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Pseudo-Octahedral Cobalt(III) Complexes of Three Flexible "Tripod-like" Tetradentate Triarsine Ligands¹

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Three series of six-coordinate cobalt(III) complexes have been isolated with the flexible tetradentate triarsine ligands $D[CH_2CH_2CH_2As(CH_3)_2]_3$ ($D = P, As, Sb$). As a result of the "tripod-like" structure of the tetradentate ligands, the cobalt complexes $[Co(ligand)X_2]^+$ possess a cis-octahedral structure. The electronic absorption spectra produce the spectrochemical series $P > As > Sb$ for the effect of the apex donor atom in the three ligands. Mixed ligand complexes of the type $[Co(ligand)XY]^{n+}$ ($X = Cl, Y = NCS; n = 1; X = Cl, Y = DMF$ or $H_2O, n = 2$) were isolated in an attempt to evaluate the trans electronic effect in these Co^{III} complexes. The $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$ complexes give the first examples of stable $Co^{III}-SbR_3$ coordinate bonds.

Introduction

Although transition metal complexes of simple arsines and phosphines have been known for a century³ and complexes of the tetraamine ligand $(NH_2CH_2CH_2)_3N$ have been investigated since 1925,⁴ the number of papers concerning cobalt(III) complexes of phosphines and arsines is rather limited. For example, most of the studies have involved the ligand *o*-phenylenebisdimethylarsine (diars).⁵⁻¹⁰ Other phosphine and arsine ligands that have given cobalt(III) complexes are: P,P,P',P' -tetraethylethylenediphosphine,¹¹ methylbis(3-dimethylarsinopropyl)arsine,¹² tris(3-dimethylarsinopropyl)arsine,¹³ tetrakis(3-dimethylarsinopropyl)-*o*-phenylenediarsine,¹⁴ triphenylphosphine, diphenylethylphosphine,¹⁵ and triethylphosphine.¹⁶ However,

correlations between electronic spectra and structure have been given only for the diarsine complexes.⁷

This paper presents the preparation and characterization of fifteen pseudo-octahedral cobalt(III) complexes of three similar tetradentate ligands, *i.e.*, the tris(3-dimethylarsinopropyl) derivatives of phosphorus, arsenic, and antimony (Figure 1). These flexible,

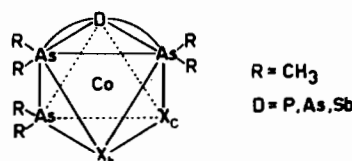


Figure 1.

potentially tetradentate ligands differ only at the apex or bridgehead atom of the "tripod-like" molecule. If a model of an octahedral metal complex of the ligands is examined, two features are apparent: the compound must possess a *cis*-structure; and the X atom (X_t) *trans* to the apex donor atom is situated in a different electronic and steric environment than the X atom (X_c) *cis* to the apex atom (Figure 2). The

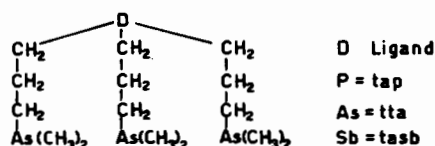


Figure 2.

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Table I. Some Physical Properties and Analytical Data for the Co^{III} Complexes of tap, tta and tasb.

Complex	Color	$\Lambda_m(\frac{\text{cm}^2}{\Omega M})^a$	%C		%H		%Halogen		%N		%Other	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Co(tap)Cl ₂]ClO ₄	Dark red	89.2	25.67	25.51	5.17	5.06					4.41 ^b	4.63
[Co(tap)Br ₂]ClO ₄	Brick red	93.1	22.79	22.94	4.59	4.44					3.92 ^b	4.10
[Co(tap)I ₂]ClO ₄	Dark brown	89.6	20.37	20.74	4.10	4.15	28.70	28.83				
[Co(tap)(NCS) ₂]ClO ₄	Orange red	90.4	27.34	28.04	4.86	4.75	4.75	4.28	3.75	3.90		
[Co(tap)(DMF)Cl](ClO ₄) ₂	Red	190	25.78	25.96	5.17	5.06	12.68	12.79	1.67	1.77		
[Co(tap)(H ₂ O)Cl](ClO ₄) ₂	Orange red	187	22.95	22.66	4.89	5.11						
[Co(tap)(NCS)Cl]ClO ₄	Red	95.9	26.54	26.68	5.01	5.24	9.74	10.58	1.93	1.75		
[Co(tta)Cl ₂]ClO ₄	Red	92.1	24.17	24.32	4.87	4.93	14.27	14.10				
[Co(tta)Br ₂]ClO ₄	Dark brown	92.2	21.59	21.84	4.35	4.43	28.73 ^c	28.92				
[Co(tta)I ₂]ClO ₄	Dark brown	94.2	19.41	19.52	3.91	4.01	41.01 ^d	41.40				
[Co(tta)(NCS) ₂]ClO ₄	Dark red	87.5	25.82	25.74	4.59	4.53					8.11 ^e	7.95
[Co(tasb)Cl ₂]ClO ₄	Dark violet	86.0	22.57	22.74	4.41	4.58	13.63	13.42				
[Co(tasb)Br ₂]ClO ₄	Green	86.8	20.44	20.45	4.12	4.10	18.34	18.13				
[Co(tasb)I ₂]ClO ₄	Black	86.4	18.47	18.42	3.72	3.51	26.03	26.79				
[Co(tasb)(NCS) ₂]ClO ₄	Orange red	78.0	24.38	24.61	4.33	4.39			3.35	3.42		

