Synthesis, crystal and electronic structure of Cd_2PCl_2: influence of cation on characteristic structural features of pnictide halides of Group 12 metals*

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Cadmium phosphide chloride Cd_2PCl_2 was prepared by the ampule synthesis method at 770 K. Crystals were obtained from the gaseous phase by the chemical transport reaction. The crystal structure of Cd_2PCl_2 is built of the P_2Cd_6 octahedra, which are linked in layers by sharing four equatorial vertices. The layers alternate in a fashion analogous to that observed in the K_2NiF_4 structural type and are linked in a three-dimensional framework through the halogen atoms. The characteristic features of the crystal and electronic structures of pnictide halides M_2PCl_2 (M = Cd or Hg) were considered based on X-ray diffraction data and results of quantum-chemical calculations.

Key words: cadmium, mercury, pnictide halides, crystal and electronic structure.

Cadmium and mercury pnictide halides belong to a broad family of ternary and quaternary phases. The main data on their crystal structures have been surveyed in the review.[1] In all phases, except for the Cd_8As_7Cl compound[2] having a unique crystal structure, the coordination environment about the pnictogen atoms is tetrahedral regardless of the presence or absence of the homonuclear pnictogen—pnictogen bonds. At the same time, the coordination environment about the cadmium and mercury atoms varies from regular octahedral[3] to nearly linear.[3,4] In spite of the fact that the stoichiometry of cadmium pnictide halides is often identical with that of mercury pnictide halides, these compounds have different crystal structures due to the difference in the coordination preference of these metals. In particular, supramolecular ensembles based on the metal—pnictogen frameworks, which are very typical of mercury,[5—12] are rarely observed for cadmium due to the fact that the linear coordination is atypical of the latter metal. Only two such compounds, *viz.*, $Cd_7P_4Cl_6$ [3] and $Cd_5P_2Br_4$,[4] are known.

In the present work, we synthesized cadmium pnictide halide Cd_2PCl_2 and studied its crystal and electronic structure. The possibility of the existence of this compound was predicted as early as 1963.[13] However, this prediction was not further confirmed.[14,15] Three other phases, *viz.*, Cd_2P_3Cl,[16] $Cd_4P_2Cl_3$,[3,13] and $Cd_7P_4Cl_6$,[3] were proved to be the only thermodynamically stable phases in the Cd—P—Cl system. By contrast, cadmium and mercury pnictide halides with the 2 : 1 : 2 stoichiometry have been documented in other systems and possess crystal structures similar to that of Cd_2PCl_2.[14,17—19] Hence, we believed that the absence of Cd_2PCl_2 was associated only with the conditions of its synthesis. The main aim of the present study was to synthesize Cd_2PCl_2, determine its structure, analyze differences between the Cd- and Hg-containing phases, and examine the relationship between the crystal and electronic structures associated with the possibility of the construction of inorganic supramolecular architectures based on metal—pnictogen frameworks.

Results and Discussion

The Cd_2PCl_2 compound was prepared by the standard ampule synthesis. We failed to prepare an individual phase upon annealing of a stoichiometric mixture by varying the temperature and annealing time. The maximum yield of the product was attained upon annealing at 770 K for 12 days with intermediate grindings. However, powder X-ray diffraction of the samples thus prepared also revealed the presence of impurities, among which only $Cd_7P_4Cl_6$ was identified. Based on analysis of the intensities of the reflections in X-ray diffraction patterns, we estimated the total content of impurities at 10—15%. The use of a larger number of intermediate grindings as well as quenching of the sample did not increase the yield of the product.

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* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 548—553, March, 2003.

We succeeded in isolating a single-phase sample and preparing single crystals suitable for X-ray diffraction analysis after the addition of tin to a mixture of the starting reagents. Apparently, crystals were grown from the gaseous phase according to the chemical transport reaction due to a certain temperature gradient in the ampule (1—3 °C). Presumably, tin chloride that formed in the course of the process served as the transporting agent. Earlier, we have demonstrated[20] that thermodynamically unstable phases could be prepared with the use of tin halides as transporting agents. Yellow crystals synthesized by the chemical transport reaction were selected mechanically in an amount necessary for powder X-ray diffraction analysis. The experimental X-ray diffraction pattern was consistent with that calculated from the structural data.

