of oxygen exchange suggests unfavorable barriers for either process.

Observation of facile oxygen exchange (process 3) suggests that water-^{18}O may be employed as a sensitive probe for oxide character in transition-metal cluster ion complexes (i.e., to distinguish dissociative from molecular chemisorption for simple oxides such as NO, CO, and CO_2). Co_3NO^+ serves as a model since we have previously demonstrated that it contains NO dissociatively chemisorbed on the cluster.[2] Competitive oxygen exchange and condensation are observed (processes 13 and 14) with water-^{18}O.

$$Co_3(N^{16}O)^+ + H_2{}^{18}O \longrightarrow Co_3(N^{18}O)^+ + H_2{}^{16}O \qquad (13)$$

$$Co_3(N^{16}O)^+ + H_2{}^{18}O \longrightarrow Co_3(N^{16}O)(H_2{}^{18}O)^+ \qquad (14)$$

CA of the water adduct $Co_3(N^{16}O)(H_2{}^{18}O)^+$ yields elimination of water as the primary fragmentation process with a statistical $H_2{}^{16}O/H_2{}^{18}O$ distribution, indicating that the oxygen atoms are rapidly interconverting. These results confirm that NO is dissociatively chemisorbed on Co_3^+.

The above results demonstrate the potential of water-^{18}O as a sensitive probe for metal oxide character in transition-metal cluster ion complexes. We are currently exploring the scope of this method for probing oxide character in a variety of transition-metal cluster ion systems. This technique may prove to be a powerful and nondestructive method for probing the structure of complex transition-metal cluster ions in the gas phase.

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Soluble Polychalcogenide Chemistry of Indium. Synthesis and Characterization of $[In_2Se_{21}]^{4-}$, the First Indium Polyselenide

Compared to transition-metal polychalcogenide chemistry, the corresponding chemistry of group III metals is virtually unexplored.[1a,b] For example, in contrast to a number of monochalcogenide compounds,[1c] no In/polychalcogenide species are known to date. As part of our continuing efforts to characterize late-transition-metal/- and main-group-metal/chalcogen chemistry, we and others recently reported the new series of $[M(Q_4)_2]^{2-}$ complex anions[2] (where M = Zn, Cd, Hg, Ni, Pd and Q = Se, Te) and their use as precursors to intermetallic solids. We also reported the unusual $[Ag(Se_4)]_n{}^{n-}$, a one-dimensional inorganic polymer.[3] We expected that at least the softer, heavier members of group III elements (i.e. In, Tl) would form analogous, stable chalcogenide complexes. The pnictide and chalcogenide binary and ternary compounds of group III metals (i.e. Al, Ga, In) are technologically important due to their promising electronic and optoelectronic properties.[4,5] Among the chalcogenides, In_2Se_3, InSe, and $CuInSe_2$ are noteworthy for their photovoltaic properties.[6] It has been recognized that, apart from the conventional high-temperature routes to such materials, molecular precursor methods are highly desirable.[7] From this perspective as well as the fact that heavier group III metals exhibit interesting structural chemistry,[8] we report here the synthesis, molecular structure, and properties of the first In/polychalcogenide complex, the Se-rich $[In_2Se_{21}]^{4-}$ (I).

