to 335 and 339 cm^{-1} for Zr^0 and Zr$^+$, respectively.[16] We do not know the exact charge of the metal, but we expect that it is about zero as in other parent compounds such as [CpTi(cot)]. The *b* and *c* coefficients are related by orthonormalization relations, but we ignore the d$_{z^2}$ coefficient *a* in the ground state. It amounts to 0.96 in [CpTi(cot)] and lies between 0.95 and 0.97 in other parent compounds such as [CpTi(cht)], [CpV(cht)], and [CpCr(cht)].[17] If we take $\lambda_{\text{eff}} = 335$ cm^{-1}, $a = 0.96$, $E(1e_1) - E(a_1) = -24\,100$ cm^{-1}, and $E(2e_1) - E(a_1) = 17\,600$ cm^{-1}, the latter being the average value deduced from the two OA bands at 528 and 618 nm, we obtain $b = 0.59$ and $c = 0.81$. We may conclude that the empty 2e$_1$ orbitals are essentially of metal character, but the 1e$_1$ orbitals have also a significant metal character although the latter is only of 8.5% in [CpTi(cot)] 1e$_1$ orbitals.[17] This high metal character of the 1e$_1$ orbitals is also confirmed by the increased intensity of ionization from this orbital in He II versus He I photoelectron spectra.[13]

Conclusion. The above EPR and proton ENDOR studies show that the electron ground state of [Cp*Zr(cot)] is nonbonding and of essentially d$_{z^2}$ character, as anticipated from MO calculations in this family of compounds. This is shown by the low spin density at protons resulting from a direct delocalization of the unpaired electron on the 1s hydrogen orbitals and confirmed by the negative spin density at 2p$_z$ orbitals of Cp carbons. The inner e$_1$ orbitals are mainly of Cp character but they are more of metal character than in the Ti analogue. This implies that the real charge on the metal is close to zero.

The presence of methyl groups hinders the Cp ring rotation up to 100 K without affecting the (cot) rotation. This situation has already been observed with [(Me-Cp)Ti(η^8-C$_8$H$_8$)].[11]

The lack of resolution of zirconium satellites in the EPR spectrum precluded measurements of ^{91}Zr ENDOR. For this purpose, we are currently undertaking investigations on zirconium paramagnetic sandwich compounds where zirconium hyperfine lines are resolved so that these measurements can be performed.

Finally, although the results described above are in agreement with what is already known on compounds of similar structure and what is expected, they provide a basis for a model since the corresponding compound has been isolated and fully characterized. This is a rare case in zirconium chemistry. On the other hand, many Zr(III) compounds have been identified in solution on various occasions but could never be isolated; however, they usually give well-resolved EPR spectra. Their study by ENDOR on frozen solutions should therefore be easy and useful to provide additional information about their spatial and electronic configurations as shown in the present case.

Registry No. [Cp*Zr(cot)], 104389-95-9.

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Unanticipated Redox Transformations in Gold Polyselenides. Isolation and Characterization of $[Au_2Se_2(Se_4)_2]^{2-}$ and $[Se_{11}]^{2-}$

