1140 *Inorg. Chem.* **1983**, *22*, 1140–1143

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Trichloro(9-methylguaninium)platinum(II) Hydrate and 9-Methylguaninium Hexachloroplatinate(IV) Dihydrate: Synthesis and Structure

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The complex trichloro(9-methylguaninium)platinum(II) hydrate, (9-MeGuaH)$PtCl_3 \cdot H_2O$, and the salt 9-methylguaninium hexachloroplatinate(IV) dihydrate, $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$, have been synthesized and their structures determined. The complex crystallizes in the orthorhombic space group $Pca2_1$ with a = 15.327 (3) Å, b = 8.672 (2) Å, c = 9.496 (2) Å, V = 1262.2 Å^3, Z = 4, D_{measd} = 2.53 g cm^{-3}, and D_{calcd} = 2.555 g cm^{-3}. The salt crystallizes in the space group $P\bar{1}$ with a = 10.425 (4) Å, b = 8.732 (3) Å, c = 6.638 (2) Å, α = 98.74 (4)°, β = 96.72 (3)°, γ = 97.00 (4)°, V = 587.1 Å^3, Z = 1, D_{measd} = 2.19 g cm^{-3}, and D_{calcd} = 2.195 g cm^{-3}. Both structures were solved by heavy-atom methods and were refined to an R index of 0.048 for the complex and 0.027 for the salt. In the complex the square-planar Pt(II) is bound to N7 of the guanine ligand, which is protonated at N3. There is no Pt–O6 interaction. In the salt, guanine is protonated at N7.

Introduction

The importance of metal ions in nucleic acid processes has stimulated considerable research in the area of metal interactions with nuclei acid constituents.[1] The interest in this research has increased with the discovery[2] that some platinum compounds, especially *cis*-$Pt(NH_3)_2Cl_2$, exhibit carcinostatic properties.[3] This has led to an increased research activity in the chemistry and structure of platinum complexes with nitrogen-containing ligands[4] as well as with nucleic acid constituents.[1b]

The nucleic acid bases are natural multisite ligands, and since investigators[5] favor the bases as the primary sites of Pt–DNA bonding, the interaction of these molecules with platinum is being studied intensively. In particular, there appears to be a distinct correlation between Pt-binding ability and the guanine–cytosine content of a polynucleotide.[6] Although a large number of crystal structures of Pt complexes of adenine and its derivatives have been studied,[1] those of guanine and its derivatives have been much less so simply because it has proven difficult to obtain crystalline complexes of guanine. Unlike the reaction of 9-methyladenine with K_2PtCl_4 in acidic medium, which yields a complex,[7] the corresponding reaction with 9-ethylguanine yields the 9-ethylguaninium tetrachloroplatinate(II) salt.[8]

Although numerous studies[9] have suggested that DNA bases are the principal target of these platinum-containing drugs, the mechanism of action remains disputed. Three major explanations for the mode of action have been proposed. One has the Pt(II) center forming an intrastrand linkage between two guanine gases bound through their N7 atoms.[10]

Table I. Summary of Crystal and Intensity Collection Data

	(9-MeGuaH)$Cl_3Pt^{II} \cdot H_2O$	$(9\text{-MeGuaH})_2Pt^{IV}Cl_6 \cdot 2H_2O$
formula	$C_6H_{10}Cl_3N_5O_2Pt$	$C_{12}H_{20}Cl_6N_{10}O_4Pt$
fw	485.63	776.17
a, Å	15.327 (3)	10.425 (4)
b, Å	8.672 (2)	8.732 (3)
c, Å	9.496 (2)	6.638 (2)
α, deg		98.74 (4)
β, deg		96.72 (3)
γ, deg		97.00 (4)
V, Å^3	1262.2	587.1
Z	4	1
D_{calcd}, g/cm^3	2.555	2.195
D_{measd}, g/cm^3	2.53	2.19
space group	$Pca2_1$	$P\bar{1}$
cryst dimens, mm	0.05 × 0.2 × 0.22	0.13 × 0.10 × 0.20
cryst shape	parallelepiped with {100}, {010}, {001}	bound by {100}, {010}, {001} and (101)
radiation	Cu K$\bar{\alpha}$ (λ 1.5418 Å)	Cu K$\bar{\alpha}$ (λ 1.5418 Å)
μ, cm^{-1}	254.4	170.9
transmission factors	0.172–0.608	0.050–0.181
scan speed, deg in 2θ/min	1.0	1.0
scan range	1.0° below Kα_1 to 1.0° above Kα_2	1.0° below Kα_1 to 1.0° above Kα_2
bkgd counting, s	20	20
2θ limit, deg	125.5	125.5
unique data measd	1087	1913
unique data used	948 with $I \geqslant 3\sigma(I)$	1913 with $I \geqslant 1\sigma(I)$
R	0.048	0.027
R_w	0.062	0.035

