Volume 25
Number 1
January 1, 1986

Inorganic Chemistry

Communications

Differences in Binding of (1,2-Cyclohexanediamine)platinum(II) Isomers with d(GpG)

Sir:

Among many *cis*-$PtCl_2(NH_3)_2$ analogues, the Pt(II) complexes involving 1,2-cyclohexanediamine, which will be abbreviated as dach, have been especially noted as a second-generation Pt drug because of its excellent activity.[1] The ligand, dach, has three isomeric forms (*R*,*R*-, *S*,*S*-, and *R*,*S*-dach). We reported that the Pt(II) complexes prepared from the separated isomers have different antitumor activities.[2] This was confirmed by antitumor tests using various tumor systems[3] and Pt(II) complexes involving other chiral chelating diamines.[4] Generally, the Pt complexes of *R*,*R*-dach have a slightly higher activity than the corresponding Pt complexes of *S*,*S*-dach, and the Pt complexes of *R*,*S*-dach are less active and less toxic. However, it is still unresolved why the Pt(II) complexes with the dach isomers have different activities. The present paper should shed a fresh light on this problem. Since DNA has a chiral structure, optically active Pt(II) complexes are expected to interact with DNA in different ways. Recent investigations indicate that intrastrand cross-link between two adjacent guanine bases is a main event in bifunctional interactions of antitumor-active Pt(II) complexes.[5] For these reasons, we have studied the difference in binding of Pt(dach isomers)$^{2+}$ with d(GpG).

The complex Pt(*R*,*R*-dach)[d(GpG)] has been prepared by reaction of $PtCl_2$(*R*,*R*-dach) with an equimolar amount of d(GpG) and by fractionation using HPLC. Pt(*S*,*S*-dach)[d(GpG)] and Pt(*R*,*S*-dach)[d(GpG)] have been prepared by the same method.[6] Since d(GpG) has a chiral structure, Pt(*R*,*R*-dach)[d(GpG)] and Pt(*S*,*S*-dach)[d(GpG)] are expected to be diastereomers that are chemically nonequivalent. In fact, they have different retention times in the HPLC study.[7] The CD spectrum of Pt(*R*,*R*-dach)[d(GpG)][8] bears a similarity to that of the structurally characterized complex *cis*-$Pt(NH_3)_2$[d(GpG)], which has the

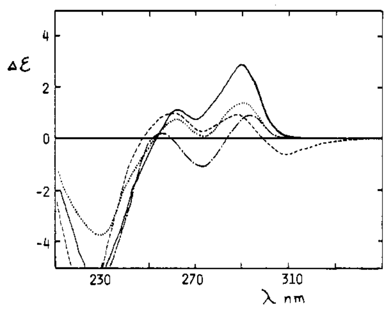

Figure 1. Circular dichroism spectra of Pt(dach isomer)[d(GpG)] compounds in 0.05 M KH_2PO_4 solution (pH 4.6): (···) *R*,*R*; (- - -) *S*,*S*; (—) *R*,*S*-**1**; (–·–) *R*,*S*-**2**.

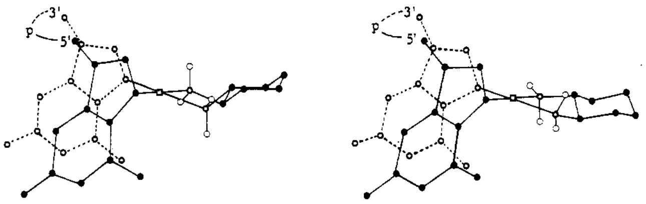

Figure 2. Schematic structures of Pt(*S*,*S*-dach)[d(GpG)] (left) and Pt(*R*,*R*-dach)[d(GpG)] (right).

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(1) (a) Clear, M. J.; Hydes, P. C.; Hepburn, D. R.; Malerbri, B. W. "Cisplatin"; Prestayko, A. W., Crooke, S. T., Carter, S. K., Eds.; Academic Press: New York, 1980; pp 149–170. (b) Hydes, P. C. "Developments in Oncology"; Hacker, M. P., Double, E. B., Krakoff, I. H., Eds.; Martinus Nijhoff Publishing: Boston, 1984; pp 216–227.

