Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond lengths around pivot atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71529 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1053]

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Acta Cryst. (1994). C**50**, 369–371

Dichloro[5,8-dimethyl-1,12-di-2-pyrrolyl-2,5,8,11-tetraaza-1,11-dodecadiene-N^2,N^5,N^8,N^{11}]cadmium(II)

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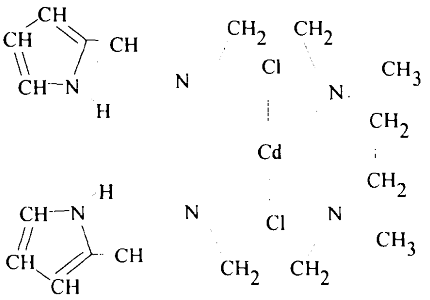
(*Received* 22 *March* 1993; *accepted* 13 *July* 1993)

Abstract

In [Cd($C_{18}H_{28}N_6$)Cl_2] the Cd atom is located on a twofold rotation axis and is octahedrally coordinated by two Cl atoms [Cd—Cl 2.533 (3) Å], two azomethine N atoms [Cd—N(2) 2.45 (1) Å] and two amino N atoms [Cd—N(1) 2.458 (9) Å] in a distorted geometry. The pyrrole N atoms are not coordinated.

Comment

The application of an electrochemical procedure to the synthesis of metal complexes with Schiff bases has been the object of several papers from our laboratory. Starting from the metal as the anode of an electrolytic cell, the synthesis of metal-pyrrolaldiminates has been described (Castro, Romero, García-Vázquez, Durán, Sousa, Castellano & Zukerman-Schpector, 1992). We have now applied the same method to the synthesis of the complex dichloro[5,8-dimethyl-1,12-di-2-pyrrolyl)-2,5,8,11-tetraaza-1,11-dodecadiene]cadmium(II) (I), and determined its structure by X-ray diffraction.



(I)

Fig. 1 shows the title molecule and the numbering scheme applied. The coordination polyhedron around the metal atom can be described as a distorted octahedron. The metal is coordinated to two Cl ligands in *cis* positions and to four N atoms from the tetradentate ligand. The two N atoms from the pyrrole rings are not coordinated to the metal. The chelate angles N(1)—Cd—N(1^{i}) and N(2)—Cd—N(2^{i}) [symmetry code: (i) $-x+1$, $-y$, z] have values of 75.8 and 71.1°, respectively, and represent the most pronounced differences from regular octahedral geometry.

The cadmium–nitrogen interatomic distances, Cd—N(azomethine) 2.45 (1) Å and Cd—N(amine) 2.458 (9) Å, are almost equal in length; they do not differ very much from those found in other hexacoordinated Cd complexes with five-membered chelate rings around the metal atom, *e.g.* in (1,2-benzenediamine-*N*)[*N*,*N*″-(2,6-pyridinediyldimethylidene)bis(1,2-benzenediamine)]cadmium(II) diperchlorate, [Cd—N(azomethine) 2.377 (10) Å and Cd—N(amine) 2.426 (12) Å (Nelson, Esho & Drew, 1982)], or in (bipy)Cd(S_2CNEt_2) [2.430 (3) Å], $(phen)_2Cd(S_2CNEt_2)_2$ [2.42 (1) Å] (Arioldi, de Oliveira, Riggiero & Lechat, 1990) and in bis[(2-aminoethyl)amine]dichlorocadmium(II) [2.37 (2) Å (Cannas, Marongin & Saba, 1980)]. This latter polymeric complex, having a CdN_4Cl_2 'core' with both bridging and terminal Cl ligands and N atoms forming five-membered chelating rings in the coordination sphere, provides the closest comparison with the subject of this paper. In fact, the bond length Cd—Cl(terminal), 2.49 (1) Å, is similar to that found in our complex, 2.533 (3) Å.

The C(5)—N(2) bonds are within the range 1.30 ± 0.04 Å proposed for a C=N bond (Brown, Towns & Trefonas, 1970). The bond lengths and angles in the ligands are close to the expected values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

An intramolecular hydrogen bond exists between the pyrrolic N atom and the Cl atom (N···Cl = 3.184 Å). This causes a shift of the ν(NH) IR band to 3200 cm^{-1}, 100–200 cm^{-1} lower than in compounds (Castro, Romero, García-Vázquez, Durán, Castiñeiras, Sousa & Fenton, 1990) without hydrogen bonding. Furthermore, a slight down-field shift of the ^{1}H NMR signal of the N—H pyrrolic proton (to 12.1 p.p.m.) is observed with respect to the aforementioned reference compounds.

