higher T_c's, and as a further test of our hypotheses (vide supra), we have synthesized β-$(ET)_2AuI_2$. This is the first linear-symmetric $(I-Au-I)^-$ triatomic metal-containing anion in an $(ET)_2X$ derivative, and one which has an anion length (~9.40 Å) intermediate between that of I_3^- and IBr_2^-. This new salt has an ambient-pressure superconducting transition temperature almost double (~5 K) that of β-$(ET)_2IBr_2$ and is the highest reported to date (vide infra).

Synthesis. Lustrous black crystals of β-$(ET)_2AuI_2$ were grown by electrocrystallization (anhydrous and light-free conditions) by use of 9.3 mg of ET (Strem Chemical Co., 1.6 mM) as organic donor and 157 mg of n-Bu_4NAuI_2 (15.1 mM) as supporting electrolyte at 23 °C in a standard H-cell. The anion and the supporting electrolyte were prepared by following a literature procedure.[18] Its purity was confirmed by its melting point (78–79 °C) and elemental analysis. Anal. Calcd (found)[19] for n-Bu_4NAuI_2: C, 27.72 (27.68); H, 5.23 (5.32); N, 2.02(1.96); I, 36.61 (36.83). Dry THF was used as solvent, and a 1.0 $\mu A/cm^2$ current density was applied. Crystal formation was observed within 24 h, and the fully grown distorted hexagons were harvested after about 1 week. The β-$(ET)_2X$ crystals are characterized by their room-temperature ESR line width of ~20 G.[20]

Single-crystal X-ray analysis[21] revealed that β-$(ET)_2AuI_2$ is clearly isostructural (space group $P\bar{1}$, V_c = 845.2 (3) Å^3, Z = 1) with β-$(ET)_2X$, X = I_3^- and IBr_2^-. The unit cell volumes for β-$(ET)_2X$, X = I_3^- and IBr_2^-, are 855.9 (2) and 828.7 (3) Å^3, respectively, which indicates that, as expected, the $(I-Au-I)^-$ anion is of length intermediate between those of the two trihalide anions. The structure consists of discrete layers of AuI_2^- anions between which is sandwiched a "corrugated sheet network"[9] of ET molecules with short ($d_{S\cdots S} \leq 3.60$ Å, the van der Waals radius sum for S) *inter*stack S···S interactions. The loosely packed stacking of the ET entities is characterized by *intra*stack S···S distances exceeding 3.60 Å.

Superconductivity. The occurrence of a superconducting state in β-$(ET)_2AuI_2$ was detected by rf penetration depth measurements at ambient pressure and at various applied magnetic fields, similar to measurements previously reported for the I_3^- and IBr_2^- derivatives.[5,6,10] Figure 1 shows the change in resonant frequency as a function of temperature at zero applied magnetic field for a sample consisting of three relatively large single crystals. This sample gave an apparent onset temperature for bulk superconductivity (T_c) of 4.97 ± 0.06 K, which is the highest T_c yet observed at ambient pressure for an organic superconductor. Like the inductive superconducting transition curves for the trihalide derivatives, this figure shows a broad transition below T_c. Measurements of the onset temperatures of the individual crystals gave T_c = 3.93 ± 0.04, 4.36 ± 0.04, and 4.98 ± 0.08 K, respectively. Thus, the crystals of β-$(ET)_2AuI_2$ have a range of T_c values like the trihalide derivatives but have a much larger spread in the extremes (~1 K in these experiments). Preliminary pressure studies using low-frequency ESR techniques described earlier[7] indicate superconductivity is strongly depressed with pressure at a rate of 1 K/kbar.

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Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atom positional and anisotropic temperature factors (Table X2) (2 pages). Ordering information is given on any current masthead page.

