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Acta Cryst. (1993). **C49**, 576–578

Structure of the Two-Coordinate Cadmium Complex Bis(pentafluorophenyl)cadmium(II), [Cd(C₆F₅)₂]

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(Received 4 February 1992; accepted 28 September 1992)

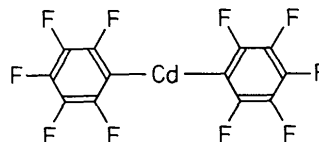
Abstract

In the neutral complex [Cd(C₆F₅)₂], the Cd atom is coordinated to two pentafluorophenyl ligands. The Cd—C bond lengths are 2.109 (3) and 2.111 (3) Å. The molecule is slightly bent at the metal atom [C—Cd—C 173.9 (1)°]. The angle between the aromatic rings of the ligands is 76.6°. There are no Cd...F contacts shorter than the van der Waals distance.

Comment

[Cd(C₆F₅)₂] has been used as a starting material in the synthesis of the multinuclear cadmium complexes [{Cd(C₆F₅)(ER)}_n] (E = O, S; R = alkyl, aryl; n = 2, 4) (Strasdeit, Duhme, Büsching, Pohl & Saak, 1992). The structure determination was performed to establish whether bridging ligands are present in the solid state. Crystals of the related compound diphenylzinc contain dimers with μ-C₆H₅ groups (Markies *et al.*, 1990), while bis(pentafluorophenyl)mercury(II) is monomeric (Kunchur & Mathew, 1966; Wilkinson, Riede & Müller, 1991). In the non-coordinating solvent C₆D₆, the title compound gives rise to a ¹³C NMR spectrum that has four multiplets, as expected for a monomeric species: δ = 119.2 [²J(C,F) 64 Hz, *ipso*-C], 137.3 [¹J(C,F) (-)255 Hz, *m*-C], 141.3 [¹J(C,F) (-)251 Hz, ²J(C,F) *ca* 14 Hz, ³J(C,F)

ca 5 Hz, *p*-C], 147.8 p.p.m. [¹J(C,F) (-)229 Hz, *o*-C]. The ¹³C, ¹⁹F coupling constants were only partly determined; ¹³C, ^{111,113}Cd couplings were not observed.



Single crystals of [Cd(C₆F₅)₂] were obtained by combined thermal decarboxylation of Cd(O₂CC₆F₅)₂ and vacuum sublimation according to a literature method (Schmeißer & Weidenbruch, 1967; Sartori & Weidenbruch, 1967). [Cd(C₆F₅)₂] is very sensitive to water and was handled under an atmosphere of dry nitrogen. The intermediate product of the hydrolysis [{Cd(C₆F₅)(μ₃-OH)}₄] has been structurally characterized (Weidenbruch, Herrndorf, Schäfer, Pohl & Saak, 1989).

[Cd(C₆F₅)₂] represents a rare example of pure (*i.e.* without additional secondary bonds) two-coordination of Cd^{II} in the solid state (Fig. 1). It is most intriguing that the two-coordination is not enforced by sterically demanding ligands such as those occurring in [Cd{C(SiMe₃)₂(SiMe₂CHCH₂)}₂] (Ayoko, Buttrus, Eaborn, Hitchcock & Smith, 1987). In this latter compound, the Cd—C bond lengths are 2.17 Å; in [Cd(C₆F₅)₂] the mean Cd—C bond length (2.11 Å) is smaller and has the same value as in gaseous CdMe₂ (Rao, Stoicheff & Turner, 1960). Using the bond-valence method (O'Keeffe & Brese, 1991), the Cd—C bond length for two-coordination is calculated to be 2.05 Å which is too low. However, for other coordination units, *e.g.* CdHal₂ and CdN₆, this method yields results that are in much better agreement with experimental values. The C—Cd—C fragment of [Cd(C₆F₅)₂] deviates from linearity by 6.1°, presumably as a result of packing forces. The aromatic rings of the two ligands form an angle of 76.6° with one another.