Another explanation involves formation of an N7,O6 chelate between the guanine base and the Pt(II) center.[11] And yet a third explanation proposes that a Pt–N1 coordination either by itself or as an N1,O6 chelation is involved.[12] We prepared the trichloro(9-methylguaninium)platinum(II) complex in order to find definitive structural evidence for either of these modes of action.

Experimental Section

A. (9-MeGuaH)$PtCl_3 \cdot H_2O$. (a) Synthesis. K_2PtCl_4 (0.415 g) and 9-methylguanine (0.170) g were dissolved separately in the minimum amount of 3 N HCl. The two solutions were mixed, and soon crystals were appearing at the bottom of the dish. The reaction was followed under the microscope, and it was clear that three types of yellow crystals were forming: needles, triclinic parallelepipeds, and octahedral-shaped ones. After as while it was noticed that the needles were slowly dissolving while the others were growing. Immediately the solution was siphoned off and the crystals were separated mechanically under the microscope. IR spectra were taken of all three

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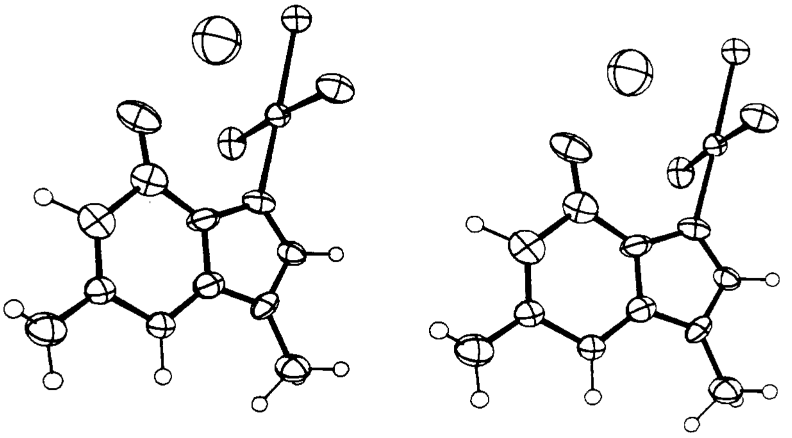

Figure 1. Stereoview of (9-MeGuaH)$PtCl_3 \cdot H_2O$ with 50% probability ellipsoids.

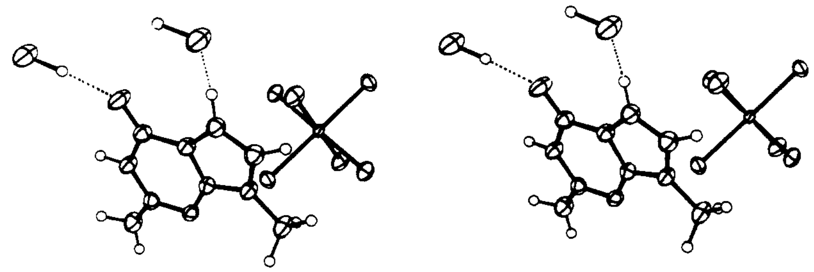

Figure 2. Stereoview of $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$ with 50% probability ellipsoids.

types of crystals and they showed that the needles and the triclinic crystals contained the ligand while the others did not. Crystallographic analysis showed that the needles, which were of rather poor quality, were the complex (9-MeGuaH)$PtCl_3 \cdot H_2O$, while the triclinic crystals, which were of good quality, were the salt $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$. We still cannot explain the presence of $PtCl_6^{2-}$. The octahedral-shaped crystals were not analyzed crystallographically.

