Pt^{2+} vs Pt^{4+} in AsS_3^{3-} Solutions and Isolation of the Clusters $[Pt(As_3S_5)_2]^{2-}$ and $[Pt_3(AsS_4)_3]^{3-}$. Observation of Unique Thioarsenate Ligands and Pt−As Bonds

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Pt^{4+} complexes are both thermodynamically stable and kinetically inert. Those with halides, pseudohalides and N-donor ligands are especially numerous.[1] While O-donor ligands also coordinate to Pt^{4+}, sulfide and selenide, and especially P- and As-donor ligands, tend to reduce it to Pt^{2+}.[2] Notable exceptions are $[Pt(S_5)_3]^{2-}$,[3] $[Pt_4S_4(S_3)_6]^{4-}$,[4] and $[Pt(Se_4)_3]^{2-}$.[5] Recently, it has been shown that hydrothermal conditions offer significant advantages in new cluster and solid state compound synthesis.[6−8] We have exploited the high reactivity and lability of the AsS_3^{3-} pyramidal unit in conjunction with elements from group 10, and other main group elements and reported on several unusual one- and two-dimensional solids containing organic cations, including $(Ph_4P)_2[InAs_3S_7]$, $(Me_4N)_2Rb[BiAs_6S_{12}]$,[9] $(Ph_4P)_2[Hg_2As_4S_9]$, and $(Me_4N)[HgAs_3S_6]$.[10] Our work with AsS_3^{3-} solutions thus far suggests the existence of very complex condensation equilibria where a variety of $[As_xS_y]^{z-}$ species might be present. The type and identity of $[As_xS_y]^{z-}$ fragments found in the isolated solids depends on the particular counterion present and on the metal size and coordination preference. Thus far, we have identified several new types of $[As_xS_y]^{z-}$ ligands including the $[As_3S_6]^{3-}$,[11] $[As_3S_7]^{5-}$,[9] and $[As_4S_9]^{6-}$ [10] anions. The chemistry of Pt^{2+} and Pt^{4+} polysulfides goes back to the beginning of this century and even to this date it has proven remarkably complex, mostly due to the lability of S_x^{2-} species and redox processes in solution. The great lability of AsS_3^{3-} and its higher $[As_xS_y]^{z-}$ homologs, and the conceptual relationship of AsS_3^{3-} to S_x^{2-} (e.g. the former derives from S_x^{2-} via a S atom substitution by an isoelectronic As^- atom) raises interesting prospects for similar chemistry in the Pt/AsS_3^{3-} system. In fact, we observed not only the familiar Pt^{2+} vs Pt^{4+} redox couple, but also an unusual kind of Pt−As bonding and several new thioarsenate ligands which emerge as new features in this chemistry. We describe here two unique clusters, $[Pt(As_3S_5)_2]^{2-}$ and $[Pt_3(AsS_4)_3]^{3-}$ formed hydrothermally.

$(Ph_4P)_2[Pt(As_3S_5)_2]$[12a,13] is relatively air stable and soluble in polar organic solvents such as DMF, CH_3CN giving orange-red solutions. $(Ph_4P)_2[Pt(As_3S_5)_2]$ is a novel molecular cage compound with discrete $[Pt(As_3S_5)_2]^{2-}$ anions, see Figure 1. There are two unique features of this compound: the unusual $[As_3S_5]^{3-}$ units and, remarkably, the presence of a Pt−As bond. The $[As_3S_5]^{3-}$ is a new thioarsenate anion and can be viewed as the two electron reduction product of a cyclic $[As_3S_6]^{3-}$ unit,[11] (see eq 1). This results in a negatively charged As atom in the $[As_3S_5]^{3-}$ unit which bonds to Pt^{4+}. The total charge of each ligand is 3−, with each of the sulfur atoms in a 2− oxidation state. We then can assign the formal oxidation states of the two As atoms that are not connected to the metal center as 3+ while the Pt-bound arsenic is assigned 1+. Despite the different oxidation states of the As atoms in the $[As_3S_5]^{3-}$ units, there is no notable difference in the As−S bond distances which vary from 2.177(5) to 2.291(5) Å.

$$[As_3S_6]^{3-} + 2e \rightarrow [As_3S_5]^{3-} + S^{2-} \qquad (1)$$

The metal in this complex is in a distorted octahedral environment coordinated by two $[As_3S_5]^{3-}$ ligands through two S and one As atom respectively. Although we started with Pt^{2+}, the geometry of the metal atom indicates it is now in the 4+ oxidation state suggesting that Pt is the reducing agent for $[As_3S_6]^{3-}$. There are two types of Pt−S bonds in the molecule. The average Pt−S bond distance where the sulfur atom is trans to an As atom is 2.428(5) Å, while the other Pt−S bond distances average at 2.355(5) Å. These distances are still within the Pt−S bond distances found in $[Pt(S_4)_3]^{2-}$ [3] which range from

