complex cation is $\Lambda\delta\delta\lambda$. A complete discussion of the molecular structure will be forthcoming.

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Registry No. $[Ni(en)_3](O_2C_2H_3)_2 \cdot 2H_2O$, 55991-04-3.

Supplementary Material Available: Table IX, listing the structure factor amplitudes for $[Ni(en)_3](O_2C_2H_3)] \cdot 2H_2O$ (9 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Hexakis(methyl isocyanide)dipalladium(I) Bis(hexafluorophosphate) Hemiacetone, $[Pd_2(CNMe)_6](PF_6)_2 \cdot {}^1/_2Me_2CO$. A Palladium(I) Dimer

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The crystal and molecular structure of the novel palladium(I) dimer hexakis(methyl isocyanide)dipalladium(I) bis(hexafluorophosphate), $[Pd_2(CNMe)_6](PF_6)_2$, has been determined as its hemiacetone solvate by three-dimensional single-crystal x-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ in a cell of dimensions $a = 12.281$ (2) Å, $b = 12.544$ (3) Å, $c = 10.388$ (2) Å, $\alpha = 111.03$ (1)°, $\beta = 111.12$ (1)°, and $\gamma = 75.95$ (1)° with two formula weights corresponding to $[Pd_2(CNMe)_6](PF_6)_2 \cdot {}^1/_2Me_2CO$ per unit cell ($\rho_{\text{exptl}} = 1.87$ (1) g/cm^3; $\rho_{\text{calcd}} = 1.87$ g/cm^3). The structure was solved by standard heavy-atom methods and refined (on F) by least squares to final discrepancy factors R_1 and R_2 of 0.045 and 0.057, respectively, for 3249 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. In the cation a metal–metal bond of length 2.5310 (9) Å joins the two Pd atoms, each of which possesses an essentially square-planar coordination geometry with the Pd–Pd bond occupying one of the coordination sites. The complex exhibits approximately D_{2d} symmetry. The Pd–"axial" C bonds are significantly longer than the Pd–"equatorial" C bonds, 2.049 (6) vs. 1.963 (5) Å, and the cis C–Pd–C bond angles average 95.0 (6)°. The bonding in this unusual dimer is discussed following the approach of Elian and Hoffmann to metal carbonyl fragments, and its stereochemical nonrigidity is considered.

Introduction

In recent years the chemistry of the platinum group metals has been vigorously pursued, in large measure stimulated by the ability of their low-valent complexes to form adducts, activate substrates and catalyze reactions.[1–12] An important class of these low-valent complexes is those which contain metal–metal bonds. Within the platinum group elements, metal–metal bonding is most often observed in carbonyl cluster compounds.[13–23] While platinum and palladium form a number of metal–metal bonded systems,[24–37] few of these contain the metal ions in their lower oxidation states.

It was therefore of structural interest when we learned of the synthesis of the Pd(I) cation dimer $[Pd_2(CNMe)_6](PF_6)_2$ by Balch and coworkers.[38] The complex was found to exhibit only a single methyl resonance at room temperature but two proton resonances in the intensity ratio 1:2 below −30°C.[39] In spite of the unusual Pd(I) oxidation state, the complex shows remarkable stability presumably arising from metal–metal bond formation. The stereochemical nonrigidity of the system and its extraordinary stability thus made the complex even more intriguing from a structural standpoint. Herein we report the crystal structure determination of $[Pd_2(CNMe)_6](PF_6)_2$ and a discussion of its bonding.

The complex $[Pd_2(CNMe)_6]^{2+}$ represents one of the few simple M_2L_6 systems known where M is a transition element.[40–46] It is formally isoelectronic with the unstable nickel(I) cyanide system $[Ni_2(CN)_6]^{4-}$ which has been extensively studied because of its interesting chemical and catalytic properties.[47–53] The structure of $[Ni_2(CN)_6]^{4-}$ has been reported[45–46] and the anion shows a short Ni–Ni bond unsupported by cyanide bridges. The title compound is also closely related to palladium(I) and platinum(I) carbonyl halide dimers $[M_2X_4(CO)_2]^{2-}$ [54] which have been reported and whose structures have been suggested on the basis of infrared spectroscopy. The present results will no doubt bear on these proposals.[84]

The structure of $[Pd_2(CNMe)_6](PF_6)_2$ has appeared in a communication.[39]

Data Collection and Reduction

A sample of $[Pd_2(CNMe)_6](PF_6)_2$ was kindly provided by Professor Alan Balch. The pale yellow crystals of the material had a cloudy appearance and were recrystallized by slow evaporation from an acetone–isopropyl alcohol solution to yield clear, well-formed crystals. Weissenberg and precession photographs showed that the crystals belonged to the triclinic system, with possible space groups of $P1$ and $P\bar{1}$.[55] A cell reduction[56] was performed on a primitive cell as obtained from the film measurements, and all further work was performed in the reduced cell. The lattice constants at 22°C were determined from a least-squares refinement of the setting angles for 12 well-resolved high-angle reflections ($2\theta \geq 35$).[57] The reflections were carefully centered, using Mo $K\alpha_1$ radiation (λ 0.709261 Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are $a = 12.281$ (2) Å, $b = 12.544$ (3) Å, $c = 10.388$ (2) Å, $\alpha = 111.03$ (1)°, $\beta = 111.12$ (1)°, $\gamma = 75.95$ (1)°, and $V = 1381.6$ (5) Å^3. The calculated density ($Z = 2$) for the compound, including a half molecule of acetone per dimer is 1.87 g/cm^3, which is in excellent agreement with the value 1.87 (1) g/cm^3, determined by flotation in a mixture of bromoform and carbon tetrachloride.

