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Hydro(methano)thermal Synthesis and Characterization of Two New Platinum Polysulfides: $[Pt_4S_{22}]^{4-}$ and $[Pt(S_4)_2]^{2-}$

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Introduction

$[Pt(S_5)_3]^{2-}$,[1] reported in 1903, is distinguished among polychalcogenide complexes by being the earliest known complex. Since then, only a few additional platinum polychalcogenide compounds such as $[Pt(S_5)_2]^{2-}$,[1c] $[Pt(Se_4)_3]^{2-}$,[2] and $[Pt(Se_4)_2]^{2-}$ [3] have been reported. The continuing success of hydrothermal synthesis in the preparation of several new metal polychalcogenide compounds[4] and the recognition that its applicability might be general urged us to use this synthetic method for the exploration of possible new Pt metal polychalcogenide compounds. Indeed, we found two previously unrecognized species in this chemistry. Here we report the synthesis and characterization of $[Pt_4Q_{22}]^{4-}$ (Q = S, Se) and $[Pt(S_4)_2]^{2-}$.

Experimental Section

Reagents. Chemicals in this work were used as purchased. K_2PtCl_4, KOH, and Ph_4PBr were from Aldrich Chemical Co. K_2S_4 and K_2Se_4 were prepared by dissolving the stoichiometric amounts of the elements in liquid ammonia. All manipulations were carried out in a glovebox under nitrogen atmosphere.

$K_4[Pt_4S_{22}]\cdot 4H_2O$. A 0.050-g (0.12-mmol) sample of K_2PtCl_4, 0.124 g (0.60 mmol) of K_2S_4, and 0.4 mL of distilled water were placed in a Pyrex tube. The tube was sealed under vacuum and heated at 130 °C for 1 day. Reddish black trigonal prismatic crystals (50% yield, based on Pt metal used) appeared while the reaction tube was kept at room temperature for several days. They were isolated by filtration and washed with ethanol. These crystals are soluble in water and DMF and slightly soluble in methanol and CH_3CN. Semiquantitative analysis of the crystals using the SEM/EDS technique showed a K:Pt:S atomic ratio of 0.9: 1.0:5.2. In this reaction the oxidation of Pt^{2+} to Pt^{4+} occurs in situ to produce S^{2-} and S_3^{2-} anions from the S_4^{2-} anion.

$K_4[Pt_4Se_{22}]$. A 0.050-g (0.12-mmol) sample of K_2PtCl_4, 0.095 g (0.24 mmol) of K_2Se_4, 0.034 g (0.61 mmol) of KOH, and 0.4 mL of distilled water were placed in a Pyrex tube. The tube was sealed under vacuum and heated at 110 °C for 2 days. The black hexagonal platelet crystals that formed (60% yield, based on Pt metal used) were isolated by filtration and washed with water and methanol. These crystals are insoluble in water and most organic solvents. Semiquantitative analysis of the crystals using the SEM/EDS technique showed a K:Pt:Se atomic ratio of 1.0: 1.0:5.5.

$(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$. A 0.050-g (0.12-mmol) sample of K_2PtCl_4, 0.124 g (0.60 mmol) of K_2S_4, 0.100 g (0.24 mmol) of Ph_4PBr, and 0.5 mL of methanol were placed in a Pyrex tube. The tube was sealed under vacuum and heated at 80 °C for 1 day. The reddish orange rectangular rod crystals that formed (40% yield, based on Pt metal used) were isolated by filtration and washed with water several times. These crystals are soluble in DMF but insoluble in water. Semiquantitative analysis of the crystals using the SEM/EDS technique showed a P:Pt:S atomic ratio of 1.7:1.0:8.0.

The homogeneity of products was confirmed by a comparison of the observed X-ray powder diffraction pattern to the one calculated from the single-crystal data.

Structure Determination. Single-crystal X-ray data were collected on a Rigaku AFC6S diffractometer using Mo radiation. The structures were solved by direct methods using the SHELXS86 software program and refined with full-matrix least-squares techniques. Empirical absorption corrections based on ψ scans of three strong reflections with $\chi \sim 90°$ were applied to each data set. DIFABS corrections after isotropic refinement of all atoms were then applied.[5] All calculations were performed on a VAXstation 3100/76 computer using the TEXSAN crystallographic software package of the Molecular Structure Corp.[6] All atoms in the anions of $K_4[Pt_4S_{22}]\cdot 4H_2O$ and $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$ were refined anisotropically. The hydrogen positions were calculated but not refined. Table I shows crystal data and details for structure analysis of both compounds. The fractional coordinates and temperature factors (B_{eq}) of all atoms and their estimated standard deviations are given in Tables II and III, and selected bond distances and angles are given in Tables IV and V.