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(12) (a) $\mathbf{(Ph_4P)_2[Pt(As_3S_5)_2]}$. A Pyrex tube (~4 mL) containing a mixture of $PtCl_2$ (65 mg, 0.25 mmol), K_3AsS_3 (144 mg, 0.75 mmol), Ph_4PBr (419 mg, 1.0 mmol) and 0.3 mL of water was sealed under vacuum and kept at 110 °C for 1 day. The large red platelike crystals formed were isolated in methanol and washed with ether. (Yield = 74.3% based on Pt.) No KCl or KBr was observed in the product. A semiquantitative elemental analysis of the red crystal using the SEM/EDS technique gave the P:Pt:As:S ratio at 2:1:5.5:10.0. (b) $\mathbf{(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5\ H_2O}$. A mixture of $PtCl_2$ (65 mg, 0.25 mmol), K_3AsS_3 (96 mg, 0.5 mmol), Ph_4PBr (419 mg, 1.0 mmol) and 0.3 mL of water was sealed under vacuum and kept at 110 °C for 1 day. A mixture of red crystals of $(Ph_4P)_2[Pt(As_3S_5)_2]$ and yellow platelike crystals of $(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5\ H_2O$ were isolated in methanol and washed with ether. (Yield = 85.4%, based on Pt.) No KCl or KBr was observed in the product. A semiquantitative elemental analysis of the yellow crystal using SEM/EDS gave K:P:Pt:As:S at 1:1.7:3:3:12. DMF solutions of $(Ph_4P)_2[Pt(As_3S_5)_2]$ and $(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O$ are orange and yellow respectively and give featureless UV/vis spectra. The far-IR spectra of $(Ph_4P)_2[Pt(As_3S_5)_2]$ and $(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O$ basically show three sets of absorptions. Absorptions in the range of 330−410 cm^{-1} are attributed to As−S vibration modes, while the peak at 300 cm^{-1} could be associated with Pt−S vibration modes. For comparison, in the far-IR spectrum of $(Ph_3P)_2Pt(S_4)$, 315 and 326 cm^{-1} peaks were assigned to the Pt−S vibration modes.[12c] The rest of the peaks in the low energy region from 230−200 cm^{-1} for $(Ph_4P)_2[Pt(As_3S_5)_2]$ could then be assigned to Pt−As vibration modes. There is also a S−S vibration at 448.9 cm^{-1} in the spectrum of $(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O$. (c) Weiss, J. *Z. Anorg. Allg. Chem.* **1986**, *542*, 137−143.

(13) Single-crystal X-ray diffraction data were collected at −110 °C on a Rigaku AFC6 diffractometer. (a) Crystal data for $(Ph_4P)_2[Pt(As_3S_5)_2]$: triclinic $P\bar{1}$ (No. 2), $a = 13.104(3)$ Å, $b = 20.519(4)$ Å, $c = 11.559(2)$ Å, $\alpha = 105.72(2)°$, $\beta = 108.09(2)°$, $\gamma = 75.11(2)°$, and $V = 2793(2)$ Å^3, $Z = 2$, $d_{calc} = 1.95$ g/cm^3, $\mu = 65.09$ cm^{-1}, $2\theta_{max}$(Mo Kα) = 45.00. Unique data: 6652. Data with $F_o^2 > 3\sigma(F_o^2)$: 3810. No. of variables: 364. Final $R = 4.7\%$ and $R_w = 5.0\%$. (b) Crystal data for $(Ph_4P)_2[Pt_3(AsS_4)_3]\cdot 1.5\ H_2O$: triclinic $P\bar{1}$ (No. 2), $a = 14.655(2)$ Å, $b = 17.852(3)$ Å, $c = 14.253(2)$ Å, $\alpha = 109.65(2)°$, $\beta = 118.89(2)°$, $\gamma = 72.08(3)°$, and $V = 3027(1)$ Å^3, $Z = 2$, $d_{calc} = 2.13$ g/cm^3, $\mu = 91.68$ cm^{-1}, $2\theta_{max}$(Mo Kα) = 45.00. Unique data: 7924. Data with $F_o^2 > 3\sigma(F_o^2)$: 3908. No. of variables: 390. Final $R = 7.7\%$ and $R_w = 9.5\%$. The structures were solved and refined by direct methods described elsewhere.[9]