The same crystal was used for the preliminary film work and data collection. The dimensions of the crystal were approximately 0.09 × 0.17 × 0.51 mm. The 11 bounding faces of the platelike crystal were identified by a comparison of diffractometer settings with optical goniometric measurements. Interplanar distances[58] were carefully measured with a Zeiss traveling hairline micrometer eyepiece. The crystal was mounted so that a^* was nearly coincident with the ϕ axis of the diffractometer. Rotation about ϕ corresponded to rotation about the longest direction of the crystal. Mosaic spread was checked by means of narrow-source, open-counter ω scans.[59] Full widths at half-maximum for some typical strong reflections were in the range 0.05–0.10°.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the x-ray tube, 1.8°, was chosen such that the intensities of typical strong reflections were roughly 80% of their maximum value as a function of takeoff angle. Data were collected at a scan rate of 1°/min and 10-sec background counts were made at each end of the scan. Scans were from 0.7° below the Mo $K\alpha_1$ peak to 0.7° above the $K\alpha_2$ peak. Brass attenuator foils were automatically inserted when the intensity of the diffracted beam reached approximately 10000 Hz with each thickness designed to yield an approximate attenuation of 0.33. The pulse height analyzer was set for a 90% window centered on Mo $K\bar{\alpha}$ radiation.

Data were collected in the range $3° \leq 2\theta \leq 50°$. Only data in the hemisphere with $h \geq 0$ were collected. Three standard reflections were monitored every 60 observations. The intensities of the standards showed a nearly uniform linear decrease of 4.68% during the period of data collection. A total of 5147 reflections were collected. The data were processed and reduced as previously described.[56,60] Corrections for Lorentz and polarization effects were included in the calculation of I and $\sigma(I)$; the value of p[61] in the expression for $\sigma(I)$ was chosen as 0.04. The data were corrected for linear decay and absorption. The absorption coefficient for Mo $K\bar{\alpha}$ radiation is 14.96 cm^{-1}.[55] The analytical method of De Meulenaer and Tompa[62] was used in calculating absorption corrections. Transmission factors ranged from 0.678 to 0.879, with a mean value of 0.822. A total of 252 reflections which are equivalent in $P\bar{1}$ were observed twice. These data were averaged, the R factor for averaging being 1.0%. The final data set consisted of 4895 independent reflections of which only the 3249 with $F^2 \geq 3\sigma(F^2)$ were used in the refinement of the structure.

Solution and Refinement of the Structure

The structure was solved and refined using standard Patterson, Fourier, and least-squares methods.[56] In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $1/\sigma(F_o)^2 = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Pd, P, F, O, N, and C were those of Cromer and Mann.[63] Corrections for anomalous dispersion of Pd and P were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[64]

The three-dimensional Patterson map was interpreted in terms of a structure in space group $P\bar{1}$ and the positions of the two crystallographically independent Pd atoms were easily obtained. The successful refinement of the structure and the excellent agreement between reflections of the type $0kl$ and $0\bar{k}\bar{l}$ confirm the choice of the centrosymmetric space group. Refinement of the metal atom positions, overall scale factor, and independent isotropic thermal parameters resulted in $R_1 = 0.37$, $R_2 = 0.46$.[65] The positions of the remaining atoms of the cation and anions were located from successive cycles of least-squares refinement and difference Fourier syntheses. Isotropic refinement of the atoms of the cation and anions yielded $R_1 = 0.118$, $R_2 = 0.170$. Anisotropic refinement reduced the R factors to 0.075 and 0.114, respectively. The prominent feature of a difference map calculated at this point was a collection of peaks near the inversion center at 0, $^1/_2$, $^1/_2$. These peaks were interpreted as a disordered acetone molecule. The acetone was treated as a rigid group with C–C = 1.52 Å, C–O = 1.23 Å, and C–C–O = 112°. An isotropic thermal parameter was refined for each atom of the group. Inclusion of the acetone in the structure factor calculation reduced R_1 and R_2 to 0.071 and 0.105, respectively. Refinement to convergence resulted in $R_1 = 0.056$ and $R_2 = 0.070$.

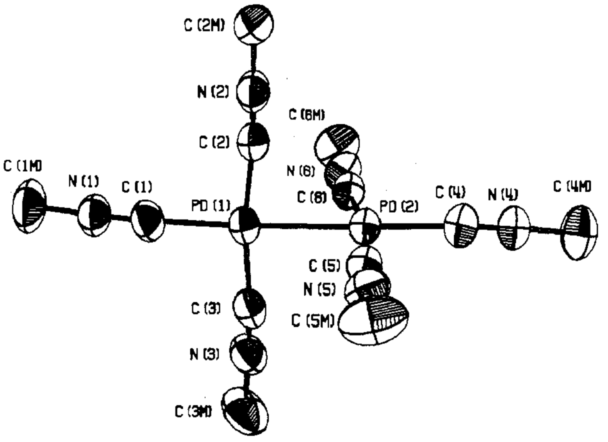


Figure 1. Perspective view of the $[Pd_2(CNMe)_6]^{2+}$ dimer.

The quantity $\sum w(|F_o| - |F_c|)^2$ showed no dependence on $|F_o|$ but was unusually large for small values of $(\sin \theta)/\lambda$. The weighting scheme was empirically altered to remove this dependence. The weights used in the final refinements were related to $\sigma(F^2)$ as before but $\sigma(F^2)$ was chosen as $(\sigma(F^2))q$ where $q = 1$ for $(\sin \theta)/\lambda > 0.45$ and $q = 3.0 - 4.44(\sin \theta)/\lambda$ for $(\sin \theta)/\lambda < 0.45$. The final R factors after convergence were $R_1 = 0.0452$, $R_2 = 0.0566$, for 3249 observations and 317 parameters. The estimated standard deviation of an observation of unit weight[65] was 1.47. The change of weights had a noticeable effect on some of the Pd–C distances.[66]

A final difference Fourier showed no peaks with intensity greater than 15% of that of a typical carbon atom. All of the most prominent peaks in the final map were in the vicinity of the PF_6^- groups. Since no definitive positions could be determined for the hydrogen atoms, they were completely omitted from all calculations.

The final positional and thermal parameters are given in Table I. A listing of the observed and calculated structure factors for those reflections used in the refinement is available.[67]

Description of the Structure

The crystal structure consists of the packing of discrete dimeric cations of formula $[Pd_2(CNMe)_6]^{2+}$, octahedral PF_6^- anions, and acetone molecules of crystallization ($^1/_2$ Me_2CO/dimer). The molecular structure of the cation is illustrated in Figure 1 and the packing arrangement is shown in Figure 2.

