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A three-dimensional framework formed from cadmium(II) cyanide and 1-methylimidazole

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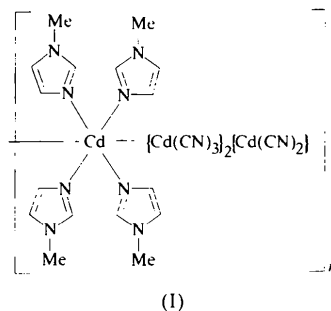
Abstract

The three-dimensional structure of octacyanotetrakis(1-methylimidazole-*N*³)tetracadmium(II) clathrate, [Cd₄(CN)₈(C₄H₆N₂)₄], contains three kinds of Cd atoms, *i.e.* tetrahedral Cd1 and octahedral Cd2 and Cd3 in a 2:1:1 ratio; atoms Cd2 and Cd3 lie on inversion centres. The Cd1 and Cd2 centres are coordinated by four and six cyano groups, respectively. The Cd3 centre is coordinated by two cyano groups and four 1-methylimidazole ligands. The three-dimensional framework provides hexagonal channels which are occupied by 1-methylimidazole ligands coordinated to the Cd3 centre.

Comment

The synthesis and characterization of polymeric multi-dimensional frameworks is of great current interest be-

cause they may be useful as catalysts, molecular sieves, optical materials *etc* (Haushalter & Mundi, 1992). As a strategy for designing infinite frameworks using cyanometallate complex hosts, Iwamoto and co-workers (Iwamoto, 1991) have employed various complementary ligands for stabilizing multi-dimensional structures. They have obtained various types of polymeric structures, such as one-dimensional chains, two-dimensional layers and three-dimensional networks (Iwamoto, 1996). Recently, Kim (1996) has studied imidazole as a complementary ligand for designing novel multi-dimensional frameworks and reported the variations of ligating behaviour of the imidazole and host topology in the resulting multi-dimensional structures. As an extension of that study, we have introduced 1-methylimidazole as a complementary ligand. We report here the novel structure of octacyanotetrakis(1-methylimidazole-*N*³)tetracadmium(II) clathrate, [Cd₄(CN)₈(C₄H₆N₂)₄], (I).



As shown in Figs. 1 and 2, the structure of (I) has cyanide bridges between the three kinds of Cd atoms, *i.e.* tetrahedral Cd1 and octahedral Cd2 and Cd3 in a 2:1:1 ratio. Cd1 is tetrahedrally coordinated by four cyano groups, Cd2 is octahedrally coordinated by six cyano groups, and Cd3 is octahedrally coordinated by two cyano groups and four 1-methylimidazole ligands. The tetrahedral Cd1 centre is linked to three octahedral Cd2 and one octahedral Cd3 *via* cyanide bridging ligands, the octahedral Cd2 centre is linked to six tetrahedral Cd1 centres *via* cyanide bridging ligands, and the octahedral Cd3 centre is linked to two tetrahedral Cd1 centres *via* cyanide bridging ligands and is also coordinated by four 1-methylimidazole ligands. The Cd—C and Cd—N bond lengths and angles (Table 1) are similar to those reported previously (Kim, 1996). The geometry of the 1-methylimidazole ligand is as expected.

As shown in Fig. 2, the three-dimensional host framework contains channels running in the *b* direction. These elongated hexagonal channels are occupied by the 1-methylimidazole ligands coordinated to the Cd3 centre. In this crystal structure, the 1-methylimidazole ligand appears to play two roles in building up the host framework; one is to block a coordination site of the Cd atom and the other is to occupy the channel space.

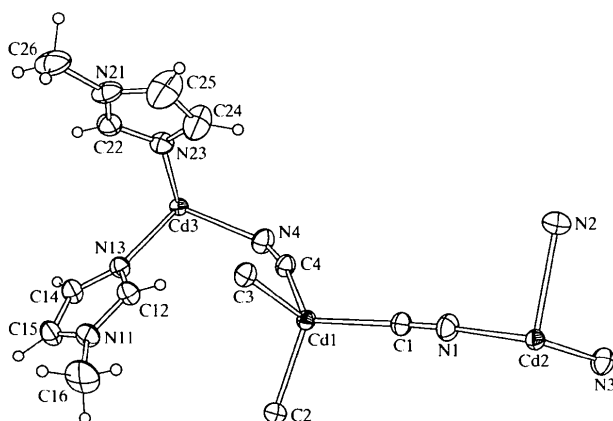


Fig. 1. The asymmetric unit of (I) with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. H atoms are shown as small circles of arbitrary radii.

