The diruthenium(II) unit is bridged by two anionic PhNpy and two neutral dmpm ligands. The arrangement of ligands is trans in nature. The geometry of Ru(1) is pseudooctahedral with one axial Cl coordination, while Ru(2) is in a square-pyramidal environment. In **2**, the axial ligand of Ru(2) was a neutral PhNHpy ligand. In **1**, the presence of two dmpm ligands makes the axial coordination on Ru(2) difficult because of the presence of methyl groups on the P atoms and the presence of two pendant phenyl groups on the amine nitrogen atoms.

The Ru(1)-Ru(2) distance in **1** is 2.340 (2) Å. The Ru-Ru distances in Ru(II)Ru(III) complexes[1-5,12-14,20,21] lie in the range 2.25-2.31 Å. In $Ru_2Cl(PhNpy)_4$,[12] **2**,[20] and $Ru_2Cl(O_2CCH_3)_4$,[3,5] the Ru-Ru bond lengths are 2.275 (3), 2.308 (1), and 2.287 (2) Å, respectively. The lengthening of the metal-metal bond in **1** could be due to the addition of one electron to the antibonding level. The other reasons could be due to a greater bite of the dmpm ligands over other ligands and due to the presence of a strong axial Ru-Cl bond. The shortest Ru-Ru distance of 2.238 (1) Å was observed[16] in $Ru_2(mhp)_4 \cdot CH_2Cl_2$ in which the metal centers do not have any axial ligand. A 2:2 arrangement of mhp ligands across the diruthenium core prohibits any kind of axial ligation. In $Ru_2(O_2CCH_3)_4(THF)_2$, the Ru-Ru distance is slightly longer, 2.260 (2) Å, and the metals have axial THF ligands. When the diruthenium core is not held by any bridging ligand, the Ru-Ru distance is long; e.g. in Ru_2L_2 (L = tetraazaannulene), the distance is 2.379 (1) Å.[22] Similarly, in $(Ru(OEP))_2$, the bond length is 2.408 (1) Å.[23]

The Ru(1)-Cl(1) distance in **1** is 2.480 (5) Å. The Ru(2)-Ru(1)-Cl(1) angle is essentially linear. As in **2**, the orientation of the PhNpy ligands in **1** is unidirectional. Such an arrangement allows the formation of a strong axial coordination on one ruthenium. In all polar molecules,[12-14] the Ru-Cl distances are short, having a value of ca. 2.43 Å, compared to those where both metal centers have axial coordinations.

The Ru-P bond lengths in **1** are in the range 2.387 (5)-2.405 (5) Å. The P-C bond lengths are normal. The P(1)-Ru(1)-P(2) and P(3)-Ru(2)-P(4) angles are 166.6 (2) and 172.0 (2)°, respectively. While the Ru-Ru-P angles are all obtuse (average 95.3°), the Cl-Ru(1)-P angles are all acute (average 83.3°). Among the Ru-N bond lengths, the Ru-N(amine) distances are shorter than the Ru-N(pyridine) bonds. This is expected if we assume the negative charge of the $PhNpy^-$ ligand to be concentrated primarily on the amine nitrogen atoms. The average value of the Ru-N distances is 2.122 [12] Å. The N-Ru-N angles are essentially linear. The Ru-Ru-N angles are all acute, but the Cl-Ru-N angles are obtuse. This could be due to the steric strain present in the molecule. Both PhNpy and dmpm ligands undergo considerable twist. The average P-Ru-Ru-P and N-Ru-Ru-N torsion angles are 22.4 and 17.3°, respectively. The torsion angles N-Ru-Ru-N observed[12,20] in **2** and $Ru_2Cl(PhNpy)_4$ are 3.2 and 22.7°, respectively.

Acknowledgment. We are grateful to the National Science Foundation for support.