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To date, soluble metal polyselenide chemistry has proven to be different from the corresponding metal polysulfide chemistry.[1] Although for a given metal polysulfide complex one might expect the analogous polyselenide or polytelluride complex to exist, the fact is that in most cases a different molecular structure or stoichiometry is adopted even under identical experimental conditions. Isostructural compounds containing all S_4^{2-}, Se_4^{2-}, and Te_4^{2-} ligands exist only in the divalent Ni and Zn groups of the periodic table[2-4] and in the Mo/Q_4^{2-} system.[5] This nonanalogous behavior can be attributed to (a) the significant variation of the chalcogen–chalcogen (Q–Q) bond as one moves from S to Te, resulting in considerably different Q_x^{2-} ligand sizes and (b) the differing reduction potentials required to split the various Q–Q bonds.[6] We have been exploring the chemistry of polyselenide and polytelluride ligands with late-transition metals and *p*-block elements because we believe that new structural motifs are possible and also that appropriate and interesting precursors to several useful chalcogenide semiconductors can be found. Interest in this aspect of polychalcogenide chemistry is intense.[7-9] Recently we reported[10] $[Ag(Se_4)]_n^{n-}$, a new one-dimensional polymer, and the discrete $[In_2(Se_4)_4(Se_5)]^{4-}$ ion.[11] In view of the absence of any known gold polyselenides and the fact that Ag$^+$ formed a very interesting polymeric structure, we set out to find analogous chemistry in the corresponding Au/Se$_x$ system. Instead, we encountered a unique and curious set of redox reactions not previously observed in the Au/S$_x$ or other M/Q$_x$ systems. We report here the formation and structural characterization of two very interesting polychalcogenides, $[Se_{11}]^{2-}$ and $[Au_2Se_2(Se_4)_2]^{2-}$, that result from a remarkable interplay of electrons transferred from Au$^+$ to Se_x^{2-} and vice versa. We note that the $[Se_{11}]^{2-}$ anion has been synthesized and structurally characterized earlier by Krebs[12] (reported by Böttcher) but unfortunately no synthetic or accurate structural details are yet available. Two reproducible syntheses of $[Se_{11}]^{2-}$ are reported herein.

Experimental Section

All work was done in a glovebox (Vacuum Atmospheres, Inc.) under a nitrogen atmosphere. The solvents were stored over 4A Linde molecular sieves for several days and distilled under vacuum or a nitrogen

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Table I. Data for Crystal Structure Analysis[a] of α-$(Ph_4P)_2[Se_{11}]$ and $[(Ph_3P)_2N]_2[Au_2Se_2(Se_4)_2]$

formula	$C_{48}H_{40}P_2Se_{11}$	$C_{72}H_{60}P_4N_2Au_2Se_{10}$
fw	1546.93	2260.32
a, Å	12.871 (3)	11.872 (4)
b, Å	14.822 (3)	11.419 (4)
c, Å	14.144 (3)	26.910 (12)
α, deg	90.00	90.00
β, deg	108.67 (2)	94.02 (6)
γ, deg	90.00	90.00
Z; *V*, Å³	2; 2556.5	2; 3639
space group	$P2_1/n$	$P2_1/n$
D_{calcd}, g/cm³	2.01	1.71
μ(Mo Kα), cm⁻¹	114.6	90.4
cryst size, mm	0.06 × 0.04 × 0.38	0.04 × 0.075 × 0.58
θ range, deg	4.0–48.0	4.0–44.0
data collcd	*h*,*k*,±*l*	*h*,*k*,±*l*
No. of data collcd	3728	5187
no. of unique data	3533	5031
no. of data used ($F_o > 3\sigma(F_o)$)	1882	3276
min, max abs cor	0.49, 0.99	0.78, 0.99
no. of variables	277	406
no. of atoms per asym unit (including H)	51	75
final R/R_w, %	6.1/6.5	4.6/5.7

[a] At 25 °C.

Table II. Positional Parameters and *B*(eq) Values for $[Se_{11}]^{2-}$ [a]

atom	*x*	*y*	*z*	*B*, Å²
Se	0.000	0.000	0.500	4.67 (7)
Se(1)	0.0900 (2)	−0.0578 (2)	0.6863 (2)	6.23 (6)
Se(2)	−0.0435 (2)	−0.1277 (2)	0.7348 (2)	6.28 (6)
Se(3)	−0.1589 (2)	−0.0128 (3)	0.7510 (2)	9.03 (8)
Se(4)	−0.2709 (2)	0.0069 (2)	0.5868 (2)	7.60 (7)
Se(5)	−0.1763 (2)	0.0942 (2)	0.5040 (2)	6.78 (7)

[a] Standard deviations are shown in parentheses.

Table III. Positional Parameters and *B*(eq) Values for $[Au_2Se_2(Se_4)_2]^{2-}$ [a]

atom	*x*	*y*	*z*	*B*, Å²
Au	0.99332 (5)	0.06784 (6)	0.43833 (3)	2.94 (1)
Se(1)	0.8324 (1)	0.0888 (2)	0.37617 (7)	3.60 (4)
Se(2)	0.8958 (2)	0.2231 (2)	0.31779 (8)	4.23 (4)
Se(3)	1.0754 (2)	0.1501 (2)	0.31220 (8)	5.05 (5)
Se(4)	1.1408 (2)	0.1688 (2)	0.39560 (8)	4.66 (5)
Se(5)	0.8639 (2)	−0.0182 (2)	0.49493 (8)	4.77 (5)

[a] Standard deviations are shown in parentheses.