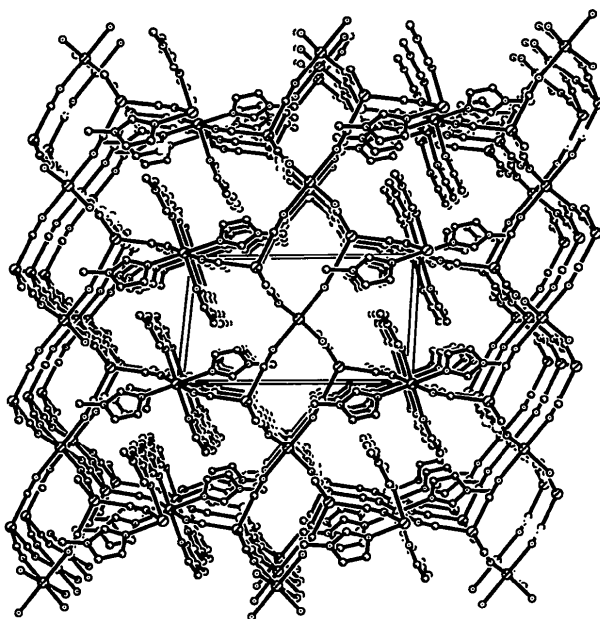


Fig. 2. Perspective view of the unit cell of (I) along the *a* axis. H atoms have been omitted for clarity.

Experimental

To an aqueous solution (200 ml) containing $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (2.28 g, 10 mmol) and $\text{K}_2[\text{Cd}(\text{CN})_4]$ (2.94 g, 10 mmol), 1-methylimidazole (1.6 ml, 20 mmol) was added. The pH of the solution was adjusted to 9 by adding 2-aminoethanol and citric acid. After the small amount of precipitate which formed was filtered off, the aqueous solution was allowed to stand in a refrigerator at 278 K. After a few weeks, colourless crystals were obtained.

Crystal data

$[\text{Cd}_4(\text{CN})_8(\text{C}_4\text{H}_6\text{N}_2)_4]$
 $M_r = 986.19$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Triclinic

$P\bar{1}$

$a = 8.3898 (10) \text{ \AA}$

$b = 8.7094 (9) \text{ \AA}$

$c = 13.8304 (17) \text{ \AA}$

$\alpha = 89.695 (9)^\circ$

$\beta = 79.108 (6)^\circ$

$\gamma = 62.568 (9)^\circ$

$V = 876.92 (18) \text{ \AA}^3$

$Z = 1$

$D_x = 1.867 \text{ Mg m}^{-3}$

$D_m = 1.87 \text{ Mg m}^{-3}$

D_m measured by flotation in mesitylene/bromofrom

Cell parameters from 39 reflections

$\theta = 5.02\text{--}12.50^\circ$

$\mu = 2.432 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block

$0.48 \times 0.37 \times 0.21 \text{ mm}$

Colourless

Data collection

Siemens *P4* diffractometer

$2\theta/\omega$ scans

Absorption correction:

empirical (North *et al.*, 1968)

$T_{\min} = 0.323$, $T_{\max} = 0.600$

4851 measured reflections

4025 independent reflections

3838 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\text{max}} = 27.5^\circ$

$h = -1 \rightarrow 10$

$k = -10 \rightarrow 11$

$l = -17 \rightarrow 17$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.077$

$S = 1.174$

4025 reflections

203 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2$

$+ 0.8502P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.773 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.906 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL97

Extinction coefficient:

0.0471 (12)