Registry No. **1**, 99582-45-3; **1** (2+ ion), 99572-92-6; **1** (3+ ion), 99572-93-7; **2**, 99572-91-5; $Ru_2Cl(O_2CCH_3)_4$, 38833-34-0.

Supplementary Material Available: Listings of bond distances, bond angles, anisotropic thermal parameters, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of a Novel Hexanuclear Complex of Platinum(II) with 2-Aminoethanethiolate

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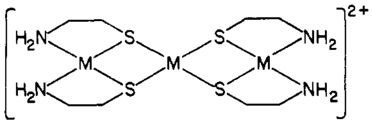
(Ethylenediamine)dibromoplatinum(II) reacts with 2-aminoethanethiol (AETH) at pH 10.5 in water to form light yellow crystals of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$. In the hexanuclear $[Pt_6(SCH_2CH_2NH_2)_8]^{4+}$ cation, which is crystallographically required to be centrosymmetric, two of the platinum atoms have a *cis*-$[Pt(AET)_2]$ square-planar (PtN_2S_2) structure, while square-planar ($PtNS_3$) geometry is achieved for the other four platinum atoms by coordination to a chelating AET ligand and two bridging sulfur atoms. The six platinum atoms do not form a regular polyhedron but rather are joined by doubly bridging thiolate sulfur atoms into three fused rings, a central Pt_4S_4 eight-membered ring and two outer Pt_3S_3 six-membered rings. All eight 2-aminoethanethiolate ligands are both chelating and bridging. The average Pt-S and Pt-N bond lengths are 2.30 (2) and 2.085 (10) Å, respectively. The compound crystallizes in the triclinic space group $P\bar{1}$, with a = 12.231 (2) Å, b = 12.400 (2) Å, c = 9.212 (1) Å, α = 107.13 (1)°, β = 108.88 (1)°, γ = 105.67 (1)°, V = 1156 Å^3, and Z = 1. The final $R(F)$ value was 0.036 for 2448 observed reflections.

Introduction

The metal complexes of 2-aminoethanethiol (AETH) were first studied by Jensen, who observed the formation of two Ni(II) complexes in solution.[1] In subsequent work, Jicha and Busch isolated two distinct types of compounds, one of which had the expected $[M(AET)_2]$ stoichiometry, M = Ni, Pd, while the other had the rather unusual formula $[M_3(AET)_4]Cl_2$.[2] The structure was proposed[2] for the trinickel(II) complex and was subsequently confirmed by single-crystal X-ray diffraction work.[3] A closely related trinickel(II) complex, $[Ni_3L_2]Cl_2 \cdot 4H_2O$, LH_2 = *N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)ethylenediamine,[4] was prepared and structurally characterized in 1975.[5]



Although mono- and trinuclear complexes of 2-aminoethanethiol with Ni(II) and Pd(II) have been thoroughly investigated,[1-3,6-8] reports of the chemistry of Pt(II) with this ligand are scarce, and for binary compounds we have found reference only

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(1) Jensen, K. A. *Z. Anorg. Chem.* **1936**, *229*, 265.
(2) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 872.
(3) Wei, C. H.; Dahl. L. F. *Inorg. Chem.* **1970**, *9*, 1878.
(4) Lippard, S. J. *Acc. Chem. Res.* **1973**, *6*, 282.
(5) Trimakis, A.; Rabinowitz, H. N.; Lippard, S. J., unpublished results from the Department of Chemistry, Columbia University, 1975. The compound $Ni_3L_2Cl_2 \cdot 4H_2O$ was prepared in CH_2Cl_2 from hydrated nickel(II) chloride and LH_2. It crystallizes in monoclinic space group $P2_1/n$ with unit cell dimensions a = 13.484 (5) Å, b = 5.442 (1) Å, c = 19.938 (5) Å, β = 101.16 (2)°, Z = 2, ρ_{calcd} = 1.693 g cm^{-3}, and ρ_{obsd} = 1.69 (1) g cm^{-3}. The structure was refined to R_1 = 0.023 and R_2 = 0.029.
(6) Schlapfer, C. W.; Nakamoto, K. *Inorg. Chim. Acta* **1972**, *6*, 177.
(7) Jayasooriya, U. A.; Powell, D. B. *Spectrochim. Acta, Part A* **1974**, *30A*, 553.
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Table I. Experimental Details of the X-ray Diffraction Study of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$ (**1**)

