Crystal Structure of Cadmium Hexacyanopalladate(IV)

By **Hans-Jorg Buser, Gideon Ron, and Andreas Ludi,*** Institut für Anorganische Chemie, Universität Bern, CH 3000 Bern 9, Switzerland
Peter Engel, Abteilung für Kristallographie, Universität Bern, CH 3012 Bern, Switzerland

The crystal structure of the title compound has been determined from diffractometer data. Crystals are cubic, $a = 10{\cdot}911(4)$ Å, $Z = 4$, space group $Fm3m$. The structure has been refined by least-squares techniques to R 0·057 for 172 observed independent reflections. Interatomic distances are: Pd–C 2·07(2), Cd–N 2·27(3), and C–N 1·11(4) Å.

THE crystal structures of a variety of cubic polynuclear transition-metal cyanides have been described in terms of a general structural model.[1] Corresponding crystallographic studies have been carried out so far with compounds of the composition $M^{II}_3[M^{III}(CN)_6]_2,xH_2O$. A particular property of these structures is given by a stoicheiometrically determined fraction of vacant lattice sites which are assumed to occur completely at random.[2] In the case of $Cd[Pd(CN)_6]$ the general model predicts a three-dimensional framework without vacancies. The present X-ray study was undertaken to test the validity of our general structural description. The determination of this structure was further initiated by the lack of structural data for cyano-complexes of palladium(IV).

EXPERIMENTAL

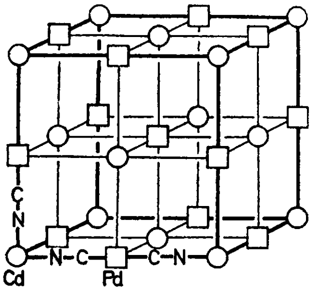
Crystals of $Cd[Pd(CN)_6]$ were prepared as described in ref. 2. The crystal used was a cube, *ca.* 0·10 × 0·10 × 0·09 mm.

Crystal Data.—$Cd[Pd(CN)_6]$, $M = 374{\cdot}9$ cubic, $a = 10{\cdot}911(4)$ Å, $U = 1299$ Å^3, $D_m = 1{\cdot}92(1)$ (by flotation), $Z = 4$, $D_c = 1{\cdot}92$, $F(000) = 688$. Filtered Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 29·5 cm^{-1}. Systematic absences: hkl if $h + k, k + l, l + h = 2n + 1$, face-centred; space group O_h^5, $Fm3m$ (by convention).[1]

The unit-cell parameter, a, was determined from silicon-calibrated high-angle Weissenberg photographs by use of Cu-K radiation [a(Si) 5·4308 Å]. Intensities for the layers $h0$—$14l$ were collected by use of a semi-automatic Supper-Pace diffractometer equipped with a scintillation detector. Scan rates were 0·5—1° min^{-1}, scan widths 2—3°. One octant of the orthorhombically indexed reciprocal lattice was included in the data collection. 541 (172 independent) reflections having $I > 2{\cdot}33\sigma(I)$ were considered observed.[3] Only 14 (13 independent) reflections with odd indices were observed.

Data reduction, including corrections for Lorentz and polarization effects but not for absorption, was carried out by use of an IBM 1620 computer. The 'X-Ray' system[4] implemented on a CDC 6400/6500 computer was used for refinement.

Solution and Refinement.—The X-ray intensities were overwhelmingly dominated by reflections with only even indices. Only a very few extremely weak reflections with odd indices were observed, which is not surprising since the scattering factors of Cd and Pd and of C and N are very similar. The dominating reflections with even indices defined a cubic primitive pseudo-cell with $a = 5{\cdot}45$ Å, *i.e.* half the edge of the complete face-centred cell. Because of the existence of the pseudo-mirror-plane intersecting the sequence M–C–N–M′, the even-index reflections did not allow a distinction to be made between Cd and Pd, or between C and N. The small number and the low intensity of the odd-index reflections provided insufficient information for us conclusively to distinguish between the possible ordered arrangements Pd–C–N–Cd and Pd–N–C–Cd, or the disordered structure (Cd,Pd)–(C,N)–(C,N)–(Cd,Pd). Further experimental data, in addition to X-ray intensities, had therefore to be used. Chemical intuition predicted the linkage Pd–C–N–Cd, by consideration of the structures of other cadmium–cyanometallates.[1] This arrangement, *i.e.* $[PdC_6]$ and $[CdN_6]$ octahedra, is in complete agreement with X-ray photoelectron spectra. The ionization potentials of the $3d_{3/2}$, $3d_{5/2}$, and $4d$ orbitals of Cd in $Cd[Pd(CN)_6]$ are 419·8, 413·0, and 19·4 eV.[5] The corresponding values for $Cd_3[Cr(CN)_6]_2,xH_2O$ with nitrogen-co-ordinated Cd are 419·6, 412·8, and 19·3 eV.[5] Conclusive evidence for the linkage Pd–C–N–Cd is also furnished by i.r. spectroscopy. The CN stretching vibration (cm^{-1}) occurs at 2145 for $K_2[Cd(CN)_4]$,[6] 2185 for $K_2[Pd(CN)_6]$,[7] and 2223 for $Cd[Pd(CN)_6]$,[2] thus showing its typical shift from a mono- to a poly-nuclear cyanide.[8] The solution of the crystal structure of $Cd[Pd(CN)_6]$ therefore relied on conclusions obtained from spectroscopic experiments, which clearly showed the linkage to be Pd–C–N–Cd. Throughout the structural calculations the distinction between Cd and Pd and between C and N was made, even though it was not apparent from consideration of the X-ray intensities.