The dimeric cation represents the first example of a Pd(I) or Pt(I) dimer containing a nonbridged metal–metal bond to be characterized by an x-ray structure determination. The geometry of the cation consists of two Pd atoms, each possessing an essentially square-planar coordination, joined by a Pd–Pd bond which occupies one of the coordination sites. The dihedral angle between the two coordination planes is about 86.4°, depending on the choice of atoms used to calculate the coordination planes, and the overall symmetry of the cation is approximately D_{2d}. Important bond distances and angles for the structure are tabulated in Tables II and III, respectively, and selected least-squares planes are presented in Table IV.

The Pd–Pd bond length of 2.5310 (9) Å is the shortest one

Table I. Final Positional and Thermal Parameters for $[Pd_2(CNMe)_6](PF_6)_2 \cdot {}^1/_2Me_2CO$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	0.115 23 (5)[b]	0.074 48 (5)	−0.245 76 (6)	79.6 (6)	96.5 (6)	156.7 (9)	−24.8 (4)	33.6 (5)	41.2 (5)
Pd(2)	0.248 89 (5)	0.200 89 (5)	−0.242 95 (6)	86.4 (6)	87.6 (6)	141.7 (9)	−21.2 (4)	36.7 (5)	37.5 (5)
P(1)	0.441 42 (21)	0.252 46 (24)	0.340 37 (27)	94.6 (20)	143.3 (25)	178 (3)	−21.9 (18)	37.1 (21)	44.8 (23)
P(2)	−0.194 12 (23)	0.303 52 (20)	0.021 47 (30)	118.0 (23)	88.3 (18)	232 (4)	−20.3 (16)	55.7 (25)	35.4 (21)
C(1)	0.008 9 (7)	−0.021 8 (8)	−0.233 6 (10)	75 (7)	120 (8)	220 (14)	−23 (6)	32 (8)	64 (9)
C(2)	0.258 7 (7)	0.005 0 (7)	−0.128 2 (9)	83 (7)	104 (7)	160 (11)	−26 (6)	35 (7)	50 (7)
C(3)	−0.012 0 (8)	0.156 7 (8)	−0.370 2 (10)	90 (8)	112 (8)	187 (12)	−37 (6)	24 (8)	45 (8)
C(4)	0.352 8 (8)	0.311 5 (8)	−0.232 9 (10)	113 (8)	99 (7)	191 (12)	−17 (7)	68 (8)	42 (8)
C(5)	0.282 0 (7)	0.077 6 (7)	−0.408 9 (9)	105 (7)	100 (7)	150 (11)	−27 (6)	38 (7)	40 (8)
C(6)	0.195 6 (7)	0.306 2 (7)	−0.077 7 (9)	93 (7)	86 (6)	167 (11)	−14 (5)	44 (7)	42 (7)
N(1)	−0.051 6 (6)	−0.068 8 (7)	−0.216 4 (8)	91 (6)	118 (7)	229 (12)	−25 (5)	38 (7)	78 (7)
N(2)	0.336 8 (7)	−0.041 3 (6)	−0.060 2 (7)	104 (7)	105 (6)	159 (9)	−36 (5)	46 (7)	36 (6)
N(3)	−0.091 0 (7)	0.199 0 (7)	−0.440 7 (9)	92 (7)	122 (7)	210 (12)	−24 (6)	21 (7)	55 (8)
N(4)	0.403 8 (6)	0.378 4 (6)	−0.228 2 (8)	107 (6)	91 (6)	194 (10)	−25 (5)	60 (7)	37 (6)
N(5)	0.306 1 (7)	0.008 3 (7)	−0.504 9 (8)	139 (8)	116 (7)	149 (10)	−16 (6)	42 (7)	46 (7)
N(6)	0.170 0 (7)	0.370 7 (6)	0.019 0 (8)	125 (7)	98 (6)	178 (10)	−8 (5)	58 (7)	52 (7)
C(1M)	−0.1275 (10)	−0.122 2 (11)	−0.187 2 (16)	124 (10)	173 (13)	386 (26)	−44 (9)	72 (14)	134 (15)
C(2M)	0.436 9 (8)	−0.100 9 (9)	0.026 9 (11)	103 (8)	138 (9)	213 (14)	−23 (7)	23 (9)	94 (10)
C(3M)	−0.193 5 (10)	0.250 5 (12)	−0.531 8 (16)	100 (9)	171 (13)	351 (25)	−18 (9)	−5 (12)	101 (15)
C(4M)	0.463 4 (11)	0.467 1 (9)	−0.223 4 (13)	174 (13)	102 (8)	288 (19)	−44 (9)	101 (13)	37 (10)
C(5M)	0.340 0 (14)	−0.080 0 (11)	−0.626 2 (12)	238 (18)	142 (11)	169 (14)	27 (11)	80 (13)	22 (10)
C(6M)	0.140 0 (11)	0.453 1 (9)	0.144 3 (11)	168 (12)	120 (9)	180 (13)	2 (8)	89 (11)	20 (9)
F(1)	0.350 1 (7)	0.199 6 (8)	0.189 9 (8)	163 (7)	243 (10)	239 (10)	−76 (7)	−8 (7)	73 (8)
F(2)	0.537 2 (8)	0.151 1 (7)	0.299 7 (9)	189 (9)	198 (9)	281 (12)	38 (7)	43 (8)	11 (8)
F(3)	0.473 5 (12)	0.323 4 (10)	0.273 2 (13)	399 (21)	287 (14)	548 (26)	−172 (15)	100 (19)	204 (16)
F(4)	0.349 8 (9)	0.348 6 (13)	0.386 9 (10)	213 (12)	442 (22)	306 (16)	154 (14)	60 (11)	37 (15)
F(5)	0.407 2 (10)	0.181 5 (12)	0.411 9 (12)	265 (14)	462 (22)	422 (20)	−145 (15)	40 (14)	277 (18)
F(6)	0.534 5 (7)	0.297 8 (7)	0.491 9 (8)	149 (7)	225 (10)	246 (11)	−18 (7)	20 (7)	−16 (8)
F(7)	−0.175 1 (7)	0.168 5 (5)	−0.018 9 (9)	217 (9)	91 (5)	373 (14)	2 (5)	104 (9)	48 (7)
F(8)	−0.309 3 (13)	0.292 7 (9)	−0.091 1 (16)	332 (20)	188 (11)	619 (33)	27 (12)	−193 (22)	79 (15)
F(9)	−0.251 4 (16)	0.309 6 (9)	0.132 5 (13)	560 (30)	214 (12)	433 (23)	−45 (15)	328 (23)	52 (13)
F(10)	−0.086 3 (13)	0.312 5 (11)	0.148 5 (22)	240 (17)	234 (15)	901 (50)	3 (13)	−158 (24)	−48 (22)
F(11)	−0.129 2 (22)	0.294 0 (9)	−0.075 1 (23)	962 (53)	177 (11)	1086 (58)	−132 (19)	908 (53)	−35 (20)
F(12)	−0.216 2 (10)	0.437 2 (5)	0.062 2 (10)	369 (16)	86 (5)	433 (18)	−20 (7)	208 (15)	42 (8)
C(Ac1)	0.007 6 (18)[c]	0.499 7 (20)	0.484 7 (25)	16.6 (12)[d]					
C(Ac2)	−0.115 5 (24)	0.548 (4)	0.497 (5)	14.1 (13)					
C(Ac3)	0.041 8 (28)	0.554 1 (26)	0.398 (3)	10.7 (7)					
O	0.072 0 (26)	0.425 1 (23)	0.539 (3)	14.8 (8)					