The crystal structure of Cd_2PCl_2 was studied by single-crystal X-ray diffraction analysis (Table 1, Fig. 1). The structure consists of the P_2Cd_6 octahedra as building blocks, inside each octahedron two closely spaced phosphorus atoms being located. The distance between the phosphorus atoms (2.18 Å) is close to the P—P single bond length.[21] The phosphorus atoms are located on the threefold pseudoaxis of the octahedron and each atom is bound to three cadmium atoms belonging to the nearest face of the octahedron to form a virtually regular tetrahedron.

Two independent cadmium atoms have different coordination environments. The coordination polyhedron about the Cd(1) atom is a strongly distorted tetrahedron formed by two P atoms and two Cl atoms (Fig. 2, *a*). The distortion is characterized by the P—Cd—P angle of 142°. The Cd(2) atom is surrounded by one P atom and four Cl atoms and its coordination can be described as intermediate between tetragonal-pyramidal and trigonal-bipyramidal (Fig. 2, *b*). The P—Cd(2)—Cl(2) angle is 157.4°, the Cd(2)—Cl(2) distance is very short (2.48 Å),

Table 1. Crystallographic parameters and main details of the refinement of the crystal structure of Cd_2PCl_2

Parameter	Characteristic
Formula	Cd_2PCl_2
Molecular weight	326.67
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.736(1)
b/Å	8.957(1)
c/Å	7.880(1)
β/deg	118.92(1)
V/Å^3	477.93(1)
Z	4
d_{calc}/g cm^{-3}	4.540
μ/mm^{-1}	10.149
Scan range	$3.04 < \theta < 34.39$
Number of measured reflections	2105
Number of reflections with $I \geq 2\sigma(I)$	1956
Number of refinable parameters	47
R_1 ($I \geq 2\sigma(I)$)	0.0455
wR_2 (for all reflections)	0.1334

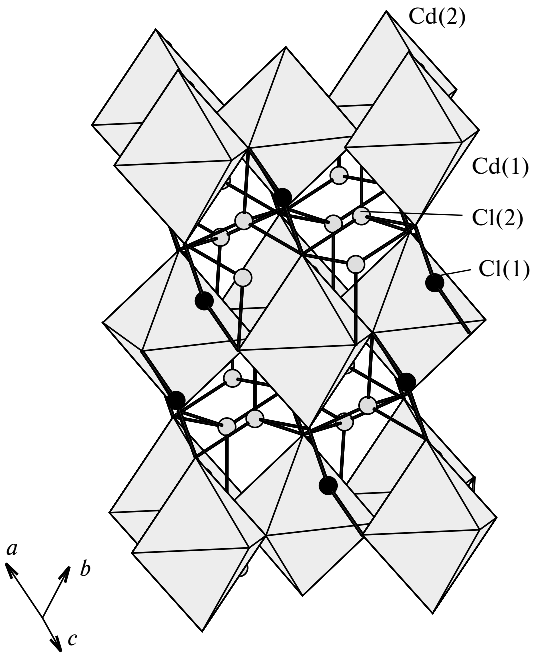

Fig. 1. Crystal structure of Cd_2PCl_2. The layers of the P_2Cd_4 octahedra and the chlorine atoms binding these layers are shown.

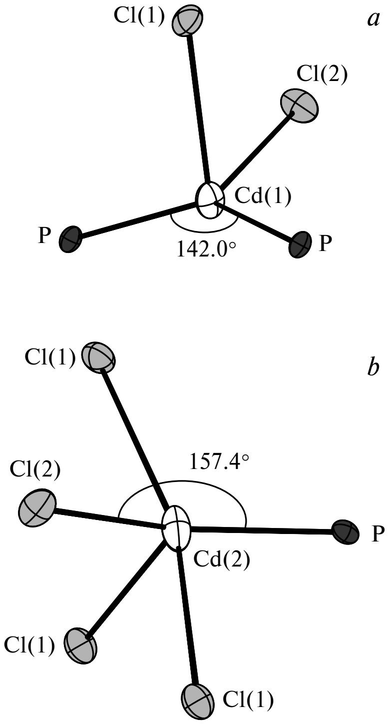

Fig. 2. Coordination about the cadmium atoms in the structure of Cd_2PCl_2 (ellipsoids are drawn at the 50% probability level).

