This work has demonstrated that homogeneous mixed-metal alloy and oxide films can be prepared by the chemical vapor deposition of Fe/Co heteronuclear organometallic clusters. This technique should in principle be extendable to clusters of various metal compositions so as to give a wide range of metal and oxide phases.[11]

Acknowledgment. We thank Dr. K. Spear and Dr. R. Messier of the Materials Research Laboratory for invaluable discussions on CVD, apparatus design, and film characterization and D. Strickler, L. Eminhizer, and N. Suhr for assistance in SEM, electron microprobe, and atomic absorption analyses, respectively. We also thank Dr. L. N. Mulay for his assistance in making and interpreting the magnetic measurements.

Supplementary Material Available: A drawing of the experimental CVD apparatus (Figure A) (1 page). Ordering information is given on any current masthead page.

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Received October 7, 1987

Articles

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Crystal Structure of a Hydroxo-Bridged Platinum(II) Tetramer, *cyclo*-Tetrakis(μ-hydroxo)tetrakis((ethylenediamine)platinum(II)) Tetranitrate

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Received March 19, 1987

The crystal structure of *cyclo*-tetrakis(μ-hydroxo)tetrakis((ethylenediamine)platinum(II)) tetranitrate has been determined by X-ray diffraction. The monoclinic crystal, space group $P2_1/c$, has cell dimensions a = 9.544 (4) Å, b = 17.683 (14) Å, c = 16.725 (18) Å, and β = 92.91 (6)° with four tetramers in the unit cell. The structure was refined to R = 0.057 and R_w = 0.048. The cation consists of an eight-membered ring with approximate symmetry S_4. Each platinum in the hydroxo-bridged tetramer has square-planar coordination. The four Pt atoms in the ring are planar with two cross-ring O atoms on one side of the plane and the other two O atoms on the other side. The cross-ring oxygen–oxygen interactions of 2.68 (3) and 2.74 (2) Å seem to indicate intramolecular hydrogen bonding. The crystal is stabilized by an extensive hydrogen-bonding system. All the amine groups are hydrogen-bonded to the nitrate ions.

Introduction

The anticancer drug cisplatin, *cis*-$[Pt(NH_3)_2Cl_2]$, has been shown to bind predominantly to d(GpG) sequences in cellular DNA.[1] The neutrality requirement of the drug is important for its passage through the cell membranes. Inside the cells, where the chloride ion concentration is much lower than in the blood plasma, the complex is hydrolyzed. At physiological pH, the predominant hydrolyzed species is *cis*-$[Pt(NH_3)_2(H_2O)(OH)]^+$, which has been shown to oligomerize quite rapidly.[2] The hydrolyzed products of cisplatin were found by ^{195}Pt NMR studies to contain monomers and hydroxo-bridged dimers and trimers. These oligomeric species are toxic[2] and might be partly responsible for the toxicity of cisplatin.

The crystal structures of the NO_3^- and CO_3^{2-} salts of the planar bis(hydroxo)-bridged dimers have been reported several years ago.[3-5] The crystal structure of the SO_4^{2-} and NO_3^- salts of a trimeric cation were also investigated.[6,7]

Chelates in which the NH_3 ligands have been replaced by 1,2-diaminocyclohexane (dach) seem to show higher antitumor activity than cisplatin with a reduced toxicity. Furthermore, the hydroxo-bridged dimers and trimers of dach–Pt(II) complexes are active anticancer agents and are less toxic than the monomer,[8] in contrast to the case for the NH_3 oligomers. This might partly account for the reduced toxicity of dach complexes. The crystal structure of the SO_4^{2-} salt of a *trans*-dach hydroxo-bridged trimer was recently reported.[9]

The antitumor activity of the chelate complex $[Pt(en)Cl_2]$ (en = ethylenediamine) is well-known. It is also less toxic than cisplatin.[10] The antitumor activity of the hydroxo-bridged dimer of en was determined by Broomhead, Fairlie, and Whitehouse, and the dimer was found to be toxic.[11] The dinuclear platinum(II) complex was prepared by a slight modification of the method used for $[Pt(NH_3)_2OH]_2(NO_3)_2$. The compound was characterized mainly by infrared spectroscopy, which showed the characteristic Pt–O–H bending vibration at 950–1100 cm^{-1}.