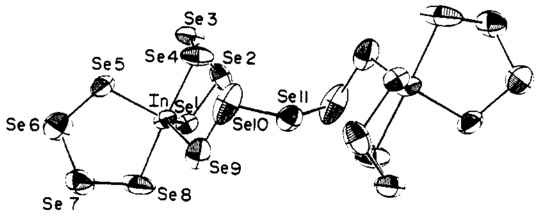

Figure 1. ORTEP projection and atom-labeling scheme of $[In_2(Se_4)_4(Se_5)]^{4-}$. Atom Se(11) is positionally disordered around a crystallographic inversion center. Only one of the Se(11) positions is shown. Individual indium–selenium bond distances are In–Se(1) = 2.663 (4) Å, In–Se(4) = 2.729 (6) Å, In–Se(5) = 2.622 (4) Å, In–Se(8) = 2.734 (6) Å, and In–Se(9) = 2.615 (5) Å. Bond distances within the $Se_4{}^{2-}$ ligands are Se(1)–Se(2) = 2.330 (7) Å, Se(2)–Se(3) = 2.334 (5) Å, Se(3)–Se(4) = 2.349 (6) Å, Se(5)–Se(6) = 2.311 (8) Å, Se(6)–Se(7) = 2.289 (7) Å, and Se(7)–Se(8) = 2.337 (5) Å. Corresponding angles are Se(1)–Se(2)–Se(3) = 100.9 (2)°, Se(2)–Se(3)–Se(4) = 99.1 (2)°, Se(5)–Se(6)–Se(7) = 102.5 (2)°, and Se(6)–Se(7)–Se(8) = 102.7 (3)°.

I was prepared according to eq 1. Slow addition of a dimethylformamide (DMF) solution of anhydrous $InCl_3$ (0.10 g,

$$2InCl_3 + 5Na_2Se_5 + 4Ph_4PCl \rightarrow [Ph_4P]_4[In_2Se_{21}] + 10NaCl \qquad (1)$$

0.452 mmol) to a mixture of Na_2Se_5[9] (0.50 g, 1.132 mmol) and Ph_4PCl (0.34 g, 0.908 mmol) in DMF caused an immediate color change from deep green to brown. Following 40 min of stirring at room temperature and removal of NaCl by filtration, the solution was diluted with ether to incipient crystallization. Within 2 days brown crystals of $[Ph_4P]_4In_2Se_{21}$ are reproducibly obtained in ca. 75% yield. Anal. Calcd for $C_{96}H_{80}P_4In_4Se_{21}$: C, 35.51; H, 2.47; In, 7.08; Se, 51.12. Found: C, 35.04; H, 2.48; In, 6.86; Se, 50.89. Care must be taken to exclude traces of water and oxygen. Although the optimum stoichiometric ratio of $In^{3+}:Se_5{}^{2-}$ is 2:5, lower yields of $[In_2Se_{21}]^{4-}$ were obtained even when the ratio was 1:2 or 1:3. This, coupled with the fact that $[In_2Se_{21}]^{4-}$

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[9] (a) This is a nominal composition. However, cation exchange with Ph_4PCl in DMF affords, in high yield, $(Ph_4P)_2Se_5$ as a black crystalline solid. (b) For more information on the crystallization of various $Se_x{}^{2-}$ species with various counterions see: Weller, F.; Adel, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1987**, *548*, 125–132.

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can be isolated with other counterions[10,11] such as Pr_4N^+ and Et_4N^+, attest to its considerable kinetic and perhaps thermodynamic stability in the solid state. However, this is not the case in polar solutions (vide infra). The nature of I was established by a single-crystal X-ray diffraction study.[12]