Results and Discussion

The structure of $[Pt_4S_{22}]^{4-}$ (**I**) is similar to that of the $[Re_4S_{22}]^{4-}$ complex.[7] Compound **I** features a cubane $[Pt_4S_4]^{4+}$ core surrounded by six S_3^{2-} ligands, as shown in Figure 1. Four Pt^{4+} metal centers and four S^{2-} ions are combined to form a Pt–S cube with six S_3^{2-} ligands connecting diagonal pairs of Pt metal ions in six faces of the cube. Thus a more descriptive formula would be $[Pt_4S_4(S_3)_6]^{4-}$. The S3 atoms of the S_3^{2-} ligands are disordered at two positions, 0.59 Å above and below the Pt–S2–S2′–Pt′ plane. The center of the cluster is sitting on the crystallographic special position (0, 0, 0) of $\bar{4}3m$ symmetry. A crystallographic 3-fold axis passes through the Pt and S1 atoms. The cluster possesses T_d symmetry, considering that disordered S3 atoms are located in the Pt–S2–S2′–Pt′ plane. The Pt–Pt distance is 3.478(4) Å, suggesting no bonding between Pt metal atoms. In the Re analog of **I** there is considerable metal–metal bonding between Re atoms (Re–Re = 2.76 Å), which causes severe distortions in the $[Re_4S_4]$ cubane core.[7] Electronically, the closest analog of **I** is $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$, a remarkable Ni^{4+} compound. In this molecule the $[Ni_4Se_4]$ cubane core is distorted due to the presence of an Se_4^{2-} chain.[8] In contrast, little distortion is observed in the Pt–S cubane core of **I**, as evidenced from the bond angles around Pt and S1 (S1–Pt–S1 = 84.4(6)°; Pt–S1–Pt = 95.3(6)°). The distance between S atoms in the Pt_4S_4 cubane core is 3.16(3) Å.

Among the four K^+ ions in $K_4[Pt_4S_{22}]\cdot 4H_2O$, two of them are found in the special positions ($^3/_4$, $^3/_4$, $^3/_4$) and ($^1/_2$, $^1/_2$, $^1/_2$), respectively. The other two K^+ ions are disordered with four water molecules, sitting in the vertices of a octahedron whose center is the special position ($^1/_4$, $^1/_4$, $^1/_4$). Four water molecules are H-bonded to each other (O–O = 2.86(5) Å) in a square planar arrangement, coordinating to two K^+ ions above and below their plane. The minimum distance between K^+ ions is 4.04(8) Å. The presence and quantity of water in the structure were confirmed by thermal gravimetric analysis (TGA) measurements.[9] The distances between K^+ ions and S atoms are in the range 3.22–3.88 Å. The far-IR spectrum (CsI pellet) of $K_4[Pt_4S_{22}]\cdot 4H_2O$ shows peaks at 463, 325, 293 (sh), 241 (sh), and 204 cm^{-1}, and its reddish brown CH_3CN solution gives a featureless UV/vis spectrum. The IR absorption at 463 cm^{-1} is

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(9) A clean weight loss of 4.5% is observed in the temperature range 125–200 °C.

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Table I. Summary of Crystallographic Data for $K_4[Pt_4S_{22}]\cdot 4H_2O$ and $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$

compd	$K_4[Pt_4S_{22}]\cdot 4H_2O$	$(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$
formula	$H_8O_4K_4Pt_4S_{22}$	$C_{49}H_{44}OP_2PtS_8$
fw	1714.13	1162.40
cryst size (mm)	0.08 × 0.08 × 0.08	0.06 × 0.08 × 0.35
temp (°C)	23	23
cryst system	cubic	orthorhombic
space group	$F\bar{4}3m$ (No. 216)	$Pna2_1$ (No. 33)
a (Å)	14.964(4)	26.888(11)
b (Å)	14.964(4)	10.163(10)
c (Å)	14.964(4)	17.630(3)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3), Z	3351(2), 4	4818(8), 4
μ(Mo Kα) (cm^{-1})	187	33.8
d_{calcd} (g/cm^3)	3.398	1.602
R/R_w (%)[a]	4.6/5.1	8.8/10.9