(b) Collection and Reduction of Intensity Data. The crystal system (orthorhombic) and the space group ($Pca2_1$; systematic absences $0kl$, $l = 2n + 1$, and $h0l$, $h = 2n + 1$) were determined (Table I) from preliminary oscillation and Weissenberg photographs as well as the density, measured by the flotation method. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 12 automatically centered reflections in the range $60° < 2\theta < 65°$ on a Picker FACS-1 diffractometer. Complete crystal data as well as parameters for data collection are reported in Table I. The crystal was mounted along its long dimension with its c axis approximately parallel to the axis of the instrument. The intensities of three standards monitored after every 60 reflections were stable with a scatter of less than 3.0% from their respective means. The data, corrected for Lorentz, polarization and absorption effects,[13] processed as previously described[7] by using a value of 0.03 for c, the "ignorance factor".

(c) Solution and Refinement of the Structure. The positional coordinates of the Pt and Cl atoms were deduced from a three-dimensional Patterson synthesis. A subsequent structure factor–Fourier calculation revealed the positions of all the non-hydrogen atoms. Several cycles of isotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o) + 0.002F_o^2$, led to an R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ value of 0.08. Two cycles of anisotropic refinement reduced the R value to 0.049. A difference Fourier synthesis at this point revealed the positions of 8 out of 10 hydrogen atoms, from within the 13 highest Fourier peaks. The hydrogen atoms of the water molecule were not located. The methyl group was idealized to a trigonal pyramid with the carbon atoms at the pivot and was refined as a rigid group. For all other hydrogen atoms the bond distances were constrained. Two final cycles of anisotropic refinement with the above mentioned constraints for the hydrogen atoms converged to an R value of 0.048. The final weighted R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2})$ was 0.062. These reflections, 020, $02\bar{2}$, and $03\bar{2}$, badly affected by secondary extinction, were given a zero weight. Anomalous dispersion corrections were applied to all non-hydrogen atoms. The final positional parameters appear in Table II, while the thermal parameters, the observed and calculated structure amplitudes, and the hydrogen parameters are available as supplementary material.[14] The final difference-Fourier map contained no peaks greater than ±0.6 e/Å^3 except one peak at 2.5 e/Å^3 near the Pt site.

B. $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$. (a) Collection and Reduction of Intensity Data. Both Weissenberg and precession photographs indicated lack of symmetry. Successful refinement of the structure of space group $P\bar{1}$ suggests it to be the correct one.

The experimental techniques described above for the collection and reduction of the data were also used for this crystal. The scatter in the standards was less than 2.5% from their respective means and the "ignorance factor" used was 0.025.

(b) Solution and Refinement of the Structure. The structure was solved by standard Patterson–Fourier techniques. Several cycles of isotropic and two of anisotropic refinement reduced R to a value of 0.031. A difference Fourier map at this point revealed the positions of 9 out of 10 hydrogen atoms. One of the water hydrogen atoms was not located. Two subsequent cycles of refinement with the above mentioned constraints for the hydrogen atoms led to convergence and a final R of 0.027 and an R_w (with $w = 1/\sigma^2(F_o)$) of 0.035. Anomalous dispersion corrections were applied to all non-hydrogen atoms. The final difference-Fourier map contained no peaks greater than ±0.5 e/Å^3. The final positional parameters appear in Table II, while the thermal parameters, the observed and calculated structure amplitudes, and the hydrogen parameters are available as supplementary material.[14]

Results and Discussion

Perspective drawings of (9-MeGuaH)$Cl_3Pt \cdot H_2O$ (*the complex*) and $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$ (*the salt*) appear in Figures 1 and 2. Bond distances and angles for both structures appear in Figure 3. Standard deviations estimated from the inverted full matrix are as follows. For *the complex*: Pt–Cl, 0.004 Å; Pt–N, 0.007 Å; C–C (or N), 0.012 Å; angles around Pt, 0.5°; angles in purine, 1°. For *the salt*: Pt–Cl, 0.002 Å; C–C (or N), 0.005 Å; angles around Pt, 0.2°; angles in purine, 0.4°.

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[13] Computer programs used: NRC-2 (data reduction); NRC-3 (absorption correction); SHELX-76 (Fourier–Pattterson least-squares refinement); OETEP (drawings).