We have recently attempted to prepare the hydroxo-bridged dimer of en by a similar method. The elemental analyses and the conductance measurements of the crystallized compound were in agreement with the dimer formulation. We chose one crystal for X-ray diffraction studies. To our surprise, we found that the compound was a hydroxo-bridged cyclic tetramer. Tetramers were suspected to exist in small quantities in solution, but no such compound of platinum(II) has been reported yet. We now report the crystal structure of *cyclo*-tetrakis(μ-hydroxo)tetrakis((ethylenediamine)platinum(II)) tetranitrate.

Experimental Section

Synthesis. $[Pt(en)Cl_2]$ (1.08 mmol) and $AgNO_3$ (2.14 mmol) were stirred together in 10 mL of water in the dark. After 24 h, the AgCl

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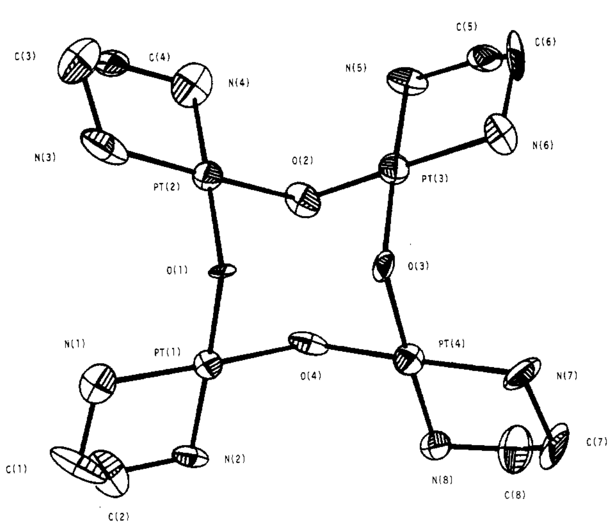

Figure 1. The hydroxo-bridged platinum(II) tetrameric cation.

precipitate was filtered out and washed twice with 2 mL of water. The filtrate was concentrated to 7–8 mL. The pH of the solution, which was about 2, was adjusted to 5.8 with 1 M NaOH. The solution was then left at room temperature for slow crystallization. The crystals were filtered out, washed with small quantities of cold water, and dried. Anal. Calcd (for dimers or tetramers): C, 7.19; H, 2.71. Found: C, 7.28; H, 2.63.

Crystal Data: $[Pt(NH_2(CH_2)_2NH_2)OH]_4(NO_3)_4$; fw = 1336.8; monoclinic; $P2_1/c$; $a = 9.544$ (4), $b = 17.683$ (14), $c = 16.725$ (18) Å; $\beta = 92.91$ (6)°; $V = 2819$ (4) Å^3; $F(000) = 2432$; $D_{calcd} = 3.149$ Mg m^{-3}; $Z = 4$; λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 200.8 cm^{-1}; $T = 293$ K.

Crystallographic Measurements and Structure Resolution. The crystals were recrystallized from water. A very pale yellow elongated plate was selected for X-ray diffraction analysis, after examination under a polarizing microscope for homogeneity. Crystals having similar shapes were separated under the microscope for density measurements. The density of the crystals from three different batches were measured in a mixture of diiodomethane–bromoethane. The average value was 3.13 (4) Mg m^{-3}. The crystal chosen for crystallographic measurements was mounted roughly along the *a* axis and had the following distances (mm) between the indicated faces: 0.024 (011–0$\bar{1}\bar{1}$) × 0.048 (01$\bar{1}$–0$\bar{1}$1) × 0.336 (110–$\bar{1}$10,$\bar{1}\bar{1}$0). The cell parameters were obtained from the refined angles of 15 well-centered reflections on a Syntex P$\bar{1}$ diffractometer using graphite-monochromatized Mo Kα radiation.

The intensity data were collected as described before.[12] A set of 4459 independent reflections $(h,k,\pm l)$ were measured up to $2\theta = 48°$ by the $2\theta/\theta$ scan technique. On the basis of the criterion $I > 2.5\sigma(I)$, a set of 2124 reflections was used for the structure resolution. The data were corrected for absorption from the equations of the crystal faces (transmission factors from 0.397 to 0.628) and for Lorentz and polarization effects.