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Fractional Atomic Coordinates and B_{eq} Values for $K_4[Pt_4S_{22}]\cdot 4H_2O$ (Estimated Standard Deviations in Parentheses)

atom	x	y	z	B_{eq} (Å^2)[a]
Pt	0.9178(1)	0.9178	0.9178	5.8730(8)
S1	0.9253(8)	−0.9253	0.9253	6.75(1)
S2	0.918(1)	0.762(1)	0.918	8.10(1)
S3	1.028(2)	0.711(1)	−1.028	12(1)
K1	$^3/_4$	$^3/_4$	$^3/_4$	6.322(5)
K2	1.0000	1.0000	$^1/_2$	18.8(6)
K3	$^3/_4$	1.115	$^3/_4$	19(1)
O1	$^3/_4$	1.115(3)	$^3/_4$	15.0

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Fractional Atomic Coordinates and B_{eq} Values for the Anion in $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$ (Estimated Standard Deviations in Parentheses)

atom	x	y	z	B_{eq} (Å^2)[a]
Pt	0.13030(9)	0.8220(3)	0.8351	3.6(1)
S1	0.0952(8)	0.647(2)	0.761(1)	5(1)
S2	0.0765(8)	0.729(2)	0.664(1)	5(1)
S3	0.140(1)	0.827(3)	0.640(1)	9(2)
S4	0.1417(7)	0.960(2)	0.735(1)	5(1)
S5	0.1167(7)	0.698(2)	0.939(1)	6(1)
S6	0.1713(7)	0.744(2)	1.019(2)	5(1)
S7	0.1552(9)	0.932(3)	1.018(1)	7(2)
S8	0.1745(7)	0.975(2)	0.904(1)	5(1)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

attributed to S–S stretches while the lower energy absorptions seem to be associated with the Pt–S framework.

The Se analog of I, $[Pt_4Se_4(Se_3)_6]^{4-}$, was similarly synthesized by a hydrothermal reaction of K_2PtCl_4 and K_2Se_4 in the presence of KOH. Its structure has been determined by a single-crystal X-ray diffraction study. Structural analysis on $K_4[Pt_4Se_{22}]$ has not been completed due to the poor quality of its data set.[10]

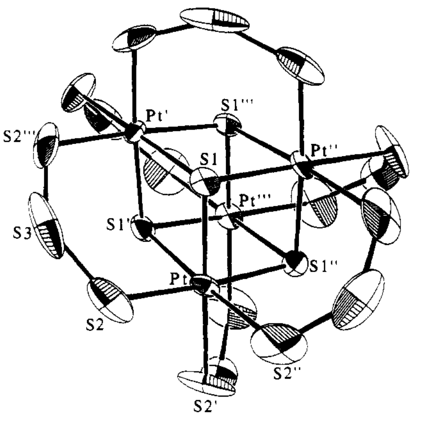

Figure 1. ORTEP drawing and labeling scheme of $[Pt_4S_{22}]^{4-}$.

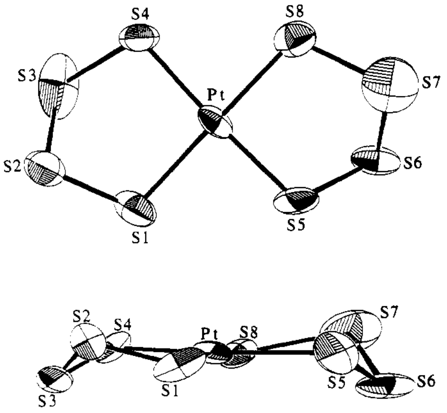

Figure 2. ORTEP drawing and labeling scheme of $[Pt(S_4)_2]^{2-}$ in two views.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in the $[Pt_4S_{22}]^{4-}$ Anion (Standard Deviations in Parentheses)

Pt–S1	2.35(1)	S2–S3	1.98(2)
Pt–S2	2.33(2)		
Pt–S(mean)	2.34(1)		
S1–Pt–S1	84.4(6)	Pt–S1–Pt	95.3(6)
S1–Pt–S2	92.6(6)	Pt–S2–S3	113(1)
S1–Pt–S2	175.9(6)	S2–S3–S2	122(2)