(2) (a) Kidani, Y.; Inagaki, K.; Tsukagoshi, S. *Gann* **1976**, *67*, 923. (b) Kidani, Y.; Inagaki, K.; Saito, R.; Tsukagoshi, S. *J. Clin. Hematol. Oncol.* **1977**, *7*, 197.

(3) (a) Kidani, Y.; Inagaki, K.; Iigo, M.; Hoshi, A.; Kuretani, K. *J. Med. Chem.* **1978**, *21*, 1315. (b) Speer, R. J.; Hall, L. M.; Stewart, D. P.; Ridgway, H. J.; Hill, J. F. M.; Kidani, Y.; Inagaki, K.; Noji, M.; Tsukagoshi, S. *J. Clin. Hematol. Oncol.* **1978**, *8*, 44. (c) Kidani, Y.; Noji, M.; Tashiro, T. *Gann* **1980**, *71*, 637.

(4) (a) Noji, M.; Okamoto, K.; Tashiro, T.; Kidani, Y. *J. Med. Chem.* **1981**, *24*, 508. (b) Okamoto, K.; Noji, M.; Tashiro, T.; Kidani, Y. *Chem. Pharm. Bull.* **1981**, *29*, 929. (c) Inagaki, K.; Tajima, K.; Kidani, Y.; Tashiro, T.; Tsukagoshi, S. *Inorg. Chim. Acta* **1979**, *37*, 547. (d) Noji, M.; Gohchi, Y.; Kidani, Y. *Chem.-Biol. Interact.* **1984**, *51*, 37. (e) Noji, M.; Motoyama, S.; Tashiro, T.; Kidani, Y. *Chem. Pharm. Bull.* **1983**, *31*, 1469. (f) Noji, M.; Goto, M.; Kidani, Y.; Tashiro, T. *J. Clin. Hematol. Oncol.* **1984**, *14*, 9.

(5) (a) Tullius, T. D.; Ushay, H. M.; Merkel, C. M.; Caradonna, J. P.; Lippard, S. J. *ACS Symp. Ser.* **1983**, *No. 209*, 51–74. (b) Caradonna, J. P.; Lippard, S. J. *Dev. Oncol.* **1984**, *17*, 15–26. (c) Marquet, J. P.; Butour, J. L.; Johnsson, N. P.; Razaka, H.; Salles, B.; Vienssens, C.; Wright, M. *Dev. Oncol.* **1984**, *17*, 27–38. (d) Reedijk, J.; den Hartog, J. H. J.; Fichtinger-Schepmann, A. M. J.; Marcelis, A. T. M. *Dev. Oncol.* **1984**, *17*, 39–50.

(6) A solution fractionated from HPLC was analyzed for Pt by AAS. From UV spectrophotometry, a molar extinction coefficient of about 24 000/mol of platinum was calculated (at $\lambda_{max} = 259$ nm). From the pH–UV titration curve, the pK_a values of N(1) of Pt(dach isomers)[d(GpG)] were in the range of 8.3–8.5, a value significantly lower than that of the ligand ($pK_a = 9.6$). No protonation reactions at N(7) were observed. Moreover, the change of the UV difference spectra arising from the deprotonation reaction at N(1) agreed with that of the N(7)-platinated guanine derivatives.[10] From these results, Pt(dach isomers)[d(GpG)] are the complexes with an interbase cross-link between the two dG bases through N(7)–N(7). In chromatographic analysis, Pt(dach isomer)[d(GpG)] accounted for more than 90% of the peak area of the products.

(7) Retention time: Pt(*R*,*R*-dach)[d(GpG)], 35.8 min; Pt(*S*,*S*-dach)[d(GpG)], 35.0 min; Pt(*R*,*S*-dach)[d(GpG)], 32.5 min (*R*,*S*-**1**) and 36.5 min (*R*,*S*-**2**). The parameters of the run of HPLC are as follows: column, TSK-Gel CM-2SW; column size, 4.6 × 500 mm; mobile phase, 0.05 M KH_2PO_4 (pH 4.6); flow rate, 0.7 mL/min; detector, UV at 260 nm.

