greater than 0.3 e$^-$/Å^3. The final standard deviation for an observation of unit weight ($[\Sigma w\Delta^2/(NO - NV)]^{1/2}$ where $\Delta = |F_o| - |F_c|$, NO is the number of observations (276), and NV is the number of variables (38)) was 0.95 electron. During the final cycle, the largest shift in any parameter was less than 0.01 times its own σ. The final positional and thermal parameters are given in Tables I and II, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle. In Table III are listed the magnitudes of the observed and calculated structure factors in electrons × 10.

Discussion

The crystal structure of tetraethylammonium hexabromoantimonate(V) is shown in Figure 1. Bond distances and angles of interest are given in Table IV and

TABLE IV

SELECTED INTERATOMIC BOND DISTANCES AND ANGLES FOR $(C_2H_5)_4NSbBr_6$[a]

Atoms	Distance, Å	Atoms	Angle, deg
Sb–Br(1)	2.536 (5)	Br(1)–Sb–Br(1)′	88.5 (3)
Sb–Br(2)	2.553 (5)	Br(1)–Sb–Br(2)′	91.2 (1)
Sb–Br(3)	2.559 (4)	Br(1)–Sb–Br(3)	91.1 (1)
Br(1)--Br(1)′	3.540 (12)	Br(2)–Sb–Br(2)′	89.0 (3)
Br(1)--Br(2)′	3.636 (5)	Br(2)–Sb–Br(3)	88.9 (1)
Br(1)--Br(3)	3.636 (5)	Br(1)–Sb–Br(2)	179.8 (5)
Br(2)--Br(2)′	3.579 (10)	Br(3)–Sb–Br(3)′	177.0 (3)
Br(2)--Br(3)	3.581 (5)	C(3)–N–C(4)	112 (3)
Br(3)---Br(3)′$_i$	3.584 (5)	C(3)–N–C(4)′	105 (3)
Br(1)---Br(2)′$_{ii}$	4.053 (6)	C(3)–N–C(3)′	113 (4)
N–C(3)	1.62 (5)	C(3)′–N–C(4)	105 (3)
N–C(4)	1.51 (5)	C(4)–N–C(4)′	109 (5)
C(3)–C(1)	1.63 (6)	N–C(3)–C(1)	101 (3)
C(4)–C(2)	1.64 (7)	N–C(4)–C(2)	113 (4)
Sb–Br(1)	2.561 (5)[b]		
Sb–Br(2)	2.564 (5)[b]		
Sb–Br(3)	2.570 (4)[b]		

[a] Primed atoms refer to the symmetry-related atom in the group (Figure 2). Other symmetry operations referred to: (i) $1 + x, y, z$; (ii) $x, \frac{1}{2} + y, \frac{1}{4} + z$. [b] Interatomic distance corrected for thermal motion using a riding model where the second atom is assumed to ride on the first.

Figure 2. The $Sb^VBr_6^-$ ion has crystallographic C_{2v} symmetry but is somewhat distorted from O_h symmetry.

The most significant deviation involves the Br(3)–Sb–Br(3)′ angle which is 177.0 (3)°. This slight distortion can be ascribed to packing effects since the closest approach between anions is 3.584 (5) Å along the *a* direction (Br(3)---Br(3)′$_i$) which is significantly shorter than the 3.9-Å sum of the van der Waals radii.[19] The average Sb–Br bond length is 2.549 (5) Å before correction for thermal motion and 2.565 (5) Å when corrected assuming a riding model. These averages are in good agreement with those previously reported.[9] The tetraethylammonium ion has the trans configuration in which the ethyl groups lie on intersecting mirror planes (C_{2v} symmetry) as required by this space group. However, the inner carbon atoms do not lie on the mirror planes and are therefore disordered with apparent D_{2h} symmetry, as shown in Figure 2. Disorder within the swastika configuration of the tetraethylammonium ion has also been reported.[20] The long bond lengths indicate that the light-atom positions are not well defined and reflect both the disorder and the heavy-atom nature of this problem.

The crystal structure (Figure 1) can be viewed as an efficient packing arrangement of the rather spherical hexabromoantimonate(V) ions and of the nearly equal in size but slightly flattened tetraethylammonium ions. The similar sizes of these two large, rather diffuse ions contribute to the crystal stability. The usual type of intervalence charge transfer cannot occur in this structure. The structure consists of only one kind of $SbBr_6$ species, has a saturated cation, and has only the one bromine---bromine contact (Br(3)---Br(3)′$_i$, 3.58 Å) which is less than the sum of the van der Waals radii. This distance does not appear to be short enough for any type of interspecies charge-transfer interaction since the Br(3)---Br(2) and Br(3)---Br(1) intraion distances are 3.58 and 3.64 Å, respectively. We believe, therefore, that the deep color of this complex probably results from normal charge transfer of the intraspecies ligand to metal type, involving transitions between molecular orbitals of the $Sb^VBr_6^-$ species.