[a] Anisotropic thermal parameters have been multiplied by 10^4. The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] In this and subsequent tables the estimated standard deviations of the least significant figures are given in parentheses. [c] Atomic positions for the atoms of acetone are derived from the group parameters for the molecule. The group is centered at C(Ac1) and has angular parameters ϕ, θ, ρ (See R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965)) or 2.042 (25), −2.491 (23), and −3.445 (21) radians, respectively. Each atom in the group is assigned a multiplier of 0.5 since the group is disordered about (0, $^1/_2$, $^1/_2$). [d] Isotropic thermal parameter B in the expression $\exp[-(B((\sin\theta)/\lambda)^2)]$.

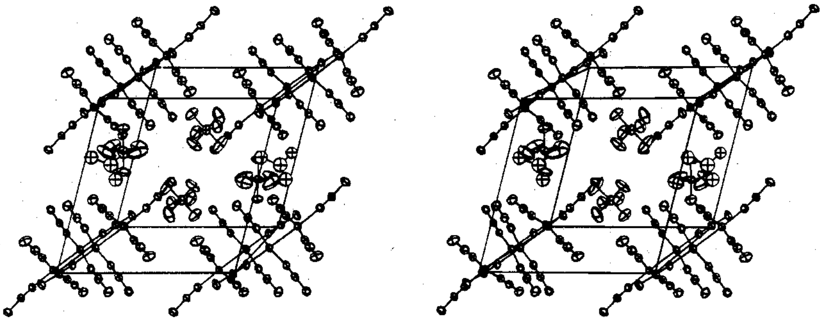


Figure 2. Stereoscopic view of the packing of $[Pd_2(CNMe)_6](PF_6)_2 \cdot {}^1/_2Me_2CO$ viewed down the c^* direction. Only one orientation of the disordered Me_2CO molecule is shown.

yet reported for a Pd(I) system. It is considerably shorter than the distance of 2.751 Å found in metallic palladium[68] and is shorter than the distances of 2.57 (1), 2.57 (1), 2.686 (7), and 2.639 (1) Å observed in the Pd(I) binuclear systems $[Pd(Al_2Cl_7)(C_6H_6)]_2$,[24] $[Pd(AlCl_4)(C_6H_6)]_2$,[24] $[Pd_2(C_3H_5)I(PPh_3)_2]$,[25] and $[Pd_2(C_5Ph_5)_2(C_2Ph_2)]$.[26] The first two of the above-mentioned compounds each contain two benzene molecules serving as π-bonded bridges in the Pd–Pd system. In $[Pd_2(C_3H_5)(PPh_3)_2I]$ the π-allyl group and iodine atom both bridge the metal–metal bond, and in $[Pd_2(C_5Ph_5)_2(C_2Ph_2)]$ there is a bridging diphenylacetylene. A novel Pt(I) system is $[Pt_2(C_5H_5)_2(C_{10}H_{10})]$[27] in which there is a metal–metal bond of 2.581 (4) Å and a bridging η^5-cyclopentadienylcyclopentadiene group. Other short Pt–Pt bond distances have been reported in $[Pt_2S(CO)(PPh_3)_3]$[28] and $[(C_8H_{12})_3Pt_3(SnCl_3)_2]$[29] which contain one bridging sulfur atom and two triply bridging $SnCl_3$ groups, respectively.

The four "equatorial" metal–carbon bonds are structurally equivalent, and their mean length is significantly shorter than that of the two "axial" Pd–C bonds, 1.963 (5) vs. 2.049 (6) Å. Similar elongation of the axial metal–carbon bonds has been observed in other dimer systems containing cyanide[69] and isocyanide[70] ligands. In the case of carbonyl complexes an axial contraction is observed.[71] The differences in bond lengths

Table II. Intramolecular Distances (Å) in $[Pd_2(CNMe)_6](PF_6)_2$

Pd(1)-Pd(2)		2.5310 (9)	N(1)-C(1M)		1.436 (12)
			N(2)-C(2M)		1.459 (12)
Pd(1)-C(1)		2.043 (8)	N(3)-C(3M)		1.444 (14)
Pd(2)-C(4)		2.055 (9)	N(4)-C(4M)		1.450 (12)
	Av[a]	2.049 (6)	N(5)-C(5M)		1.463 (14)
Pd(1)-C(2)		1.955 (9)	N(6)-C(6M)		1.446 (12)
Pd(1)-C(3)		1.973 (10)		Av	1.449 (4)
Pd(2)-C(5)		1.953 (9)	P(1)-F(1)		1.579 (7)
Pd(2)-C(6)		1.970 (9)	P(1)-F(2)		1.557 (8)
	Av	1.963 (5)	P(1)-F(3)		1.499 (8)
C(1)-N(1)		1.147 (11)	P(1)-F(4)		1.506 (9)
C(2)-N(2)		1.137 (10)	P(1)-F(5)		1.550 (9)
C(3)-N(3)		1.130 (11)	P(1)-F(6)		1.577 (7)
C(4)-N(4)		1.142 (11)	P(2)-F(7)		1.571 (6)
C(5)-N(5)		1.142 (11)	P(2)-F(8)		1.475 (11)
C(6)-N(6)		1.134 (10)	P(2)-F(9)		1.525 (10)
	Av	1.139 (3)	P(2)-F(10)		1.488 (13)
			P(2)-F(11)		1.450 (9)
			P(2)-F(12)		1.554 (7)
				Av	1.528 (13)