(8) A main component of the CD spectra is thought to arise from the exciton coupling of the d(GpG) moiety. The negative band around 310 nm of the CD spectrum of Pt(*S*,*S*-dach)[d(GpG)] is thought to arise from a chiral diamine moiety.

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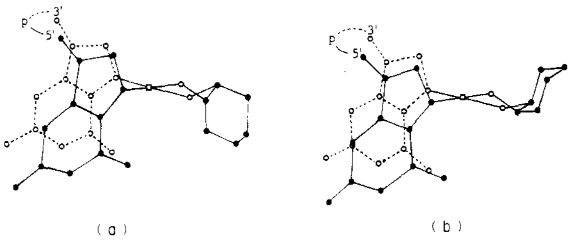

Figure 3. Schematic structures of Pt(R,S-dach)[d(GpG)] compounds, R,S-**1** and R,S-**2**.

structure with a head-to-head arrangement and an anti–anti configuration of the bases.[9] That is, the CD spectra of Pt(R,R-dach)[d(GpG)] and *cis*-Pt(NH_3)$_2$[d(GpG)] exhibited two positive bands around 290 and 260 nm and a negative band at 220–230 nm, respectively. On the other hand, the CD spectrum of Pt(R,R-dach)(dG)$_2$, in which Pt(R,R-dach)(dG)$_2$ is preferentially oriented in a head-to-tail arrangement, exhibits an inversion of CD bands (285 nm (+), 258 nm (−), and 225 nm (+)). In general the signs of CD bands are thought to be sensitive to a relative orientations of bases (changes in orientation of transition moments). Therefore, it seems reasonable to assume that Pt(R,R-dach)[d(GpG)] has a head-to-head arrangement of the bases. Pt(R,R-dach)[d(GpG)] was also a main Pt adduct produced upon the reaction of $PtCl_2$(R,R-dach) with DNA.[10] When Pt(R,R-dach)$^{2+}$ forms a cross-link between two adjacent guanine bases in DNA, a head-to-head arrangement is likely because DNA is a right-handed helical molecule with a head-to-head arrangement. Hydrogen bonds between guanine and cytosine bases are weakened, but not disrupted, by binding of *cis*-Pt(NH_3)$_2$$^{2+}$ to two adjacent guanine bases on the same strand of DNA and oligonucleotides.[11]

Molecular models indicate that one of the axial amino protons of Pt(R,R-dach)[d(GpG)] is close to O(6)-5′ (O(6) of the 5′-guanosine side) because Pt(R,R-dach)$^{2+}$ takes the λ-gauche form and that of Pt(S,S-dach)[d(GpG)] is close to O(6)-3′ because of the δ-gauche form of the chelate ring. Both the cyclohexane and chelate rings of Pt(R,R-dach)$^{2+}$ have a fixed configuration like *trans*-decalin. We have no evidence concerning the hydrogen bond between O(6) and the amino protons on the chelate ring. However, the presence of such a spacially oriented hydrogen bond was reported in the study of Pt(S,S-dach)(G)$_2$ though it has a head-to-tail structure.[12] It has often been pointed out that interaction between NH_2 groups and O(6) of the guanine base may be important for the appearance of antitumor activity.[13]