(A) Crystal Parameters[a]

a, Å	12.231 (2)	*V*, Å^3	1156
b, Å	12.400 (2)	space group	$P\bar{1}$
c, Å	9.212 (1)	*Z*	1
α, deg	107.13 (1)	*d*(calcd), g/cm^3	3.173
β, deg	108.88 (1)	*d*(obsd), g/cm^3	3.16 (1)
γ, deg	105.67 (1)	fw	2207

(B) Measurement of Intensity Data[b]

instrument: Enraf-Nonius CAD-4F κ geometry diffractometer
radiation: Mo Kα (λ = 0.71073 Å) graphite monochromatized
temp: 24 °C
takeoff angle: 2.3°
standards, measd every 1 h:[c] $(\bar{3}\bar{1}\bar{3})$, $(\bar{4}12)$, $(2\bar{3}2)$
no. of reflecns collected: 3841
data collection range: $3 \leq 2\theta \leq 25°$, $\pm h, \pm k, \pm l$; $25 < 2\theta \leq 45$, $\pm h, \pm k, l$

(C) Treatment of Intensity Data[d]

linear abs coeff[e]	221
averaging, R_{av}	0.0201
no. of unique data	2989
no. of obsd data, $I > 3\sigma(I)$	2448

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta \geq 23°$. [b] For typical procedures, see: Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379. [c] No decay in intensities was observed. [d] F_o and $\sigma(F_o)$ were corrected for background, attenuation, and Lorentz–polarization effects of X-radiation as described in footnote *b*. [e] An empirical absorption correction was performed by using PSICOR, kindly provided by J. M. Williams.

to the trans mononuclear complex.[7] Our continued interest in the aqueous chemistry of platinum(II), especially as probes of polynucleotide structure and as antitumor drugs,[9] led us to study the chemistry of (terpyridine)platinum(II) with various thiolate ligands, including 2-aminoethanethiol.[9,10] During the course of this investigation we discovered an even more complex and interesting reaction chemistry of 2-aminoethanethiol with platinum(II) than had previously been uncovered with its lighter congeners. Here we describe the synthesis and structural characterization of the novel hexanuclear complex $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$ (**1**).

Experimental Section

Preparation of $[Pt(en)Br_2]$. A solution of $[Pt(en)I_2]$[11] (1.519 g, 2.98 mmol) in water was allowed to react for 12 h in the dark with 1.00 g of $AgNO_3$. The AgI precipitate was removed by filtration, and excess (1.03 g) NaBr was added to the filtrate. The yellow precipitate (1.100 g, 91%) was filtered and washed with water, ethanol, and ether and then dried in vacuo. It was used without further purification.

Preparation of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$ (1). A 0.302-g (2.66-mmol) sample of 2-aminoethanethiol hydrochloride (purchased from Aldrich and used without further purification) was dissolved in 30 mL of deionized water, and the pH of the solution was adjusted to 10.5 with 0.5 N sodium hydroxide. A 1.100-g (2.68-mmol) amount of solid $[Pt(en)Br_2]$ was added to the thiolate solution, and the mixture was heated on a steam bath until all the solid dissolved (approximately 10 min). The solution was allowed to cool and then was filtered. Slow evaporation of this light yellow solution afforded X-ray-quality, light yellow crystals, which were filtered, washed with cold water, and then dried in vacuo. Attempts to wash the crystals with ethanol destroyed their crystallinity. The filtrate was warmed gently on a steam bath and, upon slow evaporation, a second crop of the product was harvested to give a total of 0.195 g (27% yield) of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$. Anal. Calcd for $Pt_6S_8N_8C_{16}H_{60}O_6Br_4$: C, 8.71; H, 2.74; N, 5.08; S, 11.62; Br, 14.48. Found: C, 9.13; H, 2.67; N, 5.17; S, 11.79; Br, 14.87.