[a] Average values are computed from the expression $\bar{x} = (\Sigma x_i/n)$, where $\sigma(\bar{x}) = [\Sigma(\bar{x} - x_i)^2/n(n + 1)]^{1/2}$.

Table III. Bond Angles (deg) in $[Pd_2(CNMe)_6](PF_6)_2$

Pd(1)-Pd(2)-C(4)		176.6 (2)	F(1)-P(1)-F(2)	89.6 (5)
Pd(2)-Pd(1)-C(1)		176.1 (3)	F(1)-P(1)-F(3)	89.4 (5)
	Av[a]	176.4 (3)	F(1)-P(1)-F(4)	92.1 (5)
			F(1)-P(1)-F(5)	91.1 (5)
C(1)-Pd(1)-C(2)		93.9 (3)	F(1)-P(1)-F(6)	176.5 (5)
C(1)-Pd(1)-C(3)		95.4 (3)	F(2)-P(1)-F(3)	91.7 (7)
C(4)-Pd(2)-C(5)		96.5 (3)	F(2)-P(1)-F(4)	176.9 (6)
C(4)-Pd(2)-C(6)		94.3 (3)	F(2)-P(1)-F(5)	89.5 (7)
	Av	95.0 (6)	F(2)-P(1)-F(6)	88.2 (4)
C(2)-Pd(1)-C(3)		170.6 (3)	F(3)-P(1)-F(4)	90.9 (9)
C(5)-Pd(2)-C(6)		169.2 (3)	F(3)-P(1)-F(5)	178.7 (8)
	Av	169.9 (7)	F(3)-P(1)-F(6)	93.3 (6)
			F(4)-P(1)-F(5)	87.9 (8)
Pd(2)-Pd(1)-C(2)		84.8 (2)	F(4)-P(1)-F(6)	90.0 (5)
Pd(2)-Pd(1)-C(3)		86.0 (2)	F(5)-P(1)-F(6)	86.2 (5)
Pd(1)-Pd(2)-C(5)		86.7 (2)	F(7)-P(2)-F(8)	87.1 (5)
Pd(1)-Pd(2)-C(6)		82.5 (2)	F(7)-P(2)-F(9)	89.4 (5)
	Av	85.0 (9)	F(7)-P(2)-F(10)	91.6 (6)
Pd(1)-C(1)-N(1)		174.3 (9)	F(7)-P(2)-F(11)	88.7 (5)
Pd(1)-C(2)-N(2)		174.5 (6)	F(7)-P(2)-F(12)	178.4 (5)
Pd(1)-C(3)-N(3)		174.4 (7)	F(8)-P(2)-F(9)	89.7 (11)
Pd(2)-C(4)-N(4)		175.3 (8)	F(8)-P(2)-F(10)	171.9 (14)
Pd(2)-C(5)-N(5)		176.5 (7)	F(8)-P(2)-F(11)	95.3 (13)
Pd(2)-C(6)-N(6)		175.9 (7)	F(8)-P(2)-F(12)	92.0 (6)
	Av	175.1 (4)	F(9)-P(2)-F(10)	82.3 (11)
			F(9)-P(2)-F(11)	174.5 (13)
C(1)-N(1)-C(1M)		176.6 (11)	F(9)-P(2)-F(12)	89.3 (5)
C(2)-N(2)-C(2M)		179.9 (9)	F(10)-P(2)-F(11)	92.7 (14)
C(3)-N(3)-C(3M)		178.5 (9)	F(10)-P(2)-F(12)	89.1 (7)
C(4)-N(4)-C(4M)		177.3 (9)	F(11)-P(2)-F(12)	92.7 (5)
C(5)-N(5)-C(5M)		178.6 (11)		
C(6)-N(6)-C(6M)		178.7 (9)		
	Av	178.3 (5)		

[a] See footnote *a* in Table II.

Table IV. Weighted Least-Squares Planes[a] through Different Coordination Planes in $[Pd_2(CNMe)_6]^{2+}$

Atom	Plane 1	Plane 2	Plane 3	Plane 4
Pd(1)	0.027[b]	0.0000 (6)	−0.0002 (6)	−0.036
Pd(2)	−0.0003 (6)	0.012	−0.166	0.0001 (6)
C(1)	−0.081 (10)		0.005 (10)	
C(2)	0.050 (8)		0.020 (8)	
C(3)	0.066 (9)		0.026 (9)	
C(4)		−0.010 (9)		−0.002 (9)
C(5)		0.007 (8)		−0.007 (8)
C(6)		0.007 (8)		−0.007 (8)

Coefficients of Plane

Coeff	Plane 1	Plane 2	Plane 3	Plane 4
A	4.197	5.811	3.670	5.900
B	−4.482	−6.177	−5.030	−6.081
C	−7.569	5.779	−7.282	5.739
D	1.983	−1.211	1.838	−1.148

Interplanar Dihedral Angles, Deg

Plane 1–plane 2	86.3	Plane 2–plane 3	86.5
Plane 1–plane 3	3.2	Plane 2–plane 4	0.5
Plane 1–plane 4	86.3	Plane 3–plane 4	86.4

[a] Equation of the plane is of the form $AX + BY + CZ - D = 0$, referred to triclinic coordinates; see W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). [b] Deviation, in Å, from the plane. Where an estimated error for the deviation is not given, the atom was given zero weight in the calculation.

have been interpreted[69] in terms of the σ- and π-bonding abilities of CO, CNR, and CN^-. The metal–carbon bond lengths observed in this study are in good agreement for those in some other palladium and platinum isocyanide systems.[60b,72] In the cases of *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$[73a] and *cis*-$[PtCl_2(CNPh)_2]$,[73b] shorter Pt–C bond distances have been reported (1.83 (4) and 1.896 (16) Å, respectively).