The antitumor activity of the geometrical isomer, Pt(R,S-dach)$^{2+}$, shows a definitive difference in comparison with that of Pt(II) complexes involving R,R-dach and S,S-dach. In the Pt(R,S-dach)$^{2+}$ complex, the two amino groups are bound to the cyclohexane ring with axial and equatorial orientations, and two λ and δ conformations are interconvertible, with a simultaneous inversion of the cyclohexane ring. Reaction of $PtCl_2$(R,S-dach) with d(GpG) yielded two equal amounts of Pt adducts (R,S-**1** and R,S-**2**). Each adduct was fractionated with use of HPLC. The CD spectra of R,S-**1** and R,S-**2** seem to have characteristic features of a head-to-head arrangement. The cyclohexane ring of Pt(R,S-dach)$^{2+}$ is almost perpendicularly oriented with respect to the platinum coordination plane. Conformations such as torsion angle about glycosyl bonds and puckering of furanose rings may be affected by the axially standing cyclohexane ring. The following two platinum binding modes would be expected. One is the structure where the cyclohexane ring faces the side of O(6) of the guanines (Figure 3a), and the other is the structure in which the cyclohexane ring is oriented to the opposite side (Figure 3b). The proposed structures seem to be reasonable on the basis of the following experiments. (1) If the proposed arrangements are true, it should not be expected that R,S-**1** and R,S-**2** are in an equilibrium state. An exchange reaction between R,S-**1** and R,S-**2** was not observed even if each adduct was heated at 95 °C. (2) Reaction of $PtCl_2$(1,3-dach) with d(GpG) also yielded two Pt adducts.[14] Pt(1,3-dach)$^{2+}$ has a symmetry plane involving Pt, C(2), and C(5),[15] and the cyclohexane ring of Pt(1,3-dach)$^{2+}$ is almost perpendicularly oriented with respect to the platinum coordination plane. Therefore, reaction of Pt(1,3-dach)$^{2+}$ with d(GpG) is expected to form diastereomers. In fact, the reaction yielded two Pt(1,3-dach)[d(GpG)] compounds. No exchange reaction between the two Pt adducts was observed.

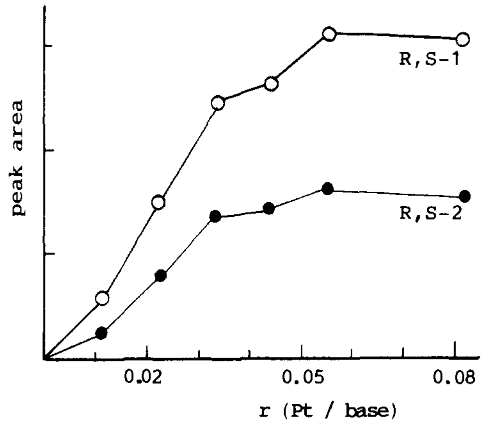

Figure 4. Variation of peak area of Pt(R,S-dach)[d(GpG)] compounds R,S-**1** and R,S-**2**, obtained from Pt-modified DNA as a function of r. DNA was allowed to react with various concentrations of $PtCl_2$(R,S-dach) in 0.01 M phosphate buffer (pH 7.3) at 37 °C for 4 days, and the resulting Pt-modified DNA was digested by the enzymes.[10]

We also examined whether or not the proposed arrangements can take place in reaction with DNA. Pt(R,S-dach)$^{2+}$-modified DNA obtained from the reaction of $PtCl_2$(R,S-dach) with calf thymus DNA was digested by the enzymes deoxyribonuclease I, snake venom phosphodiesterase, alkaline phosphatase, and calf spleen phosphodiesterase, reported in a previous paper.[10] The HPLC study of the digested products indicates the following: (1) Pt(R,S-dach)[d(GpG)] compounds, R,S-**1** and R,S-**2**, are preferential Pt adducts, especially when $r < 0.06$ (r = amount of Pt added/amount of base). (2) Formation of R,S-**1** and R,S-**2** increases with increasing r and tends to saturate at about $r = 0.06$ (Figure 4).[16,17] (3) There is a significant difference in the relative ratio of R,S-**1** and R,S-**2** when compared with the case of the reaction with d(GpG), and the ratio (R,S-**1**:R,S-**2** = 1.0:0.59)

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[9] (a) Girault, J.-P.; Chottard, G.; Lallemand, J.-Y.; Chottard, J.-C. *Biochemistry* **1982**, *21*, 1352. (b) den Hartog, J. H. J.; Altona, C.; Chottard, J.-C.; Girault, J.-P.; Lallemand, J.-Y.; de Leeuw, F. A. A. M.; Marcelis, A. T. M.; Reedijk, J. *Nucleic Acids Res.* **1982**, *10*, 4715.

