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.

Acknowledgment.—We are pleased to acknowledge support of this work by the Office of Naval Research, Power Branch.

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

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Received July 8, 1970

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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TABLE I

ELEMENTAL ANALYSES AND MOLECULAR WEIGHTS OF THE COMPOUNDS

Compound	% calcd			% found[a]			Mol wt	
	C	H	S	C	H	S	Calcd	Found[b]
$Co(sacsac)_2P(C_6H_5)_3$	57.62	5.00	21.98	57.81	5.02	21.88	583	597
$Co(sacsac)_2As(C_6H_5)_3$	53.59	4.66	20.44	53.67	4.76	20.16	620	618
$Co(sacsac)_2Sb(C_6H_5)_3$	49.90	4.34	19.06	49.86	4.40	18.87	675	655
$Co(sacsac)_2Bi(C_6H_5)_3$	44.15	3.83	16.84	44.35	3.81	17.00	762	696

[a] Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Cryoscopic in benzene.

TABLE II

SOLUTION OPTICAL SPECTRA AND MAGNETIC MOMENTS OF $Co(sacsac)_2L$

	$P(C_6H_5)_3$		$As(C_6H_5)_3$		$Sb(C_6H_5)_3$		$Bi(C_6H_5)_3$		$Co(sacsac)_2$	
	ν[a]	ϵ[b]	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ
	6,800	17	6,750	18.3	6,800	25	6,900	21	5,240	<10
	8,300 sh				8,000 sh		8,200 sh		6,750	22
	11,000	23.5	11,000	25	11,100	27	11,100	29.5	10,000	31
	15,200 sh	525	14,900 sh	270	15,200 sh	526	15,200 sh	490	14,900 sh	350
	17,700	4,330	17,800	2,360	17,900	4,120	17,800	4,620	17,500	4,070
	21,800	3,790	21,850	3,680	21,900	3,540	21,900	3,980	21,650	3,240
	23,900 sh	4,100	23,900 sh	4,380	23,900 sh	3,650	23,800 sh	4,130	24,000 sh	5,000
	28,500	14,500	27,800	13,300	27,800	12,900	27,500	13,700	28,000 sh	14,500
									29,500	15,000
μ_{eff}, BM	2.60		2.30		2.23		2.01			

[a] In cm^{-1}. Bands in the near-ir and visible regions. [b] In $l. mol^{-1} cm^{-1}$.

TABLE III

SOLID-STATE OPTICAL SPECTRA (CM^{-1}) OF $Co(sacsac)_2L$ AND $[Co(AP)_2X]ClO_4$

$[Co(AP)_2Cl]ClO_4$	$[Co(AP)_2Br]ClO_4$	$[Co(AP)_2I]ClO_4$	$Co(sacsac)_2P(C_6H_5)_3$	$Co(sacsac)_2As(C_6H_5)_3$	$Co(sacsac)_2Sb(C_6H_5)_3$	$Co(sacsac)_2Bi(C_6H_5)_3$
6,900	6,800	6,750	6,800	6,850	6,900	6,850
			8,300 sh	8,300 sh	8,350 sh	8,350 sh
11,000	11,000	11,000	11,000	11,100	11,100	11,100
12,500	12,400 sh	12,000 sh	15,200 sh	15,000 sh	15,000 sh	14,500
	14,000	15,700	17,300	17,500	17,500	17,450
21,900	21,600	20,750	21,650	21,900	21,900	21,850
		22,820	23,800 sh	23,900 sh	23,600	23,600
28,500	28,200	28,600	28,500 sh			

$Co(sacsac)_2P(C_6H_5)_3$, only a very slow quaternization takes place, and this is evident only after several minutes of standing at room temperature. The above data clearly show that the group V ligand is coordinated to cobalt.

The evidence at hand favors the square-pyramidal structure rather than the trigonal-bipyramidal arrangement, mostly on the basis of electronic spectra. The optical spectra of $Co(sacsac)_2L$, although shifted somewhat, are very similar to those of $Co(AP)_2X^+$, both in solution and in the solid state. Arguments advanced by Dyer and Meek[12] for the interpretation of the optical spectra of $Co(AP)_2X^+$ in terms of a square-pyramidal arrangement also apply here for $Co(sacsac)_2L$. On the other hand, electronic spectra of some known trigonal-bipyramidal molecules show spectra which are similar to each other (compare, *e.g.*, $Co(QP)X^+$[7] with $Co(CR)X^+$[14]) but are significantly different from the spectra of $Co(sacsac)_2L$ and $Co(AP)_2X^+$.

The similarity in electronic spectra taken in solution and in the solid state indicates that $Co(sacsac)_2L$, as well as $Co(AP)_2X^+$, does not alter its structure upon dissolution. This also means that these compounds might possess only limited catalytic activity.

Acknowledgment.—We are grateful to Professor D. W. Meek of The Ohio State University for kindly supplying us with samples of $[Co(AP)_2X]ClO_4$.

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Electrochemistry of Tantalum Bromide Cluster Compound

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Received July 9, 1970

The divalent tantalum bromide cluster ion $Ta_6Br_{12}^{2+}$ has been shown to be chemically oxidizable to the tri- and quadrivalent ions $Ta_6Br_{12}^{3+}$ and $Ta_6Br_{12}^{4+}$ in aqueous solutions.[2,3] Estimated values of the redox potentials for these two reactions

$$Ta_6Br_{12}^{3+} + e^- = Ta_6Br_{12}^{2+} \quad E_1° \tag{1}$$

$$Ta_6Br_{12}^{4+} + e^- = Ta_6Br_{12}^{3+} \quad E_2° \tag{2}$$

suggested a relatively large calculated value of K_{eq} for the reproportionation reaction

$$Ta_6Br_{12}^{2+} + Ta_6Br_{12}^{4+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2Ta_6Br_{12}^{3+} \tag{3}$$

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