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cd1—C1	2.205 (3)	Cd2—N1	2.335 (3)
Cd1—C2	2.217 (3)	Cd2—N2	2.349 (3)
Cd1—C4	2.221 (3)	Cd3—N23	2.292 (3)
Cd1—C3	2.241 (3)	Cd3—N13	2.335 (3)
Cd2—N3	2.323 (3)	Cd3—N4	2.430 (3)
C1—Cd1—C2	109.49 (13)	N3—Cd2—N1	88.97 (12)
C1—Cd1—C4	122.18 (13)	N3—Cd2—N2	92.93 (12)
C2—Cd1—C4	107.49 (13)	N1—Cd2—N2	91.54 (11)
C1—Cd1—C3	104.47 (13)	N23—Cd3—N13	85.02 (11)
C2—Cd1—C3	110.17 (13)	N23—Cd3—N4	90.18 (12)
C4—Cd1—C3	102.46 (13)	N13—Cd3—N4	91.93 (11)

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1056). Services for accessing these data are described at the back of the journal.

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A coordination compound of (–)-ephedrine and palladium(II)

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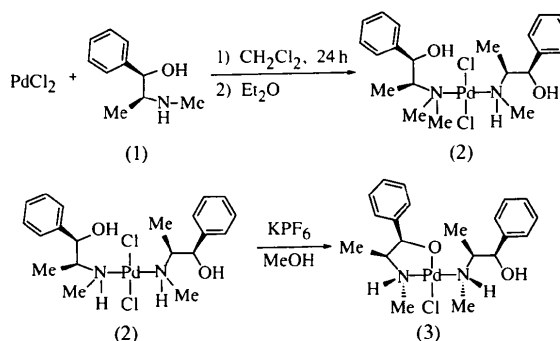
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Abstract

The reaction of (–)-ephedrine with PdCl₂ in the presence of NaPF₆ leads to chloro[(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol-*N*][(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-olato-*N,O*]palladium(II), [PdCl(C₁₀H₁₄NO)(C₁₀H₁₅NO)]. The crystal structure determination shows two (–)-ephedrine [(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol] ligands, one as a chelating moiety and the other as a monodentate ligand in which only the N atom is coordinated to the Pd^{II} atom. An extensive hydrogen-bond network ensures the three-dimensional cohesion of the atomic arrangement.

Comment

Complexes of Pd^{II} are of interest both in radio-pharmaceutical chemistry as β-emitters for radiotherapy applications (with ¹¹¹Pd) and in homogeneous catalysis. Ephedrine derivatives have aroused increasing interest as chiral ligands for catalytic enantioselective reactions (Mortezaei *et al.*, 1988), such as the asymmetric tautomerization of prochiral enols produced under Pd-induced domino reactions (Jamal Aboulhoda *et al.*, 1995) or the Pd-catalyzed enantioselective hydrogenation of α,β-unsaturated ketones (Thorey *et al.*, 1996). Very recently, complexes formed by the coordination of enantiopure β-amido alcohols to cationic η³-allylpalladium units have been suggested by Bäckvall's group as the most important intermediates for the enantioselective 1,4-dialkoxylation of 1,3-dienes (Itami *et al.*, 1998), the chiral ligands being synthesized from β-amino alcohols and hydroquinone-type compounds (for the coordination of racemic β-amino alcohols to Pd^{II}, see Andrieu *et al.*, 1998). Although van Koten's group has already characterized alkoxopalladium(II) complexes derived from achiral amino alcohol ligands (Kapteijn *et al.*, 1997), little is known about the structure of their chiral counterparts. Therefore, a part of our work has concerned the complexation of (–)-ephedrine, (1), and palladium chloride and we present here the characterization of a new and unexpected Pd^{II} complex, namely chloro[(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-ol-*N*][(1*R*,2*S*)-2-methylamino-1-phenylpropan-1-olato-*N,O*]palladium(II), (3), obtained under particular experimental conditions.



The reaction of PdCl₂ with two equivalents of (1) at room temperature leads to a new compound identified as (2) from IR and NMR spectroscopic and elemental analysis (see Scheme above). Crystallization of (2) under special conditions (see *Experimental*) led to compound (3), whose crystal presents characteristics suitable for X-ray analysis (see Scheme above).

The X-ray structure of (3) (Fig. 1) shows the unusual structure of this complex. One of the two amino alcohol ligands is selectively deprotonated to give an *N,O*-chelate, resulting in the expulsion of one chloride ligand, while the other amino alcohol ligand remains coordinated to Pd^{II} through the N atom. To our knowl-