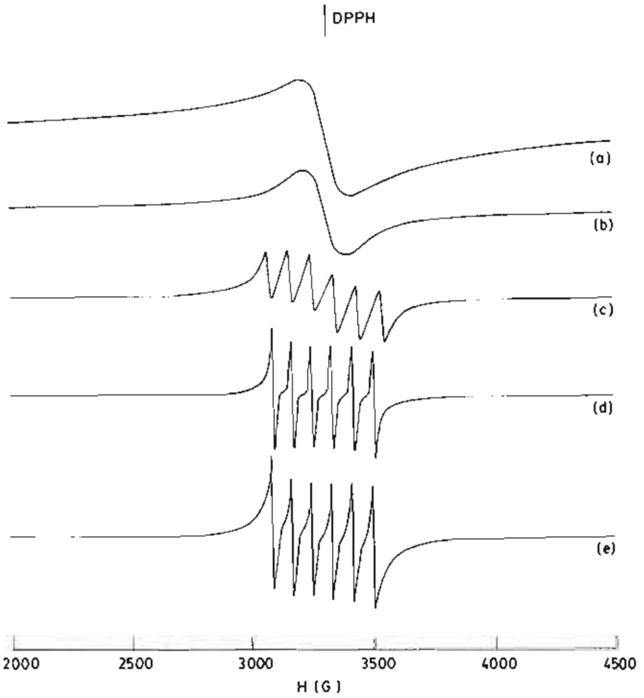

Figure 2. First-derivative EPR spectra (X-band, 9.4 GHz) at 298 K: (a) **1** in polycrystalline form; (b) **2** in polycrystalline form; (c) **2** in DMF; (d) **2** doped (1%) into [(bpy)$_2$Co(μ-S)$_2$WS$_2$] in polycrystalline form; (e) **2** doped (1%) into [(bpy)$_2$Zn(μ-S)$_2$WS$_2$] in polycrystalline form.

magnetic cobalt (g = 2.002, A = 84 G) and the diamagnetic zinc (g = 2.002, A = 84 G) host lattices suggest that Co–Co spin interaction is very fast with no interaction between Mn and Co.[13] The line width of the derivative curve is approximately 8 G for Mn-doped complexes, and the isotropic nitrogen superhyperfine splitting could not be seen. From the intensity ratio between the forbidden lines ($\Delta M_I = \pm 1$) and the allowed lines ($\Delta M_I = 0$)[14] an approximate value of D, the axial field splitting parameter, has been estimated to be on the order of 15.6×10^{-4} cm^{-1}. Thus in **2** (and also in **1**), though the central Mn(II) contains a N$_4$S$_2$ donor site, it still retains a nearly octahedral symmetry.

Our attempts to incorporate another [MS$_4$]$^{2-}$ ligand in **1** or **2** at the expense of a 2,2′-bipyridine ligand and to utilize the terminal sulfide groups in **1** or **2** for further coordination with a third metal have not been successful.

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Pressure-Induced Skeletal Isomerization of [Au$_9$(PPh$_3$)$_8$][PF$_6$]$_3$ in the Solid State

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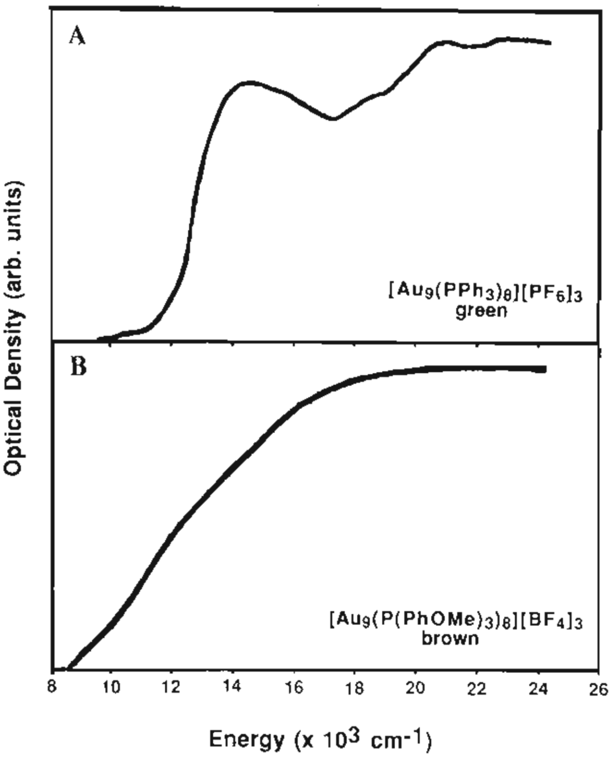
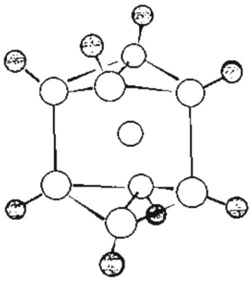


Figure 1. Optical absorption spectra for (A) "green" [Au$_9$(PPh$_3$)$_8$][PF$_6$]$_3$ and (B) "brown" [Au$_9$(P(p-C$_6$H$_4$OMe)$_3$)$_8$][BF$_4$]$_3$.

