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Chemistry of Quinquevalent Chromium. 2,2'-Bipyridinium Oxopentabromochromate(V)

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We report here for the first time the isolation of oxopentabromochromate(V), $[\text{CrOBr}_5]^{2-}$, as the bipyridinium salt, using a method similar to that used by one of the authors to synthesize oxopentabromomolybdates,¹⁻³ with some necessary modifications. Similar oxopentachlorochromates(V) have been isolated long ago⁴⁻⁸ and studied,^{9,10} but corresponding bromo complexes could not be isolated, presumably due to the fact that reduction of Cr(VI) with hydrobromic acid proceeds to Cr(III) at ordinary temperatures. However it has been observed, that the Cr(V) which is formed as an intermediate can be trapped at low temperatures and the $[\text{CrOBr}_5]^{2-}$ species has been isolated as the corresponding bipyridinium salt. The salt isolated is fairly stable but, when kept for weeks, slowly decomposes, especially in the presence of moisture, chromium being reduced to Cr(III), while the bromide is oxidized to bromine. Thus, the analysis and measurements were carried out with freshly prepared samples.

Experimental Section

Preparation of 2,2'-Bipyridinium Oxopentabromochromate(V), $\text{BpyH}_2[\text{CrOBr}_5]$. About 1 g of $\text{K}_2\text{Cr}_2\text{O}_7$ was finely ground and cooled to -5°C in a freezing mixture. Saturated hydrobromic acid (saturated by passing hydrobromic acid gas through available AR hydrobromic acid at 0°C) was cooled to -5°C and was added slowly and dropwise with stirring till the dichromate dissolved, the temperature being kept always below 0°C . To this was added the hydrobromide of 2,2'-bipyridyl (prepared by adding saturated hydrobromic acid slowly and dropwise with stirring to 1 g of 2,2'-bipyridyl, till it dissolved and the solution was just acidic). A brownish yellow solid was obtained which was quickly filtered under cold conditions, drained under suction, washed once with ice-cold saturated hydrobromic acid, and dried under vacuum over solid KOH; yield 3.3 g.

Analysis. Chromium in the compound was estimated by oxidizing with sodium peroxide, adding ferrous ammonium sulfate solution along with excess silver sulfate to precipitate bromide, destroying excess silver ion with HCl, and then back-titrating the excess ferrous ion with standard potassium dichromate solution (the modifications being necessary due to the presence of bromide).

Bromide in the compound was estimated as silver bromide and nitrogen was estimated using the semimicro Kjeldahl method.

The conductance measurement was carried out in freshly distilled nitrobenzene (as the compound decomposes in water at ordinary temperature).

Magnetic susceptibility was measured on a Gouy balance at room temperature using a field strength of 10160 G.

The ir spectrum was recorded on a Perkin-Elmer 621 spectrophotometer using a KBr pellet.

The ESR spectrum was recorded in powder form using an Alfa EPR spectrophotometer, Model No. 340, by keeping the frequency constant at 340 MHz and changing the magnetic field at a rate of 32 G/min and at a run rate of 0.5 in./min. The spectrum is shown in Figure 1.

Results

The molar conductance value of the compound in nitrobenzene using a saturated solution at 38°C was found to be $42.2 \text{ ohm}^{-1} \text{ cm}^2$. The molar magnetic susceptibility (after

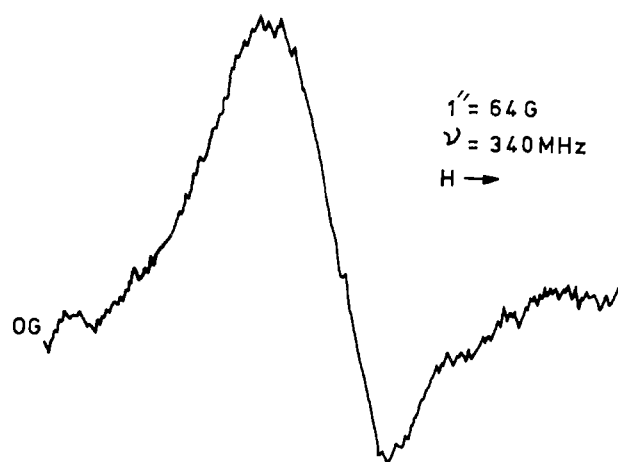


Figure 1. First-derivative ESR absorption spectrum of $\text{bpyH}_2[\text{CrOBr}_5]$ in solid powder form.

diamagnetic correction) was found to be 1245.7 cgsu at 308 K, from which the effective magnetic moment is calculated to be 1.75 BM. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{CrOBr}_5$: Cr, 8.31; Br, 63.89; N, 4.47. Found: Cr, 8.40; Br, 64.52; N, 4.24.