The coordinates of the four Pt atoms were determined by direct methods on a Nicolet SHELXTL system. The positions of all the other non-hydrogen atoms were obtained by structure factor and difference-Fourier calculations. The refinement on $|F|$ was done by block-diagonal least-squares calculations. The H atoms could not be located, but they were fixed at the calculated positions with isotropic $B = 6.0$ Å^2 (N–H = 0.85 Å, C–H = 0.95 A). Individual weights $w = 1/\sigma^2(F)$ were applied. The refinement of the scale factor, coordinates, and anisotropic temperature factors of all atoms converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.048$. The refined coordinates are listed in Table I.

The scattering curves of Cromer and Waber[13] were used, except for hydrogen.[14] The anomalous dispersion terms[15] of Pt were included in the structure factor calculations. The calculations were done on a Cyber 830 computer with programs already described.[12]

Table I. Refined Coordinates (×10^4 for Pt, ×10^3 for Other Atoms) and Equivalent Isotropic Temperature Factors (×10^4)[a]

atom	x	y	z	U_{eq}, Å^2
Pt(1)	3703 (1)	7067 (1)	6109 (1)	289
Pt(2)	2515 (1)	5629 (1)	4930 (1)	308
Pt(3)	1246 (1)	6808 (1)	3528 (1)	322
Pt(4)	2321 (1)	8356 (1)	4617 (1)	322
O(1)	194 (2)	649 (1)	569 (1)	284
O(2)	305 (2)	641 (1)	408 (1)	386
O(3)	95 (2)	747 (1)	453 (1)	317
O(4)	383 (2)	758 (1)	501 (1)	436
N(1)	369 (2)	651 (1)	717 (1)	365
N(2)	539 (2)	767 (1)	663 (1)	329
N(3)	207 (3)	483 (1)	573 (1)	575
N(4)	299 (3)	474 (1)	420 (1)	503
N(5)	149 (3)	620 (1)	254 (1)	496
N(6)	−45 (2)	726 (1)	286 (1)	317
N(7)	87 (3)	914 (1)	414 (2)	540
N(8)	355 (3)	926 (1)	472 (1)	388
N(9)	548 (3)	569 (1)	272 (1)	568
N(10)	251 (3)	310 (1)	17 (2)	575
N(11)	6 (3)	403 (1)	301 (2)	582
N(12)	257 (4)	463 (2)	137 (2)	1073
C(1)	449 (3)	698 (2)	776 (2)	586
C(2)	591 (3)	724 (2)	738 (2)	590
C(3)	201 (3)	402 (2)	532 (2)	539
C(4)	315 (3)	406 (2)	474 (2)	504
C(5)	78 (4)	655 (2)	182 (2)	438
C(6)	−67 (3)	677 (2)	214 (2)	425
C(7)	139 (4)	992 (2)	426 (2)	755
C(8)	302 (4)	984 (2)	414 (2)	564
O(5)	456 (2)	593 (1)	229 (1)	674
O(6)	534 (3)	512 (1)	315 (1)	636
O(7)	661 (3)	595 (2)	269 (2)	1231
O(8)	351 (3)	323 (2)	−19 (2)	1151
O(9)	139 (3)	332 (2)	−1 (2)	1268
O(10)	268 (4)	273 (2)	75 (2)	1450
O(11)	−73 (2)	373 (1)	249 (1)	600
O(12)	95 (2)	357 (1)	335 (1)	594
O(13)	20 (2)	468 (1)	320 (1)	686
O(14)	187 (4)	504 (2)	110 (2)	1402
O(15)	377 (3)	452 (2)	112 (2)	1067
O(16)	249 (4)	430 (2)	198 (2)	1445

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \bar{a}_i \cdot \bar{a}_j$.