Molecular gold clusters are of widespread interest from a standpoint of structure, bonding, and reactivity.[1] Clusters of high nuclearity have been isolated,[2] most of which possess terminal triarylphosphines as ligands. One particularly interesting class gold compounds are clusters of the core formula [Au$_9$(PPh$_3$)$_8$]$^{3+}$, for which two different structural forms have been isolated and crystallographically identified.[1,3,4] The first is the "green" form (**1**), viewed as a D_{2h} fragment of an icosahedron, while the second is the "brown" form (**2**), described in terms of a D_{4d} centered-crown structure. The observed geometry under ambient conditions is highly dependent upon the choice of triarylphosphine ligand and counterion. We report in this work the ability of pressure to transform the cluster [Au$_9$(PPh$_3$)$_8$][PF$_6$]$_3$ from an initial "green" form to the "brown" form, as detected by changes in its optical spectrum. Pressure-induced structural rearrangements have been observed previously for monometallic copper complexes[5] and also



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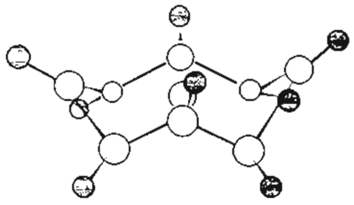

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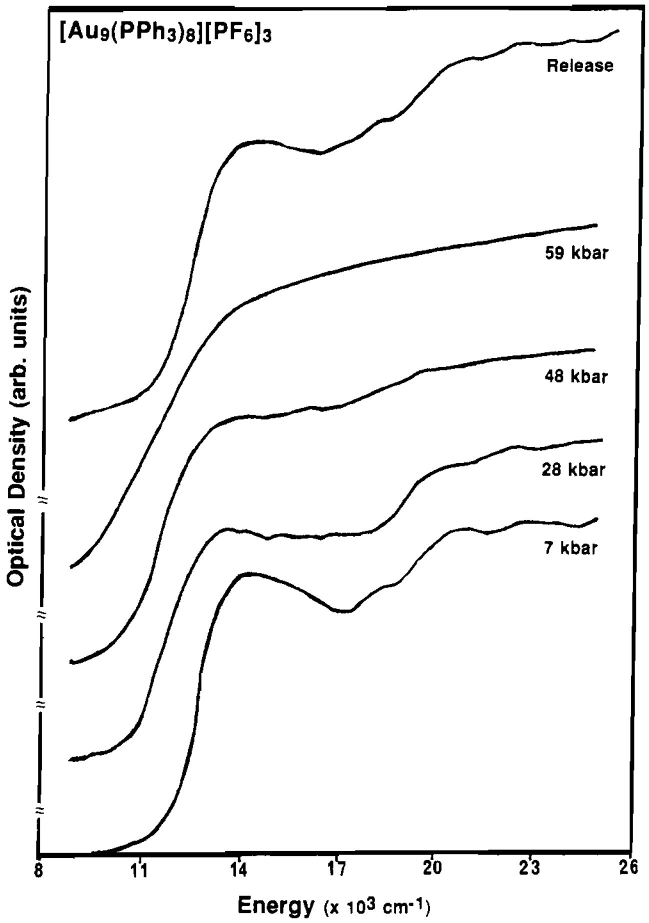

Figure 2. Effect of pressure on the optical absorption spectrum of a crystalline sample of $[Au_9(PPh_3)_8][PF_6]_3$.

for dinuclear rhenium compounds,[6] but to our knowledge, no precedent exists for such a piezochromic transformation in the case of a high nuclearity metal cluster.

Experimental Section and Results

$[Au_9(PPh_3)_8][NO_3]_3$ was synthesized according to a literature procedure.[7] The $[PF_6]^-$ salt was prepared by metathesis with $[NBu_4]PF_6$ in ethanol. Crystalline samples of each were loaded into a diamond-anvil cell (DAC) and examined by using Nujol as a pressure-transmitting medium. All runs were reproduced at a minimum of two separate loads. The ruby fluorescence method was utilized for pressure calibration. The light source employed was a 100-W Oriel tungsten halogen lamp, dispersed by a Kratos 1/4m monochromator using either a 1000 or 450 blaze grating. Light in the visible region was detected by EMI 9558 or 9658 photomultiplier tubes, along with an Ortec photon counting system interfaced to an IBM PC-XT computer.