[14] See paragraph at end of paper regarding supplementary material.

Table II. Positional Parameters (×10^4) for the Non-Hydrogen Atoms

atom	*x*	*y*	*z*
		$(9\text{-MeGuaH})PtCl_3 \cdot H_2O$	
Pt	4040.0 (3)	2094.1 (5)	7501
Cl1	4826 (2)	3001 (4)	5604 (4)
Cl2	3816 (2)	4557 (3)	8298 (4)
Cl3	3195 (2)	1126 (3)	9298 (4)
O6	6046 (6)	609 (9)	8197 (9)
OW	6862 (7)	2578 (10)	6194 (10)
N1	6357 (4)	−1865 (9)	7723 (8)
N3	5457 (5)	−3541 (9)	6484 (9)
N7	4227 (4)	−90 (8)	6860 (8)
N9	4064 (4)	−2373 (9)	5871 (9)
N11	6828 (7)	−4313 (8)	7164 (9)
C2	6244 (5)	−3233 (8)	7156 (8)
C4	4847 (5)	−2361 (9)	6504 (9)
C5	4995 (5)	−992 (9)	7094 (9)
C6	5805 (6)	−597 (10)	7695 (9)
C8	3723 (6)	954 (9)	6115 (9)
C10	3692 (6)	3547 (10)	4988 (11)
		$(9\text{-MeGuaH})PtCl_6 \cdot 2H_2O$	
Pt	0	0	0
Cl1	1989 (1)	296 (1)	2038 (2)
Cl2	933 (1)	1401 (1)	−2281 (2)
Cl3	491 (1)	−2296 (1)	−1809 (2)
O6	5251 (4)	−3695 (5)	−2765 (5)
OW	2854 (4)	−6556 (5)	−4602 (6)
N1	5698 (4)	−1888 (4)	190 (5)
N3	4386 (4)	−1700 (4)	2874 (5)
N7	2863 (4)	−4911 (5)	−869 (6)
N9	2534 (4)	−3760 (4)	2135 (5)
N11	6242 (4)	45 (5)	3022 (6)
C2	5421 (4)	−1197 (5)	2065 (6)
C4	3642 (4)	−2942 (5)	1667 (6)
C5	3839 (4)	−3672 (5)	−229 (6)
C6	4941 (4)	−3156 (5)	−1117 (6)
C8	2093 (5)	−4938 (5)	578 (6)
C10	1922 (5)	−3373 (6)	3999 (7)

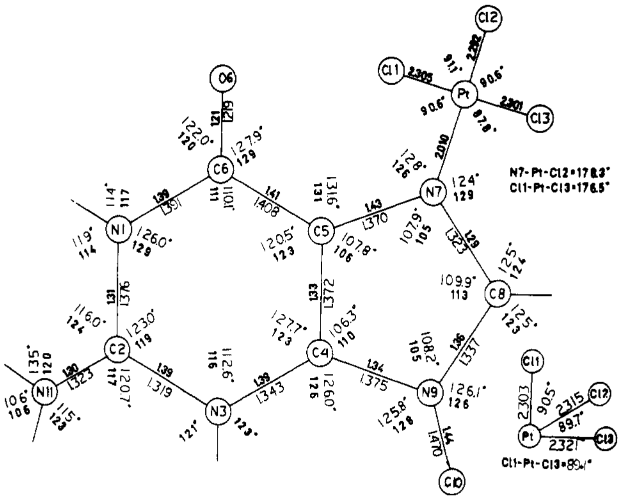


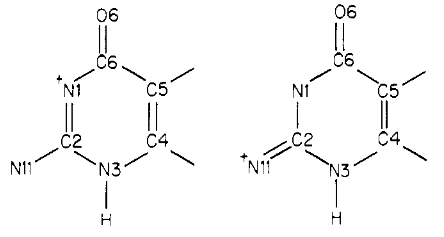
Figure 3. Interatomic bond distances and angles: heavy characters for $(9\text{-MeGuaH})PtCl_3 \cdot H_2O$; light characters for $(9\text{-MeGuaH})_2PtCl_6 \cdot 2H_2O$ (see text for standard deviations).

