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cis-Bis[1,3-bis(2-fluorophenyl)triazenido-κ^2N^1,N^3]bis(pyridine-κN)cadmium(II)

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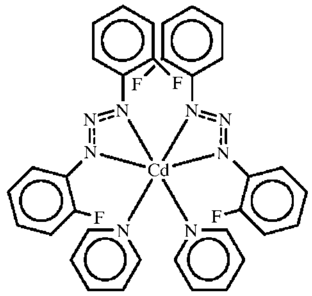
In the title compound, $[Cd(C_{12}H_8F_2N_3)_2(C_5H_5N)_2]$, the Cd atom lies on a crystallographic twofold axis in space group *Iba*2. The coordination geometry about the Cd^{II} ion corresponds to a rhombically distorted octahedron, with two deprotonated 1,3-bis(2-fluorophenyl)triazenide ions, *viz*. $FC_6H_4NNNC_6H_4F^-$, acting as bidentate ligands (four-electron donors). Two neutral pyridine (py) molecules complete the coordination sphere in positions *cis* with respect to one another. The triazenide ligand is not planar (r.m.s. deviation = 0.204 Å), the dihedral angle between the phenyl rings of the terminal 2-fluorophenyl substituents being 24.6 (1)°. The triazenide and pyridine Cd—N distances are 2.3757 (18)/2.3800 (19) and 2.3461 (19) Å, respectively. Intermolecular C—H⋯F interactions generate sheets of molecules in the (010) plane.

Comment

The synthesis of the first cadmium(II) 1,3-diaryl-substituted triazenide complex, $Cd(ArNNNAr)_2$ (Ar = *p*-$C_6H_4NO_2$), was reported in 1887, while the analogous complex with 1,3-diphenyltriazene was prepared in 1963 (Moore & Robinson, 1986, and references therein). More recently, cadmium(II) diaryltriazenide complexes have received attention in connection with the spectrophotometric determination of cadmium based on the chromogenic behaviour of triazene derivatives (Hayashibe & Sayama, 1996). To date, only two diaryltriazenide cadmium(II) complexes have been characterized by single-crystal X-ray diffraction, namely $[Cd\{PhN_3(H)C_6H_4N_3(H)Ph\}\{PhN_3C_6H_4N_3(H)Ph\}_2]$, (II), in which the Cd atom is coordinated by one neutral 1,2-bis(phenyltriazeno)benzene ligand and two monodentate 1-(phenyltriazenido)-2-(phenyltriazeno)benzene anions in a distorted-tetrahedral arrangement, and $K[Cd(O_2NC_6H_4NNNC_6H_4NO_2)_3]$, (III), an anionic cadmium complex in which the Cd atom is coordinated in a trigonal-prismatic arrangement by three chelating deprotonated 1,3-bis(4-nitrophenyl)triazenide ions (Hörner *et al.*, 1996; Hörner, Carratu *et al.*, 2003). In this work, we report the synthesis and structural characterization of the title complex, (I), an axially symmetric mononuclear Cd^{II} complex with a symmetrically disubstituted 1,3-diaryltriazenide ion and pyridine (py) as ligands.



(I)

Complex (I) has a structure analogous to that of the related Co^{II} complex $[Co(C_{12}H_{10}N_3)_2(C_5H_5N)_2]$, (IV) (Peng *et al.*, 1985). The crystal structure of (I) consists of discrete mononuclear complexes in which the Cd^{II} ion has a rhombically distorted octahedral coordination geometry. Two deprotonated 1,3-bis(2-fluorophenyl)triazenide ions act as (N11)-η^1,(N13)-η^1 bidentate (four-electron donor) ligands, while two neutral pyridine molecules are coordinated *cis* with respect to one another (Fig. 1).

In the molecule of (I), which has site symmetry 2, the Cd^{II} ion is located in a distorted square-planar base formed by atoms N13, N13^i, N31 and N31^i [r.m.s. deviation = 0.286 Å; symmetry code: (i) $-x, 1-y, z$]. The crystallographic twofold-symmetry axis bisects the N13—Cd—N13^i [89.09 (9)°] and N31—Cd—N31^i [91.40 (10)°] angles, and the N11—Cd—N11^i axial angle [141.42 (8)°]. These values are in good agreement with the angles found in (IV) [N3—Co—N3^i = 90.3 (1)°, N4—Co—N4^i = 89.6 (1)° and N1—Co—N1^i = 149.6 (1)°, *i.e.* Co is also on a twofold axis; Peng *et al.* (1985)].