Collection and Reduction of X-ray Data. A light yellow crystal was mounted with epoxy resin on the end of a glass fiber. It had approximate dimensions of 0.11 mm × 0.15 mm × 0.17 mm. Open-counter ω scans of low-angle reflections revealed structureless profiles, and the peak widths were judged to be acceptable ($\Delta\bar{\omega}_{1/2} = 0.23°$). Intensity data and unit cell parameters were measured with a single-crystal diffractometer as described in Table I. The space group could be either *P*1 (C_1^1) or $P\bar{1}$ (C_i^1).[12] Statistical analysis of the data suggested the centrosymmetric space group, and this choice was confirmed by successful refinement of the structure.

Table II. Final Positional Parameters for $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$ (**1**)[a]

ATOM	X	Y	Z
Pt1	0.60488(5)	0.18096(6)	0.34242(7)
Pt2	0.35543(5)	0.01503(6)	0.43350(7)
Pt3	0.36789(6)	0.30417(6)	0.40808(7)
S12	0.6825(4)	0.0333(4)	0.3552(5)
S21	0.3959(4)	0.0502(4)	0.2201(5)
S31	0.5440(4)	0.3431(4)	0.3625(5)
S32	0.4327(4)	0.2245(4)	0.5975(5)
N1	0.7924(11)	0.3023(12)	0.4410(16)
N2	0.2835(13)	-0.1729(12)	0.2702(15)
N31	0.2962(12)	0.3616(12)	0.2212(15)
N32	0.2087(13)	0.2840(12)	0.4534(16)
C11	0.8515(13)	0.1311(16)	0.445(2)
C12	0.8708(15)	0.2372(16)	0.398(2)
C21	0.3738(14)	-0.1057(15)	0.0981(19)
C22	0.2639(15)	-0.1934(16)	0.0982(18)
C31	0.4709(15)	0.3365(16)	0.1518(20)
C32	0.3914(15)	0.4159(15)	0.165(2)
C33	0.3254(16)	0.2451(16)	0.6864(20)
C34	0.1978(16)	0.2084(16)	0.551(2)
Br1	0.0873(3)	0.1234(3)	0.8445(3)
Br2	0.8177(2)	0.49526(18)	0.2479(3)
OW1	0.9830(13)	0.1381(12)	0.1313(16)
OW2	0.9973(13)	0.3456(13)	0.8753(18)
OW3	0.0928(16)	0.4566(17)	0.2409(19)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme.

Solution and Refinement of the Structure. The platinum atoms were located by using the direct-methods program MULTAN.[13] All the remaining nonhydrogen atoms were found in subsequent difference Fourier maps. Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were obtained from ref 14. Anisotropic thermal parameters were used for the non-hydrogen atoms. All hydrogen atoms were placed in their calculated positions (d(C–H) = 0.95 Å) and constrained to "ride" on the atoms to which they are attached. The hydrogen atoms were assigned a common isotropic thermal parameter, which converged at $U = 0.02$ Å^2.

With use of SHELX-76,[15] full-matrix least-squares refinement was carried out on 218 variable parameters. The refinement converged at $R_1 = 0.0355$ and $R_2 = 0.0512$.[16] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.2389/[\sigma^2(F_o) + 0.000625(F_o)^2]$. The maximum parameter shift in the final cycle of refinement was 0.01σ, and the largest peaks on the difference maps (2.9, 1.9 e/Å^3) were located at distances of approximately 1 Å from the platinum atoms.