Results and Discussion

The crystal consists of cyclic hydroxo-bridged $[Pt(en)OH]_4^{4+}$ cations as shown in Figure 1. The complex cation is formed of four square-planar $[Pt(en)(OH)_2]$ units sharing both OH corners. Its structure may be visualized as consisting of a tetrahedral core of oxygen atoms, with platinum atoms bridging four of the six edges of the tetrahedron. The four Pt atoms define a plane and are located approximately on the corner of a square with sides of 3.378 (2), 3.321 (2), 3.418 (2), and 3.582 (2) Å. These distances are about 10% longer than in the ammine dimer (3.09 Å).[3] The vertices of the oxygen tetrahedron lie approximately 1 Å above and below the plane defined by the four Pt atoms. The eight-membered ring has approximate S_4 symmetry. The deviations from the best plane through the four Pt atoms are as follows (Å): Pt(1), 0.006 (1); Pt(2), −0.007 (1); Pt(3), 0.007 (1); Pt(4), −0.006 (1); O(1), −1.15 (2); O(2), 1.11 (2); O(3), −1.08 (2); O(4), 1.00 (2). A similar structure has been reported for dimethylgold(III) hydroxide, $[(CH_3)_2AuOH]_4$.[16] A comparison of the torsion angles (Table S6, supplementary material) in the Pt_4O_4 ring (−69.3, −76.4, 76.6, 72.5, −76.2, −68.5, 67.8, and 74.3°) with those of the gold tetramer (−58, −90, 61, 82, −57, −87, 57, and 83°) clearly indicates similar conformations in the two compounds.

The coordination around each platinum atom is square planar. The deviations from the four best planes are shown in Table S4 (supplementary material). The angles around each platinum atom are close to the expected 90 and 180° (Table II), but there are some slight deviations due to a slight strain caused by the bidentate ligand. The chelate angles N–Pt–N are smaller (83–85 (1)°) than the other angles as observed in other Pt–ethylenediamine struc-

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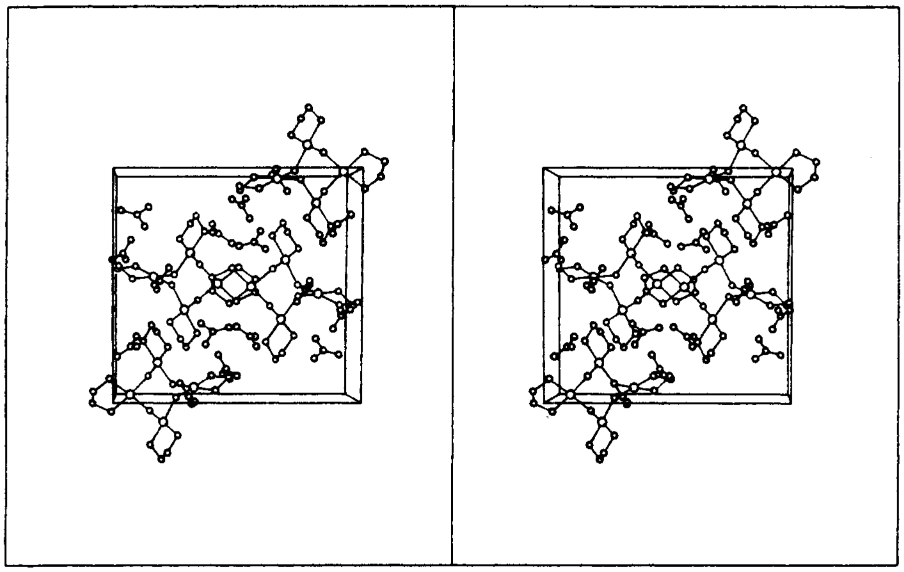

Figure 2. Packing within the unit cell (*b* axis horizontal, *c* axis vertical).

tures.[17-19] The O–Pt–O angles (87–91°) are normal, and the Pt–O–Pt angles (108–120°) are close to the tetrahedral values as observed in the three reported Pt trimers[6,7,9] and the Au tetramer.[16] This is in contrast to the four-membered ring in bis(μ-hydroxo) Pt dimers,[3-5,20,21] where the Pt–O–Pt angles are constrained to 100° and the O–Pt–O angles to 80°. These structural results, demonstrating one way of achieving an unstrained ring system and tetrahedral angles about the bridging O atoms, provide some evidence for the fundamental instability of the dimer with its strained bond angles about the O and Pt atoms.

The Pt–N and Pt–O distances (average 2.04 (2) and 2.06 (2) Å, respectively) agree with the values found in the hydroxy-bridged Pt dimers and trimers mentioned above. The bond lengths and angles within the en ligands are normal (Table II). The torsion angles have been calculated (Table S6).