As a result of the bidentate coordination mode of the triazenide ligand, the N—N bond lengths are equal to within three standard deviations, with a mean value of 1.307 (4) Å (Table 1). These bond lengths are longer than the typical value for a double bond (1.24 Å; *International Tables for Crystallography*, 1995, Vol. C), and are similar to the N—N distances observed in the anionic triazenide complex (II) [1.310 (5) and 1.317 (6) Å]. On the other hand, both the N11—C11 [1.398 (3) Å] and N13—C21 [1.405 (3) Å] bonds are shorter than expected for an N—C$_{aryl}$ single bond (1.452 Å for secondary amines, NHR_2, with $R = Csp^2$; Orpen *et al.*, 1989). These values, together with the observed N—N bond distances, which imply partial double-bond character, provide evidence for the delocalization of the π electrons on the N—N=N triad towards the terminal 2-fluorophenyl substituents.

The Cd—N11 [2.3757 (18) Å] and Cd—N13 [2.3800 (19) Å] bonds are both longer than the sum of the covalent radii (2.27 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960) and correspond to covalent single bonds. These values are in good agreement

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with those found in (II) [2.350 (5) and 2.397 (4) Å] and (III) [2.350 (4) and 2.376 (4) Å].

The bidentate coordination mode of the triazenide ligand, together with the acute N11—Cd—N13 angle [53.33 (6)°], give rise to a strained Cd/N11–N13 four-membered ring. The bond angle of the triazenide moiety [109.46 (17)°] deviates only slightly from the angles observed in complexes such as *trans*-[Pd(FC$_6$H$_4$—N═N—NC$_6$H$_4$NO$_2$)$_2$(C$_5$H$_5$N)$_2$] [111.0 (3)°; Hörner *et al.*, 2002] and [Au(O$_2$NC$_6$H$_4$N═N—N—C$_6$H$_4$NO$_2$)-{P(C$_6$H$_5$)$_3$}] [110.0 (4)°; Hörner, Casagrande *et al.*, 2003], in which the triazenide ligand is monodentate.

The terminal 2-fluorophenyl substituents form a dihedral angle of 24.6 (1)°, indicating the lack of planarity of the triazenide ligand.

The crystal structure of (I) reveals molecules linked into chains along the [001] direction *via* intermolecular C—H···F interactions [C24^{ii}···F1 = 3.351 (3) Å and C24^{ii}—H24^{ii}···F1 = 101.12°; symmetry code: (ii) $-x$, y, $-\frac{1}{2}+z$]; these chains, related by the axial *c*-glide plane, generate sheets of molecules in the (010) plane (Fig. 2). These values are comparable to those found for C—H···F interactions in the crystal structure of the fluorobenzene C$_6$HF$_5$ (C6···F11 = 3.46 Å and C6—H1···F11 = 120.4°; Thalladi *et al.*, 1998).

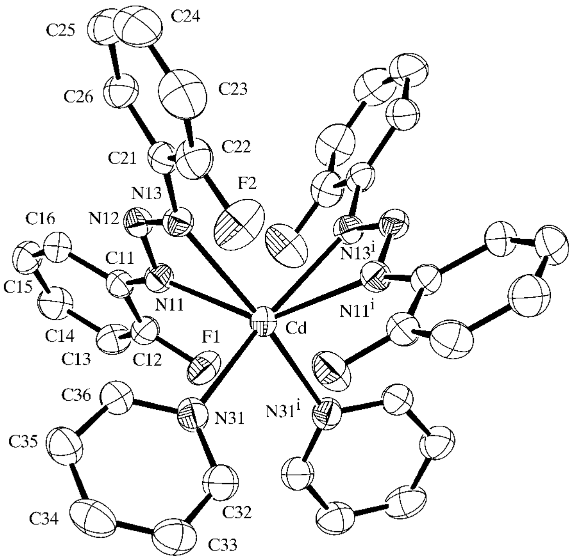

Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids for non-H atoms. H atoms have been omitted for clarity. [Symmetry code: $-x$, $1-y$, z.]