Final non-hydrogen atom positional parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles with their estimated standard deviations are given in Table III. Listings of final observed and calculated structure factors, anisotropic thermal parameters, and final hydrogen atom positional and

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(10) Dewan, J. C.; Lippard, S. J.; Bauer, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 858.
(11) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2600.
(12) Hahn, T., Ed. "International Tables for X-ray Crystallography"; D. Reidel Publishing Co.: Dordrecht, Holland, 1983; Vol. A, pp 102–105.
(13) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.
(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.
(15) SHELX-76: Sheldrick, G. M. In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 34–42.
(16) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

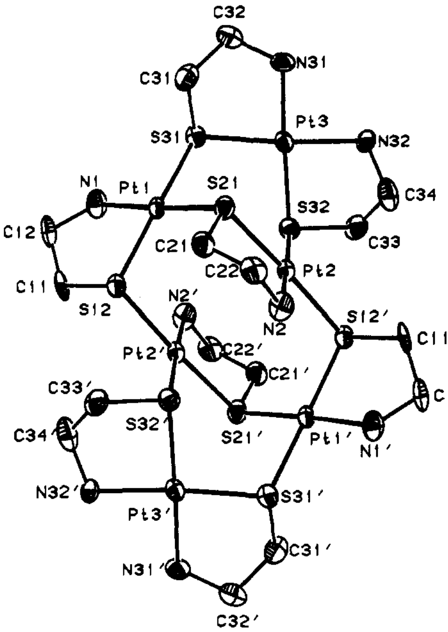

Figure 1. Structure of the $[Pt_6(AET)_8]^{4+}$ cation showing the 40% probability thermal ellipsoids and atom-labeling scheme.

Table III. Interatomic Distances (Å) and Angles (deg) for $[Pt_6(AET)_8]Br_4{\cdot}6H_2O$[a]

Coordination Sphere			
Pt1 - N1	2.08(1)	Pt1 - S21	2.287(4)
Pt1 - S12	2.293(5)	Pt1 - S31	2.303(5)
Pt2 - N2	2.10(1)	Pt2 - S21	2.305(5)
Pt2 - S32	2.310(4)	Pt2 - S12'	2.341(5)
Pt3 - N31	2.08(2)	Pt3 - N32	2.08(2)
Pt3 - S31	2.276(5)	Pt3 - S32	2.278(5)
N1 - Pt1 - S21	176.5(5)	N1 - Pt1 - S12	85.8(4)
N1 - Pt1 - S31	90.0(4)	S21 - Pt1 - S12	96.0(2)
S21 - Pt1 - S31	88.5(2)	S12 - Pt1 - S31	173.2(1)
N2 - Pt2 - S21	84.7(5)	N2 - Pt2 - S32	176.2(4)
N2 - Pt2 - S12'	91.9(5)	S21 - Pt2 - S32	91.7(2)
S21 - Pt2 - S12'	175.9(2)	S32 - Pt2 - S12'	91.7(2)
N31 - Pt3 - N32	90.7(6)	N31 - Pt3 - S31	86.5(5)
N31 - Pt3 - S32	175.0(3)	N32 - Pt3 - S31	175.1(4)
N32 - Pt3 - S32	87.5(5)	S31 - Pt3 - S32	95.6(2)
Ligand Geometry			
S12 - C11	1.83(1)	S21 - C21	1.82(2)
S31 - C31	1.82(2)	S32 - C33	1.79(2)
N1 - C12	1.48(3)	N2 - C22	1.45(2)
N32 - C34	1.48(3)	N31 - C32	1.50(3)
C11 - C12	1.48(3)	C21 - C22	1.48(3)
C31 - C32	1.57(3)	C33 - C34	1.49(2)
C11 - S12 - Pt1	98.5(7)	C11 - S12 - Pt2'	107.8(7)
Pt1 - S12 - Pt2'	104.0(2)	C21 - S21 - Pt1	109.9(6)
C21 - S21 - Pt2	97.6(7)	Pt1 - S21 - Pt2	106.2(1)
C31 - S31 - Pt3	97.1(6)	C31 - S31 - Pt1	108.8(7)
Pt3 - S31 - Pt1	110.0(2)	C33 - S32 - Pt3	95.2(7)
C33 - S32 - Pt2	106.4(5)	Pt3 - S32 - Pt2	104.3(1)
C12 - N1 - Pt1	111.7(8)	C22 - N2 - Pt2	113.(1)
C34 - N32 - Pt3	111.(1)	C32 - N31 - Pt3	113.(1)
C12 - C11 - S12	111.(1)	C11 - C12 - N1	110.(2)
C22 - C21 - S21	108.(1)	N2 - C22 - C21	111.(1)
C32 - C31 - S31	106.(1)	N31 - C32 - C31	108.(2)
C34 - C33 - S32	111.(1)	N32 - C34 - C33	109.(1)

