Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(μ-*N*,*N*-dimethyldithiocarbamato-$\kappa^3S,S':S'$)bis[(dimethoxyphenylphosphane-κP)(*N*,*N*-dimethyldithiocarbamato-κ^2S,S')cobalt(III)] bis(hexafluorophosphate)

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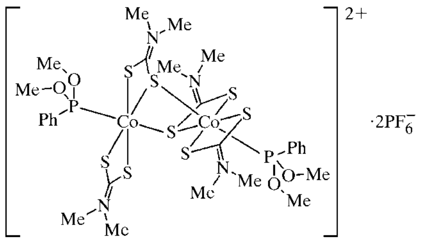
Received 28 August 2001
Accepted 31 October 2001
Online 23 January 2002

Purple prismatic crystals of the title compound, $[Co_2(C_3H_6NS_2)_4(C_8H_{11}O_2P)_2](PF_6)_2$, were obtained by repeated recrystallization of *trans*-$[Co(C_3H_6NS_2)_2(C_8H_{11}O_2P)_2]PF_6$ from CH_3CN/Et_2O and then from MeOH/CH_2Cl_2; during recrystallization one of the $P(OMe)_2Ph$ ligands was dissociated from the Co^{III} center and the resulting Co^{III} complex fragment underwent dimerization. The complex cation has a dinuclear structure bridged by one S atom of each of two of the *N*,*N*-dimethyldithiocarbamate ligands, and has crystallographically imposed C_2 symmetry. Two $P(OMe)_2Ph$ ligands are coordinated at the *transoid* positions of the $Co_2(\mu\text{-}C_3H_6NS_2)_2(C_3H_6NS_2)_2$ moiety, with Co—P bond lengths of 2.1921 (11) Å.

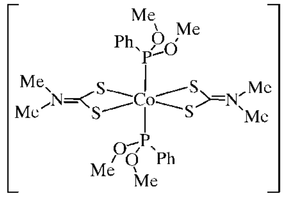
Comment

We have undertaken the systematic syntheses and comparison of the structures, together with the chemical and spectroscopic properties, of several series of cobalt(III) complexes containing monodentate *P*-donor ligands, such as $[Co(acac)_2(\text{P-ligand})_2]^+$ (acac = pentane-2,4-dionate) and $[Co(dtc)_2(\text{P-ligand})_2]^+$ (dtc = *N*,*N*-dimethyldithiocarbamate). It was possible to synthesize a series of dtc complexes with diphenylphosphine (Suzuki, Iwatsuki *et al.*, 2001), phosphites (Matsui *et al.*, 1993), phosphonites and phosphinites (Kashiwabara *et al.*, 2002), as well as tertiary phosphines (Suzuki, Kashiwamura & Kashiwabara, 2001), while only tertiary phosphine complexes have been prepared for the series of acac complexes (Suzuki *et al.*, 1998, 2000). It was suggested that dtc is the best ligand to stabilize the Co^{III}—P bond due to its steric compactness and electronic softness (Suzuki, Kashiwamura *et al.*, 2001).

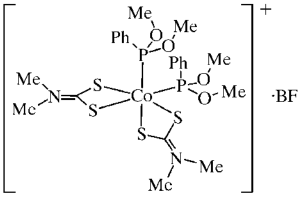
The title compound, $[Co_2\{\mu(S)\text{-dtc}\}_2(dtc)_2\text{-}\{P(OMe)_2Ph\}_2](PF_6)_2$, (I), was the unexpected product of the attempted recrystallization of *trans*-$[Co(dtc)_2\{P(OMe)_2Ph\}_2]PF_6$, (II), in the course of which the mononuclear molecules of (II) each lost one $P(OMe)_2Ph$ ligand thus permitting the formation of dinuclear complex (I) in which the Co centres are bridged by one S atom of each of two dtc ligands (Fig. 1).



(I)



(II)

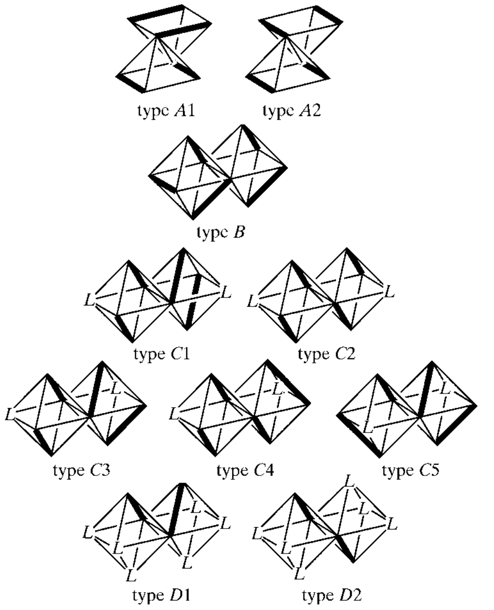


(III)