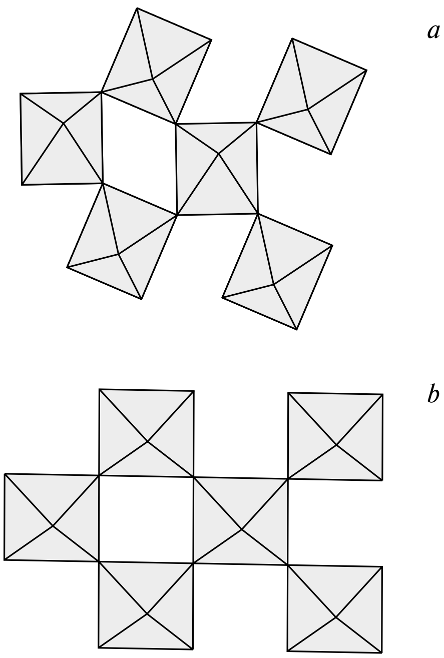

Fig. 3. Top views of the layers of the P_2Cd_4 octahedra in the crystal structure of Cd_2PCl_2 (*a*) and layers of the P_2Hg_4 octahedra in Hg_2PCl_2 (*b*).

and all other distances between the Cd and Cl atoms are substantially longer and are in the range of 2.64—2.98 Å typical of the cadmium—chlorine covalent bond (2.66 Å in $CdCl_2$,[22] 2.62—2.86 in $Cd_4P_2Cl_3$).[3]

The P_2Cd_6 octahedra share the equatorial vertices occupied by the Cd(1) atoms to form layers of the general formula P_2Cd_4 (Fig. 3). The layers are linked to each other through the chlorine atoms. The mode of alternation of the layers composed of the octahedra is typical of the K_2NiF_4 structural type.[22] Two other cadmium pnictide halides, *viz*., Cd_2AsCl_2 [14] and Cd_2SbBr_2,[17] (Table 2) belong to the same structural type. However, the difference in the relative size of the halogen and pnictogen atoms is responsible for the fact that the former compound is characterized by a stronger distortion of the coordination polyhedra about cadmium, whereas the crystal structure of the latter loses a center of symmetry. The crystal structure of Cd_2PCl_2 differs much from the structures of mercury analogs, Hg_2PCl_2 [18] and the non-isostructural Hg_2AsCl_2 compound[19] (see Table 2). Although the general motif is retained, the difference between the structures of the cadmium- and mercury-containing phases is that both the octahedra within each layer and the layers themselves in Hg_2PCl_2 are arranged "properly" in a manner similar to the K_2NiF_4 structural type (due to the fact that the P—Hg—P angle is 180°), whereas the analogous layers in Cd_2PCl_2 are rotated with respect to each other (see Fig. 3). In addition, the mercury atoms in Hg_2PCl_2 are characterized by the *trans*-2+4 coordination in which two short bonds are formed with phosphorus atoms (Hg(1) atom) or phosphorus and chlorine atoms (Hg(2) atom).

The difference between mercury- and cadmium-containing pnictide halides with the 2 : 1 : 2 stoichiometry can be attributed to different coordination requirements of Cd^{II} and Hg^{II}. The divalent mercury atoms are involved in two short collinear bonds, thus providing the formation of K_2NiF_4-like layers, whereas cadmium tends primarily to have a tetrahedral coordination, which leads to a distortion of these layers. As a consequence, the role of the halogen atoms changes. Thus, the Cl(1) atom in Cd_2PCl_2 is surrounded by the tetrahedral Cd atoms, whereas the Cl(2) atom serves as an angular bridge between the axial Cd atom of one layer of octahedra and the equatorial Cd atom of the adjacent layer. In Hg_2PCl_2, one-half of the halogen atoms are terminal.