The structure of the $[In_2Se_{21}]^{4-}$ ion is shown in Figure 1, and it consists of two $[In(Se_4)_2]^-$ units bridged by a Se_5^{2-} chain. Therefore, a more descriptive formation for I would be $[In_2(Se_4)_4(Se_5)]^{4-}$. The In^{3+} center is chelated by two Se_4^{2-} ligands and bound to a terminal Se atom of the Se_5^{2-} chain. This five-coordination geometry around the In atom can be clearly described as a trigonal bipyramid with two axial selenium atoms, Se(4) and Se(8), and three equatorial atoms, Se(1), Se(5), and Se(9). Although five-coordination is uncommon for an all-chalcogen In environment, the trigonal-bipyramidal geometry can be rationalized in terms of valence electron pair repulsion (VSEPR) theory. The axial Se(4)–In–Se(8) angle is 175.7 (1)°. The corresponding equatorial angles are Se(1)–In–Se(5) = 118.9 (2)°, Se(5)–In–Se(9) = 117.1 (2)°, and Se(1)–In–Se(9) = 123.6 (2)°. The In, Se(1), Se(5), and Se(9) atoms do not deviate more than 0.02 Å from the corresponding least-squares plane. The conformations of the chelating Se_4^{2-} ligands in I differ from those in other polyselenide complexes (i.e. $[MSe(Se_4)_2]^{2-}$, M = Mo, W[13,14]) in that they adopt an envelope vis â vis puckered configuration. Atoms Se(3) and Se(7) lie an average of 1.28 Å away from the InSe(1)Se(2)Se(4) and InSe(5)Se(6)Se(8) basal planes, respectively.[15] We have encountered this envelope conformation in the $M(Q_4)$ moieties of the structures of $[Ag(Se_4)]_n^{n-}$,[3] $(Ph_4P)_2Hg(Se_4)_2$,[2,16] $[\text{Na-15-crown-5}]_2Hg(Se_4)_2$,[2b] and $[(Ph_3P)_2N]_2Hg(Te_4)_2$.[2,16] It has also been observed in $[Cr(CO)_4(Te_4)]^{2-}$.[17] The average In–Se bond is 2.673 Å. Individual indium–selenium bond distances and angles are given in the caption of Figure 1. Although $[In_2(Se_4)_4(Se_5)]^{4-}$ itself lacks a center of symmetry, a crystallographically imposed center of symmetry lying halfway between the In···In vector induces a positional disorder of the central Se(11) atom of the Se_5^{2-} chain. Thus, in the solid state two different conformations of the Se_5^{2-} chain are observed. The interatomic distances in the Se_5^{2-} moiety are Se(9)–Se(10) = 2.383 (9) Å, Se(10)–Se(11) = 2.322 (9) Å, and Se(10)′–Se(11) = 2.171 (9) Å. In view of the disorder present in this portion of the Se_5^{2-} chain and the marginal quality of the data, we do not place any significance in the short length of this bond. $[In_2(Se_4)_4(Se_5)]^{4-}$ is the first discrete In/polychalcogenide complex to be reported. In the absence of other congeners we feel that the trigonal-bipyramidal geometry[18] around In is unprecedented among indium chalcogenide compounds, in which In is normally found either tetrahedrally (i.e. $CuInSe_2$,[19] $[In_4Se_{10}]^{8-}$[20]) or octahedrally coordinated (i.e. $NaInSe_2$[21]). The dimeric structure of I bears some resemblance to that of $[Bi_2S_{34}]^{4-}$,[22] which consists of two tetragonal-pyramidal $[Bi(S_7)_2]^-$ units bridged by a S_6^{2-} chain. To the best of our knowledge, pentaselenide ligands have not been reported to bridge in a $\mu\text{-}\eta^1\text{-}Se_5^{2-}$ fashion (where each terminal Se atom is bonded to a different metal atom) two otherwise unsupported metal centers. Examples of bridging $\mu\text{-}\eta^1\text{-}Se_2^{2-}$ diselenides, however, are found in $[Cp_2Mn_2(CO)_4Se_2]^+$[23] and the recently reported $Nb_4Se_{22}^{6-}$ ion.[24]

UV/vis and ^{77}Se NMR spectroscopic as well as cyclic voltammetric studies in DMF solutions show that I does not maintain its integrity in this solvent. The electronic spectrum of I in DMF shows two absorptions at 450 (sh) nm (ϵ = 12 855 $M^{-1}\ cm^{-1}$) and 649 nm (ϵ = 2789 $M^{-1}\ cm^{-1}$), respectively, while the corresponding spectrum in the solid state (KBr pellet) is different and features a rising absorbance, completely void of absorption bands (300–900-nm region). It appears that the UV/vis solution spectrum of I arises from selenium radical anion species such as Se_3^- (not unlike S_3^-[25]), and it is very similar (vide infra) to that of Na_2Se_5 or $(Ph_4P)_2Se_5$ under the same conditions.