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

thermal parameters are available in Tables S1–S3, respectively, supplied as supplementary material. Figure 1 depicts the molecular geometry along with the atom-labeling scheme, and Figure 2 displays a stereoview of the unit cell packing.

Results and Discussion

Synthesis. The pale yellow compound $[Pt_6(AET)_8]Br_4{\cdot}6H_2O$ (**1**) is prepared by allowing solid $[Pt(en)Br_2]$ to react with a basic solution of 2-aminoethanethiol. Warming the reaction mixture results in dissolution of solid $[Pt(en)Br_2]$ to give a clear yellow solution from which crystals of $[Pt_6(AET)_8]Br_4{\cdot}6H_2O$ eventually deposit. Attempts to react $[Pt(en)Br_2]$ with 2-aminoethanethiol at neutral pH were unsuccessful, with no reaction being observed after an equivalent period of warming. Briefly warming $[Pt(en)Br_2]$ with NaOH (pH 10.5) did not result in formation of the clear yellow solution, but after prolonged heating a clear red solution was obtained. Thus, in order to obtain the clear yellow solution from which the hexanuclear platinum complex may be isolated, both base and 2-aminoethanethiol must be present.

Formation of the cyclic hexanuclear complex probably proceeds through a complicated multistep mechanism[17] in rather low yield (27%). Despite the low yield, the synthesis is reproducible. In the hexanuclear complex, only 2-aminoethanethiolate ligands are bound to platinum and thus both the bromide ions as well as the chelating ethylenediamine ligands have been displaced. Substitution of chelating di- and triamines from Pt and Pd has been studied previously, but mainly in acidic media, where ligand release is assisted by protonation of the amine groups.[17] Only a few studies have been carried out on base hydrolysis of chelating diamines bound to platinum and palladium. Nord suggested that base hydrolysis of $[Pt(bpy)_2]^{2+}$ proceeds through a five-coordinate intermediate in which hydroxide ion is added to the coordination sphere.[18] Gillard et al. propose preliminary addition of a hydroxyl group to the α-carbon atom prior to decomplexation.[19]

Although we have not studied the mechanism of the reaction, it is intuitively appealing to postulate base-promoted substitution of bromide by a thiolate ligand as the initial step. Subsequent displacement of the chelating ethylenediamine moiety is favored by the strong trans-labilizing ability of the thiolate ligands and closure of the N–Pt–S chelate ring. The mechanism of the subsequent condensation steps to form the hexanuclear and other, unidentifield, products is obscure. Unfortunately, the very low solubility of the hexanuclear complex in common solvents prevented us from obtaining its solution properties.