[10] Inagaki, K.; Kasuya, K.; Kidani, Y. *Chem. Lett.* **1984**, 171–174.

[11] (a) Miller, S. K.; VanDerveer, D. G.; Marzilli, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 1048. (b) den Hartog, J. H. J.; Altona, C.; van Boom, J. H.; van der Marel, G. A.; Haasnoot, C. A. G.; Reedijk, J. *J. Am. Chem. Soc.* **1984**, *106*, 1528. (c) van Hemelryck, B.; Guittet, E.; Chottard, G.; Girault, J.-P.; Huynh-Dinh, T.; Lallemand, J.-Y.; Igolen, J.; Chottard, J.-C. *J. Am. Chem. Soc.* **1984**, *106*, 3037. (d) den Hartog, J. H. J.; Altona, C.; van Boom, J. H.; Reedijk, J. *FEBS Lett.* **1984**, *176*, 393.

[12] Gullotti, M.; Pacchioni, G.; Pasini, A.; Ugo, R. *Inorg. Chem.* **1982**, *21*, 2006–2014.

[13] Leh, H. K. V.; Wolf, W. *J. Pharm. Sci.* **1976**, *65*, 315.

[14] Abbreviation: 1,3-dach, *cis*-1,3-cyclohexanediamine.

[15] (a) Srneski, F. E.; Mcphail, A. T.; Onan, K. D. *J. Am. Chem. Soc.* **1977**, *99*, 7736. (b) Saito, R.; Kidani, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 57. (c) Kamisawa, K.; Matsumoto, K.; Ooi, S.; Kuroya, H.; Saito, R.; Kidani, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2330.

[16] At $r = 0.055$, sum of the peak area of R,S-**1** and R,S-**2** occupies about 75% of the peak area of all the Pt adducts.

[17] The nearest-neighbor frequency of the d(GpG) sequence in calf thymus DNA (GC content 42%) is about 7%. If Pt(R,S-dach)$^{2+}$ binds only to d(GpG) moieties in DNA, the d(GpG) moieties will be saturated at $r = 0.035$.[18] If saturation observed in Figure 4 is assumed to correspond with the maximum attainable number (35 cross-links per 1000 nucleotides), 28 cross-links (i.e., Pt(R,S-dach)[d(GpG)]) per 1000 nucleotides are counted at $r = 0.035$. This value clearly indicates a preferential binding of Pt(R,S-dach)$^{2+}$ to d(GpG).

[18] Fichtinger-Schepman, A. M. J.; van der Veer, J. L.; den Hartog, J. H. J.; Lohman, P. H. M.; Reedijk, J. *Biochemistry* **1985**, *24*, 707.

does not depend on *r*. The enzymatic digestion of Pt(1,3-dach)-DNA also indicates similar results, and the difference in the relative ratio of the two Pt(1,3-dach)[d(GpG)] compounds becomes much greater (1.0:0.26). Stereoselectivity observed in the experiment with the DNA presumably arises from a steric hindrance, being caused by the axially standing cyclohexane ring. Such steric hindrance may impede an approach toward DNA. This may be the reason for its weaker antitumor activity and toxicity.

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Received April 23, 1985

Synthesis of the Octathiotritungstate Anion, $W_3S_8^{2-}$. First Example of Square-Planar Coordination about a Tungsten Atom

Sir:

In recent years the WS_4^{2-} anion has been extensively used as a versatile bidentate ligand and for the syntheses of a variety of soluble binary or ternary metal sulfides.[1] In all these complexes derived from WS_4^{2-} the coordination geometries about the W atoms are either tetrahedral or square pyramidal.[2-8] Here we report the synthesis and structure of $[PPN]_2[W_3S_8]$ (PPN = bis(triphenylphosphoranylidene)ammonium). The central W atom in the $W_3S_8^{2-}$ ion is at the center of a square plane of S atoms; to our knowledge this is the first example in the coordination chemistry of W where square-planar geometry is observed.