Calculations of the band structures of Cd_2PCl_2 and Hg_2PCl_2 in the framework of the extended Hückel theory (EHT)[23] demonstrated that the individual features of the

Table 2. Crystallographic data for cadmium and mercury pnictide halides with the 2 : 1 : 2 stoichiometry

Compound	Space group	Unit cell parameters						Reference
		a/Å	*b*/Å	*c*/Å	α	β	γ	
					deg			
Cd_2PCl_2	*P*2$_1$/*n*	7.736	8.957	7.880	—	118.92	—	Present study
Cd_2AsCl_2	*P*2$_1$/*c*	7.858	9.193	8.189	—	119.95	—	14
Cd_2SbBr_2	*P*2$_1$	8.244	9.920	8.492	—	116.80	—	17
Hg_2PCl_2	*I*2/*m*	7.643	7.977	8.539	—	115.23	—	18
Hg_2AsCl_2	*C*2/*m*	13.914	8.210	8.896	—	97.61	—	19
$Hg_{19}As_{10}Br_{18}$*	$P\bar{1}$	11.255	11.348	12.295	105.73	105.72	109.15	19
Hg_2SbBr_2**	*P*2$_1$/*c* (?)	8.899	9.911	13.995	—	92.92	—	15

* Phase differs in the stoichiometry, but has a similar structure formed as a result of the ordered removal of 1/20 of the Hg atoms and 1/10 of the Br atoms. ** Crystal structure is unknown.

crystal structures of cadmium and mercury phoshpide chlorides associated with the difference in the coordination of the metal atoms are manifested in substantial differences in their band structures (Figs. 4 and 5). Analysis of the density of states (DOS) curves demonstrated that there is the separation in energy between the valence band and conduction band in the band structure of Cd_2PCl_2, the top of the valence band being composed predominantly from the p orbitals of the phosphorus atoms and the s and p orbitals of the cadmium atom. The Hg_2PCl_2

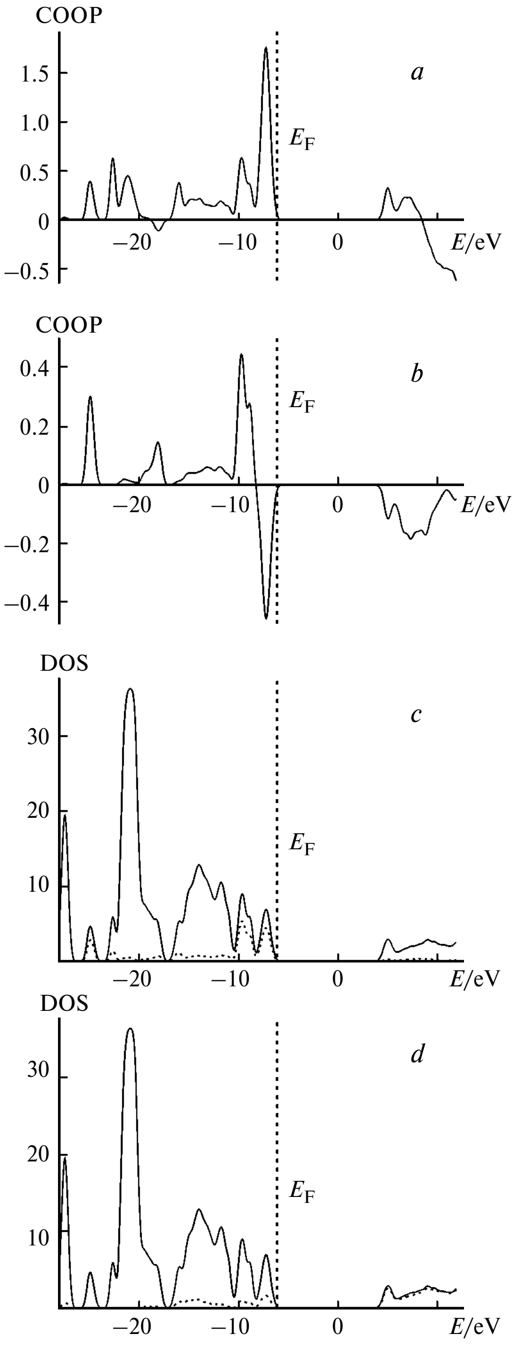

Fig. 4. Band structure of Cd_2PCl_2: *a*, COOP of the Cd—P bond; *b*, COOP of the P—P bond; *c*, total DOS and the contribution of the orbitals of the P atoms; *d*, total DOS and the contribution of the s and p orbitals of the Cd atoms.