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(21) X-ray data were collected on a Syntex $P2_1$ diffractometer, and the triclinic unit cell data (space group $P\bar{1}$, Z = 1) are as follows (298 K): a = 6.603 (1) Å, b = 9.015 (2) Å, c = 15.403 (4) Å, α = 94.95 (2)°, β = 96.19 (2)°, γ = 110.66 (1)°, V = 845.2 (3) Å^3 ρ_{obsd} = 2.39 (8) g/cm^3, and ρ_{calcd} = 2.40 g/cm^3. Diffraction data (ω scan, Mo K$\bar{\alpha}$ radiation, graphite monochromator, λ = 0.7107 Å) were collected at 298 K in the range $4° < 2\theta < 50°$, and 3406 data were averaged ($R_{av}(F)$ = 1.6%) to yield 2969 independent reflections, which were corrected for absorption (μ = 71.15 cm^{-1}), with T_{min} = 0.136 and T_{max} = 0.588. Full-matrix least-squares refinement (all atoms except hydrogen were refined with anisotropic temperature factors, 178 parameters) yielded $R(F)$ = 4.3% and $R_w(F)$ = 3.4% (GOF = 1.85). The crystal structure is fully ordered, and the $(I-Au-I)^-$ anion Au–I bond distance is 2.5610 (6) Å.
(22) M.A.F., K.S.W., and L.N. are student research participants sponsored by the Argonne Division of Educational Programs from Indiana University of Pennsylvania, Indiana, PA, St. Michael's College, Winooski, VT, and DePaul University, Chicago, IL.

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Transformation of Monoclinic $CfBr_3$ to Orthorhombic $CfBr_3$ by the Application of Pressure

Sir:

It has been shown previously that the orthorhombic form of anhydrous $CfBr_3$ can be synthesized by preparing $^{249}BkBr_3$ in its orthorhombic form and waiting for the ^{249}Bk ($t_{1/2}$ = 325 d) to transmute to ^{249}Cf ($t_{1/2}$ = 351 y) by β^- decay.[1] Both absorption spectrophotometric and X-ray powder diffraction analysis confirmed that, within the limits of sensitivity of these analytical techniques, the product of this transmutation is orthorhombic ($PuBr_3$-type structure) $CfBr_3$. Up to now this has been the only way known to prepare the orthorhombic modification of $CfBr_3$. Two other structural forms are known for $CfBr_3$: $AlCl_3$-type monoclinic and $FeCl_3$-type rhombohedral.[2] We report here a new synthetic route to the orthorhombic form of $CfBr_3$. The advantage of this route, which requires the application of pressure, is that it is an active rather than passive one, thus giving control over the process to the experimenter.

A few micrograms of monoclinic $CfBr_3$ was loaded into a triangular-shaped diamond anvil pressure cell similar to that reported by Merrill and Bassett.[3] A detailed description of the pressure cell and its use for spectral studies of actinide materials under pressure in conjunction with our microscope spectrophotometer[4] will be published separately. The $CfBr_3$ was handled in a helium-atmosphere glovebox and was placed, along with silicone oil and ruby chips, in the 0.2 mm diameter hole of an Inconel gasket mounted on one of the diamond anvils. The oil