Cyclic voltammetric studies of I in DMF solutions show an irreversible oxidation wave at −0.35 V, which is accompanied by two reduction waves at −0.82 and −1.25 V. The last two cathodic processes appear after the initial anodic scan has ensued and therefore are not due to species originally present in solution. It should be noted that a similar cyclic voltammogram is observed in solutions of $(Ph_4P)_2Se_5$ in this solvent. It is thus clear that the redox-active species in solutions of Se_5^{2-} and I in DMF are similar in nature. This supports the contention that I is dissociated in solution, with Se_x^- radicals being a significant species in the resulting equilibria. Further elaboration on the nature of this dissociation must await an urgently needed, complete characterization of polar (i.e. DMF) polychalcogenide solutions.[26]

The dissociation of I is also consistent with its ^{77}Se NMR spectra, which show three resonances (in DMF) at 643, 197, and −244 ppm (vs Me_2Se). By analogy to other systems,[14,27] the first two resonances are attributed respectively to the terminal, metal-bound Se atoms and middle atoms of the Se_4^{2-} ligands. In solution all Se_4^{2-} ligands become equivalent. The third resonance at −244 ppm arises from a thus far unidentified Se_x^{2-} species. The Se_x^- radical anions are not detected by NMR[25,26] spectroscopy. The analogous S_3^- radicals, which derive from S_x^{2-} solutions ($x > 4$–6[25]), have been shown to exist in liquid ammonia and polar solvents such as DMF and are relatively well characterized. In contrast few analogous[28a] studies on the Se_x^{2-} system exist, al-

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(10) Unpublished results in this laboratory. The structures of both Pr_4N^+ and Et_4N^+ salts were solved and refined by X-ray crystallographic techniques. The $[In_2Se_{21}]^{4-}$ anions in these salts possess (within experimental error) structures identical with the one reported here. The yields from the synthesis of these materials are good and range from 50 to 80%. Crystal data for $(Et_4N)_4[In_2(Se_4)_4(Se_5)]$: triclinic, $P\bar{1}$, a = 12.428 (3) Å, b = 17.540 (4) Å, c = 15.781 (3) Å, α = 89.47 (2)°, β = 94.47 (2)°, γ = 97.90 (2)°, V = 3397 Å^3, Z = 2. Crystal data for $(Pr_4N)_4[In_2(Se_4)_4(Se_5)]$: monoclinic, $P2/c$, a = 15.168 (2) Å, b = 17.376 (3) Å, c = 15.997 (3) Å, β = 94.56 (1)°, V = 4203 Å^3, Z = 2.

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(12) Crystals of $(Ph_4P)_4[In_2(Se_4)_4(Se_5)]$ are triclinic, $P\bar{1}$, with a = 11.417 (3) Å, b = 12.733 (9) Å, c = 20.188 (8) Å, α = 96.03 (5)°, β = 94.68 (3)°, γ = 111.68 (4)°, V = 2689 Å^3, Z = 1, D(calcd) = 2.05 g/cm^3, and μ = 79 cm^{-1}. Single-crystal X-ray diffraction data were collected (at 23 °C) on a Nicolet P3 four-circle diffractometer (Mo Kα radiation), with a $\theta/2\theta$ scan, $4° < 2\theta < 45°$, and 2426 reflections with $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction was applied, the number of variables was 319, and final R = 0.073. The structure was solved with SHELXS-86 and was refined with the SDP package of crystallographic programs. The Ph_4P^+ cation features the expected structural characteristics and calls for no further comment. The anions have a crystallographically imposed inversion center and are disordered at the central Se(11) atom.

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though some qualitative observations have been reported.[28b,29]

Thermolysis experiments, under flowing Ar, show that the Ph$_4$P$^+$ salt of I does not show any appreciable weight loss below 350 °C. Its decomposition is smooth and continuous and is complete at 536 °C. The final product was unequivocally identified by its X-ray powder diffraction pattern as β-In$_2$Se$_3$.[30] This behavior is not shared by the Et$_4$N$^+$ and Pr$_4$N$^+$ salts, which, although they begin to decompose at lower temperature, convert to β-In$_2$Se$_3$ via intermediate, Se-rich phases. Further studies on the thermolysis of these compounds are in progress.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms in the anion (7 pages); a listing of calculated and observed (10F_o/10F_c) structure factors (43 pages). Ordering information is given on any current masthead page.