Table V. Selected Bond Distances (Å) and Bond Angles (deg) in the $[Pt(S_4)_2]^{2-}$ Anion (Standard Deviations in Parentheses)

Pt–S1	2.40(2)	S1–S2	1.97(3)
Pt–S5	2.25(2)	S5–S6	2.09(3)
Pt–S4	2.29(2)	S4–S3	2.14(3)
Pt–S8	2.31(2)	S8–S7	2.12(3)
		S2–S3	2.03(3)
		S6–S7	1.96(3)
Pt–S(mean)	2.31(6)	S–S(mean)	2.05(8)
S1–Pt–S5	88.1(8)	Pt–S1–S2	105(1)
S1–Pt–S4	94.9(7)	Pt–S5–S6	108(1)
S1–Pt–S8	172.1(7)	Pt–S4–S3	102(1)
S5–Pt–S4	175.9(7)	Pt–S8–S7	104(1)
S5–Pt–S8	91.8(7)	S1–S2–S3	100(1)
S4–Pt–S8	85.7(7)	S4–S3–S2	100(1)
		S5–S6–S7	93(1)
		S8–S7–S6	99(1)

The structure of $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$ was revealed by a single-crystal structure analysis. It is composed of $[Pt(S_4)_2]^{2-}$ (**II**) anions with noninteracting Ph_4P^+ cations. Complex **II** is a new member of the well-known metal octachalcogenide family. The other two members in the Ni triad, $[Ni(S_4)_2]^{2-}$[11] and $[Pd(S_4)_2]^{2-}$,[11a] are known as Et_4N^+ and Ph_4P^+ salts and the Se analog, $\{Pt(Se_4)_2]^{2-}$,[3] is also known. Figure 2 shows two different views of **II**, and Table III gives selected bond distances and angles. The average Pt–S and S–S distances are 2.31(6) and 2.05(8) Å, respectively. The Pt metal center has a square planar coordination geometry. The $Pt(S_4)$ five-membered ring in **II** has been found previously in neutral compounds such as $(R_3P)_2Pt(S_4)$.[12] The far-IR spectrum (CsI pellet) of $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$ shows

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(10) Kim, K.-W.; Kanatzidis, M. G. Work in progress. Although $[Pt_4Se_{22}]^{4-}$ is isostructural to $[Pt_4S_{22}]^{4-}$, it does not crystallize in the same space group. Crystal data for $K_4[Pt_4Se_{22}]$: hexagonal $P6_3/m$ (No. 176), $Z = 4$, $a = 10.642(6)$ Å, $c = 39.377(20)$ Å, $V = 3862(6)$ Å^3 at 23 °C.

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peaks at 482, 442, 338, 303, 270, and 200 (sh) cm^{-1}, and its reddish brown DMF solution gives a featureless UV/vis spectrum.

The stabilization of **I** and **II** marks the most significant development in platinum polysulfide chemistry since the structure determination of $K_2Pt(S_5)_3$. The reports for the corresponding Pt^{2+} complex $[Pt(S_5)_2]^{2-}$ are based primarily on elemental analytical data. It was proposed to be a square planar complex chelated with two S_5^{2-} ligands.[1c] The absence of a crystal structure for this material coupled with the considerable stability of the five-membered ring $M(S_4)$ with M = Ni, Pd, and Pt raises the need for a reexamination of K_2PtS_{10}. $[Pd(S_3N)(S_5)]^-$ [13] is one exception to the generality of the $M(S_4)$ unit. K_2PtS_{10} was proposed to contain the mononuclear $[Pt(S_5)_2]^{2-}$ anion. We note, however, that as similar as Pd and Pt may be in their respective chemistries, their polychalcogenide chemistry is not always analogous. Therefore, despite $[Pd(S_3N)(S_5)]^-$, the existence of the $Pt^{II}(S_5)$ ring will remain unclear until the $[Pt(S_5)_2]^{2-}$ complex is structurally characterized.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates of all atoms, anisotropic thermal parameters, bond distances and angles, and calculated and observed powder patterns for $K_4[Pt_4S_{22}]\cdot 4H_2O$ and $(Ph_4P)_2[Pt(S_4)_2]\cdot CH_3OH$ (14 pages). Ordering information is given on any current masthead page.

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