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Notes

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Bromine Perchlorate

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Recently we reported the synthesis of a novel chlorine oxide, chlorine perchlorate.[1] This preparation was accomplished by the reaction

$$MClO_4 + ClSO_3F \longrightarrow MSO_3F + ClOClO_3 \quad (M = NO_2, Cs) \quad (1)$$

It has now been found that the related bromine compound bromine perchlorate can be prepared by this method using bromine(I) fluorosulfate.

$$MClO_4 + BrSO_3F \xrightarrow{-20^\circ} MSO_3F + BrOClO_3 \quad (2)$$

In addition, a second method involving the oxidation of elemental bromine with chlorine perchlorate was discovered

$$Br_2 + 2ClOClO_3 \xrightarrow{-45^\circ} Cl_2 + 2BrOClO_3 \quad (3)$$

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TABLE I

INFRARED SPECTRA OF $BrOClO_3$ AND RELATED COMPOUNDS

Freq, cm^{-1}, and rel intens						
$HOClO_3$[a]	$FOClO_3$[b]	$ClOClO_3$[c]	$BrOClO_3$		Assignment in point group C_s	Approx description of mode
Gas	Gas	Gas	Gas	Matrix		
			2300 w		$\nu_2 + \nu_9$ (A'') = 2299	
1326 s 1263 vs	1298 vs	1282 vs	1275 vs	1279 vs 1262 vs 1253 m	ν_1 (A') ν_9 (A'')	$\nu_{asym}(ClO_3)$
1050 s	1049 s	1041 s	1039 s	1037 s	ν_2 (A')	$\nu_{sym}(ClO_3)$
3560 s	885 m	752 w	683[d] m	686 m	ν_3 (A')	ν(O–X)
725 s	666 s	652 s	648 s	651 vs 643 ms	ν_4 (A')	ν(–Cl–O)
579 s		561 ms	570 ms	572 mw 566 m	ν_5 (A') ν_{10} (A'')	$\delta_{sciss}(ClO_2)$ $\delta_{asym}(ClO_3)$
519 w		511 w	509 m	516 m	ν_6 (A')	$\delta_{umbrella}(ClO_3)$
430 w				387 w	ν_{11} (A'')	$\delta_{twist}(ClO_2)$

[a] Reference 3. [b] Only four bands reported.[2] [c] Reference 1. [d] A comparable band has been observed at 690 cm^{-1} in the spectrum of $BrONO_2$: C. J. Schack, unpublished results.

This reaction proceeded quantitatively and yielded a purer product than the fluorosulfate reactions.

Bromine perchlorate is a red liquid which freezes below −78°. It is unstable at ambient temperature and decomposes slowly at approximately −20°. A reproducible, measurable vapor pressure of 5 mm was obtained at −23°. The instability of the compound precluded reliable measurements at higher temperatures. The formulation as $BrOClO_3$ is based on the quantitative synthesis according to eq 3, its elemental analysis, and the infrared spectrum. Further support for this formulation was obtained from the quantitative reaction with HBr to form Br_2 and $HClO_4$ and the qualitative reaction with AgCl to form Br_2, Cl_2, and $AgClO_4$.

Figure 1 shows the replotted infrared spectrum of gaseous and matrix-isolated $BrOClO_3$. Good-quality spectra were difficult to obtain owing to the thermal instability of the compound. The vibrational spectrum of $BrOClO_3$ is very comparable to that of other covalent perchlorates—$ClOClO_3$,[1] $FOClO_3$,[2] and $HOClO_3$.[3] From the vibrational spectrum a structure of symmetry C_s (*i.e.*, the only symmetry element is a symmetry plane in the plane of the paper) can be derived for $BrOClO_3$

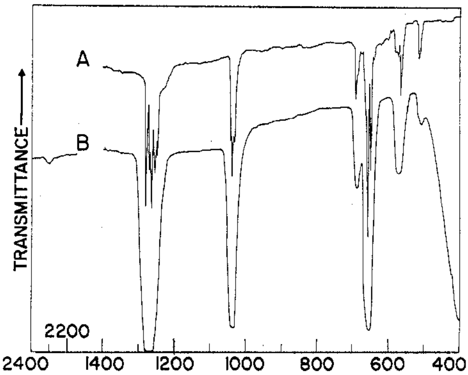
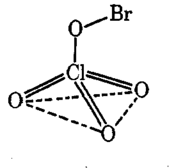


Figure 1.—Infrared spectra of $BrOClO_3$: trace A, 2.5 μmol of sample in Ar matrix (mixture ratio 400) at 4°K; trace B, gas at 20 mm pressure in a cell of 5-cm path length.