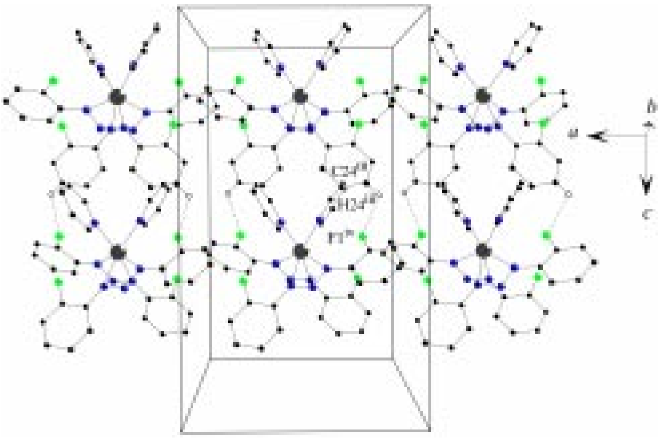

Figure 2
The unit cell of (I), in a view slightly inclined from [010]. The intermolecular C—H···F interactions are shown as dashed lines. [Symmetry codes: (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, z; (iv) $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$.]

The pyridine ring (N31/C32–C36) makes a dihedral angle of 56.4 (6)° with the N11—Cd—N11^{i} moiety. The Cd—N31 bond distance [2.3461 (19) Å] in (I) is longer than the sum of the covalent radii (2.27 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960) and is comparable to the mean Cd—N bond length found in Cd(py)$_4$Cr$_2$O$_7$ [2.347 (5) Å; Norquist *et al.*, 2001].

Experimental

Yellow 1,3-bis(2-fluorophenyl)triazene (46.6 mg, 0.2 mmol) was dissolved in methanol (20 ml) and treated with two pellets of KOH, whereupon the solution changed colour to deep red. A solution of cadmium(II) acetate dihydrate (26.7 mg, 0.1 mmol) in methanol (10 ml) was added slowly with continuous stirring; the reaction mixture changed colour to orange–red. The mixture was stirred for 1 h at room temperature, after which pyridine (2 ml) was added and stirring continued for a further 24 h. Orange–red prism-shaped crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvent at room temperature (yield 42.6 mg, 58%; m.p. 413 K).

Crystal data

[Cd(C$_{12}$H$_8$F$_2$N$_3$)$_2$(C$_5$H$_5$N)$_2$]
M_r = 735.03
Orthorhombic, *Iba*2
a = 9.835 (3) Å
b = 19.229 (2) Å
c = 16.750 (6) Å
V = 3167.6 (15) Å^3
Z = 4
D_x = 1.541 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.7–14.0°
μ = 0.75 mm^{-1}
T = 208 (2) K
Prism, orange–red
0.35 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Spek, 1990)
$T_{\min}$ = 0.779, $T_{\max}$ = 0.864
4462 measured reflections
3800 independent reflections
3233 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 28.0°
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 25$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.053
S = 1.03
3800 reflections
214 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.7633P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ < 0.001
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00193 (13)
Absolute structure: Flack (1983), 1829 Friedel pairs
Flack parameter = −0.03 (2)

Table 1
Selected geometric parameters (Å, °).

Cd—N31	2.3461 (19)	N11—C11	1.398 (3)
Cd—N11	2.3757 (18)	N12—N13	1.303 (3)
Cd—N13	2.3800 (19)	N13—C21	1.405 (3)
N11—N12	1.311 (2)		
N31—Cd—N31^i	91.40 (10)	N31—Cd—N13	91.44 (6)
N31—Cd—N11	94.24 (6)	N11^i—Cd—N13	97.26 (6)
N31^i—Cd—N11	112.80 (6)	N11—Cd—N13	53.33 (6)
N11^i—Cd—N11	141.42 (8)	N13^i—Cd—N13	89.09 (9)
N31—Cd—N13^i	166.03 (6)	N13—N12—N11	109.46 (17)

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

The positional parameters of the H atoms were obtained geometrically and refined as riding (C—H = 0.93 Å for Csp^2 atoms), with isotropic displacement parameters of $1.2U_{\rm eq}$ of the attached Csp^2 atom. Friedel opposites were not averaged before refinement. The Flack (1983) parameter was obtained by refinement. The F atoms show large thermal motion, indicated by their elongated displacement ellipsoids (Fig. 1). Split peaks for these atoms were not observed and consequently a disorder model was not used.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1048). Services for accessing these data are described at the back of the journal.

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