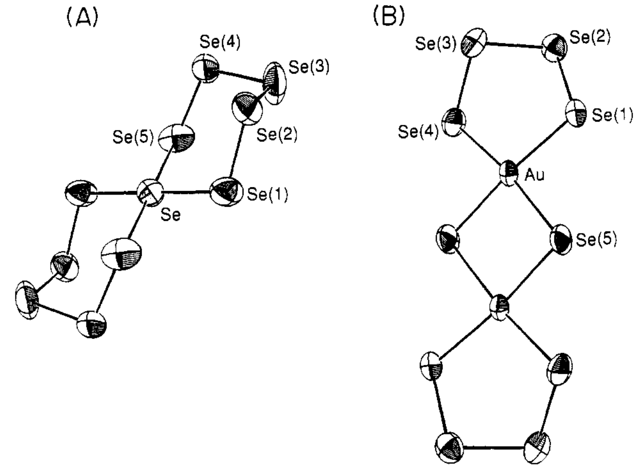

Figure 1. (A) ORTEP drawing of the $[Se_{11}]^{2-}$ ion with labeling scheme. Selected distances and angles: Se–Se(1) = 2.659 (2) Å, Se–Se(5) = 2.680 (3) Å, Se(1)–Se(2) = 2.320 (4) Å, Se(2)–Se(3) = 2.319 (4) Å, Se(3)–Se(4) = 2.327 (3) Å, Se(4)–Se(5) = 2.332 (4) Å; Se(1)–Se–Se(5)(intra-ring) = 104.49 (8)°. (B) ORTEP drawing of the $[Au_2Se_{10}]^{2-}$ ion with labeling scheme. Selected distances and angles: Au–Se(1) = 2.461 (2) Å, Au–Se(4) = 2.450 (2) Å, Au–Se(5) = 2.444 (2) Å, Au–Se(5)′ = 2.449 (2) Å, Se(1)–Se(2) = 2.357 (3) Å, Se(2)–Se(3) = 2.304 (3) Å, Se(3)–Se(4) = 2.332 (3) Å; Se(1)–Au–Se(4) = 100.43 (7)°, Se(1)–Au–Se(5) = 88.31 (6)°, Se(5)–Au–Se(5) = 82.95 (6)°.

blanket prior to use. Gold chloride was purchased from Alfa Products. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All compounds gave satisfactory elemental analyses. Sodium pentaselenide was prepared in liquid ammonia from sodium metal and elemental selenium in a 2:5 ratio.

Preparation of α-$(Ph_4P)_2[Se_{11}]$ (I). The dropwise addition of a 20-mL dimethylformamide (DMF) solution of 0.091 g (0.30 mmol) of $AuCl_3$ to a stirred 30-mL DMF solution of 0.270 g (0.61 mmol) of Na_2Se_5 and 0.228 g (0.61 mmol) of Ph_4PCl results in an immediate color change from dark green to brown. The stirring continued for 1 h, after which the solution was filtered to remove NaCl and then diluted with ether. When the mixture was allowed to stand for 3 days, red-brown needle crystals of $(Ph_4P)_2[Se_{11}]$ were isolated in 50% yield.

Preparation of β-$(Ph_4P)_2[Se_{11}]$ (I′). To a stirred 50-mL DMF solution of 0.270 g (0.60 mmol) of Na_2Se_5 and 0.220 g (0.60 mmol) of Ph_4PCl was added dropwise 10 mL of a DMF solution of 0.150 g (0.60 mmol) of I_2. After 10 min, the resulting solution was filtered and the filtrate was diluted with ether. When the mixture was allowed to stand for a day, red-brown crystals of β-$(Ph_4P)_2[Se_{11}]$ were isolated in 72% yield. As this method affords a different crystalline modification of I, a crystal structure determination was carried out to verify the presence of $[Se_{11}]^{2-}$.[13]

Preparation of $[(Ph_3P)_2N]_2[Au_2Se_2(Se_4)_2]$ (II). The procedure was identical with the one described above except AuCN was used. Analytically pure orange-brown needles of II were isolated in 69% yield. UV/vis spectrum (in DMF): 312 nm (ε = 28 200 M⁻¹ cm⁻¹), 392 nm (ε = 11 290 M⁻¹ cm⁻¹), 590 (sh) nm (ε = 2248 M⁻¹ cm⁻¹).