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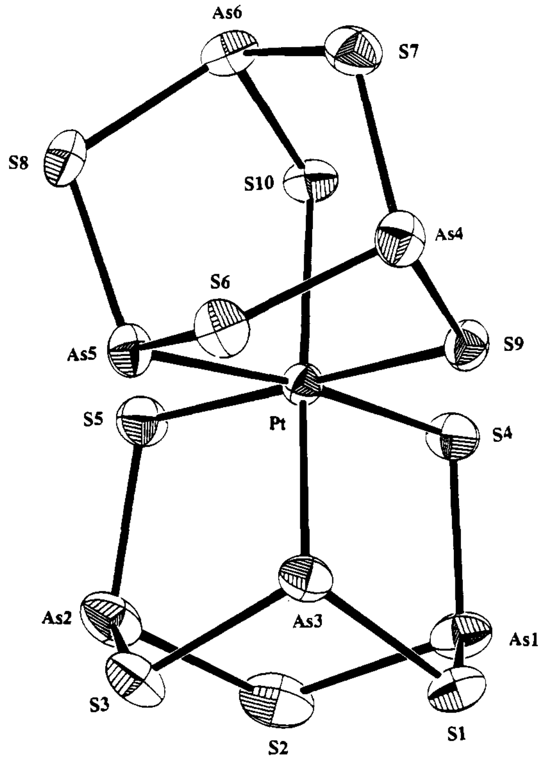
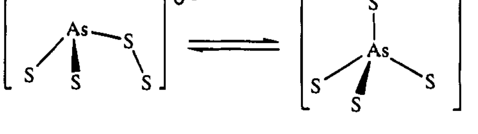


Figure 1. Structure of $[Pt(As_3S_5)_2]^{2-}$. Selected bond distances (Å): Pt−As3 2.453(2), Pt−As5 2.455(2), Pt−S4 2.430(5), Pt−S5 2.351(5), Pt−S9 2.358(5), Pt−S10 2.425(5), As1−S1 2.245(5), As1−S2 2.285(7), As1−S4 2.177(5), As2−S2 2.253(7), As2−S3 2.229(5), As2−S5 2.189(6), As3−S1 2.261(5), As3−S3 2.291(5), As4−S6 2.214(6), As4−S7 2.281(6), As4−S9 2.196(5), As5−S6 2.277(5), As5−S8 2.263(6), As6−S7 2.282(6), As6−S8 2.236(5), As6−S10 2.177(5). Selected bond angles (deg): As3−Pt−As5 79.83(7), As3−Pt−S4 98.3(1), As3−Pt−S5 100.5(1), As3−Pt−S9 80.9(1), As3−Pt−S10 171.9(1), As5−Pt−S4 171.8(1), As5−Pt−S5 81.9(1), As5−Pt−S9 99.9(1), As5−Pt−S10 97.7(1), S4−Pt−S5 90.7(2), S4−Pt−S9 87.6(2), S4−Pt−S10 85.3(2), S5−Pt−S9 177.9(2), S5−Pt−S10 86.6(2), S9−Pt−S10 92.1(2), S1−As1−S2 103.2(2), S1−As1−S4 100.1(2), S2−As1−S4 107.7(2), S2−As2−S3 102.6(2), S2−As2−S5 106.5(2), S3−As2−S5 102.4(2), Pt−As3−S1 104.7(1), Pt−As3−S3 103.8(1), S1−As3−S3 101.5(2), S1−As3−S3 101.5(2), S6−As4−S7 105.8(2), S6−As4−S9 101.3(2), S7−As4−S9 105.1(2), Pt−As5−S6 103.5(1), Pt−As5−S8 105.7(1), S6−As5−S8 100.6(2), S7−As6−S8 103.8(2), S7−As6−S10 107.1(2), S8−As6−S10 100.9(2).

2.332 to 2.479 Å. The As−S distances and S−As−S angles are normal. To the best of our knowledge, and with the exception of solid state platinum arsenides, the $[Pt(As_3S_5)_2]^{2-}$ anion offers the first observation of a Pt−As bond in an all-inorganic molecule. Such a bond is somewhat surprising considering that it involves a highly oxidized metal center and that it formed in aqueous solution.

When the amount of $AsS_3{}^{3-}$ is decreased the above redox chemistry is avoided and the Pt^{2+} cluster $(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O$ forms in very good yield.[12b,13b] $(Ph_4P)_2K[Pt_3(AsS_4)_3]$ contains discrete trinuclear anions of $[Pt_3(AsS_4)_3]^{3-}$, see Figure 2. Each Pt atom is coordinated by four S atoms in a distorted square planar fashion. The formal oxidation state of the metal center is 2+. The most unique feature of the compound is the presence of a new kind of $[AsS_4]^{3-}$ ligand, which can be viewed as the oxidative coupling product between $[AsS_3]^{3-}$ and S^{2-}. This anion contains As^{3+} and it is different from the well-known tetrahedral, $[AsS_4]^{3-}$, which is a As^{5+} species. The two isomers are related via an internal redox equilibrium according to eq 2.