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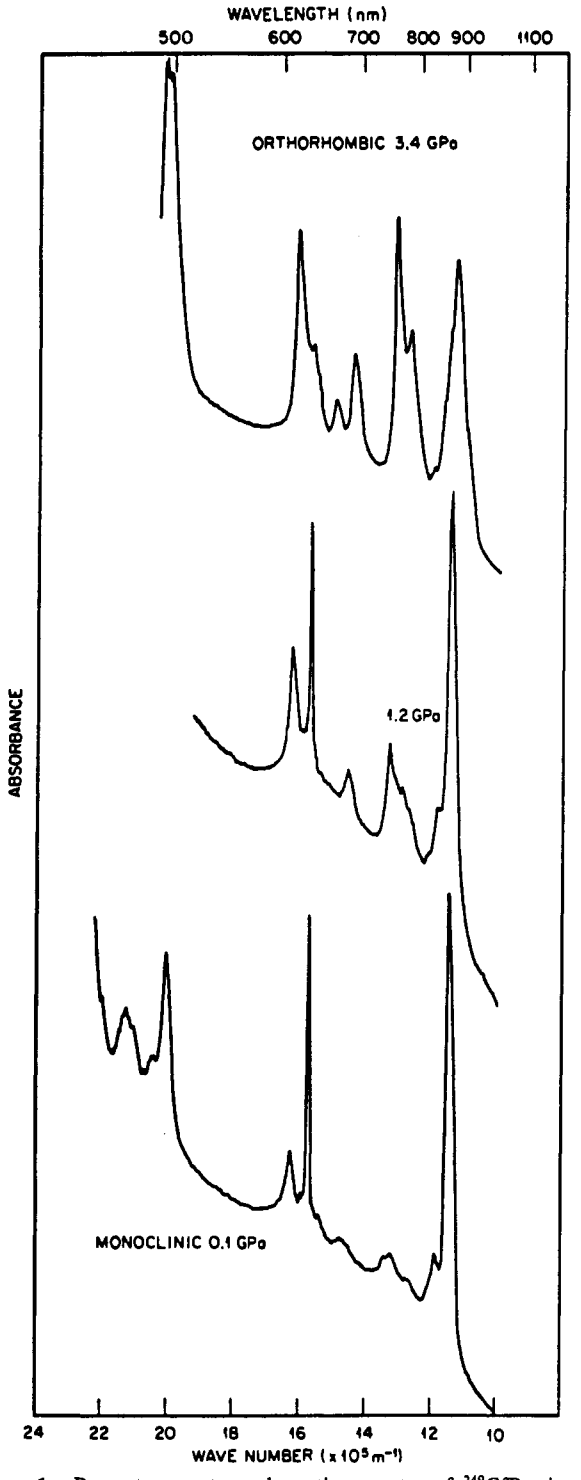

Figure 1. Room-temperature absorption spectra of $^{249}CfBr_3$ in two crystallographic forms ($AlCl_3$-type monoclinic, $PuBr_3$-type orthorhombic) at various pressures.

served as the pressure-transmitting medium, while the ruby allowed determination of the applied pressure by means of the ruby fluorescence technique using the nonlinear scale.[5] The ruby was excited by the 514.5-nm radiation of an argon ion laser, and its fluorescent line near 694.2 nm was measured in a back-scattering mode with a Raman microprobe attached to a Ramanor HG-2S spectrometer. Spectrophotometric analysis of the $CfBr_3$ in the sealed pressure cell was carried out at room temperature in air. Pressure on the $CfBr_3$ sample was increased in steps by tightening screws at the corners of the triangular cell. The absorption spectrum of the $CfBr_3$ sample and the fluorescent emission of ruby were obtained at each step. Assignment of the crystal structure exhibited by the $CfBr_3$ sample in this work was based on matching its absorption spectrum with those obtained from previous $CfBr_3$ samples that were sealed in silica capillaries and subjected to analysis by both absorption spectrophotometry and X-ray powder diffraction.[1]

Three of the absorption spectra obtained in the present work are shown in Figure 1. The spectral features stem from La-porte-forbidden f–f transitions in Cf(III). The bottom spectrum is that of monoclinic $CfBr_3$ (the starting material) in the pressure cell at 0.1 GPa. It is identical with the spectrum we reported earlier for this form of $CfBr_3$.[1] The middle spectrum, obtained at a pressure of 1.2 GPa, still exhibits most of the features characteristic of monoclinic $CfBr_3$ but with an increased intensity of the absorption envelope around 13.2×10^5 m^{-1} relative to that of the peak at 11.4×10^5 m^{-1}. Whether this spectral change reflects the beginning of the transformation from monoclinic $CfBr_3$ to orthorhombic $CfBr_3$ or just the effect of pressure on the spectrum of monoclinic $CfBr_3$ is not known. It should be noted that the top spectrum, obtained at 3.4 GPa, matches the absorption spectrum of orthorhombic $CfBr_3$ obtained via transmutation of orthorhombic $BkBr_3$.[1]