This structure is analogous to those of the related molecules $ClOClO_3$, $FOClO_3$, and $HOClO_3$. Table I lists the observed frequencies together with their assignment for symmetry C_s and the values for comparable bands in similar compounds. The decreasing thermal stability of the halogen perchlorates in the order $FOClO_3$ > $ClOClO_3$ > $BrOClO_3$ might be related by the increasing polarizability of the terminal halogen atoms.

Experimental Section

Materials and Apparatus.—All materials were handled in a well-passivated (with ClF_3 followed by covalent perchlorates) 304 stainlesss steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellow-seal valves (Hoke Inc., 4251F4Y). Outside of the vacuum line materials were manipulated in the dry nitrogen atmosphere of a glove box. The apparatus used for the low-temperature matrix-isolation study has been described elsewhere[4] and was directly connected to a metal–Teflon FEP vacuum system. The $BrOClO_3$–Ar mixtures were prepared in a mole ratio of 1:400 by standard manometric techniques using research grade Ar (99.9995% minimum purity from The Matheson Co.). Owing to the thermal instability of $BrOClO_3$, preparation of the gas mixture and its deposition on the cold (4°K) CsI window was done in less than 2 min. The infrared spectra of gases were taken in stainless steel cells of 5-cm path length equipped with AgCl windows. All spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points.[5]

Preparation of $BrOClO_3$. Method A.—Prepassivated 30-ml stainless steel cylinders were loaded with weighed amounts of either NO_2ClO_4 or $CsClO_4$ in the drybox. A less than equimolar amount of $BrSO_3F$ was then condensed into the cylinder from the vacuum line and the reaction was allowed to proceed at −20° for 5 days or longer. On cooling the cylinder to −196°, varying small amounts of noncondensable gases were observed. The volatile products were separated by fractional condensation in U traps cooled to −45, −64, and −196°. Unreacted $BrSO_3F$, if present, was retained at −45° while the trap cooled to −196° contained only small amounts of the by-products $FClO_2$ and $FClO_3$. Bromine perchlorate was trapped at −64°.

Method B.—A prepassivated 30-ml stainless steel cylinder was loaded at −196° with Br_2 (1.36 mmol) that had been dried over P_2O_5 followed by $ClOClO_3$ (2.76 mmol). The cylinder was left at −45° for 5 days. After recooling first to −78° and later at −64° the material volatile at those temperatures was pumped out and trapped at −78, −112, and −196°. This consisted of Cl_2 (1.38 mmol), $ClOClO_3$ (0.04 mmol), and $BrClO_4$ (0.1 mmol) as indicated by their vapor pressure and/or infrared spectra. Based on one Cl_2 molecule from each Br_2 reacted, the Cl_2 yield was quantitative within experimental error. The product $BrOClO_3$ (0.469 g, 2.61 mmol) was decomposed by heating at 50° for 3 days. The evolved O_2 was identified by its vapor pressure at −196° and by mass spectroscopy. The halogens were separated

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by fractional condensation after the small amount of BrCl present was thermally decomposed at reduced pressure. Recovered Br_2 (1.30 mmol), Cl_2 (1.32 mmol), and O_2 (5.14 mmol) gave an observed mole ratio of 1.00:1.02:3.95 (theory 1:1:4). *Anal.* Calcd for $BrClO_4$: Br, 44.55; Cl, 19.76; O, 35.68. Found: Br, 44.3; Cl, 20.0; O, 35.1.

Bromine Perchlorate Reactions.—The reaction of $BrOClO_3$ and AgCl was examined only qualitatively. Thus, samples of $BrOClO_3$ were allowed to stand in infrared cells with AgCl windows for several hours. Bands due to $BrOClO_3$ gradually disappeared and those of the ClO_4^- ion[6] grew and were accompanied by the bands of ClO_2 which was formed in minor amounts. In addition, Br_2, Cl_2, and small quantities of gases not condensable at -196° were generated.