Unit cell of $Cd[Pd(CN)_6]$ with most of the C and N atoms omitted for clarity

Since the unit cell contains four formula units $Cd[Pd(CN)_6]$, the metal atoms Cd and Pd have to occupy the two four-fold positions 4*a* and 4*b* of space group $Fm3m$ (see Figure), so

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that carbon and nitrogen are on two non-equivalent sets of the twenty-four-fold position 24*e*. Only two positional parameters, *x*(C) and *x*(N) had therefore to be determined. Atomic scattering factors from ref. 9 were used for all atoms with corrections for the effects of anomalous dispersion for the two metal atoms. Starting parameters for the least-squares refinement were chosen by consideration of the C–N and Cd–N distances in $Cd_3[Cr(CN)_6]_2,xH_2O$.[10]

The starting thermal parameters affected the phase angle of the odd-index reflections, because for these reflections the contribution of the two metal atoms to the structure factor was almost equal, but opposite in sign. All even-index reflections, however, have zero phase-angle (disregarding the effects of anomalous dispersion), because all metal atoms scatter in-phase with the Cd atom at the origin. Two least-squares calculations were carried out, starting with $B(Cd) > B(Pd)$, and $B(Cd) < B(Pd)$, respectively, in order to distinguish between the two possible sign assignments for the odd reflections. The function minimized was $\Sigma w(F_o - F_c)^2$ and the weight was chosen [3] as $1/\sigma^2(F_o)$. After four cycles of isotropic refinement for both cases, all parameter shifts were $<\sigma$. Results are presented in Table 1. The *R* factors and the C–N distances clearly favour the assignment of a positive sign to the structure factors with odd indices. Final parameters, corresponding to *R* 0·057, are in Table 2. Final observed and calculated structure factors are in Supplementary Publication No. SUP 21079 (3 pp., 1 microfiche).* A difference-Fourier map, calculated with the final parameters, showed a diffuse maximum around $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, corresponding to *ca.* 25% of the electron density of the carbon atom, and may be assigned to some residual zeolitic water molecules. Such zeolitic water molecules located within the cell octants have been found in the structures of other polynuclear cyanides.[1] Analytical data [2] for $Cd[Pd(CN)_6]$ indeed show a small amount of water corresponding to about two water molecules per unit cell.

TABLE 1

Results from least-squares calculations for phase assignment

		+ ve *	−ve *
All reflections	*R*	0·057	0·062
	R′	0·034	0·033
Odd only	*R*	0·231	0·326
	R′	0·107	0·188
B/Å²	Cd	0·73	3·6
	Pd	3·7	0·64
	C	4·1	2·0
	N	4·6	10
C–N/Å		1·11	1·03

* Sign of most odd-index structure factors.

TABLE 2

Atomic co-ordinates (fractional) and thermal parameters, with estimated standard deviations in parentheses

	x	*y*	*z*	*B* (mean)
Cd	0	0	0	2·2(2)
Pd	0·5	0	0	
C	0·3102(30)	0	0	4·4(7)
N	0·2081(18)	0	0	

RESULTS AND DISCUSSION

The poor distinction between Cd and Pd by the *X*-ray intensities is reflected by a least-squares correlation coefficient of −0·81 between the two thermal parameters. The corresponding value for C and N is −0·84. The mean values *B*(Cd,Pd) and *B*(C,N) are therefore more meaningful than the individual temperature factors.

The crystal structure of $Cd[Pd(CN)_6]$ fits completely within the general scheme of the structural chemistry of polynuclear transition-metal cyanides. It consists of an uninterrupted cubic Pd–C–N–Cd framework. Both metal ions sit in a perfectly octahedral co-ordination geometry with the following interatomic distances: Pd–C 2·07(2), Cd–N 2·27(3), and C–N 1·11(4) Å. Since no other data for the bond-length Pd^{IV}–C are available, this distance may be compared with the isoelectronic Ru^{II}–C bond distance (2·03 Å) in $Mn_2[Ru(CN)_6],8H_2O$.[11] The values of the Cd–N and C–N distances are in agreement with those found in other cyano-compounds.[1,12]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

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