The reactions of WS_4^{2-} with acids are known to lead to a mixture of thiotungstate anions,[3,8] although there are no previous reports of the $W_3S_8^{2-}$ ion. We have prepared it as $[PPN]_2[W_3S_8]$ by the reaction of $[NH_4]_2[WS_4]$ with H_2SO_4 according to the stoichiometry shown in (1), followed by addition of [PPN]Cl in

$$3WS_4^{2-} + 4H^+ \rightarrow W_3S_{9-x}^{2-} + 2H_2S + (1 + x)S\downarrow \qquad x = 0 \text{ or } 1 \tag{1}$$

methanolic solution. Although by following the stoichiometry shown in (1) we minimized the formation of $W_4S_{12}^{2-}$, it appears from the IR spectral data[9] that anions such as $W_3S_8O^{2-}$ and $W_3S_9^{2-}$ are also formed. Attempts to precipitate one of these thiotungstate anions selectively with the use of different tetraalkylammonium salts or separation of the anions by chromatographic techniques have not been successful. However, fractional crystallization by the slow diffusion of hexane into a dichloromethane solution of the crude product gives orange needle-like crystals of $[PPN]_2[W_3S_8]$ suitable for characterization by X-ray[10] and other physical methods.[9,11]

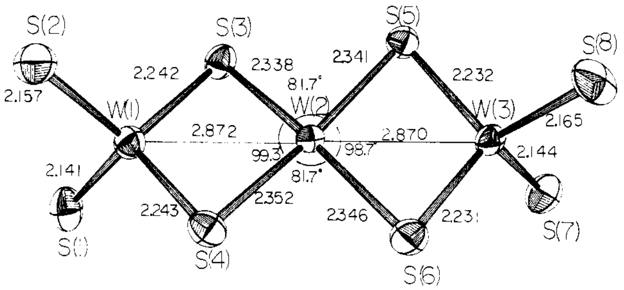

Figure 1. Structure of the $W_3S_8^{2-}$ ion. The labeling scheme and some bond distances and bond angles are shown. The estimated standard deviations in the W-W and W-S bond distances and the S-W-S bond angles are 0.001 Å, 0.004 Å, and 0.1°, respectively.

Table I. Comparisons of Thiotungstate Anions

anion	mean W-W, Å	formal oxidn states	no. of d electrons per W-W bond
$[W_4S_{12}]^{2-a}$	3.027	+6, +5, +5, +6	$^2/_3$
$[W_3S_8O]^{2-b}$	2.961	+6, +4, +6	1
$[W_3S_9]^{2-c}$	2.965	+6, +4, +6	1
$[W_2S_4(S_2C_2H_4)_2]^{2-d}$	2.862 (1)[f]	+5, +5	2
$[W_3S_8]^{2-e}$	2.871 (1)	+6, +2, +6[g]	2

[a] Reference 3. [b] Reference 2. [c] Reference 7. [d] Reference 5. [e] This work. [f] Estimated standard deviation of the mean is given only in those cases where equivalent distances were averaged. [g] An alternative assignment is +5, +4, +5, but this seems less likely because the terminal tungsten atoms have nearly perfect tetrahedral environments characteristic of the +6 state. With either assignment the number of d electrons per bond remains the same.

The structure of the $W_3S_8^{2-}$ ion is shown in Figure 1. The ion has pseudo-D_{2h} symmetry with tetrahedral coordination around the terminal W atoms. The central W atom has square-planar coordination of S atoms with a very slight tetrahedral distortion: deviations from the best weighted least-squares plane are W(2) = -0.0032 (6), S(3) = -0.179 (4), S(4) = 0.188 (4), S(5) = 0.167 (4), S(6) = -0.210 (4) Å.