Based on our analysis of the absorption spectra obtained from the $CfBr_3$ sample at several pressures up to 3.4 GPa, we conclude that the structural transformation of monoclinic $CfBr_3$ to orthorhombic $CfBr_3$ takes place between 1.7 and 3.4 GPa. As the pressure was further increased up to a maximum of 12.5 GPa and then released in the usual stepwise manner, several reversible spectral features were noted, as well as the irreversibility of the structural transformation. The relative heights of the two peaks at 11.4 and 13.2×10^5 m^{-1} change with pressure. At higher pressures the peak at 13.2×10^5 m^{-1} is the more intense; at lower pressures, the 11.4×10^5 m^{-1} peak is the more intense one. The latter situation describes the absorption spectrum previously identified as that of orthorhombic $CfBr_3$.[1] Another reversible spectral change with pressure observed for orthorhombic $CfBr_3$ was a shift to lower energies with increasing pressure of the cutoff of transmitted light. This shift probably results from the pressure-induced shortening of the ligand-to-metal bond. Such a change decreases the energy of the ligand-to-metal charge-transfer band. A somewhat similar effect was noted recently in a study of the effect of pressure on the spectral and structural properties of AmI_3.[6] In the AmI_3 case, however, the shift was further into the visible-wavelength region, occurred at a lower pressure, and was irreversible. It was postulated that this spectral shift may have resulted from the generation of a trace amount of elemental iodine as a consequence of applying pressure on AmI_3.[6]

As mentioned above, the structural transformation of monoclinic $CfBr_3$ to orthorhombic $CfBr_3$ is irreversible with pressure. This transformation may relate to the relative packing efficiencies of the two crystal structures. On the basis of their crystallographic studies of a number of lanthanide trihalides under pressure, Beck and Gladrow proposed the following order of trihalide structures with respect to packing efficiency as pressure is increased: $AlCl_3$-type monoclinic (least efficient space filling) < BiI_3 ($FeCl_3$)-type rhombohedral < UCl_3-type hexagonal < $PuBr_3$-type orthorhombic (most efficient space filling).[7] The present result is consistent with this sequence. In our previous work we demonstrated the conversion of orthorhombic $CfBr_3$ to monoclinic $CfBr_3$ at normal pressure by heating the former to 360 °C.[1] Our direct synthesis of $CfBr_3$ via hydrobromination of Cf_2O_3 or $CfCl_3$ always results in monoclinic $CfBr_3$. Annealing monoclinic $CfBr_3$ at various temperatures down to 250 °C does not transform it to the orthorhombic form.

The present result of finding a controllable synthetic route to the orthorhombic form of $CfBr_3$ opens up the possibility of using applied pressure to produce new modifications of other actinide

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compounds, as well as to produce entirely new compounds such as californium monoxide. Leger and co-workers have already employed pressure-induced reactions to synthesize some lanthanide monoxides.[8] Further work in our laboratory will explore these possibilities along with increasing our understanding of the effects of pressure, as observed by changes in the optical absorption spectra, on actinide halides.

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Articles

Contribution from the Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan, and Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 466, Japan

Equilibria and Kinetics of the Reactions of Water-Soluble Molybdenum(V) Porphyrins with Hydrogen Peroxide in Aqueous Solutions[1]