X-ray Crystallographic Studies. All crystallographic data sets were collected on a P3 Nicolet four-circle diffractometer using a θ/2θ scan mode and Mo Kα radiation. The crystals were mounted inside glass capillaries and sealed. Crystal data and details for data collection and refinement are shown in Table I. The intensities of three check reflections were monitored every 100 reflections and did not show any appreciable decay during the data collection period. An empirical absorption correction was applied to all data based on ψ scans. The structures were solved with direct methods using SHELXS-86 and were refined with the SDP package of crystallographic programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated but not refined. The final coordinates and average temperature factors of the atoms in the anions of I and II are shown in Tables II and III.

Results and Discussion

The reaction of $AuCl_3$ with Na_2Se_5 results in the isolation of a homogeneous product that is devoid of Au and has the stoichiometry $(Ph_4P)_2[Se_{11}]$. The formation of $[Se_{11}]^{2-}$ is a product of oxidation of the pentaselenide ligand by Au^{3+} ions. The structure of I is identical with that reported by Böttcher[12] and is shown in Figure 1A. Given the existence of various Se_x^{2-} species (*x* = 3,[14] 4,[15] 5,[15,16] 6,[17]), all of which are helical chain structures, approximately representing fragments of the infinite one-dimensional structure of hexagonal polymeric selenium,[18] the structure of $[Se_{11}]^{2-}$ is intriguing. Instead of the more intuitive chain conformation, I consists of a central Se atom (situated at an inversion center) chelated by two Se_5^{2-} ligands. Formally, the central four-coordinate selenium atom can be thought of as a Se^{2+} center. This explains, according to valence-shell electron-pair repulsion theory (VSEPR), its square-planar geometry, and the very long bonds to the ligated pentaselenide ligands. These bonds are Se–Se(1) = 2.659 (2) Å and Se–Se(5) = 2.680 (3) Å. Selected distances and angles for I are given in Figure 1. The square-planar

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(13) Crystal data for β-$(Ph_4P)_2[Se_{11}]$ (I′): monoclinic $P2_1/n$, *Z* = 2, *a* = 9.667 (3) Å, *b* = 13.889 (4) Å, *c* = 18.668 (4) Å, β = 102.60 (3)°, *V* = 2522 Å³ at 25 °C. The structural details of this phase will be reported elsewhere.

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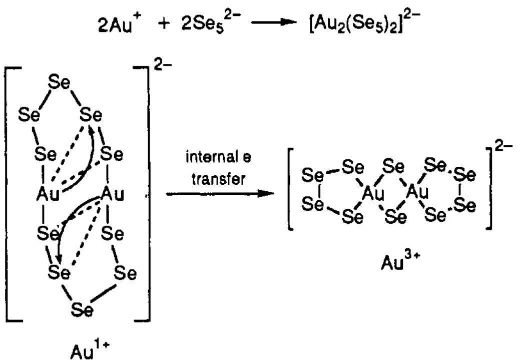
Scheme I



32e $SeSe_4$ fragment of I is isoelectronic to analogous $TeTe_4$ fragments found in solid-state alkali-metal polychalcogenides (e.g. Cs_2Te_5,[19] Rb_2Te_5,[20] Rb_2SnTe_5[21]). The fact that a chain polyselenide version of I (or even $[Se_{10}]^{2-}$) does not arise, attests to the instability of such species in the solid state or even in solution and may imply that, beyond a certain polyselenide chain length, internal electron transfer within the chain is favorable, resulting in a more compact, chelated, and presumably more stable molecule. In fact, $[Se_{11}]^{2-}$ forms in good yields by oxidation of $[Se_5]^{2-}$ using other oxidants such as iodine. A more efficient delocalization of the dinegative charge over I compared to the hypothetical linear isomer may be partly responsible for the stability of the former. It should be noted that, to date, deliberate efforts to synthesize longer ($x > 6$) chain Se_x^{2-} species as well as theoretical calculations have not been reported and are highly desirable to test this notion. The fate of gold in this reaction remains unknown.[22]