Molecular Structure of $[Pt_6(AET)_8]Br_4{\cdot}6H_2O$. Figure 1 displays the structure of **1**, metrical parameters for which are summarized in Table III. The molecule is comprised of two $[Pt_3(AET)_4]^{2+}$ units related by a crystallographically imposed center of symmetry at ($^1/_2$, 0, $^1/_2$) (Figure 2) to give a cyclic hexanuclear complex. The platinum atoms can be divided into two groups on the basis of their coordination spheres. Pt(3) and its symmetry-related mate Pt(3)′ are chelated by two cis-oriented 2-aminoethanethiolate ligands, which provide an N_2S_2 coordination environment around these two platinum atoms. Atoms Pt(1) and Pt(2) have an NS_3 coordination sphere generated by one chelating 2-aminoethanethiolate ligand and two bridging thiolate sulfur atoms. All eight 2-aminoethanethiolates are both chelating and bridging, as commonly found for this class of ligands.[3-5,20]

The coordination geometry around each platinum atom is approximately square-planar, and the deviations of the atoms from the best plane defined by the platinum and its four donor atoms do not exceed 0.088 Å. The deviations from the calculated planes as well as the interplanar dihedral angles are listed in Table S4. The average Pt–N bond length is 2.085 (10) Å, and the average Pt–S bond length is 2.30 (2) Å, values comparable to those in $\{[Pt(terpy)(AET)]_2Pt\}^{4+}$.[10] There are no significant differences between chelating and nonchelating Pt–S bond lengths, nor do sulfur atoms trans to sulfur form substantially larger Pt–S bonds than those trans to nitrogen. The fact that all sulfur atoms are

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(17) For a general review of substitution reactions of square-planar complexes involving polydentate ligands see: Mureinik, R. J. *Rev. Inorg. Chem.* **1979**, *1*, 11.

(18) Nord, G. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 270.

(19) Bielli, E.; Gillard, R. D.; James, D. W. *J. Chem. Soc., Dalton Trans.* **1976**, 1837.

(20) Hu, W. J.; Barton, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 1170.

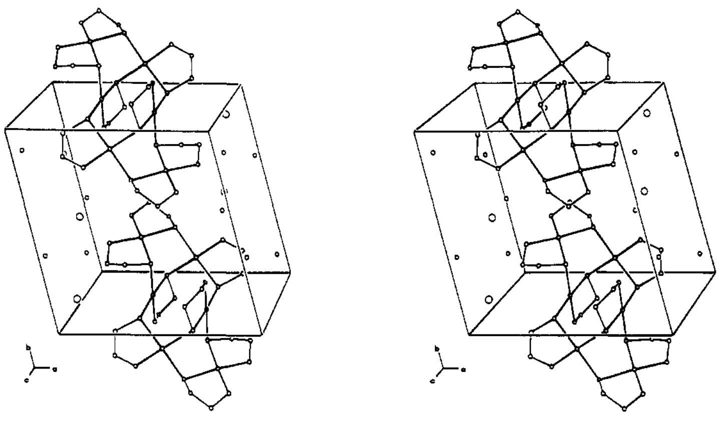

Figure 2. Stereoview of the crystal packing of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$. The bromide ions are shown as open circles.

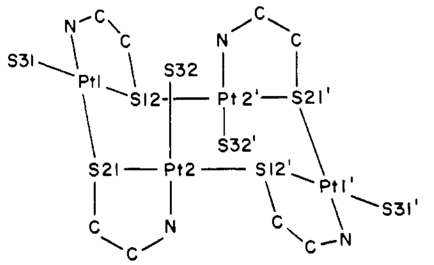

Figure 3. Line drawing of the central, eight-membered ring in the $[Pt_6(AET)_8]^{4+}$ structure (see text).

bridging is probably related to the absence of a pronounced trans influence in **1**, although close inspection of Table III reveals a slight elongation of trans-Pt–S bonds. All the sulfur–sulfur distances are greater than 3.2 Å and are nonbonded.

The *cis*-$M(AET)_2$ moiety can interact with additional metal atoms to form polynuclear complexes either by bridging to a single metal atom, as in the case of $[Ni_3(AET)_4]^{2+}$ (vide supra), or by binding two different metal atoms, as in the case of $\{[Pt(terpy)(AET)]_2Pt\}^{4+}$.[10] In the present work we observe the latter kind of interaction, although the two platinum atoms (Pt(1) and Pt(2)) are further linked by bridging thiolate ligands.

