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References


Structure of Bis(cyclopentadienyl)bis(pyridine)cadmium(II)

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Abstract. [Cd(C₅H₅)₂(C₅H₅N)₂], Mr= 400.8, monoclinic, P2₁/n, a = 12.79 (1), b = 10.093 (4), c = 14.38 (1) Å, β = 107.20 (8)°, V = 1773 (2) Å³, Z = 4, Dₐ = 1.501 g cm⁻³, Mo Kα, λ = 0.71073 Å, μ = 12.3 cm⁻¹, F(000) = 808, T = 294 K, R = 0.0326 for 2407 observed reflections with I > 2σ(I). The Cd atom is pseudo-tetrahedrally coordinated by the two N atoms of the pyridine molecules and by two C atoms of the η⁴-bonded Cp moieties.

Introduction. Bis(cyclopentadienyl)cadmium [Cd(Cp)₂] was prepared to compare its reactivity with the related [Zn(Cp)₂] as part of an investigation on the reactions of (cyclopentadienyl)zinc compounds with Ni⁰ complexes (Budzelaar, Boersma, van der Kerk, Spek & Duisenberg, 1985a,b; Fischer, Boersma, Kojić-Prodić & Spek, 1985). Single crystals of the present pyridine complex were obtained by slow crystallization from pyridine. An X-ray study of this complex was undertaken in order to establish the molecular geometry of the first known example of a cyclopentadienyl–Cd compound. A preliminary report of this study was given previously (Fischer, van Mier, Boersma, Smeets & Spek, 1987).

Experimental. Yellowish crystal 0.58 x 0.25 x 0.20 mm suitable for X-ray diffraction was sealed under nitrogen in a Lindemann-glass capillary. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo Kα radiation, cell constants from the angular settings of 25 reflections with 16.3 < 0< 20.4°. Intensity data of 4074 unique reflections were collected within a quarter of the reflection sphere: 0<h<16; 0<k<13; -18 < l < 17; (sinθ)/λ < 0.65 Å⁻¹; ω/2θ scan mode with Δω = (0.70 + 0.35 tanθ)°. Three reference reflections [200 (e.s.d. = 0.64%); 020 (e.s.d. = 0.51%); 002 (e.s.d. = 0.68%)], measured every hour showed a linear decay of 0.2% during the 77 hours of X-ray exposure time. The intensity data were corrected for this decay and for Lorentz–polarization effects. No correction for absorption was applied in view of the small intensity variation of 6% about the mean of the 360° ψ scan of the 404 reflection. Standard deviations in the intensities were increased according to an analysis of the variance © 1987 International Union of Crystallography
The structure was solved by standard Patterson (SHELX84; Sheldrick, 1984) and difference Fourier methods. All non-H atoms were refined anisotropically (on F) by blocked full-matrix least-squares techniques. H atoms were introduced on calculated positions and included in the refinement with individual positional parameters and one overall isotropic thermal parameter. Weights were introduced in the final refinement cycles. Convergence with 269 parameters was reached at $R = 0.0326$, $wR = 0.0185$, $w = 1/\sigma^2(F)$, $S = 1.67$, $(\Delta / \sigma)_{\text{max}} = 0.044$. The final difference Fourier synthesis revealed max. and min. residual densities of 0.62 and $-0.41 \text{ eÅ}^{-3}$ near the Cd atom.

**Discussion.** Fractional atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table 1.* Bond lengths and bond angles are listed in Table 2. The molecular structure of the title compound and the adopted atom numbering are presented in Fig. 1.

The crystal structure consists of four discrete molecules contained in the monoclinic unit cell with no unusual intermolecular contacts. The Cd atom is pseudo-tetrahedrally coordinated by the two N atoms of the pyridine molecules and by the two $\eta^1$-bonded C atoms of the Cp moieties. This is illustrated by the six relevant pseudo-tetrahedral angles which are in the range of 96.4 (1)-129.1 (2)$^\circ$ [average = 109 (1)$^\circ$].

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and geometrical data concerning H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43683 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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![PLUTO (EUCLID) version; Spek, 1982](drawing of the title compound with the adopted atom numbering.)
The Cd−N and Cd−C distances for the four coordinating atoms are 2.307 (5), 2.309 (3), 2.353 (5) and 2.360 (3) Å for C(6), N(1), C(1) and N(2) respectively.Comparable Cd−N distances have been found in other pyridine-containing Cd complexes such as trans-diiodotetrakis(pyridine)cadmium(II) with Cd−N distances of 2.368 (6) and 2.454 (9) Å (Ito, Shibata & Saito, 1984), in bis(o-hydroxybenzoate)tris(pyridine) cadmium(II) with Cd−N distances in the range 2.350 (2)−2.372 (2) Å (Charles, Griffith, Rodesiler & Amma, 1983) and in bis(nitrato)tris(pyridine) cadmium(II) with Cd−N distances of 2.301 (9) and 2.360 (3) Å (Cameron, Taylor & Nuttall, 1972). The deviation of the Cd atom from the least-squares planes through the N(1) and N(2) pyridine rings is 0-50 (1) and 0.119 (4) Å respectively.

Both Cp rings are η1-bonded to the Cd atom; the angles between the Cd−C(η1) bonds and the Cp ring planes are 80.1 (2) and 80.9 (3)° for the C(1) and C(6) rings respectively. The ring slippage [distance between ring centroid and the perpendicular projection of the Cd atom on the ring plane] is 1.424 (6) and 1.454 (7) Å for the C(1) and C(6) Cp rings respectively.

The cyclohexane ring is in the chair conformation and the tert-butyl radical is nearly staggered with respect to the cyclohexane. The average deviation from a perfectly staggered disposition is 15°. The six independent molecules in the asymmetric unit are interconnected through a complex network of hydrogen bonds. The O⋯O distances in the 12 hydrogen bonds range from 2.691 (4) to 2.832 (4) Å.

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The X-ray data were collected by Dr A. J. M. Duisenberg.

References


La Structure à 173 K d'un tert-Butyl-3 Cyclohexanediol-1,2 qui Cristallise avec Six Molecules Distinctes

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Abstract. C10H20O2, Mw = 172-27, triclinic, P1, a = 12.640 (6), b = 14.404 (5), c = 18.459 (6) Å, α = 96.99 (6), β = 106.00 (3), γ = 100.03 (7)°, V = 3129.7 Å3, Dx = 1.096 Mg m−3, Z = 12, F(000) = 1152, λ(Cu Kα) = 1.54178 Å, μ(Cu Kα) = 0.55 mm−1. T = 173 K, R = 0.075 for 6142 observed reflections.

The cyclohexane ring is in the chair conformation and the tert-butyl radical is nearly staggered with respect to the cyclohexane. The average deviation from a perfectly staggered disposition is 15°. The six independent molecules in the asymmetric unit are interconnected through a complex network of hydrogen bonds. The O⋯O distances in the 12 hydrogen bonds range from 2.691 (4) to 2.832 (4) Å.

Introduction. Une première étude cristallographique de ce composé entreprise il y a une dizaine d’années, en capillaire, à la température ambiante, n’avait révélé clairement que cinq des six molécules dans l’unité asymétrique. Une succession de synthèses de Fourier différence et d’affinements faisait difficilement ressortir la sixième molécule. Cependant l’affinement des données fractionnaires qui se comportait raisonnablement bien pour les cinq premieres molécules n’a jamais pu converger de manière satisfaisante pour la sixième molécule. Les longueurs de liaisons et les angles de valence de cette dernière prenaient des valeurs bien trop éloignées de leurs homologues dans les autres molécules. Ayant maintenant à notre disposition un...