After the apparent proclivity of the Au^{3+}/Se_5^{2-} couple to redox chemistry, we proceeded towards a gold polyselenide complex using AuCN as a Au^+ source. To our surprise, we isolated $[Au_2Se_2(Se_4)_2]^{2-}$, a Au^{3+} polyselenide. Although this behavior is not presently understood, it is analogous to the Tl^+/I_3^- system in which Tl^{3+} is susceptible to rapid and complete reduction to Tl^+ by I^- solution. Curiously, however, the reaction of Tl^+ with excess I_3^- results in the tetrahedral Tl^{3+} complex $[TlI_4]^-$.[23]

The structure of II is shown in Figure 1B and consists of a hitherto unknown (in discrete polyselenides[24]) planar $[Au_2Se_2]^{2+}$ core (see Figure 1) with a nonbonding Au–Au distance of 3.660 (1) Å and Au–Se–Au angle of 96.70 (1)°. The $[Au_2Se_2]^{2+}$ core in II is situated on crystallographic center of symmetry. The two independent intracore Au–Se bonds are 2.444 (2) and 2.448 (2) Å, respectively. The Au^{3+} centers show the expected (d^8 configuration) square-planar geometry.[25] Two chelating Se_4^{2-} ligands complete the coordination of the $[Au_2Se_2]^{2+}$ core. Selected Au–Se and Se–Se distances are given in Figure 1. The five-membered $AuSe_4$ rings develop the twist-boat conformation. We found that I and II are best prepared when Se_5^{2-} is used. The use of Se_4^{2-} in the synthetic procedure yields gold(I) polyselenides that upon standing convert to II.[26]

Assuming that the initial step in the reaction of AuCN with Se_5^{2-} is a simple coordination, to form a Au^+ intermediate (e.g. $[Au_2(Se_5)_2]^{2-}$ (III)), the formation of Au^{3+} can be envisioned via an internal two-electron-transfer process from the gold atom to the terminal Se–Se bond of the Se_5^{2-} ligand. This will result in the splitting of the Se–Se bond, creating Se^{2-} and Se_4^{2-} ligands. Scheme I illustrates a possible pathway for the formation of II.

III is a reasonable intermediate because a close structural sulfur analogue, $[Au_2(S_4)_2]^{2-}$, exists and features linear Au^+ centers.[27] Since it is more difficult to reductively cleave the Se–Se bond than it is to cleave the S–S bond, the formation of $[Au_2Se_2(Se_4)_2]^{2-}$ and the stability of $[Au_2(S_4)_2]^{2-}$ (instead of $[Au_2S_2(S_4)_2]^{2-}$) seems counterintuitive. Although Au^{3+} square-planar complexes with all-sulfur coordination are known (e.g. $Au(S_2C_2(CN)_2)_2^{2-}$[28]), no analogous gold(III) polysulfide compounds have been reported thus far. Other structurally characterized binary anionic gold polychalcogenides include $[Au(S_9)]^-$[29] and $[Au_2(Te_2)_2]^{2-}$,[30] also featuring linear gold geometry. The existence of two gold(II) polysulfides, $[Au(CH_2)_2P(C_6H_5)_2]_2S_x$ (x = 8, 9) is also noteworthy.[31] At this stage there appears to be no obvious reason as to why a sulfide analogue of II should not exist. Further information on this issue must await the systematic study of the little-investigated Au/S_x system.

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Registry No. I, 123881-60-7; II, 123881-62-9; Na_2Se_5, 12439-18-8.

Supplementary Material Available: Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all non-hydrogen atoms (12 pages); a listing of calculated and observed ($10F_o/10F_c$) structure factors (51 pages). Ordering information is given on any current masthead page.

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