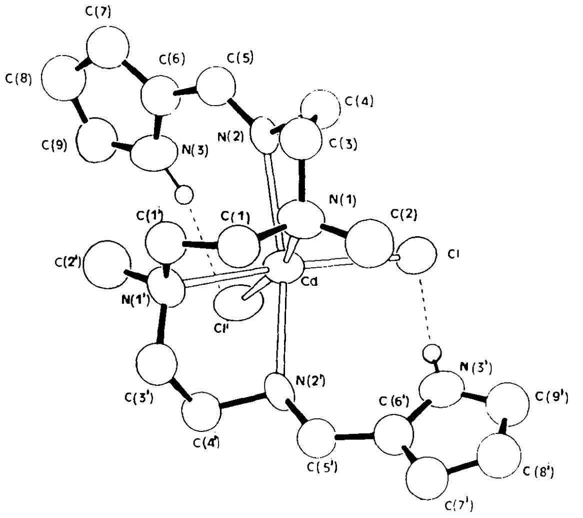


Fig. 1. The molecular structure of [Cd($C_{18}H_{28}N_6$)Cl_2] together with the atomic numbering system. H atoms are omitted for clarity.

Experimental

The compound was obtained using an electrochemical method similar to that described by Habeeb, Tuck & Walters (1978). The solution phase was prepared by reaction of equimolar amounts of 2-pyrrolecarbaldehyde (2.1588 g) and *N*-methylethylenediamine (1.782 g) in benzene until the theoretical amount of water was collected in a Dean-Stark trap. The resulting oil was washed with diethyl ether and 1,2-dichloroethane. The solvents were removed in a rotary evaporator and replaced by acetonitrile prior to the cadmium(II) complex formation. This solution was then placed in a 100 ml tall-form beaker while the platinum wire cathode and the cadmium anode, suspended on a second platinum wire, were introduced through a rubber bung. Electrolysis with an applied voltage of 25 V and a current of 10 mA during 2 h resulted in the evolution of H_2 at the cathode and the smooth dissolution of 85.4 mg from the cadmium anode (E_F = 0.51 mol F^{-1}). The reaction mixture was filtered to remove any precipitated particles of metal and the remaining solution phase was concentrated at room temperature; the oil obtained was washed with diethyl ether and *n*-hexane and finally recrystallized from 1,2-dichloroethane to give crystals suitable for X-ray diffraction.

Infrared spectra were recorded in KBr mulls on a Perkin-Elmer 180 spectrophotometer. Proton NMR spectra were recorded in $CDCl_3$ or DMSO solutions using a Bruker WM 250 MHz spectrometer; chemical shifts were determined with respect to TMS as the internal standard. The ^{1}H NMR spectrum of the complex showed a signal at 12.1 p.p.m. attributable to the pyrrolic proton; the signal of the azomethine H atom appeared upfield (8.6 p.p.m); the signals of the pyrrolic rings were observed between 7.2 and 6.3 p.p.m.; three signals corresponding to the ethylene bridges of the complex were found at 3.9, 3.4 and 2.2 p.p.m.

Crystal data

[Cd($C_{18}H_{28}N_6$)Cl_2]
M_r = 511.75
Orthorhombic
*Pnc*2
a = 9.2228 (8) Å
b = 11.7012 (8) Å
c = 9.8752 (9) Å
V = 1065.7 (3) Å^3
Z = 2
D_x = 1.588 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 46–58°
μ = 10.918 mm^{-1}
T = 293 K
Prismatic
0.2 × 0.2 × 0.2 mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans [width (1.05 + 0.15tanθ)°, speed variable]
Absorption correction: empirical
T_{min} = 0.46, T_{max} = 0.99
1775 measured reflections
923 independent reflections

764 observed reflections [$I > 1.5\sigma(I)$]
R_{int} = 0.064
θ_{max} = 70°
h = 0 → 10
k = 0 → 11
l = −13 → 13
3 standard reflections
frequency: 90 min
intensity variation: −1.5%

Refinement

Refinement on F
R = 0.042
wR = 0.049
S = 1.15
764 reflections
78 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.011

$\Delta\rho_{max}$ = 1.1 e Å^{-3}
$\Delta\rho_{min}$ = −0.8 e Å^{-3}
Extinction correction: $F_c' = F_c[1.0 + (k \times F_c^2/\sin 2\theta)]^{1/4}$ (Zachariasen, 1963)
Extinction coefficient: $k = 1.21 \times 10^{-6}$
Atomic scattering factors from *SDP* (Frenz, 1985)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for Cd, Cl and N atoms.

	x	y	z	B_{iso}/B_{eq}
Cd	1/2	0	0	3.81 (2)
Cl	0.6986 (3)	0.0309 (3)	−0.1734 (2)	4.81 (4)
N(1)	0.6515 (8)	0.049 (1)	0.1964 (7)	4.9 (2)
N(2)	0.5231 (5)	−0.205 (1)	0.0425 (7)	3.7 (2)
N(3)	0.8328 (7)	−0.201 (1)	−0.0605 (8)	5.2 (2)
C(1)	0.583 (1)	−0.0061 (9)	0.3184 (9)	5.1 (2)