Some of the nitrate ions are disordered as shown by the high thermal factors. Values of U_{eq} up to 0.145 Å^2 have been observed. But the compound is really a tetranitrate salt, since exclusion of the most disordered nitrate ion (N(12), O(14), O(15), O(16)) in the structure refinement considerably increased the *R* factor. The N–O bond distances vary from 1.10 (5) to 1.28 (3) Å with an average value of 1.20 Å (Table S3, supplementary material), and the O–N–O angles vary from 109 (4) to 130 (3)° with an average value of 120°.

The packing of the ions within the unit cell is shown in Figure 2. It consists of layers of cations parallel to the *ab* plane centered at $z = 0$ and $^1/_2$. The cations are held together by an extensive hydrogen-bonding system involving the nitrate ions. The distances and angles involving possible hydrogen bonds are shown in Table S5 (supplementary material). The short distances O(1)- - -O(3) (2.74 (2) Å) and O(2)- - -O(4) (2.68 (3) Å) might indicate transannular hydrogen bonding between opposite bridging hydroxo groups. The bridging ligands O(1)–H and O(2)–H would be hydrogen-bonded to O(3) and O(4), respectively, while O(3)–H and O(4)–H would be hydrogen-bonded to the oxygen atoms of the nitrate ions. The angles Pt–O(1)- - -O(3) and Pt–O(2)- - -O(4) range from 97 (1) to 101 (1)° (Table S5). A molecular model has shown that the H atoms on O(1) and O(2) can point directly toward O(3) and O(4), respectively, assuming tetrahedral angles around the O atoms.

Table II. Bond Distances (Å) and Angles (deg)

Pt(1)–O(1)	2.06 (2)	Pt(1)–N(1)	2.02 (2)
Pt(1)–O(4)	2.07 (2)	Pt(1)–N(2)	2.08 (2)
Pt(2)–O(1)	2.08 (2)	Pt(2)–N(3)	2.00 (2)
Pt(2)–O(2)	2.05 (2)	Pt(2)–N(4)	2.05 (2)
Pt(3)–O(2)	2.04 (2)	Pt(3)–N(5)	1.99 (2)
Pt(3)–O(3)	2.07 (2)	Pt(3)–N(6)	2.07 (2)
Pt(4)–O(3)	2.05 (2)	Pt(4)–N(7)	2.09 (2)
Pt(4)–O(4)	2.07 (2)	Pt(4)–N(8)	1.99 (2)
N(1)–C(1)	1.48 (4)	N(5)–C(5)	1.49 (4)
N(2)–C(2)	1.53 (4)	N(6)–C(6)	1.49 (4)
N(3)–C(3)	1.59 (4)	N(7)–C(7)	1.46 (4)
N(4)–C(4)	1.52 (4)	N(8)–C(8)	1.49 (4)
C(1)–C(2)	1.58 (4)	C(5)–C(6)	1.55 (4)
C(3)–C(4)	1.50 (4)	C(7)–C(8)	1.58 (5)
Pt(1)- - -Pt(2)	3.378 (2)	Pt(2)- - -Pt(3)	3.321 (2)
Pt(1)- - -Pt(4)	3.582 (2)	Pt(3)- - -Pt(4)	3.418 (2)
Pt(1)–O(1)–Pt(2)	109.4 (8)	O(1)–Pt(1)–N(1)	90.8 (8)
Pt(1)–O(4)–Pt(4)	120.1 (9)	O(1)–Pt(1)–N(2)	174.6 (8)
Pt(2)–O(2)–Pt(3)	108.4 (8)	O(1)–Pt(2)–N(3)	91.8 (9)
Pt(3)–O(3)–Pt(4)	112.3 (8)	O(1)–Pt(2)–N(4)	176.6 (9)
O(1)–Pt(1)–O(4)	90.3 (8)	O(2)–Pt(2)–N(3)	176.9 (9)
O(1)–Pt(2)–O(2)	91.0 (7)	O(2)–Pt(2)–N(4)	91.8 (9)
O(2)–Pt(3)–O(3)	88.6 (7)	O(2)–Pt(3)–N(5)	93.4 (9)
O(3)–Pt(4)–O(4)	87.2 (7)	O(2)–Pt(3)–N(6)	173.8 (8)
O(3)–Pt(3)–N(5)	177.8 (9)	O(4)–Pt(4)–N(7)	175.7 (9)
O(3)–Pt(3)–N(6)	94.6 (8)	O(4)–Pt(4)–N(8)	96.1 (8)
O(3)–Pt(4)–N(7)	94.2 (8)	O(4)–Pt(1)–N(1)	175.9 (8)
O(3)–Pt(4)–N(8)	176.3 (8)	O(4)–Pt(1)–N(2)	93.8 (8)
N(1)–Pt(1)–N(2)	85 (1)	N(5)–Pt(3)–N(6)	83 (1)
N(3)–Pt(2)–N(4)	85 (1)	N(7)–Pt(4)–N(8)	83 (1)
Pt(1)–N(1)–C(1)	107 (2)	Pt(3)–N(5)–C(5)	112 (2)
Pt(1)–N(2)–C(2)	108 (2)	Pt(3)–N(6)–C(6)	107 (2)
Pt(2)–N(3)–C(3)	111 (2)	Pt(4)–N(7)–C(7)	111 (2)
Pt(2)–N(4)–C(4)	106 (2)	Pt(4)–N(8)–C(8)	109 (2)
N(1)–C(1)–C(2)	108 (2)	N(5)–C(5)–C(6)	101 (2)
N(2)–C(2)–C(1)	103 (2)	N(6)–C(6)–C(5)	110 (2)
N(3)–C(3)–C(4)	103 (2)	N(7)–C(7)–C(8)	104 (3)
N(4)–C(4)–C(3)	112 (2)	N(8)–C(8)–C(7)	106 (2)