A sample of $BrOClO_3$ (2.2 mmol) contained in a 30-ml cylinder was allowed to react with HBr (3.21 mmol) for 1 hr at -78°. Vacuum fractionation of the volatile products at -30, -78, and -196° gave unreacted HBr (1.02 mmol), identified by its infrared spectrum, and Br_2 (2.18 mmol), identified by its vapor pressure. The least volatile fraction was a nearly colorless liquid of low volatility, identified as $HClO_4$ by its infrared spectrum[8] and vapor pressure.[7] No unreacted $BrOClO_3$ was observed.

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Some Five-Coordinate, Low-Spin Cobalt(II) Complexes

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Whereas the most common examples of five-coordination are found among Ni(II) complexes, increasing reports of five-coordinate Co(II) have appeared so that examples of the latter metal are nearly as numerous as the former.[1] Perhaps the most important five-coordinate d^7 complex in homogeneous catalysis is $Co(CN)_5^{3-}$, which functions somewhat like a free radical in promoting certain organic reactions.[2] Most low-spin five-coordinate Co(II) complexes have been found with soft donor ligands,[1] particularly, phosphorus,[3-10] arsenic,[11] unsymmetrical bidentates containing phosphorus–sulfur, phosphorus–selenium, and phosphorus–arsenic,[12] and isonitriles.[13] Recently, some low-spin five-coordinate Co(II) complexes containing a tetradentate of nitrogen donors were reported.[14]

This paper reports the synthesis and properties of some $(C_6H_5)_3Y$ (Y = P, As, Sb, Bi) adducts of bis(dithioacetylacetonato)cobalt(II), $Co(sacsac)_2$; these compounds are of interest as potential catalysts, studies on which are currently in progress.

Experimental Section

Starting Materials.—Benzene, methylene chloride, and methanol were dried with 4A molecular sieves and deoxygenated by purging with nitrogen gas. The triphenyl–group V ligands were purchased from Eastman Organic Chemicals and used as received. $Co(sacsac)_2$ was prepared according to methods described in the literature.[15]

Preparation of the Complexes.—Triphenylphosphine, -arsine, -stibine, and -bismuthine adducts of $Co(sacsac)_2$ were prepared by mixing equimolar amounts of $Co(sacsac)_2$ and the appropriate ligand in dry, deoxygenated benzene and stirring for 72 hr at room temperature in an inert atmosphere. The crude product was obtained after the solvent was removed by gentle suction at 30–35°. The product was obtained pure after recrystallization from benzene–pentane or methylene chloride–pentane and drying under high vacuum. Table I gives the elemental analyses of the complexes prepared.

Physical Studies.—The magnetic moments of the complexes were obtained after their susceptibilities were measured by the nmr technique described by Evans,[16] using CH_2Cl_2 solutions containing ~10% v/v of TMS. The temperature of the probe area was calibrated by means of a methanol standard.

Ligand field spectra were recorded on a Perkin-Elmer Model 450 recording spectrophotometer in CH_2Cl_2 solution. Electronic spectra were also recorded as Nujol mulls on Whatman No. 1 filter paper according to the method described by Lee, *et al.*[17] Mull spectra were also recorded on $[Co(AP)_2X]ClO_4$[12] (AP = diphenyl(*o*-diphenylarsinophenyl)phosphine; X = Cl, Br, I) for comparison.

Results and Discussion

All the five-coordinate complexes, like $Co(sacsac)_2$, are very dark red (nearly black) solids and dissolve in a wide range of organic solvents to give intensly dark solutions. They are very stable thermally; there is no apparent melting or decomposition when the compounds are heated up to 300°.

The solution optical spectra and magnetic moments are shown in Table II; the mull spectra of the compounds prepared in this work, along with those of Dyer and Meek,[12] are shown in Table III.

There is ample evidence for five-coordination. Besides elemental analyses and molecular weight data, the optical spectra of the adducts, while similar to each other, are somewhat different from that reported for $Co(sacsac)_2$[15] and also obtained under our conditions and shown in Table II for comparison. In addition, the magnetic moments of the $Co(sacsac)_2L$ complexes are different from the values reported for $Co(sacsac)_2$: 2.3 BM from a bulk susceptibility measurement[15] and 2.1 BM[18] from the nmr technique, used in this paper. The magnetic moments range from 2.0 to 2.6 BM, which are intermediate in the range between those of low-spin octahedral (1.8–2.0 BM) and square-planar (2.3–2.9 BM) Co(II) complexes. Intermediate values would be expected for five-coordination.[19] Furthermore, whereas quaternization of phosphorus begins immediately upon addition of a solution of CH_3I to one of $P(C_6H_5)_3$, when CH_3I is added to a solution of

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