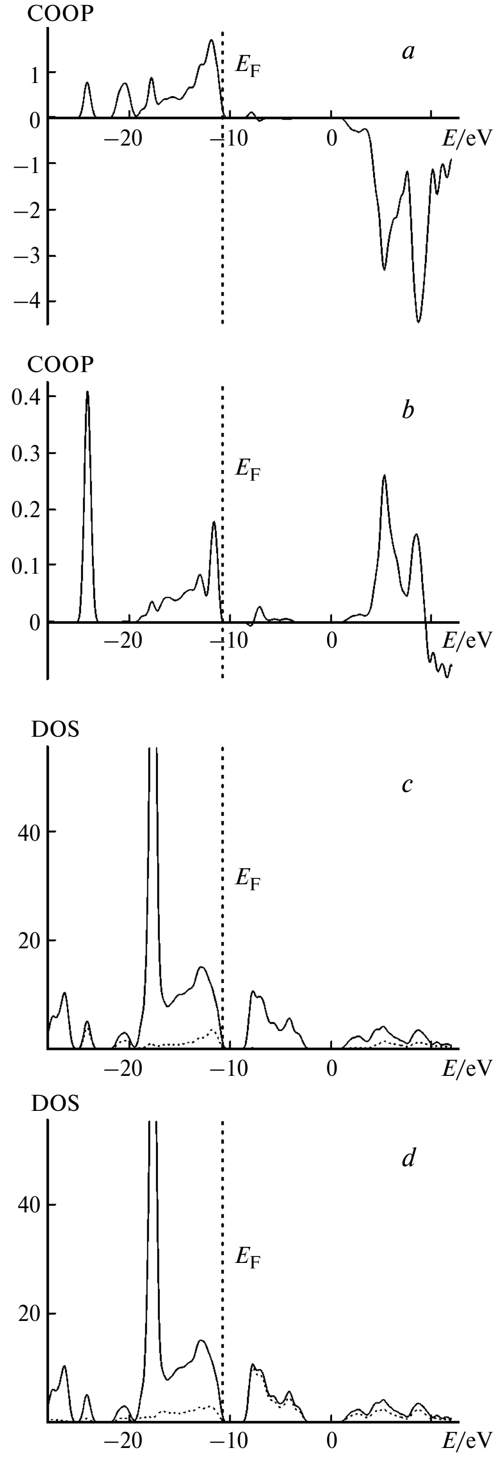

Fig. 5. Band structure of Hg_2PCl_2: *a*, COOP of the Hg—P bond; *b*, COOP of the P—P bond; *c*, total DOS and the contribution of the orbitals of the P atoms; *d*, total DOS and the contribution of the s and p orbitals of the Hg atom.

compound has a different band structure in which a rather narrow band formed almost completely from the mercury p orbitals is located between the valence and conduction bands. As can be seen from the crystal orbital overlap population (COOP) curves, these orbitals are virtually nonbonding. A more detailed analysis of orbital interactions showed that the d orbitals of mercury make a substantial contribution to the Hg—P bonding interaction at the top of the valence band. This leads to a stronger and shorter Hg—P bond compared to the Cd—P bond (2.40 [18] and 2.46—2.49 Å, respectively).

In both structures, the P—P distances have equal values. The corresponding Mulliken populations determined from the analysis of the band structures also have equal values. By contrast, the Mulliken populations of the metal—chlorine bonds are substantially different (0.11 and 0.06 for cadmium and mercury, respectively). After subtraction of the contribution of the short Cd(2)—Cl(2) bond, the corresponding Mulliken population remains virtually unchanged, whereas the subtraction of the contribution of the short Hg—Cl bond leads to a decrease in the population to 0.04. In spite of the fact that the absolute values of the Mulliken populations do not provide complete information on the bond strength, a comparison of the values of like compounds enables one to reveal the tendency for a change in the strength of covalent interactions. The results of our study demonstrated that the metal—chlorine bond in Hg_2PCl_2 is weaker than that in Cd_2PCl_2, and more remote chlorine atoms in the former structure make only a slight contribution to this bond.