Platinum Coordination. In *the complex* the compound exists as discrete molecules in which the platinum has a square-planar coordination with a small tetrahedral distortion; while Pt is in the "plane" of Cl1, Cl2, Cl3, and N7, the best plane calculations indicate that Cl1 and Cl3 are 0.04 Å above the "plane" while Cl2 and N7 are 0.04 Å below the "plane". We have observed the same distortion in the corresponding adeninium complex.[7]

The Pt–Cl_3 best plane makes an angle of 79.1° with the guanine (N1–N9) best plane. This torsion angle is rather flexible, and it accommodates itself to the environment of the $PtCl_3$ unit. In the adeninium complex,[7] where one of the chlorine atoms formed a hydrogen bond to the C6 amine group, the torsion angle was 62.6°. The Pt–Cl and Pt–N7 bond distances are in excellent agreement with those in the adeninium complex.[7] We fine no Pt···O6 interaction at a Pt–O6 distance of 3.40 Å.

In *the salt*, the platinum atom occupies a crystallographic center of symmetry. It has a slightly distorted octahedral coordination with four chlorine atoms in the square plane at an average distance of 2.318 Å and two axial chlorine atoms at 2.303 Å. In K_2PtCl_6, where Pt occupies a position with *m*3*m* symmetry,[15] the Pt–Cl distance is 2.323 (1) Å.

The Guaninium Ion. The evidence from the difference-Fourier map for the position of H3, the extra hydrogen needed to neutralize the negative charge on *the complex*, was not very strong. H3 was a peak at 0.5 e/Å^3 in a map that contained several unassigned peaks of 0.6 e/Å^3, which were considered as noise. A much stronger indication that N3 is protonated comes from the angle C2–N3–C4. It has been pointed out[16] that the magnitude of the valence angle of nitrogen atoms in six-membered heterocyclic rings depends on the exocyclic attachment to the nitrogen atoms. The angle is significantly larger when the nitrogen is protonated than when it is not. This effect has been established for adenine[7] and caffeine[17] and noted[8,19] for guanine. We have examined eight structures[8,18–23] with guanine present. When N3 is not protonated,[8,18,20–23] the angle C2–N3–C4 ranges from 111.7 to 114.1° with an average value of 112.4°. The angle C2–N3–C4 in our complex is 116 ± 1°, significantly larger, and we believe that N3 is protonated. This is in agreement with the earlier work of Ringertz,[24] in which he tabulated the effect of exocyclic attachment (H, CH_3, NH_2, O, and S) on the internal ring angles of purines, and also with the case of the $(GuaH)CuCl_3$[19] complex, in which Cu is coordinated at N9 and the authors presumed N3 to be protonated on the basis of the C2–N3–C4 angle which was 118.1°. Another indication that N3 is protonated comes from the increase of both bond lengths adjacent to N3, N3–C2 and N3–C4, both at 1.39 Å as compared to 1.322 and 1.354 Å, respectively, in the protonated cases.[8,18,20–23] The increase in these two bond lengths along with the decrease in N1–C2 and C2–N11 (Figure 3) indicates a major contribution of the structures



for the protonated case. We have observed analogous effects in the case of adenine.[7] We note that metal coordination to N7 (specifically Pt(II) and Cu(II)) is much less effective than a proton is inducing molecular structural changes. In two

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Table III. Possible A–H···B Hydrogen Bonds

A	B	A···B, Å	H···B, Å	A–H···B, deg
		(9-MeGuaH)PtCl$_3$·H$_2$O		
N1	Cl3	3.25	2.28	163
N3	Cl1	3.26	2.28	163
N11	OW	2.85	1.95	158
OW	O	2.85		
OW	Cl1	3.19		
		(9-MeGuaH)$_2$PtCl$_6$·2H$_2$O		
N1	Cl1	3.25	2.25	175
N7	OW	2.67	1.65	162
N11	N3	3.06	2.15	152
OW	O	2.80	1.81	156
OW	Cl1	3.23		
OW	Cl2	3.20		

Cu(II) complexes[20,22] and the present Pt(II) complex, the angle C5–N7–C8 ranges from 104.5 to 105.0°, which is very close to the unprotonated case of 104.2°. This effect has been noted before[7] and established in Hodgson's review paper.[1b]