But these transannular O- - -O distances are also close to the sum of the van der Waals radii (2.8 Å). The above proposed hydrogen-bonding scheme is asymmetric since O(1) and O(2) donate H bonds without accepting any, while O(3) and O(4) accept and dónate H bonds. This asymmetry should be reflected in the Pt–O distances. We have observed very similar Pt–O bonds, but the standard deviations on these distances are very high. We favor at the moment the transannular hydrogen bonding, especially since there are no other acceptor atoms around O(1) and O(2)

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(below 3.25 Å). All the amine groups are also involved in hydrogen bonding with the nitrate ions.

The analyzed crystal was synthesized by a method used for the synthesis of hydroxo-bridged dimers[11] involving the equations

$$\begin{tikzcd}{[Pt(en)X_2]} + 2AgNO_3 \arrow[r, "H_2O"] & {[Pt(en)(H_2O)_2](NO_3)_2} + 2AgX\downarrow \arrow[d, "NaOH"', "pH\sim 6"] \\ & {[Pt(en)OH]_2(NO_3)_2}\end{tikzcd}$$

The method used by Broomhead, Fairlie, and Whitehouse[11] to synthesize $[Pt(en)OH]_2^{2+}$ is not well-described, and the authors have characterized their compound only by elemental analyses, conductance measurements, and the Pt–O–H bending vibration at 950–1100 cm^{-1} in the infrared spectrum. We do not believe that these methods are sufficient to identify different oligomers. ^{195}Pt NMR is a much better technique to identify such species. We have measured the ^{195}Pt NMR spectra of the products of the above reaction, and we have found the presence of several species. The proportion of each species depends on the pH, concentration, time of reaction, and halide anions. We have not identified all the different species yet, but we believe that the hydrolyzed product is a mixture of monomeric and oligomeric species (dimers, trimers, and tetramers). Attempts to grow crystals of the hydroxo-bridged dimer for structure determination were not successful. The work is continuing especially with methyl derivatives of en. We hope that the presence of bulky alkyl substituents on the coordinating amine will reduce the number of species formed. Therefore, the ^{195}Pt NMR spectra should be easier to interpret.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR (Québec) for financial support.

Registry No. $[Pt(NH_2(CH_2)_2NH_2)OH]_4(NO_3)_4$, 111380-02-0; $[Pt(en)Cl_2]$, 14096-51-6.