The CNMe ligands of $[Pd_2(CNMe)_6]^{2+}$ coordinate in an essentially linear manner with an average bond angle at the donor C atom of 175.1 (4)°. The isocyanide ligands are themselves linear with an average C–N–Me bond angle of 178.3 (5)°. The average bond lengths within the ligand are 1.139 (3) Å for C≡N and 1.449 (4) Å for N—Me.

The bond angles about each Pd atom show significant deviation from a square coordination. The equatorial isocyanide ligands bend away from the axial ligand giving rise to values of 95.0 (6)° for the mean C(axial)–Pd–C(equatorial) angle and 85.0 (9)° for the mean C(equatorial)–Pd–Pd angle. A similar type of distortion has been observed in M_2X_{10} systems and will be discussed below in terms of the Elian and Hoffmann molecular fragment approach.[74]

The hexafluorophosphate anions have the expected octahedral geometry. As in other structures containing this anion,[75–79] the bond distances span a rather wide range of values (1.488 (13)–1.579 (7) Å, mean 1.528 (13) Å) and the fluorine atoms show a large amount of anisotropic thermal motion (Figure 2 and Table V). Although there was no evidence for disorder, the shape of the thermal ellipsoids suggests that there is considerable librational motion about the axes defined by F(1)–P(1)–F(6) and F(7)–P(2)–F(12).

Discussion

The Pd(I) dimeric cation is formally isoelectronic with the unstable nickel(I) cyanide system $[Ni_2(CN)_6]^{4-}$ which has been the subject of many earlier investigations.[79–81] The structure of the Ni(I) dimer has been determined recently as both the K^+ [45] and Rb^+ [46] salts. The results of these structure determinations reveal a geometry for $[Ni_2(CN)_6]^{4-}$ essentially the same as that reported in the present study. These two dimer systems represent the only structurally characterized M_2L_6 complexes in which the metal atoms bond directly and possess square-planar coordination. Other M_2L_6 systems where M is a transition element have been studied by single-crystal x-ray methods, and different structural types have been observed. The binuclear complexes $Mo_2(CH_2SiMe_3)_6$[42] and $W_2(NMe_2)_6$[43] each possess a "staggered ethane" type structure of approximate D_{3d} symmetry if only the donor atoms of the ligands are considered. The coordination geometry about the metal atoms in these systems is essentially tetrahedral with the metal–metal bond occupying one of the coordination sites. On the other hand, the Pt(II) system $[Pt_2Br_6]^{2-}$ [41] has no M–M bond and a square-planar coordination about each Pt(II) ion. The square planes share a common edge through the occurrence of Br ligand bridges and the complex exhibits overall D_{2h} symmetry. In $[Cu_2Cl_6]^{2-}$ [44] there are also ligand bridges but the coordination geometry about each Cu(II) is distorted between square-planar and tetrahedral geometries.

In light of the molecular structure, it is interesting to

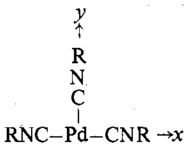
Table V. Root-Mean-Square Amplitudes of Vibration (Å × 10^3)

Atom	Min	Intermed	Max
Pd(1)	206.1 (8)	255.5 (8)	266.5 (8)
Pd(2)	211.2 (8)	247.9 (8)	253.7 (8)
P(1)	245 (3)	279 (3)	315 (3)
P(2)	240 (3)	275 (3)	322 (3)
C(1)	211 (10)	273 (9)	316 (10)
C(2)	207 (9)	254 (10)	278 (9)
C(3)	217 (9)	280 (10)	299 (10)
C(4)	233 (10)	263 (10)	298 (10)
C(5)	230 (9)	256 (9)	277 (10)
C(6)	226 (9)	247 (9)	270 (9)
C(1M)	217 (11)	325 (13)	421 (14)
C(2M)	245 (9)	256 (10)	340 (11)
C(3M)	246 (12)	333 (13)	425 (15)
C(4M)	233 (10)	309 (12)	375 (13)
C(5M)	247 (12)	317 (13)	434 (16)
C(6M)	236 (11)	313 (11)	343 (12)
N(1)	219 (9)	264 (8)	327 (8)
N(2)	213 (8)	262 (7)	291 (9)
N(3)	240 (9)	283 (8)	317 (9)
N(4)	220 (9)	262 (8)	297 (8)
N(5)	247 (8)	283 (8)	304 (9)
N(6)	244 (8)	266 (9)	294 (8)
F(1)	273 (12)	369 (7)	423 (8)
F(2)	297 (9)	335 (8)	494 (8)
F(3)	256 (10)	479 (8)	575 (12)
F(4)	283 (14)	361 (9)	696 (10)
F(5)	288 (18)	391 (8)	601 (10)
F(6)	284 (7)	328 (8)	481 (10)
F(7)	246 (7)	380 (8)	408 (8)
F(8)	292 (10)	378 (11)	749 (21)
F(9)	330 (10)	385 (10)	620 (17)
F(10)	327 (12)	380 (12)	841 (24)
F(11)	268 (9)	337 (10)	910 (24)
F(12)	240 (7)	385 (8)	507 (11)
C(Ac1)	458 (16)[a]		
C(Ac2)	423 (19)[a]		
C(Ac3)	368 (13)[a]		
O	432 (12)[a]		

[a] Atom refined isotropically.

speculate about the electronic structural description of $[Pd_2(CNMe)_6]^{2+}$. Usually metal–metal bond formation between low-valent metal atoms occurrs with each atom achieving the next inert-gas configuration. In the present case, however, the coordination geometry about each Pd atom is nearly square planar and thus similar to that found in most Pd(II) complexes. Square-planar coordination in d^8 complexes is coordinatively unsaturated in that only eight of the nine valence shell orbitals are utilized in the formation of bonds and the storage of metal-based electron pairs.