As is usually observed[25] in nine-atom framework of the purine is significantly nonplanar. The dihedral angle between the highly planar imidazole ring and the pyrimidine ring, which retains some degree of nonplanarity (largest deviation from the plane if 0.039 Å for C6) is 3.0°. The Pt atom is in the imidazole plane. In *the salt* the 9-methylguaninium ion is protonated at N1 and N7 and the valence angles at N1, N7, and the unprotonated N3 are in agreement with the above mentioned rule. The bond lengths and angles are in excellent agreement with those in 9-ethylguaninium ion,[8] with generally no more than twice the estimated standard deviation (0.005 Å, 0.4°) difference. Both the imidazole and the pyrimidine rings are highly planar with an angle of 2.7° between them.

Crystal Packing. The hydrogen bonding in these structures is extensive. There are many potential donor and acceptor sites and almost all of them are used. The hydrogen bonds are listed in Table III and shown in Figures 4[14] and 5.[14] The criterion used for inclusion of an interaction is that of Hamilton and Ibers,[26] who note that a A–H···B hydrogen bond probably exists if both A–H and H···B separations are less than the sum of the van de Waals radii of the two atoms. When the hydrogen position was not known, the A···B separation was used and compared with similar literature[8] values. In *the complex* long zigzag "chains" are formed in which consecutive molecules are held together by hydrogen bonds N3–H3···Cl1 and via the water molecule. The interchain hydrogen bond is N1–H1···Cl3 (Figure 4). In *the salt* the packing is quite different. Two bases form a "planar" dimer across a center of symmetry via hydrogen bonds between N3 and N11. These dimers are joined across another center of symmetry, via the water molecules, to form extended "planar" chains. Except for a weak base stacking arrangement at 3.30 Å, there is no interaction between these "planar" chains. Interspersed between these chains are the PtCl$_6^{2-}$, ions which hold the structure together via hydrogen bonds (Figure 5).

Registry No. (9-MeGuaH)PtCl$_3$, 84433-30-7; (9-MeGuaH)$_2$PtCl$_6$, 84433-31-8; K$_2$PtCl$_4$, 10025-99-7.

Supplementary Material Available: Listings of hydrogen atom parameters, observed and calculated structure amplitudes, and thermal parameters for the non-hydrogen atoms (Table IV) and packing diagrams (Figures 4 and 5) (16 pages). Ordering Information is given on any current masthead page.

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Notes

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Structural Characterization of a $B_{11}H_{11}^{2-}$ Derivative: Molecular Structure of $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$

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The eleven-vertex polyhedral borane $B_{11}H_{11}^{2-}$ has long been of interest due to its remarkably facile fluxional behavior in solution.[1-4] Neither its solid-state nor solution limiting structure is known, though molecular orbital calculations suggest the closo-C_{2v} octadecahedral geometry [C_{2v}-$(1v^62v^4422)$-Δ^{18}-*closo*] to be the most probable (Figure 1). Only one derivative of $B_{11}H_{11}^{2-}$ has been characterized crystallographically. This is the unusual $B_{11}H_9Se_3^{2-}$ species prepared by Todd and co-workers from $B_{11}H_{14}^-$ and polyselenide.[6] The cage geometry was found to be similar to that of the isoelectronic $C_2Me_2B_9H_9$ carborane structure.[7] In both cases, the closo-C_{2v} deltahedral geometry was observed. An analogous geometry was also found in the 11-vertex cage in the metallacarborane $(C_5H_5Co)C_2B_8H_{10}(CoC_2B_8H_{10})$.[8] The lone exception to this structural preference is the $C_2Me_2B_9H_6(OH)_2Br$ structure reported by Scholer where the carborane cage is distorted toward a C_{5v} nido-icosahedral fragment.[9]

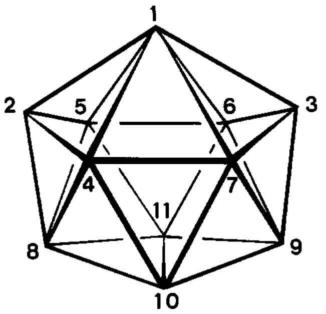

Figure 1. The closo-C_{2v} deltahedron with numbering scheme.

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