Therefore, the difference in the coordination about the mercury and cadmium atoms is responsible for substantial differences in the band structures of the corresponding phosphide chlorides. The tendency of mercury to have a linear coordination atypical of cadmium is manifested, on the one hand, in the formation of "proper" layers of octahedra typical of the K_2NiF_4 structural type and, on the other hand, in the occurrence of a narrow unoccupied band formed by the p orbitals, which are not involved in covalent bonding, between the Fermi level and the conduction band. The presence of such a band in mercury-containing compounds is, apparently, the necessary condition for the formation of weak guest—host interactions in supramolecular ensembles.[7,11,12]

Experimental

High-purity cadmium (>99.99%) and red phosphorus (97%) were used as the starting compounds. Phosphorus was purified by washing with a 30% KOH aqueous solution, water, ethanol (two times), and ether followed by vacuum drying. Anhydrous cadmium chloride was synthesized by heating cadmium metal under a stream of dried HCl at 670 K followed by the purification of the product by sublimation. All operations with moisture-sensitive cadmium chloride were carried out in a dry box.

The preparation was carried out by the standard ampule synthesis. Equimolar amounts of cadmium, phosphorus, and cadmium chloride (total weight was 1 g) were placed in a quartz ampule. The ampule was sealed *in vacuo* and placed in a furnace. Annealing was carried out at 770 K for 6 days and then the mixture was annealed once again under the same conditions after intermediate grinding.

Single crystals of Cd_2PCl_2 were prepared from a mixture of cadmium chloride, phosphorus, tin, and cadmium in a molar ratio of 3 : 4 : 1 : 3. Annealing was carried out at 820 K for 2 days and then the temperature was lowered to 775 K during 6 h. The reaction mixture was kept at this temperature for 4 days and then furnace-cooled.

Powder X-ray diffraction analysis was carried out on a STADI-P (STOE) powder diffractometer (Cu-Kα_1 radiation). The phase analysis was performed with the use of the automated PDF-1 database.

A suitable single crystal of Cd_2PCl_2 was mounted on a goniometric head of an automated Nonius CAD-4 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ~20 °C, ω-2θ scanning technique). The crystallographic parameters and main details of the refinement of the crystal structure of Cd_2PCl_2 are given in Table 1. The absorption correction was applied using the standard DIFABS program.

Analysis of the observed systematic absences indicated the only possible space group $P2_1/n$ (No. 14, non-standard setting). The crystal structure of Cd_2PCl_2 was solved by direct methods, which made it possible to locate the positions of the cadmium atoms. The remaining atoms were revealed from a series of subsequent difference Fourier syntheses alternated with cycles of the least-squares refinement. Since the experimental data were collected to $\theta = 35°$, it was unambiguously determined that the metal positions were occupied only by cadmium atoms, whereas tin atoms with a similar scattering power are not involved in the structure. (The cadmium and tin atoms have 48 and 50 electrons, respectively, and, hence, posses close scattering properties. The difference in the scattering power increases as the θ angle increases. The X-ray data collected to large θ angles from a high-quality crystal makes it possible to distinguish these atoms.) The final anisotropic refinement was carried out against F^2. The principal interatomic distances and bond angles are given in Table 3. All calculations were carried out using the SHELX97 program package.[24,25]*

Calculations of the band structures were carried out in the tight-binding approximation using the MO LCAO method within the limits of the extended Hückel theory. The Slater-type atomic orbital parameters, *viz.*, ionization potentials and atomic orbital exponent, were taken from the literature.[26] The geometric parameters of Cd_2PCl_2 and Hg_2PCl_2 were taken from the X-ray diffraction study and literature, respectively.[18] The calculations were carried out using the BICON-CEDiT program package.[27]

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* More detailed data on the study of the crystal structure can be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 412647.

Table 3. Principal bond lengths (*d*) and bond angles (ω) in the structure of Cd_2PCl_2

Bond	*d*/Å	Angle	ω/deg
Cd(1)—P	2.488(1)	P—Cd(1)—P	142.00(5)
Cd(1)—P	2.493(1)	P—Cd(2)—Cl(2)	157.36(5)
Cd(1)—Cl(2)	2.703(1)	P—P—Cd(2)	108.76(8)
Cd(1)—Cl(1)	2.799(1)	P—P—Cd(1)	111.12(8)
Cd(2)—P	2.461(1)	P—P—Cd(1)	111.80(7)
Cd(2)—Cl(2)	2.477(1)	Cd(2)—P—Cd(1)	108.07(5)
Cd(2)—Cl(1)	2.636(1)	Cd(2)—P—Cd(1)	107.82(5)
Cd(2)—Cl(1)	2.841(1)	Cd(1)—P—Cd(1)	109.13(5)
Cd(2)—Cl(1)	2.979(1)		
P—P	2.183(2)		

This study was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32539a).