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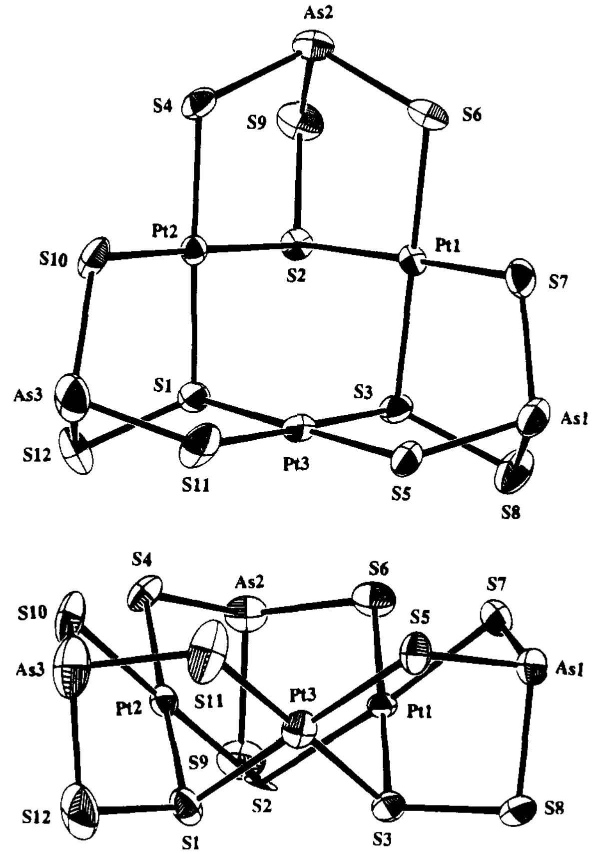

Figure 2. Two views of the structure of $[Pt_3(AsS_4)_3]^{3-}$. Selected bond distances (Å): Pt1−S2 2.315(5), Pt1−S3 2.323(6), Pt1−S6 2.341(7), Pt1−S7 2.362(7), Pt2−S1 2.314(8), Pt2−S2 2.298(6), Pt2−S4 2.353(6), Pt2−S10 2.294(6), Pt3−S1 2.324(5), Pt3−S3 2.285(6), Pt3−S5 2.345(7), Pt3−S11 2.292(7), As1−S5 2.208(6), As1−S7 2.215(7), As1−S8 2.254(7), As2−S4 2.216(7), As2−S6 2.202(7), As2−S9 2.232(6), As3−S10 2.246(7), As3−S11 2.195(7), As3−S12 2.264(7), S1−S12 2.074(8), S2−S9 2.101(8), S3−S8 2.105(7). Selected bond angles (deg): S2−Pt1−S3 85.6(1), S2−Pt1−S6 94.8(1), S2−Pt1−S7 174.2(1), S3−Pt1−S6 178.0(1), S3−Pt1−S7 94.5(1), S6−Pt1−S7 84.8(1), S1−Pt2−S2 84.0(1), S1−Pt2−S4 178.6(1), S1−Pt2−S10 95.5(1), S2−Pt2−S4 95.0(1), S2−Pt2−S10 178.8(1), S4−Pt2−S10 85.5(1), S1−Pt3−S3 84.6(1), S1−Pt3−S5 179.0(1) S1−Pt3−S11 94.4(1), S3−Pt3−S5 94.4(1), S3−Pt3−S11 178.8(1), S5−Pt3−S11 86.6(2).

Each $[AsS_4]^{3-}$ ligand binds to two Pt atoms employing all its terminal S atoms. The central cluster Pt_3S_3 core is in a distorted "cyclohexane-chair" conformation forming a partial cube which derives from a hypothetical Pt_4S_4 cube by removing a S and a Pt atom lying on a body diagonal. Interestingly, a cluster with a Pt_4S_4 cubane core has recently been described.[4]

The presence of the new $[As_3S_5]^{3-}$ and the $[AsS_4]^{3-}$ ligands in these two compounds suggests that in addition to the already complex condensation equilibria between the various $[As_xS_y]^{z-}$ species,[9,10] redox reactions also exist in solution. Therefore, the thioarsenate systems are much more complicated in nature than the pure polychalcogenide anions. The two novel Pt-based clusters reported here represent significant extensions of the long known platinum polysulfide chemistry. That, coupled with the observation of the novel arsenide species expressed in a stable Pt−As bond, justifies further investigations in this area of chemistry. The introduction of a trivalent As atom in a polychalcogenide chain generates additional structural complexity that is not possible with polychalcogenides only.

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Supplementary Material Available: Tables of fractional atomic coordinates, bond distances, bond angles, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms (30 pages). Ordering information is given on any current masthead page.