C(2)	0.797 (1)	0.006 (1)	0.181 (1)	6.6 (3)
C(3)	0.3423 (9)	−0.174 (1)	0.2157 (9)	5.0 (2)
C(4)	0.3748 (7)	−0.237 (1)	0.0862 (9)	4.5 (2)
C(5)	0.6217 (8)	−0.286 (1)	0.0634 (9)	4.4 (2)
C(6)	0.7727 (8)	−0.281 (1)	0.0226 (9)	4.7 (2)
C(7)	0.8737 (9)	−0.358 (1)	0.059 (1)	5.2 (2)
C(8)	1.007 (1)	−0.320 (1)	0.002 (2)	5.8 (2)
C(9)	0.9779 (9)	−0.228 (2)	−0.077 (1)	5.6 (2)

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

Cd—Cl	2.533 (3)	Cd—N(1)	2.458 (9)
Cd—N(2)	2.45 (1)	C(1)—N(1)	1.50 (2)
C(1)—C(1^{i})	1.55 (2)	N(1)—C(2)	1.44 (2)
N(2)—C(4)	1.48 (1)	N(2)—C(5)	1.33 (1)
N(3)—C(6)	1.36 (2)	N(3)—C(9)	1.39 (1)
C(3)—C(4)	1.51 (1)	C(5)—C(6)	1.45 (1)
C(6)—C(7)	1.35 (2)	C(7)—C(8)	1.43 (2)
C(8)—C(9)	1.35 (3)		
Cl—Cd—Cl^{i}	95.0 (2)	Cl—Cd—N(1)	95.1 (3)
Cl—Cd—N(1^{i})	167.8 (3)	Cl—Cd—N(2)	101.1 (1)
Cl—Cd—N(2^{i})	92.2 (2)	N(1)—Cd—N(1^{i})	75.8 (5)
N(1)—Cd—N(2)	92.5 (3)	N(1)—Cd—N(2^{i})	71.7 (3)
N(2)—Cd—N(2^{i})	160.3 (4)	N(1)—C(1)—N(1^{i})	112.1 (8)
C(1)—N(1)—C(2)	109 (1)	C(4)—N(2)—C(5)	114 (1)
C(6)—N(3)—C(9)	108 (1)	N(2)—C(4)—C(3)	108.0 (9)
N(2)—C(5)—C(6)	125 (1)	N(3)—C(6)—C(5)	126 (1)
N(3)—C(6)—C(7)	110.0 (9)	C(5)—C(6)—C(7)	124 (1)
C(6)—C(7)—C(8)	106 (1)	C(7)—C(8)—C(9)	108 (1)
N(3)—C(9)—C(8)	108 (1)		

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

Lp corrections were applied to intensity data. The heavy-atom method (Cd atom) followed by difference Fourier syntheses revealed the positions of all non-H atoms. The positions of the H atoms were calculated geometrically and were not refined but included in F_c calculations [C—H = 0.98 Å; B(H) = 1.3B(C)]. A full-matrix least-squares refinement was used with anisotropic thermal parameters for Cd, Cl and N atoms, isotropic for C and H. Calculations were performed on a VAXstation 3100 computer with the *SDP* programs (Frenz, 1985); molecular graphics were produced using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71503 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1057]

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Acta Cryst. (1994). C**50**, 371–375

A Series of Osmium Carbonyl Complexes with Related Terminal, Bridging and Capping Phosphorus Ligands

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(*Received* 1 *December* 1992; *accepted* 16 *July* 1993)

Abstract

The structures of a series of three triosmium carbonyl clusters containing closely related phosphorus ligands have been determined: decarbonyl-1κ^3C,2κ^3C,3κ^4C-(dimethylphosphine-1κP)-μ-hydrido-1:2κ^2H-hydrido-2κH-*triangulo*-triosmium(3 Os—Os), [$Os_3(CO)_{10}H(\mu_2\text{-}H)(PMe_2H)$] (1), contains a terminal $PHMe_2$ ligand; decacarbonyl-1κ^3C,2κ^3C,3κ^4C-(μ-dimethylphosphino-1:2κ^2P)-μ-hydrido-1:2κ^2H-*triangulo*-triosmium(3 Os—Os), [$Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}PMe_2)$] (2), has a PMe_2 group bridging two of the osmium centres; in nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-bis-μ-hydrido-2:3κ^2H;1:3κ^2H-(μ_3-methylphosphinidene-κ^3P)-*triangulo*-triosmium(3 Os—Os), [$Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}PMe)$] (3), the PMe group caps all three metals. In (1) the terminal Os—P distance is 2.316 (18) Å and in (2) the two Os—P distances of 2.360 (4) and 2.365 (4) Å do not differ significantly. However, the μ_3-PMe group in (3) does not cap symmetrically: at 2.350 (5) Å, one of the Os—P distances is significantly longer than the remaining two, 2.318 (5) and 2.317 (5) Å.

Comment

Many structure determinations have been reported of triosmium carbonyl clusters containing terminal phosphines but there are relatively few reports of such clusters with bridging (μ_2) PR_2 ligands

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