References

1. A. V. Shevelkov and M. M. Shatruk, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 321 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 337].
2. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, *J. Solid State Chem.*, 1997, **134**, 282.
3. A. V. Shevelkov, L. N. Reshetova, and B. A. Popovkin, *J. Solid State Chem.*, 1998, **137**, 138.
4. M. M. Shatruk, L. N. Reshetova, A. V. Shevel´kov, and B. A. Popovkin, *Zh. Neorg. Khim.,* 2000, **45**, 565 [*Russ. J. Inorg. Chem.*, 2000, **45**, 495 (Engl. Transl.)].
5. A. V. Olenev, A. I. Baranov, A. V. Shevel´kov, and B. A. Popovkin, *Eur. J. Inorg. Chem.*, 2000, 265.
6. A. V. Olenev and A. V. Shevelkov, *Angew. Chem., Int. Ed.*, 2001, **40**, 2353.
7. A. V. Olenev, A. I. Baranov, A. V. Shevelkov, and B. A. Popovkin, *Eur. J. Inorg. Chem.*, 2002, **2**, 547.
8. A. V. Olenev, A. V. Shevel´kov, and B. A. Popovkin, *Zh. Neorg. Khim.,* 1999, **44**, 1911 [*Russ. J. Inorg. Chem.*, 1999, **44**, 1814 (Engl. Transl.)].
9. A. V. Olenev, A. V. Shevel´kov, and B. A. Popovkin, *Zh. Neorg. Khim.,* 1999, **44**, 1957 [*Russ. J. Inorg. Chem.*, 1999, **44**, 1853 (Engl. Transl.)].
10. J. Beck and U. Neisel, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1620.
11. J. Beck and U. Neisel, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2016.
12. A. V. Olenev and A. V. Shevelkov, *J. Solid State Chem.*, 2001, **160**, 88.
13. L. Suchow and N. R. Stemple, *J. Electrochem. Soc.*, 1963, **110**, 766.
14. A. Rebbah, J. Yazbeck, A. Leclaire, and A. Deschanvres, *Acta Crystallogr.*, 1980, **B36**, 771.
15. H. Puff and H. Gotta, *Z. Anorg. Allg. Chem.*, 1966, **B343**, 225.
16. P. C. Donohue, *J. Solid State Chem.*, 1972, **5**, 71.
17. L. N. Reshetova, A. V. Shevel´kov, and B. A. Popovkin, *Koord. Khim.,* 1999, **25**, 875 [*Russ. J. Coord. Chem.*, 1999, **25**, 819 (Engl. Transl)].
18. A. V. Olenev, A. V. Shevelkov, and B. A. Popovkin, *J. Solid State Chem.*, 1998, **142**, 14.
19. A. V. Shevel´kov, E. V. Dikarev, and B. A. Popovkin, *Zh. Neorg. Khim.,* 1995, **40**, 1496 [*Russ. J. Inorg. Chem.*, 1995, **40** (Engl. Transl.)].
20. M. M. Shatruk, K. A. Kovnir, A. V. Shevelkov, and B. A. Popovkin, *Angew. Chem., Int. Ed.*, 2000, **39**, 2508.
21. H. G. von Schnering and W. Hönle, *Chem. Rev.*, 1988, **88**, 243.
22. A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1986.
23. J. H. Ammeter, H. B. Bürgi, J. C. Thibeaut, and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686.
24. G. M. Sheldrik, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen (Germany), 1997.
25. G. M. Sheldrik, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (Germany), 1997.
26. P. Pyykkö and L. L. Lohr, Jr., *Inorg. Chem.*, 1981, **20**, 1950.
27. M. Brändle, R. Rytz, and G. Calzaferri, *BICON-CEDiT. Manual*, University of Bern, Bern (Switzerland), 1997.

Received September 27, 2002;
in revised form January 14, 2003