^a conductivity values of 10⁻³M nitromethane solutions. ^b % phosphorus. ^c total halogen calcd. as % Br. ^d total halogen calcd. as % I. ^e % sulfur.

the apex donor atom is changed from phosphorus to arsenic to antimony. The tasb compounds are the first examples of cobalt(III)-stibine complexes.

Experimental Section

The preparations of tap,¹⁷ tta^{13,18} and tasb¹⁹ have been described previously.

[CoLX₂]ClO₄ Complexes (L = tap, tta, tasb; X = Cl, Br, I, NCS). The dihalocobalt(III) complexes were all prepared according to the following general method. A warm, filtered, deaerated solution of 2 mmoles of cobalt(II) halide and 1.2 mmoles of lithium or sodium perchlorate in 30 ml of absolute ethanol was treated under a nitrogen atmosphere with 1 mmole of ligand. The resulting dark solution was stirred for about 5 minutes under an inert atmosphere and then the complex was stirred overnight open to the air at room temperature. The resulting reaction mixture was combined with a large volume of ether and filtered. The solid was extracted with dichloromethane until a clear extract was obtained. Usually a small amount of an insoluble green solid remained. About 50 ml of anhydrous ethanol was added to the dichloromethane solution and the volume was slowly reduced on a hot plate until crystals started to form. The flask was stoppered and cooled in a refrigerator overnight. The resultant solid was collected on a glass frit, washed with a small amount of cold ethanol followed by ether and then air dried. Finally it was dried *in vacuo*. The yield was usually ca. 60%, based on the amount of ligand used. If the ratio of starting materials was 1 mole of Co salt per 1 mole of ligand, the product yields were ~40%. The color and the analytical data are given in Table I for the isolated dihalo complexes. The individual preparations are described in the theses.²⁰⁻²²

Diisothiocyanato cobalt(III) complexes of tap, tta and tasb can be prepared by a procedure similar to that described for the dihalo complexes or by a metathetical reaction between [Co(lig)Br₂]ClO₄ and NaSCN. The tap and tta thiocyanate complexes were recrystallized as described above for the dihalo complexes. The analytical data are given in Table I.

Chloro-N,N-dimethylformamide-tris(3-dimethylarsinopropyl)phosphinecobalt(III) perchlorate, [Co(tap)(DMF)Cl](ClO₄)₂. One gram of [Co(tap)Cl₂]ClO₄ (0.0014 mol) dissolved in 30 ml of DMF was mixed with 0.296 g of anhydrous AgClO₄ (0.0014 mol) dissolved in 7.4 ml of DMF at 60°C for 10 min. The reaction mixture was placed in a freezer overnight; then it was filtered through asbestos to remove the AgCl. The solvent was removed *in vacuo* at 30°C, and the red residue was recrystallized from DMF-ethanol.

Chloroisothiocyanatotris(3-dimethylarsinopropyl)-phosphinecobalt(III) perchlorate, [Co(tap)(NCS)Cl]ClO₄. A solution of 0.5 g of [Co(tap)(DMF)Cl](ClO₄)₂ (0.61 mmol) in 15 ml of DMF was mixed with 0.05 g of NaSCN (0.61 mmol) dissolved in 10 ml of DMF. After the reaction mixture stood overnight, a mixture of 160 ml of ether and 40 ml of ethanol was added. The [Co(tap)(NCS)Cl]ClO₄ was precipitated from the reaction liquor by addition of more ether. The red solid was recrystallized twice from methanol, washed with ether and dried *in vacuo*.

Chloroaquatris(3-dimethylarsinopropyl)phosphinecobalt(III) perchlorate, [Co(tap)(H₂O)Cl](ClO₄)₂. A solution of 0.3 g of AgClO₄ (0.0014 mol) in 20 ml of 95% methanol was added to a refluxing solution of 1 g of [Co(tap)Cl₂]ClO₄ (0.0014 mol) in 150 ml of absolute methanol; the resultant solution was refluxed ten minutes. After the AgCl was separated by filtration, the [Co(tap)(H₂O)Cl](ClO₄)₂ was precipitated from the solution with ether, then recrystallized

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from absolute methanol.

Characterization and Measurements. Elemental analyses were done by MHW Laboratories, Garden City, Michigan or Galbraith Laboratories, Inc., Knoxville, Tennessee.