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Equilibria of (5,10,15,20-tetrakis(4-*N*-methylpyridiniumyl)porphine(2+))oxomolybdenum(V) (Mo(V)-TMPyP complex) and its reaction with hydrogen peroxide have been investigated in aqueous solutions at I = 1.00 M by ESR and visible spectroscopies. The Mo(V)-TMPyP complex hydrolyzes and dimerizes to give rise to the following four species: $[Mo^{V}O(tmpyp)OH_2]^{5+}$ (**1**), $[Mo^{V}O(tmpyp)OH]^{4+}$ (**2**), the bis(μ-hydroxo) dimer $[(tmpyp)OMo^{V}(\mu\text{-}OH)_2Mo^{V}O(tmpyp)]^{8+}$ (**3**), and the (μ-hydroxo)(μ-oxo) dimer $[(tmpyp)OMo^{V}(\mu\text{-}O)(\mu\text{-}OH)Mo^{V}O(tmpyp)]^{7+}$ (**4**). Equilibrium constants were obtained to be $K_{a1} = [\mathbf{2}][H^+][\mathbf{1}]^{-1} = 10^{-7.18\pm0.02}$ M, $K_{a2} = [\mathbf{4}][H^+][\mathbf{3}]^{-1} = 10^{-10.0\pm0.1}$ M, and $K_D = [\mathbf{3}][\mathbf{2}]^{-2} = 10^{6.00\pm0.05}$ M^{-1} at 25 °C. The rate law for the dissociation of dimer **3** to give monomers **1** and **2** is $-d[\mathbf{3}]/dt = k_d[\mathbf{3}][H^+]$ with $k_d = (4.1 \pm 0.2) \times 10^4$ M^{-1} s^{-1} at 25 °C over the pH range 7.1-7.6. The reaction of the Mo(V)-TMPyP complex with hydrogen peroxide gives three types of peroxo complexes. Over the pH range 5-8 the peroxomolybdenum(V) complex $[Mo^{V}O(O_2)(tmpyp)]^{3+}$ (**5**) was obtained, while in acidic aqueous solution **1** is oxidized by hydrogen peroxide to produce $[Mo^{VI}(O_2)(tmpyp)OH_2]^{6+}$ (**6**). The substitution of the coordinated water molecule in **6** by hydrogen peroxide yielded a third type of the peroxo complex, $[Mo^{VI}(O_2)_2(tmpyp)]^{4+}$ (**7**). Formation constants of **5** and **7** were determined to be $K_{Mo(V)} = [\mathbf{5}][H^+]^2[\mathbf{1}]^{-1}[H_2O_2]^{-1} = 10^{-9.02\pm0.03}$ M and $K_{Mo(VI)} = [\mathbf{7}][H^+]^2[\mathbf{6}]^{-1}[H_2O_2]^{-1} = 10^{-8.16\pm0.03}$ M, respectively, at 25 °C. The formation of **6** is second order with respect to the concentration of hydrogen peroxide and first order with respect to that of **1**, and activation parameters were estimated as follows: k_{TMPyP}(25 °C) = 3.27 × 10^{-4} M^{-2} s^{-1}, $\Delta H^{\ddagger} = 74 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -63 \pm 3$ J K^{-1} mol^{-1}, $\Delta V^{\ddagger} = 1.3 \pm 0.3$ cm^3 mol^{-1}. The mechanism of formation of **5** from **1** and H_2O_2 includes a preequilibrium hydrolysis of **1**, followed by the rate-determining substitution. Activation parameters for the latter are k_f(25 °C) = 1.05 × 10^3 M^{-1} s^{-1}, $\Delta H^{\ddagger} = 37 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -63 \pm 3$ J K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -0.2 \pm 0.3$ cm^3 mol^{-1}. An interchange mechanism is most probably operative in this reaction.

Introduction

In recent years the chemistry of molybdenum porphyrins has been extensively investigated. Studies include the synthesis, structural characterization, and chemical reactivities of their dioxygen complexes.[3-6] Complexes of early transition metals in high oxidation state have been known to react with hydrogen peroxide to produce peroxo complexes. Molybdenum(V) porphyrins give rise to the corresponding peroxomolybdenum(VI) complexes in organic media. Chevrier et al. first reported on the synthesis and crystal structure of diperoxomolybdenum(VI) porphyrin, $Mo^{VI}(O_2)_2(tptp)$.[3,7] Photochemical[4] and electro-

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