A reasonable starting point to a description of the bonding in $[Pd_2(CNMe)_6]^{2+}$ is to consider the complex composed of two $Pd(CNMe)_3^+$ fragments of known electronic structure. The planar $Pd(CNMe)_3^+$ moiety, I, has C_{2v} symmetry with three corners of a square occupied by methyl isocyanide ligands and the fourth corner vacant for metal–metal bonding.



$$\begin{array}{c} y \\ \uparrow \\ \mathrm{R} \\ \mathrm{N} \\ \mathrm{C} \\ | \\ \mathrm{RNC{-}Pd{-}CNR} \rightarrow x \end{array}$$

I

Isci and Mason[82] have recently given the molecular orbital energy level ordering for square-planar tetrakis(alkyl isocyanide) complexes as $b_{1g}(x^2 - y^2) > e_u(\pi^*) > a_{2u}(\pi^*) > a_{1g}(z^2) > e_g(xz,yz) > b_{2g}(xy)$ with a ground-state term of $...(b_{2g})^2(e_g)^4(a_{1g})^2 = {}^1A_{1g}$ for d^8 systems. In going from the $M(CNR)_4^{n+}$ complex to the $Pd(CNMe)_3^+$ moiety, the major change in the ordering is expected to occur in the position of the MO mainly composed of $d_{x^2-y^2}$ which is σ antibonding with respect to the metal–ligand bonds. Other changes take place in the positions of the d_{yz} and d_{xy} levels because of reduced metal–ligand π interaction. The ordering for the $Pd(CNMe)_3^+$ moiety is therefore proposed as ligand π^* levels $> a_1(x^2 - y^2) > b_1(xy) > b_2(yz) > a_1(z^2) > a_2(xz)$ with the $a_1(x^2 - y^2)$ orbital singly occupied (note that because the y axis is the principal symmetry axis, the irreducible representations of the d orbitals differ from those given in standard character tables where z is assumed as the major symmetry axis).

The lowering of symmetry from D_{4h} to C_{2v} (with a change in principal symmetry axis) also allows mixing of metal-based orbitals transforming according to the same irreducible representation. This latter aspect results in hybridization of the orbital to be used in metal–metal bonding in a manner completely analogous to that developed by Elian and Hoffmann[74] in their discussion on bonding in carbonyl fragments. Hybridization of the $x^2 - y^2$ orbital, a_1 in C_{2v}, involves the mixing in of the energetically more unstable s and p_y orbitals in order that the antibonding nature of $a_1(x^2 - y^2)$ be diminished. The resultant a_1 orbital has decreased electron density along the y axis in the direction of the CNMe ligand and increased spatial extent toward the missing ligand position.

Up to this point the $Pd(CNMe)_3^+$ fragment has been considered to have cis bond angles of 90° but there is no reason a priori why the bond angles should remain fixed at this value. We therefore apply the arguments developed by Elian and Hoffmann[74] to consider what happens to the molecular orbital energies when the cis bond angles θ are allowed to vary. For the orbitals d_{z^2}, d_{yz}, and d_{xz}, there will be essentially no change in energy as θ varies in the range 80–100°. (Any possible shifting in the position of the a_2–d_{xz} level because of a change in the d_{xz}–π^* interaction is expected to be extremely slight.)

The d_{xy} orbital in square-planar complexes is involved in in-plane π bonding. In $Pd(CNMe)_3^+$ this interaction is preserved for the three isocyanide ligands and is maximized when θ equals 90°. Variation of θ from 90° results in an increase in the energy of the d_{xy} level through two factors: first, there is a decrease in the d_{xy}–π^* in-plane overlap and hence a decrease in metal–ligand in-plane π bonding, and, second, the d_{xy} orbital is allowed to mix in an antibonding manner with the ligand b_1 combination of orbitals along the x axis and thus acquire σ^* character.

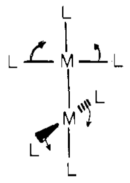
The remaining orbital to consider is the σ^* function composed mainly of $d_{x^2-y^2}$ which is hybridized in C_{2v} symmetry as discussed above. Movement of the isocyanide ligands in I to bond angles greater than 90° stabilizes this level by decreasing the metal–ligand σ^* interaction and by permitting the orbital to participate in metal–isocyanide in-plane π bonding. Stabilization of the a_1–$d_{x^2-y^2}$ level is a key feature of the system, and this is achieved in part by increasing the cis bond angle θ beyond 90°. In the $Pd(CNMe)_3^+$ moiety, the ground-state configuration is $...(a_2)^2(a_1)^2(b_2)^2(b_1)^2(a_1)^1$ and the most stable geometry is anticipated to have $\theta > 90°$ as is observed. The average C–Pd–C cis bond angle in the present structure is 95.0 (6)°.

The formation of the metal–metal bond between two $Pd(CNMe)_3^+$ fragments then occurs through the interaction of the singly occupied hybrid orbitals which have maximum directional character toward the vacant corner of their respective squares. The resultant σ-bonding molecular orbital is doubly occupied, producing a metal–metal bond. The metal–metal σ^* function is vacant in the ground state and it lies either above or below the methyl isocyanide π^* levels which Mason and Isci[82] suggested as being below $d_{x^2-y^2}$ in the square-planar systems $M(CNR)_4^{n+}$. It is interesting to note that each metal center in $[Pd_2(CNMe)_6]^{2+}$ is coordinatively unsaturated and this raises some interesting possibilities regarding potential catalytic activity.

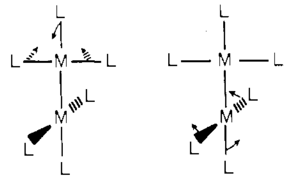
The fluxional behavior of $[Pd_2(CNMe)_6]^{2+}$ [39] merits comment in light of the structural results and the bonding considerations. Equilibration of the two different types of isocyanide ligands may take place by a number of different pathways including (a) intermolecular exchange, (b) deformation at each metal center to allow equilibration of axial and equatorial isocyanides, and (c) formation of a bridged intermediate in order to interchange all six isocyanide ligands. In recent studies Balch and coworkers[83] have examined the variable-temperature NMR spectrum of the monosubstituted derivative $[Pd_2(CNMe)_5(PPh_3)]^{2+}$ and they observed two different temperature-dependent processes. The lower temperature process shows equilibration of the MeNC ligands at the unsubstituted metal center, while the higher temperature process, which is promoted by traces of free MeNC, involves equilibration of all isocyanide ligands.