The C—C bond lengths do not differ significantly. In contrast, two groups of C—F bonds can be discerned. The average length of the four *ortho* C—F

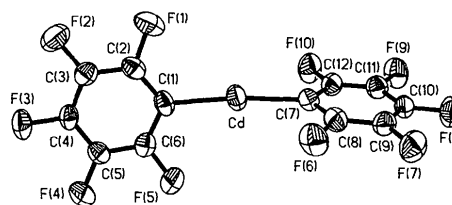


Fig. 1. View of [Cd(C₆F₅)₂] showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

bonds is 1.355 Å, while the mean value of the remaining six C—F bonds is 1.343 Å. As the e.s.d. of an individual bond is 0.003 Å and the spread within each group is small, the difference is considered to be significant. The C₆ rings show angular distortions typical of C₆F₅ groups. For example, the C—C—C angles at the *ipso* C atoms are considerably smaller than 120°; the value in the present complex (115.8°) may be compared to the mean value (114.7°) calculated from several other metal—C₆F₅-containing structures (Jones, 1988).

The analogous mercury complex [Hg(C₆F₅)₂] crystallizes in a different space group (*P*2₁2₁2₁, Kunchur & Mathew, 1966). Its X-ray structure has been redetermined recently (Wilkinson, Riede & Müller, 1991). The mean Hg—C bond length (2.05 Å) is remarkably short, 0.06 Å less than the mean Cd—C bond in [Cd(C₆F₅)₂].

Crystals of the title compound consist of discrete molecules (Fig. 2). The shortest intermolecular Cd···F contact is 2.973 Å [to F(2ⁱ); (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. It corresponds to the sum of the van der Waals radii of 2.9–3.0 Å (Bondi, 1964; Nyburg & Faerman, 1985). All other Cd···F distances, including the intramolecular ones, are larger than 3.1 Å. The absence of any significant Cd···F interactions is in accordance with the low affinity of Cd^{II} to fluoride (Hefter, Tioh & Chan, 1990). For other metals, secondary aryl F···M bonds have been observed in a number of complexes (Kulawiec & Crabtree, 1990). The shortest Cd···Cd distance in [Cd(C₆F₅)₂] is 5.605 Å.

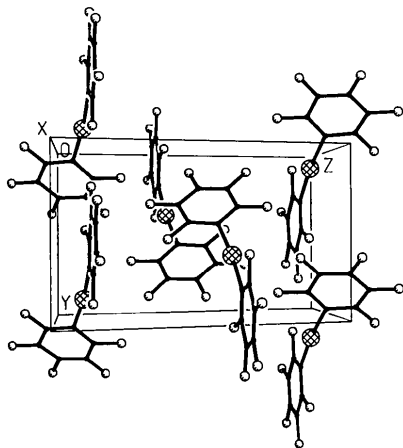


Fig. 2. View of the crystal packing.

The X-ray structures of [Zn(R_f)₂], [Cd(R_f)₂-(CH₃CN)] and [Hg(R_f)₂] [R_f = 2,4,6-tris(trifluoromethyl)phenyl] have been reported recently (Brooker, *et al.*, 1992). As a solvent adduct of a diarylcadmium species, [Cd(R_f)₂(CH₃CN)] is closely related to [Cd(C₆F₅)₂]. However, in contrast to the latter, it contains three-coordinate cadmium.