The infrared spectrum of the compound shows the following absorption bands (in cm^{-1}): 365 s, 390 w, 585 m, 605 w, 755 vs, 895 s, 940 vs, 990 m, 1032 m, sh, 1085 s, 1150 s, 1170 s, 1218 s, sh, 1240 m, 1270 s, 1300 s, 1320 s, 1350 w, 1425 s, 1465 vs, 1518 vs, 1580 vs, 1595 vs, sh (w = weak, m = medium, s = strong, sh = shoulder, vs = very strong).

The first derivative of the ESR absorption is shown in Figure 1. The $\langle g \rangle$ value has been calculated using the relation $h\nu = g\beta H$ where h is Planck's constant, ν is the frequency of absorption, g is the gyromagnetic ratio, β is the Bohr magneton ($0.927120 \times 10^{-20} \text{ erg/Oe}$), and H is the magnetic field strength. The $\langle g \rangle$ value has been found to be 1.999.

Discussion

The value of the molar conductance in nitrobenzene is in conformity with that of a 2:2 electrolyte in nitrobenzene,¹¹ which is expected for the compound.

The value of the magnetic moment obtained from the bulk susceptibility measurement and the $\langle g \rangle$ value from the ESR spectrum show that the orbital moment is quenched in a low-symmetry ligand field as is expected in these types of compounds, the distortion being caused by the presence of a strong metal-oxygen bond. The presence of the metal-oxygen multiple bond is clearly proved by the presence of a very strong absorption band at 940 cm^{-1} in the infrared spectrum which is observed in similar chloro complexes^{9,10} and corresponding molybdenum complexes.¹²⁻¹⁵ The metal-halogen bond in the compound is characterized by a strong infrared absorption at 365 cm^{-1} as in the case of corresponding chloro complexes.^{9,10}

The nature of the ESR spectrum in powder form also shows that there is a distortion from octahedral symmetry because in pure octahedral symmetry there would be excited states close to the ground state causing short spin-lattice relaxation times and very broad absorption lines at most temperatures. The situation is similar to that of corresponding chloro complexes.¹⁶⁻¹⁸

In view of the observations mentioned above we conclude that we have been able to isolate for the first time a species containing the $[\text{CrOBr}_5]^{2-}$ ion having chromium in the +5 oxidation state and bromide ion together. The anion is expected to belong to the C_{4v} point group, which is indicated by the presence of a metal-oxygen multiple bond observed in the infrared spectrum and a fairly narrow line width in the ESR spectrum.

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Registry No. $K_2Cr_2O_7$, 7778-50-9; hydrobromic acid, 10035-10-6; 2,2'-bipyridinium oxopentabromochromate(V), 57527-51-2.

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Isolation of Thermally Stable Compounds Containing the Dimethylaurate(I) and Tetramethylaurate(III) Anions¹

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Lithium dimethylaurate(I) has been reported by Tamaki and Kochi to be quite stable in diethyl ether solution but to decompose at -78° when freed of ether and to yield rather unstable bis(pyridine) and 2,2'-bipyridyl adducts.^{2,3} In a recent communication,⁴ we found the corresponding gold(III) complex, lithium tetramethylaurate(III), to be equally stable in ether solution but also unstable when freed of ether. We now report the isolation of remarkably stable solid derivatives of both the permethylaurate(I) and -(III) moieties, obtained by complexing the lithium ion with the aprotic polyamine N,N,N',N'',N''' -pentamethyldiethylenetriamine. Analogous reactions with polyethers also are discussed.

Experimental Section

Diethyl ether was distilled from CaH_2 under dry nitrogen immediately before use. All manipulations of methyl lithium and permethylaurates were performed under dried argon using Schlenk-type glassware and syringe techniques. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by the departmental microanalytical laboratory or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. N,N,N',N'',N''' -Pentamethyldiethylenetriamine (PMDT) was obtained from K & K Laboratories and used without further purification. Diethylene glycol dimethyl ether (diglyme) was distilled from metallic sodium under argon.

Synthesis of [Li(PMDT)][(CH₃)₂Au]. To $CH_3AuP(C_6H_5)_3$ was added with stirring slightly more than 1 equiv of halide-free CH_3Li prepared from $(CH_3)_2Hg$ and lithium sand. When dissolution of the solid was complete, PMDT was added dropwise. The mixture was slightly turbid until more than 1 equiv of PMDT had been added, when a fine white precipitate formed all at once. The precipitate was collected on a frit inside the apparatus, washed twice by slurrying with small portions of dry ether, and dried thoroughly under vacuum. The solid was crushed by manipulating the stirring bar with a hand-held magnet, and a portion of the resulting powder was shaken into an attached collection tube (Ace Glass "sample loader") which was then sealed off under vacuum. Other sampling devices were