Typical absorption spectra are shown in Figure 1, and the effect of applied pressure on the optical spectrum of the salt of green $[Au_9(PPh_3)_8]^+$ is shown in Figure 2, both introduced in the next section.

Discussion

The existence of two structural isomers for a gold cluster framework was first established by Mingos,[3] who found that $[Au_9(PR_3)_8]^{3+}$ crystallizes as the green D_{2h} structure, when R = C_6H_5 or p-$C_6H_4CH_3$ and the anion is $[PF_6]^-$ but as the brown D_{4d} crown-shaped structure, when R = p-$C_3H_4OCH_3$ and the anion is $[BF_4]^-$. Furthermore, for $[Au_9(P(p\text{-}C_6H_4CH_3)_3)_8]^{3+}$, changing the anion to $[NO_3]^-$ results in cocrystallization of both structural forms.[4] Each form possesses its own distinct optical and ^{31}P NMR spectrum in the solid state. However, the observation that the two isomers show identical ^{31}P NMR and optical absorption spectra in solution suggests possible rapid interconversion between the two structural forms.

Typical absorption spectra of green $[Au_9(PPh_3)_8][PF_6]_3$ and brown $[Au_9(P(p\text{-}C_6H_4OMe)_3)_8][BF_4]_3$ are shown in Figure 1. In previous accounts the solid-state optical spectra of both structural types has only been reported to 750 nm,[3] but the asymmetry in the absorption maximum near 700 nm for $[Au_9(PPh_3)_8][PF_6]_3$ led us to suspect that there was significant peak intensity at lower energies for the spectrum of this cluster. Extending the lower limit of the energy scale to 10.0×10^3 cm^{-1} (1140 nm) shows that this is indeed the case. The green isomer possesses a distinct absorption maximum near 1.40×10^3 cm^{-1}, followed by several overlapping bands of varying intensity at higher energy. On the other hand, the optical spectrum of the brown form consists of a continuous edge for which the onset of absorption begins around 9.0×10^3 cm^{-1}.

The effect of applied pressure on the optical spectrum of green $[Au_9(PPh_3)_8]^+$ is shown in Figure 2. With increasing pressure the absorption intensity near 15.5×10^3 cm^{-1} increases, with the most significant changes occurring in the 45–60-kbar range. By ca. 60 kbar, the spectral appearance is that of a continuous edge, analogous to that observed for an authentic, isolated brown isomer. At higher pressures, this edge does not change shape, but it tends to shift to lower energy up to the highest pressures measured (80 kbar). Upon gradual release of the cell back to atmospheric pressure, the spectrum reverts back to its original "green" type. Given these dramatic changes in spectral shape that occur with pressure, we ascribe them to a pressure-induced reversible change in cluster geometry from the D_{2h} icosahedral-fragment form to the D_{4d} centered-crown form. It is apparent from the core geometries shown for **1** and **2** that a relatively small "twist" of the "top" four Au atoms relative to the "bottom" four Au atoms concomitant with realignment of "bonding" Au–Au interactions suffices to interconvert the two forms.

It is known for the case of $[Au_9(Pp\text{-}C_6H_4OCH_3)_3)_8][NO_3]_3$ that the cluster volume for the green isomer is smaller than that of the brown (4098 Å^3 vs 4232 Å^3)[4]. If one combines this observation with the pressure-induced behavior of $[Au_9(PPh_3)_8][PF_6]_3$, it is apparent that the driving force for the green to brown transition is a energetically favorable change in the intermolecular forces (cation–cation, cation–anion) governing the lattice structure. In thermodynamic terms, the crown-shaped structure is the more compressible form. This observation is a salient point not fully appreciated in the literature, i.e., that increases in pressure and temperature can often direct the same phenomenon. A conceptually similar precedent exists in the case of thermo- and piezochromic behavior of the salicylidene anils, where the effect of increasing pressure or increasing temperature induces the same dramatic changes in the optical spectrum of the system.[8]

By rapid crystallization of $[Au_9(PPh_3)_8][NO_3]_3$ (e.g., addition of hexane to a methanol solution), a sample of this cluster appearing to possess only the brown centered-crown geometry was obtained. The effect of increasing pressure on the optical spectrum of this sample resulted in an overall growth of intensity and slight red shift of the absorption edge in ca. 50 kbar. However, no changes indicative of a phase transition were detected in the optical spectrum.

In summary, through changes in optical spectra, we have detected a novel example of pressure-induced solid-state skeletal isomerization for the case of a Au_9 cluster. This rearrangement confirms the "soft" energy barrier between the two structural forms and further extends the boundaries of piezochromic phenomena to metal clusters of high nuclearity.

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