Experimental

Crystal data

[Cd(C₆F₅)₂]
M_r = 446.53
 Monoclinic
*P*2₁/*n*
a = 12.030 (1) Å
b = 7.792 (1) Å
c = 13.711 (1) Å
 β = 108.94 (1)°
V = 1215.7 Å³
Z = 4
D_x = 2.440 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 42 reflections
 θ = 16–20°
 μ = 1.86 mm⁻¹
T = 297 K
 Truncated parallelepiped
 0.38 × 0.27 × 0.23 mm
 Colourless

Data collection

Siemens/Stoe AED-2 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 $T_{\min} = 0.2657$, $T_{\max} = 0.3288$
 2987 measured reflections
 2648 independent reflections

2226 observed reflections [$I > 2\sigma(I)$]
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 27^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 9$
 $l = -17 \rightarrow 17$
 3 standard reflections
 frequency: 45 min
 intensity variation: -3%

Refinement

Refinement on *F*
 Final *R* = 0.027
 $wR = 0.029$
 2213 reflections
 208 parameters
 $w = 0.8996/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cd	0.15716 (2)	0.38081 (3)	0.40269 (2)	0.0512 (1)
F(1)	0.2590 (2)	0.6580 (3)	0.2681 (1)	0.0708 (5)
F(2)	0.4495 (2)	0.8637 (3)	0.3254 (2)	0.0692 (5)
F(3)	0.5928 (2)	0.8662 (2)	0.5236 (2)	0.0602 (5)
F(4)	0.5375 (2)	0.6812 (3)	0.6685 (1)	0.0637 (5)
F(5)	0.3491 (2)	0.4729 (3)	0.6132 (1)	0.0619 (5)
F(6)	0.1676 (2)	-0.0274 (3)	0.3967 (2)	0.0679 (5)
F(7)	0.0066 (2)	-0.2764 (2)	0.3758 (2)	0.0690 (6)
F(8)	-0.2183 (2)	-0.1926 (3)	0.3551 (2)	0.0686 (5)
F(9)	-0.2846 (2)	0.1406 (3)	0.3467 (2)	0.0716 (6)
F(10)	-0.1230 (2)	0.3912 (2)	0.3697 (2)	0.0728 (6)
C(1)	0.2971 (2)	0.5583 (4)	0.4395 (2)	0.0439 (6)
C(2)	0.3261 (3)	0.6603 (4)	0.3694 (2)	0.0450 (6)
C(3)	0.4231 (3)	0.7655 (4)	0.3954 (2)	0.0446 (6)
C(4)	0.4947 (2)	0.7702 (3)	0.4967 (2)	0.0421 (6)
C(5)	0.4676 (2)	0.6746 (4)	0.5701 (2)	0.0427 (6)
C(6)	0.3697 (2)	0.5708 (3)	0.5395 (2)	0.0427 (6)
C(7)	0.0270 (3)	0.1896 (4)	0.3807 (2)	0.0447 (6)
C(8)	0.0550 (3)	0.0190 (4)	0.3821 (2)	0.0462 (6)
C(9)	-0.0254 (3)	-0.1108 (4)	0.3721 (2)	0.0472 (7)
C(10)	-0.1397 (3)	-0.0679 (4)	0.3605 (2)	0.0475 (7)
C(11)	-0.1722 (3)	0.1011 (4)	0.3581 (2)	0.0479 (7)
C(12)	-0.0885 (3)	0.2262 (4)	0.3687 (2)	0.0463 (6)

Table 2. Geometric parameters (Å, °)