The coordination mode for dithiocarbamates (R_2dtc: $R_2NCS_2^-$) bridging two metal centers by one of the S atoms, $\mu_2(S)$-R_2dtc-$\kappa^3S{:}S,S'$, has often been observed; the April 2001 release of the Cambridge Structural Database (Allen & Kennard, 1993) contains more than 60 reports of compounds with such an R_2dtc coordination mode. Typical examples involving bis$\{\mu_2(S)$-R_2dtc-$\kappa^3S,S,S'\}$ ligands are the dinuclear complexes composed of two edge-sharing square-pyramidal polyhedra, each of which consists of the square-planar $M^{II}(dtc)_2$ (M = Mo, Fe, Cu, Zn, Cd or Hg) moiety and an apical bridging S atom (types *A*1 and *A*2 in the scheme below, in which bold lines represent R_2dtc chelates). $[Co_2(Et_2dtc)_5]BF_4$ (Hendrickson *et al.*, 1975) is the only example within Co^{III} complexes, and the structure of the cation is illustrated in the scheme below as type *B*; it consists of two edge-sharing octahedra, $[Co(Et_2dtc)_3]$ and *cis*-$[Co(Et_2dtc)_2]^+$. This type of dinuclear species was also found for $[Rh_2(dtc)_5]BF_4$ (Hendrickson *et al.*, 1976) and $[Ru_2(^iPr_2dtc)_5]^+$ (Raston & White, 1975*a*). The structure of the complex cation in (I) can be categorized as type *C*1; two $P(OMe)_2Ph$ ligands are sited at the *transoid* positions of two edge-sharing octahedra. The complex cation has C_2 symmetry, so it can be considered as a type *A*1 species with two monodentate ligands added. This kind of structure has already been found in $[Ru_2(Et_2dtc)_4(CO)_2]$ (Raston & White, 1975*b*) and $[Re_2(Et_2dtc)_4\{NB(C_6F_5)_3\}_2]$ (Abram, 1999). Interestingly, all three examples of the $[M_2(\mu\text{-}R_2dtc)_2(R_2dtc)_2L_2]$ structure are of type *C*1. There are four other possible isomers for the $[M_2(\mu\text{-}R_2dtc)_2(R_2dtc)_2L_2]$ type of dinuclear complex (*i.e.* types *C*2, *C*3, *C*4 and *C*5), but no complex having these structures has been reported to date. Furthermore, for the related $[M_2(\mu\text{-}R_2dtc)_2L_6]$ type dinuclear complexes, $[Pt_2(\mu\text{-dtc})_2(CH_3)_6]$

DOI: 10.1107/S0108270101018406

(Heard *et al.*, 2000), $[Ru_2(\mu\text{-dtc})_2([9]aneS_3)_2]^{2+}$ (Landgrafe & Sheldrick, 1994) and $[Mo_2(\mu\text{-}Et_2dtc)_2(CO)_4(NO)_2]$ (Shiu *et al.*, 1995), all the reported structures are of type *D*1 rather than type *D*2.



The two bridging Co—S bond lengths in (I) are 2.2757 (10) and 2.3865 (11) Å. The latter [Co—S1($-x, y, \frac{1}{2}-z$) bond] is appreciably longer than those [2.298 (8) and 2.333 (8) Å] in $[Co_2(Et_2dtc)_5]BF_4$ (Hendrickson *et al.*, 1975), suggesting that the bridge which forms the dinuclear structure is not as strong in (I) as it is in $[Co_2(Et_2dtc)_5]BF_4$. The structure of the $Co(dtc)_2\{P(OMe)_2Ph\}$ moiety is similar to that of the $Co(dtc)_2(PMe_2Ph)$ moiety in *trans*-$[Co(dtc)_2(PMe_2Ph)_2]BF_4$ (Suzuki, Kashiwamura & Kashiwabara, 2001), the phenyl ring being located directly above one of the S atoms, S4 in (I), with a stacking interaction to the dtc plane. The dihedral angle between the phenyl ring and the dtc mean plane is 19.6 (2)°. The S—Co—S bite angles, 77.68 (4) and 77.10 (4)°, of dtc in (I) are comparable to those in *trans*-$[Co(dtc)_2(PMe_{3-n}Ph_n)_2]BF_4$ (Suzuki, Kashiwamura & Kashiwabara, 2001) and $[Co(dtc)_3]$ (Iwasaki & Kobayashi, 1980).

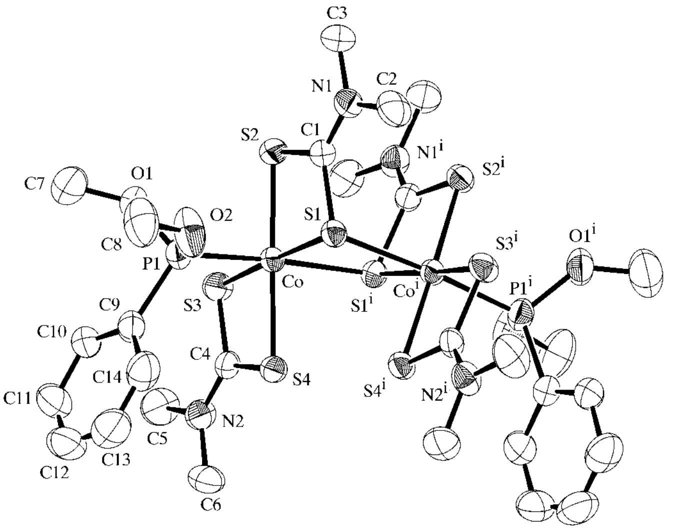


Figure 1

A perspective view of the complex dication in (I). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

