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1κ^4N,N',O,O':2κ^2O,O';3κ^4N,N',O,O':2κ^2O,-O'-tricadmium(II), [Cd{Cd(C$_{17}$H$_{16}$N$_2$O$_2$)(CH$_3$CO$_2$)}$_2$], consists of a doubly oxygen-bridged linear homotrinuclear complex. The outer Cd$^{\rm II}$ ions, related by an inversion centre, have an irregular square-pyramidal coordination. The central Cd$^{\rm II}$ ion has an irregular octahedral coordination and lies on an inversion centre. The metal–metal bridging distance is 3.2582 (3) Å.

Comment

The structures and syntheses of several oxygen-bridged dimeric and trimeric linear homo- or heteronuclear metal complexes have been studied in our laboratories recently; examples include [Cu$_2$(C$_{11}$H$_{10}$ClNO$_2$)$_2$] (Tahir *et al.*, 1996), [Cu$_2$(C$_{14}$H$_{11}$NO$_2$)$_2$] (Ülkü, Ercan, Atakol, Ercan & Gencer, 1997), [Ni$_3${(SALPD)(CH$_3$CO$_2$)-[(CH$_3$)$_2$SO]}$_2$] (Ülkü, Ercan, Atakol & Dinçer, 1997), [Cd{Ni(SALPD)(CH$_3$CO$_2$)[(CH$_3$)$_2$NCHO]}$_2$] (Ülkü, Tahir *et al.*, 1997), [Cu$_2$(C$_{12}$H$_{13}$NO$_2$)$_2$] (Atakol *et al.*, 1997), [Cu$_2$(C$_{12}$H$_{13}$NO$_2$)$_2$] (Ülkü *et al.*, 1998), [Ni$_2${Cu-