The six platinum atoms in **1** do not form a regular polyhedron but are joined in three fused rings by the bridging sulfur atoms. Two six-membered Pt_3S_3 rings are formed, Pt(1)–S(31)–Pt(3)–S(32)–Pt(2)–S(21) and the centrosymmetrically related set of atoms, each having the symmetric skew-boat conformation. These are fused to a central eight-membered ring constituted by the Pt_4S_4 atom set Pt(1)–S(21)–Pt(2)–S(12)′–Pt(1)′–S(21)′–Pt(2)′–S(12). This eight-membered ring adopts a chairlike conformation, as can be seen in Figure 3. The structure thus differs from that of $[Ni(SC_2H_5)_2]_6$, which has a regular planar-hexagonal array of six nickel atoms linked into a 12-membered ring by bridging thiolate ligands.[21] From the Pt–Pt distances (Pt(1)–Pt(2) = 3.672 (1) Å; Pt(1)–Pt(3) = 3.751 (1) Å; Pt(2)–Pt(3) = 3.624 (1) Å) within the six-membered ring and the shortest Pt–Pt distance (Pt(2)–Pt(2)′ = 3.507 (1) Å) across the inversion center (eight-membered ring) it is clear that no metal–metal bonding occurs.

The internal geometry of the AET ligands is normal within the limits of error. The four bromide anions and the six water molecules in the unit cell participate in few hydrogen-bonding interactions. The bromide anions exhibit no appreciable hydrogen-bonding interactions, while only one water molecule, O(W1), is hydrogen bonded to an amine ligand, N(32). The remaining water molecules are hydrogen bonded only to each other.

It is interesting to note that the stoichiometry of this hexametallic complex cation, $[M_6(AET)_8]^{4+}$, is identical with that of the previously reported trimetallic ones, $[M_3(AET)_4]^{2+}$. This stoichiometry is not unexpected if we view the polymetallic complexes of the nickel triad with 2-aminoethanethiolate as being comprised of M^{2+}, $M(AET)^+$, and $M(AET)_2$ building blocks. The stoichiometry for such complexes will be $[M_{p+q+r}(AET)_{q+2r}]^{(2p+q)+}$, where p is the number of M^{2+} units, q the number of $M(AET)^+$ units, and r the number of $M(AET)_2$ units. If we further assume that all the 2-aminoethanethiolate ligands are bridging as well as chelating and that the geometry around the metal atoms is square-planar, then only compounds where $4p + q - 2r = 0$ are possible. This situation obtains both for the hexanuclear complex, which is comprised of two $Pt(AET)_2$ units ($r = 2$) and four $Pt(AET)^+$ units ($q = 4$), and for the trinuclear complexes, which contain two $M(AET)_2$ ($r = 2$) and one M^{2+} unit ($p = 1$).[22]

Conclusions. We have demonstrated that, under basic conditions in the presence of 2-aminoethanethiolate, the complex $[Pt(en)Br_2]$ can be solubilized, presumably by initial substitution of the bromides by AET to yield a soluble cation. Further condensation of this postulated intermediate, facilitated by the strong trans effect of the thiolate ligands, leads to the formation of the hexaplatinum(II) cation **1**, which has been crystallographically characterized. The hexanuclear complex presents a new type of geometry for 2-aminoethanethiolate complexes of square-planar metal atoms.

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Supplementary Material Available: Tables S1–S4 reporting respectively observed and calculated structure factors, anisotropic thermal parameters, positional and thermal parameters of the hydrogen atoms, and best planes and dihedral angles for **1** (14 pages). Ordering information is given on any current masthead page.

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[21] Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251.

[22] We thank a reviewer for this insight.