Table I. Raman Frequencies of Permethylaurates

Compd	$\nu(Au-CH_3)$, cm^{-1}	$\delta_s(CH_3)$, cm^{-1}
Li[(CH ₃) ₄ Au] ^a	530 p, 522 dp, 484 dp	1212 p, 1176 dp
[Li(PMDT)]-[(CH ₃) ₄ Au] ^b	529, 520, 490	1208, 1168
Li[(CH ₃) ₂ Au] ^a	526, 490	1173
[Li(PMDT)]-[(CH ₃) ₂ Au] ^b	525, 492	1168

^a Ether solution; from ref 4. ^b Microcrystalline solid.

charged by transferring the apparatus to an argon-filled glovebag. Anal. Calcd for $C_{11}H_{29}N_3LiAu$: C, 32.4; H, 7.18; N, 10.3; Li, 1.70; Au, 48.4. Found (duplicate analyses): C, 32.2, 32.2; H, 7.33, 7.01; N, 10.5, 10.4; Li, 1.50, 1.51; Au, 48.8, 48.1; mp $120-123^\circ$ dec. The compound decomposes in seconds upon exposure to moist air and upon contact with solvents such as water, methanol, and chloroform. Attempts to prepare $Na[(CH_3)_2Au]$ from a solution containing a mixture of $Li[(CH_3)_2Au]$ and $P(C_6H_5)_3$ in ether by addition of THF or pyridine solutions of $NaClO_4$ gave solutions which precipitated $CH_3AuP(C_6H_5)_3$ upon addition of methanol or water, whereas ether solutions of $Li[(CH_3)_2Au]$ react violently with methanol or water to form only metallic gold.

Synthesis of [Li(PMDT)][(CH₃)₄Au]. This was prepared from $(CH_3)_3AuP(C_6H_5)_3$ by a procedure identical with that given above, except that the reaction mixture was permitted to stand 15 min prior to addition of PMDT to allow completion of the slower methylation. Anal. Calcd for $C_{13}H_{35}N_3LiAu$: C, 35.7; H, 8.07; N, 9.61; Li, 1.59; Au, 45.0. Found: C, 35.5; H, 8.00; N, 9.75; Li, 1.80; Au, 45.3. The compound melts at $86-88^\circ$ with effervescence, but there is no discoloration until 185° . The compound decomposes only slowly upon exposure to moist air. It is not soluble in water and is not rapidly attacked by it. It dissolves readily in moist methanol, showing no evidence of colloidal gold for up to 30 sec.

Synthesis of [Li(PMDT)][I]. This was prepared by addition of 1 equiv of PMDT to anhydrous LiI in ether and was collected and washed in the same manner as the aurates. Anal. Calcd for $C_9H_{23}N_3LiI$: C, 35.3; H, 7.55; N, 13.7. Found: C, 34.9; H, 7.76; N, 13.4.

Attempted Synthesis of [Li(diglyme)][(CH₃)₂Au] and [Li(diglyme)][(CH₃)₄Au]. The syntheses described above were repeated substituting diglyme for PMDT. The addition of diglyme to ether solutions of $Li[(CH_3)_2Au]$ or $Li[(CH_3)_4Au]$ gave white precipitates. The gold(III) compound developed a purple color due to some decomposition on washing with ether, but neither showed further decomposition when sealed off under vacuum. These are nonstoichiometric and appear to contain ca. 1.5 mol of diglyme/mol of Li^+ .

Raman Spectra. Spectra of solids were obtained with a Jarrell-Ash 25-300 spectrophotometer using 632.8-nm He-Ne excitation. Samples were contained in sealed capillaries, and the transillumination technique was employed. The frequencies of sharp bands should be accurate to ± 2 cm^{-1} .

Results and Discussion

The observed Raman bands of $[Li(PMDT)][(CH_3)_4Au]$ and $[Li(PMDT)][(CH_3)_2Au]$ are collected in Table I along with those from the previously reported⁴ anion spectra for diethyl ether solutions. The spectra indicate that the change in state has little effect on the structure of the aurates. Presumably the interaction of a permethylaurate anion with $Li(PMDT)^+$ in the crystal is comparable to the interaction with solvated Li^+ via ion pairing in ether solution. In all cases, the anions are perturbed from the expected symmetries of the free ions, and the number of Raman bands in the $\nu(Au-C)$ region is greater than predicted for D_{4h} and $D_{\infty h}$ symmetry. The solid-state spectra confirm conclusions drawn from the solution Raman and proton NMR spectra.⁴ The assignments of the solid-state spectra are unambiguous because of the very weak scattering of PMDT which was studied with $[Li(PMDT)][I]$.

The $[Li(PMDT)][(CH_3)_nAu]$ complexes are extremely stable gold alkyls, though quite reactive ones. Both are stable for months at room temperature, and they do not photolyze either in fluorescent lighting for that time or in periods of up