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Heterobimetallic Au-Pd Phosphine Cluster Complexes. X-ray Crystal and Molecular Structure of [Au$_8$Pd(PPh$_3$)$_8$](NO$_3$)$_2$

A large number of transition-metal-gold cluster compounds have been prepared containing transition metals such as V, Cr, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Pt, and Ag.[1-12] There have not, however, been any reports of well-characterized compounds containing Au-Pd bonds.[13-15] Because Pd is a catalytically important metal and gold-palladium heterogeneous catalysts are known and used commercially for oxidation catalysis,[16-18] and because we are interested in developing a better understanding of the role of Au in bimetallic catalysis,[19-26] we have devoted a

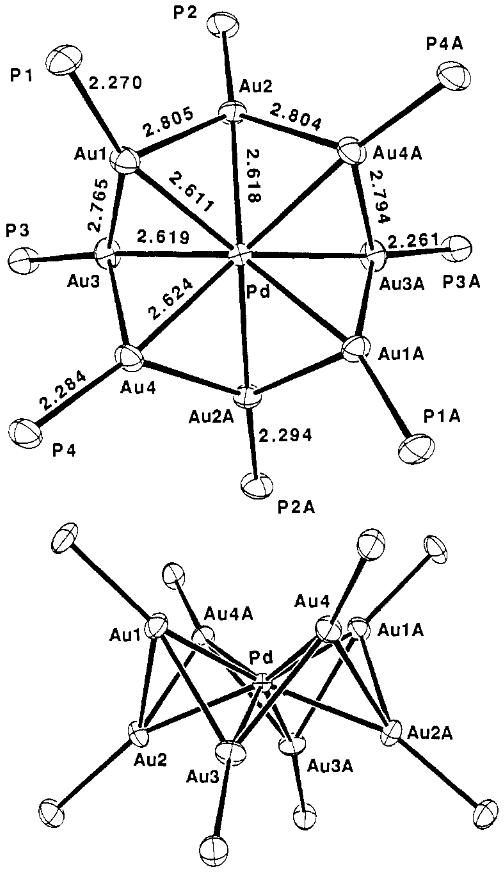

Figure 1. ORTEP drawings (two views) of the coordination core of the cation of **1** with selected bond distances (Å). Ellipsoids are drawn with 50% probability boundaries. Phenyl rings have been omitted for clarity. Atoms with the "A" label are related to their counterparts, e.g., Au4A and Au4, by a crystallographic C_2 axis that passes through the Pd atom. Selected angles (deg) are as follows, wherein numbers refer to respective Au atoms: Pd-1-P1 = 153.6 (2); Pd-2-P2 = 160.3 (2); Pd-3-P3 = 164.1 (2); Pd-4-P4 = 163.5 (2); 1-Pd-1A = 132.7 (1); 1-Pd-2 = 64.88 (5); 1-Pd-2A = 135.93 (4); 1-Pd-3 = 63.83 (5); 1-Pd-3A = 145.11 (4); 1-Pd-4 = 74.80 (6); 1-Pd-4A = 88.71 (7); 2-Pd-2A = 137.0 (1); 2-Pd-3 = 77.14 (7); 2-Pd-3A = 82.92 (7); 2-Pd-4 = 133.42 (5); 2-Pd-4A = 64.68 (5); 3-Pd-3A = 123.6 (1); 3-Pd-4 = 64.39 (5); 3-Pd-4A = 140.09 (5); 4-Pd-4A = 138.5 (1). Average esd's for Au-Pd, Au-Au, and Au-P distances are 0.002, 0.002, and 0.007, respectively.

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