Three different types of W-S bonds, four around the central W atom, four terminal ones, and four bonds involving terminal W and bridging S atoms, with average values 2.344 (3), 2.152 (6), and 2.237 (3) Å, respectively, are observed. The last two values are very close to the corresponding distances in the WS_4^{2-} anion and in bis(tetrathiotungstato) complexes.[1,12-15]

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(1) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934-955.
(2) Secheresse, F.; Lavigne, G.; Jeannin, Y.; Lefebvre, J. *J. Coord. Chem.* **1981**, *11*, 11-16.
(3) Secheresse, F.; Lefebvre, J.; Daran, J. C.; Jeannin, Y. *Inorg. Chem.* **1982**, *21*, 1311-1314.
(4) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 672-678.
(5) Pan, W.-H.; Chandler, T.; Enemark, J. H.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 4265-4269.
(6) Müller, A.; Hellmann, W.; Römer, C.; Römer, M.; Bögge, H.; Jostes, R.; Schimanski, U. *Inorg. Chim. Acta* **1984**, *83*, L75-L77.
(7) Müller, A.; Bögge, H.; Krickemeyer, E.; Henkel, G.; Krebs, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1014-1019.
(8) Königer-Ahlborn, E.; Müller, A. *Angew. Chem.* **1975**, *87*, 598.
(9) $[PPN]_2[W_3S_8]$ has IR bands at 495, 490, and 440 cm^{-1}. Bands (cm^{-1}) in related compounds as described by the authors are as follows: for $W_3S_8O^{2-}$,[2] 970 (W-O), 495 (W-S_{term}), 465 and 453 (W-S-W); for $W_3S_9^{2-}$,[8] 525 (W-S_{apex}), 490 and 485 (W-S_{term}), 465 and 435 (W-S-W); for $W_4S_{12}^{2-}$,[3] 525 (W-S_{apex}), 495 and 485 (W-S_{term}), 448 and 350 (W-S-W). From the relative intensities of the characteristic IR bands, less than 20% of the crude product is $[PPN]_2[W_3S_8]$ while more than 50% is $[PPN]_2[W_3S_9]$.
(10) Crystal data for $[PPN]_2[W_3S_8]$, $C_{72}H_{60}N_2P_4S_8W_3$: triclinic, C_i^1-$P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 11.548$ (2) Å, $b = 15.175$ (5) Å, $c = 22.181$ (5) Å, $\alpha = 104.90$ (2)°, $\beta = 90.80$ (2)°, $\gamma = 110.31$ (2)°, and $V = 3500$ Å^3 at -150 °C. A total of 13 088 intensities were measured out to 2θ(Mo Kα_1) = 40° to yield 6512 unique reflections after correction for absorption and averaging. Refinement was by full-matrix least-squares methods on F^2 with all unique data used. All non-hydrogen atoms were refined anisotropically. The positions of the H atoms were idealized and their contributions to F_o^2 included. The final cycle of refinement of 802 variables and 6512 observations converged to $R(F^2) = 0.064$. The conventional R index, $R(F)$, for the 4060 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.037. A list of positional parameters is provided in Table II (supplementary material).
(11) Magnetic susceptibility measurements over the range 5-290 K indicate that $[PPN]_2[W_3S_8]$ is diamagnetic. The ^{1}H NMR spectrum of the material from -60 to +5 ppm shows no resonances that can be ascribed to possible W-H bonds, nor are there any characteristic IR bands for W-H stretching modes in the region 2200-1600 cm^{-1}. The cyclic voltammogram of $[PPN]_2[W_3S_8]$ (2.0 mM in acetonitrile) shows no reversible or quasi-reversible oxidation or reduction peaks between +2.0 and -2.0 V.
(12) Sasvări, K. *Acta Crystallogr.* **1963**, *16*, 719-724.
(13) Müller, A.; Paulat-Böschen, I.; Krebs, B.; Dornfeld, H. D. *Angew. Chem.* **1976**, *88*, 691-692.
(14) Müller, A.; Dornfeld, H.; Henkel, G.; Krebs, B.; Viegers, M. P. A. *Angew. Chem.* **1978**, *90*, 57-58.
(15) Paulat-Böschen, I.; Krebs, B.; Müller, A.; Königer-Ahlborn, E.; Dornfeld, H.; Schulz, H. *Inorg. Chem.* **1978**, *17*, 1440-1443.

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