The Co—P bond lengths in (I) are 2.1921 (11) Å. There are only a few reports of structural analyses of Co^{III} complexes containing $P(OMe)_2Ph$. Except for four organometallic Co^{III} complexes, complex (I) is only the third example of such non-organometallic Co^{III}–$P(OMe)_2Ph$ complexes, the other two being *trans*-$[Co(Hdmg)_2Cl\{P(OMe)_2Ph\}]$ (Hdmg is the dimethylglyoximate monoanion; Bresciani-Pahor *et al.*, 1982) and *cis*-$[Co(dtc)_2\{P(OMe)_2Ph\}_2]PF_6$ (Kashiwabara *et al.*, 2002), where the Co—P bond lengths are reported as 2.213 (2) Å and an average of 2.218 (3) Å, respectively.

Experimental

Reaction of $Co(BF_4)_2\cdot6H_2O$, $P(OMe)_2Ph$ and tetramethylthiuram disulfide (molar ratio 2:4:1) in $MeOH/CH_2Cl_2$ afforded *cis*-$[Co(dtc)_2\{P(OMe)_2Ph\}_2]BF_4$, (III). UV irradiation for 5 h of an MeOH solution of (III) and NH_4PF_6 afforded thin brown plate-like crystals of the *trans* isomer, (II). Repeated recrystallization of (II) from CH_3CN/Et_2O and then from $MeOH/CH_2Cl_2$ gave purple prismatic crystals of (I) whose ^1H NMR spectrum was consistent with the dinuclear structure. The ^1H NMR data of (I) in CD_3CN (303 K, 400 MHz) are: δ 2.852 (*s*, $-NCH_3$, 3H), 2.903 (*s*, $-NCH_3$, 3H), 3.235 (*s*, $-NCH_3$, 3H), 3.273 (*s*, $-NCH_3$, 3H), 3.825 (*d*, $-OCH_3$, J = 10.8 Hz, 3H), 3.915 (*d*, $-OCH_3$, J = 10.4 Hz, 3H), and 7.40–7.71 (*m*, $-C_6H_5$, 5H).

Table 1

Selected geometric parameters (Å, °).

Co—P1	2.1921 (11)	S2—C1	1.696 (4)
Co—S1	2.2757 (10)	S3—C4	1.716 (4)
Co—S2	2.2493 (11)	S4—C4	1.713 (4)
Co—S3	2.2633 (11)	P1—O1	1.594 (4)
Co—S4	2.2793 (11)	P1—O2	1.578 (3)
Co—S1ⁱ	2.3865 (11)	P1—C9	1.804 (4)
S1—C1	1.766 (4)		
P1—Co—S2	88.43 (4)	P1—Co—S1ⁱ	175.94 (4)
P1—Co—S3	86.99 (4)	S1—Co—S1ⁱ	83.41 (4)
S2—Co—S3	102.76 (4)	C1—S1—Co	84.86 (12)
P1—Co—S1	97.13 (4)	C1—S1—Coⁱ	108.26 (12)
S2—Co—S1	77.68 (4)	Co—S1—Coⁱ	95.11 (4)
P1—Co—S4	93.06 (4)	C1—S2—Co	87.30 (13)
S3—Co—S4	77.10 (4)	C4—S3—Co	85.92 (12)
S1—Co—S4	102.35 (4)	C4—S4—Co	85.49 (13)

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

Crystal data

$[Co_2(C_3H_6NS_2)_4(C_8H_{11}O_2P)_2](PF_6)_2$
M_r = 1228.91
Monoclinic, $C2/c$
a = 26.454 (3) Å
b = 14.499 (3) Å
c = 14.517 (3) Å
β = 120.276 (10)°
V = 4808.8 (16) Å^3
Z = 4

D_x = 1.697 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 14.7–15.0°
μ = 1.26 mm^{-1}
T = 296 (2) K
Square prism, purple
0.28 × 0.26 × 0.18 mm

m96 Takayoshi Suzuki et al. • $[Co_2(C_3H_6NS_2)_4(C_8H_{11}O_2P)_2](PF_6)_2$ Acta Cryst. (2002). C58, m95–m97

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.744$, $T_{\max} = 0.798$
7153 measured reflections
7017 independent reflections
3741 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 37$
$k = 0 \rightarrow 20$
$l = -20 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.164$
$S = 1.04$
7017 reflections
284 parameters
H-atom parameters constrained (see text below)

$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 1.623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}

Methyl H atoms attached to the N atoms of the dimethyldithiocarbamate ligands were located from ΔF syntheses and refined as parts of rigid groups which were allowed to rotate but not tip or distort, and with C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Other H atoms were placed geometrically and refined using a riding model with C—H = 0.96 (for methyl H) or 0.93 Å (for phenyl H), and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Rigaku, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1475). Services for accessing these data are described at the back of the journal.

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