Cd—C(1)	2.109 (3)	C(1)—C(2)	1.377 (4)
Cd—C(7)	2.111 (3)	C(1)—C(6)	1.369 (4)
C(2)—F(1)	1.361 (3)	C(2)—C(3)	1.374 (4)
C(3)—F(2)	1.345 (3)	C(3)—C(4)	1.376 (4)
C(4)—F(3)	1.344 (3)	C(4)—C(5)	1.374 (4)
C(5)—F(4)	1.340 (3)	C(5)—C(6)	1.377 (4)
C(6)—F(5)	1.352 (3)	C(7)—C(8)	1.370 (4)
C(8)—F(6)	1.353 (3)	C(7)—C(12)	1.376 (4)
C(9)—F(7)	1.343 (3)	C(8)—C(9)	1.375 (4)
C(10)—F(8)	1.342 (3)	C(9)—C(10)	1.373 (5)
C(11)—F(9)	1.346 (3)	C(10)—C(11)	1.371 (4)
C(12)—F(10)	1.353 (3)	C(11)—C(12)	1.374 (4)
C(1)—Cd—C(7)	173.9 (1)	Cd—C(7)—C(8)	121.0 (2)
Cd—C(1)—C(2)	125.1 (2)	Cd—C(7)—C(12)	123.0 (2)
Cd—C(1)—C(6)	119.1 (2)	C(8)—C(7)—C(12)	115.9 (3)
C(2)—C(1)—C(6)	115.7 (3)	C(7)—C(8)—F(6)	119.5 (3)
C(1)—C(2)—F(1)	120.2 (3)	C(9)—C(8)—F(6)	117.1 (3)
C(3)—C(2)—F(1)	116.5 (3)	C(7)—C(8)—C(9)	123.4 (3)
C(1)—C(2)—C(3)	123.3 (3)	C(8)—C(9)—F(7)	121.3 (3)
C(2)—C(3)—F(2)	122.1 (3)	C(10)—C(9)—F(7)	120.1 (3)
C(4)—C(3)—F(2)	119.3 (3)	C(8)—C(9)—C(10)	118.6 (3)
C(2)—C(3)—C(4)	118.6 (3)	C(9)—C(10)—F(8)	119.5 (3)
C(3)—C(4)—F(3)	119.9 (3)	C(11)—C(10)—F(8)	120.2 (3)
C(5)—C(4)—F(3)	119.8 (3)	C(9)—C(10)—C(11)	120.3 (3)
C(3)—C(4)—C(5)	120.3 (3)	C(10)—C(11)—F(9)	119.4 (3)
C(4)—C(5)—F(4)	119.8 (3)	C(12)—C(11)—F(9)	121.6 (3)
C(6)—C(5)—F(4)	121.6 (3)	C(10)—C(11)—C(12)	119.0 (3)
C(4)—C(5)—C(6)	118.6 (3)	C(7)—C(12)—F(10)	119.8 (3)
C(1)—C(6)—F(5)	119.7 (3)	C(11)—C(12)—F(10)	117.3 (3)
C(5)—C(6)—F(5)	116.7 (3)	C(7)—C(12)—C(11)	122.9 (3)
C(1)—C(6)—C(5)	123.5 (3)		

Data collection and cell refinement: *DIF4* (Stoe, 1985a). Data reduction: *REDU4* (Stoe, 1985b). Structure solution: *SHELXS86* (Sheldrick, 1986). Structure refinement: *SHELXL76* (Sheldrick, 1976). Molecular graphics: *XP (SHELXTL-Plus)*; Sheldrick, 1990).

The authors wish to thank W. Saak for technical assistance and the Deutsche Forschungsgemeinschaft for financial support.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55621 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1005]

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Acta Cryst. (1993). **C49**, 578–580

Structure of Bis[pentaamminechloro-iridium(III)] Hexachloroplatinate(IV) Dichloride

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(Received 4 June 1992; accepted 23 September 1992)

Abstract

The crystal is built up from octahedral PtCl_6^{2-} and nearly octahedral $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ ions; the electro-neutrality is assumed by the Cl^- ions. The structure can be described as comprising layers of PtCl_6^{2-} and layers containing $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ and Cl^- , parallel to (001). The layers are stabilized by electrostatic interactions, and numerous $\text{N—H}\cdots\text{Cl}$ hydrogen bonds possibly take part in the packing of the ions.

Comment

The title compound is one of a series of inorganic Pt–Ir complexes which are reforming-catalyst precursors. The reaction of $\text{Ir}(\text{NH}_3)_5\text{Cl}_2$ and K_2PtCl_6 leads to $\text{Ir}(\text{NH}_3)_5\text{ClPtCl}_6$ (Michelot, Ouali, Blais,