Supplementary Material Available: Anisotropic temperature factors (Table S1), fixed coordinates of the hydrogen atoms (Table S2), bond distances and angles in the nitrate ions (Table S3), weighted least-squares planes (Table S4), distances and angles involving possible hydrogen bonds (Table S5), and torsion angles (Table S6) (9 pages); observed and calculated structure factor amplitudes (Table S7) (17 pages). Ordering information is given on any current masthead page.

Contribution from the Institute for Molecular Science,
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Syntheses and Properties of Monochalcogenide-Substituted Hexamolybdenum Halide Clusters

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Received April 15, 1987

Syntheses and properties of three types of monochalcogenide-substituted hexamolybdenum clusters are reported. $Cs_3[(Mo_6Cl_7S)Cl_6]\cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.213$ (2) Å, $b = 13.021$ (1) Å, $c = 9.367$ (1) Å, $\alpha = 95.71$ (1)°, $\beta = 105.92$ (1)°, $\gamma = 90.61$ (1)°, $V = 1307.5$ (3) Å^3, and $Z = 2$. $Cs_3[(Mo_6Cl_7Se)Cl_6]\cdot H_2O$ crystallizes also in the triclinic space group $P\bar{1}$ with $a = 11.238$ (2) Å, $b = 13.077$ (3) Å, $c = 9.398$ (2) Å, $\alpha = 95.57$ (2)°, $\beta = 105.65$ (1)°, $\gamma = 90.62$ (2)°, $V = 1322.6$ (4) Å^3, and $Z = 2$. In both crystals the chalcogenide is disordered among the eight capping sites. The Mo–Mo distances are 2.609 (2) and 2.612 (2) Å for the sulfide and the selenide complexes, respectively, and are similar to those of other complexes with the isoelectronic Mo_6 (12+) core. The ^{95}Mo NMR signals of clusters with mixed capping ligands in acetonitrile split into two in the range 2488–3617 ppm, indicating significant lower field shift despite their low formal oxidation number. The terminal chloride ions are replaced by the solvent molecule easily in water but difficultly in acetonitrile. Absorption spectra of $[(Mo_6Cl_7S)Cl_6]^{3-}$, $[(Mo_6Cl_7Se)Cl_6]^{3-}$, and $[(Mo_6Br_7S)Cl_6]^{3-}$ in the 250–600-nm region are similar to one another but change slightly depending on the terminal ligand. Their oxidation potentials ($E_{1/2}$) in acetonitrile are lower than those of the $Mo_6X_8^{4+}$ (X = halide) core by more than 0.8 V. A change in the terminal ligand seems to affect the $E_{1/2}$ value to a much less extent.

Introduction

The chemistry of cluster complexes with the hexamolybdenum core and various ligands has become attractive in recent years. Chevrel phase compounds $[M_xMo_6X_8$ (M = Fe, Cu, Pb, etc.; X = S, Se, Te)] are nonstoichiometric superconductors,[1] whereas halide clusters $[[(Mo_6X_8)Y_6]^{2-}$ (X, Y = Cl, Br, I)] are discrete luminescent ions.[13–17] The total oxidation number of the hexamolybdenum core is 12+–16+ in Chevrel phases[1–6] (i.e. Mo_6S_8 (16+), $Cu_2Mo_6S_8$ (14+), $Cu_4Mo_6S_8$ (12+), etc.), whereas only the 12+ state is known for the halide clusters. The X-ray structure and electronic absorption, infrared absorption (IR), and X-ray photoelectron spectra (XPS)[7–12] as well as the electrochemistry[14,15] were studied on halide clusters with various terminal ligands. Little information is available, however, concerning hexamolybdenum clusters with mixed capping ligands. Crystals of a $[(Mo_6Cl_7S)Cl_6]^{3-}$ (**1**) salt were synthesized by Michel and McCarley,[18] and those of $[(Mo_6Cl_7Se)Cl_{6/2}]$ by Perrin et al.[19] Their X-ray structures and IR and XPS spectra (pyridinium salt of **1**) were reported, but the properties in solution including electronic absorption, ^{95}Mo NMR, and electrochemical behavior remain unknown. Systematic studies of such cluster complexes with mixed

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0020-1669/88/1327-0013$01.50/0 © 1988 American Chemical Society