The lower temperature process in the monophosphine derivative, which may also be operative in the parent compound, is of particular interest in that it portends deformation at the metal center. Since the only vacant MO in $[Pd_2(CNMe)_6]^{2+}$ composed mainly of metal d functions is the σ^* orbital of the M–M bond and since this would not be expected to change assuming other reasonable geometries, one might anticipate that metal center deformations in this system should be facile.

In view of the fact that distortions occur along the normal modes of vibration we have considered a symmetry analysis of the normal modes in $[Pd_2(CNMe)_6]^{2+}$ assuming D_{2d} symmetry and monoatomic ligands. Of the 18 normal modes of vibration in this M_2L_6 system, eleven are associated with bending motions and other deformations. The two most important of them which make possible an equilibration of the axial and equatorial isocyanide ligands are an A_1 mode, illustrated as II, which involves deformation of the cis angles θ, and an E mode, III, which is a linear combination of E modes based on deformations of the L–M–M and L–M–L trans angles. When these two normal modes of vibration are superimposed, a possible resultant motion of the M_2L_6 molecule is deformation to a staggered ethane type structure, IV, in which the L ligands at each metal center become equivalent. As we have noted above, there are structural precedents for this type of geometry in transition metal systems. Relaxation of structure IV back to the D_{2d} ground-state structure then permits equilibration of the L ligands as shown according to (1).

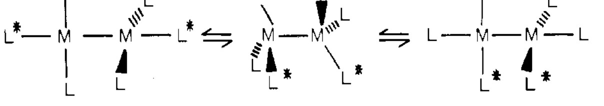


II



a b

III



(1)

IV

In conclusion, it seems clear that the stable binuclear complex $[Pd_2(CNMe)_6]^{2+}$, its Pt analogue, and their derivatives possess an interesting structural and dynamic chemistry.

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Registry No. $[Pd_2(CNMe)_6](PF_6)_2 \cdot {}^1/_2Me_2CO$, 57636-56-3.

Supplementary Material Available: table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(58) The distances, in mm, of the bounding faces from an arbitrary origin are $d_{100} = 0$, $d_{010} = 0$, $d_{101} = 0$, $d_{0\bar{1}0} = 0.089$, $d_{\bar{1}00} = 0.512$, $d_{10\bar{1}} = 0.047$, $d_{\bar{1}01} = 0.417$, $d_{00\bar{1}} = 0.177$, $d_{001} = 0.115$, $d_{01\bar{1}} = 0.106$, $d_{0\bar{1}1} = 0.117$.

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(66) M–C bonds were lengthened by ~0.03 Å but Pd(2)–C(6) was shortened by 0.003 Å and Pd(2)–C(4) was lengthened by only 0.008 Å. C–N and N–Me bonds were shortened by 0.01–0.04 Å.

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(84) **Note Added in Proof.** The crystal and molecular structure of $[(n\text{-}Pr)_4N]_2[Pt_2Cl_4(CO)_2]$ has recently been reported [A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1516 (1975)]. The structure of the anion is similar to that reported here except the two coordination planes have a dihedral angle of ca. 60° between them.

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Preparation and Nuclear Magnetic Resonance Studies of Stereochemically Nonrigid Magnesium, Zinc, and Cadmium Derivatives of Hexaborane(10). Crystal and Molecular Structure of $Mg(THF)_2(B_6H_9)_2$[1]

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Hexaborane(10) has been deprotonated by methylmagnesium halides and the dimethyl derivatives of magnesium, zinc, and cadmium to form a new series of metalloboranes: $Mg(THF)_2(B_6H_9)_2$, $Zn(THF)_2(B_6H_9)_2$, and $Cd(B_6H_9)_2$ which were isolated as crystalline solids. Variable-temperature ^1H NMR spectra of these compounds indicate that they are stereochemically nonrigid with bridging hydrogens and metal being involved in the dynamic processes. At low temperatures the spectra are consistent with metal insertion into a basal boron–boron bond of the anion. The crystal and molecular structure of $Mg(THF)_2(B_6H_9)_2$ has been determined. Each $B_6H_9^-$ anion is coordinated to magnesium through one of its two nonadjacent basal boron–boron bonds. Three-dimensional x-ray data were collected on an automated diffractometer with monochromatized Mo Kα radiation. The structure was solved in the space group $P4_12_12$ with four molecules in the unit cell for which $a = 11.20$ (1), $c = 16.52$ (2) Å (−70°); $a = 11.38$ (1), $c = 16.42$ (2) Å (22°). The calculated densities are 1.02 and 0.99 g/cm^3, respectively. The structure was refined by full-matrix least squares to a final conventional R index of 0.055 for 482 unique reflections with $I \geq 3\sigma(I)$ obtained at −70°. The Mg–B distances are 2.38 (1) and 2.48 (1) Å, and the Mg–O bond distance is 2.019 (5) Å. Bond distances and angles within the B_6H_9 and THF units appear normal; the THF rings are distorted from planarity.

Introduction

The Bronsted acidity of hexaborane(10) is well established and several nonahydrohexaborate(1−) salts have been isolated.[2-5] Deprotonation of B_6H_{10} has been shown to occur by the removal of a bridging proton from one of the four B–H–B bridges. Boron-11 and ^1H NMR spectra of the $B_6H_9^-$ anion in solution suggest rapid exchange of the three remaining bridge hydrogens on the ^1H NMR and boron-11 NMR time scales[3,6] (Similar rapid exchange of the bridge protons in hexaborane(10) has recently been established.[7]) However, the solid-state structure of the nonahydrohexaborate(1−) anion has remained unknown.

The only reported metalloborane involving the nonahydrohexaborate(1−) anion is $[(C_6H_5)_3P]_2CuB_6H_9$.[8] Spectral evidence suggested that the copper had been inserted into a basal boron–boron bond of the anion.

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