Conductance values were obtained on an Industrial Instruments, Inc., Model RC-16B2, conductivity bridge with a Lab-Line conductivity cell, cat. No. 11200, ($k = 0.1037$). The electronic spectra were obtained on a Cary Model 14 spectrophotometer. The solvents used were "spectroquality" or reagent grade and were used without further purification. Routine vibrational spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. The samples were obtained as Nujol mulls between KBr disks or as KBr pellets. The polystyrene spectrum was used for calibration. Accurate peak positions, when desired, were obtained on a Beckman IR-9 spectrophotometer and are accurate to $\pm 1 \text{ cm}^{-1}$ in the 2100 cm^{-1} region.

Fischer Scientific certified nitromethane was stirred over Linde 4A molecular sieves before use as the conductivity solvent.

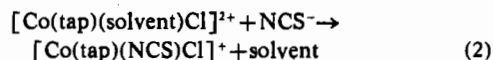
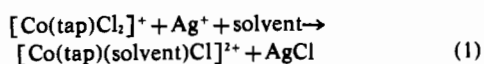
Sodium-dried diethylether was prepared by storing anhydrous ether over clean sodium wire.

Results and Discussion

The cobalt(III) halide and thiocyanate complexes can be prepared easily by the addition of the appropriate tetradentate ligand to a cobalt(II) salt dissolved in absolute ethanol, followed by air oxidation. Addition of lithium or sodium perchlorate to the reaction mixture facilitates isolation and purification of the $[\text{CoLX}_2]^+$ cations, as the perchlorate compounds are easily recrystallized. If a large anion, e.g., perchlorate, is not added to the reaction mixture, an insoluble material (probably $[\text{CoLX}_2]_2[\text{CoX}_4]$) is obtained, which is very difficult to characterize.

The thiocyanate complexes were also prepared *via* metathetical reactions on the $[\text{CoLBr}_2]\text{ClO}_4$ complexes. Attempts to prepare the corresponding cyanide or selenocyanate complexes, either by direct combination of the reactants or by a metathetical reaction with a dihalo compound, were not successful.

The mono-solvent complexes $[\text{Co}(\text{tap})(\text{DMF})\text{Cl}](\text{ClO}_4)_2$ and $[\text{Co}(\text{tap})(\text{H}_2\text{O})\text{Cl}](\text{ClO}_4)_2$ were prepared by mixing one equivalent of $[\text{Co}(\text{tap})\text{Cl}_2]\text{ClO}_4$ with one equivalent of anhydrous silver perchlorate in DMF and 95:5 methanol-water, respectively. The complexes were precipitated from the solvents with diethyl ether and recrystallized from methanol containing a small amount of DMF or water, as appropriate. The thiocyanato-chloro complex $[\text{Co}(\text{tap})(\text{NCS})\text{Cl}]\text{ClO}_4$ was obtained by mixing one equivalent of sodium thiocyanate with one equivalent of $[\text{Co}(\text{tap})(\text{DMF})\text{Cl}](\text{ClO}_4)_2$ in DMF. The mixed complex was precipitated with ether and recrystallized from methanol. Equations 1 and 2 summarize the syntheses of the solvent and mixed complexes. It seems likely that an



extensive series of mixed complexes could be prepared by varying the starting complex, the polar solvent, or the anion added in the final step, *i.e.*, in Equation 2. However, attempts to replace DMF with CN^- , NO_2^- or SeCN^- in a manner analogous to the preparation of $[\text{Co}(\text{tap})(\text{NCS})\text{Cl}]\text{ClO}_4$ generally yielded a small amount of the starting complex $[\text{Co}(\text{tap})\text{Cl}_2]\text{ClO}_4$ but none of the desired mixed complexes.

Even if air is carefully excluded from the reaction mixture, only cobalt(III) complexes are isolated when ClO_4^- was used as the counterion. However, when the larger BPh_4^- anion was used, an unstable intermediate (presumably of Co^{II}) could be obtained. For example, a deaerated alcohol solution of equimolar amounts of $\text{Co}(\text{SCN})_2$ and NaBPh_4 was treated under N_2 with one equivalent of tap. A green precipitate was noted immediately. If this green solid was stirred overnight in absolute ethanol or methanol, the orange $[\text{Co}(\text{tap})(\text{NCS})_2]^+$ complex was obtained. Even the dried green powder turned orange over a period of several weeks. Thus, it appears that the tap ligand strongly favors Co^{III} complexes. Presumably tta and tasb would behave similarly, although no attempts were made to isolate Co^{II} salts with these ligands.

All of the complexes isolated in this study are diamagnetic, as expected for an octahedral d^6 complex containing strong-field ligands. The conductivity values for the $[\text{CoLX}_2]\text{ClO}_4$ and $[\text{Co}(\text{tap})(\text{solvent})\text{X}](\text{ClO}_4)_2$ complexes in nitromethane are characteristic of univalent-univalent and divalent-univalent electrolytes, respectively. The infrared spectra of all the halide complexes with a given ligand from 4000 to 400 cm^{-1} are virtually identical; they show ionic perchlorate groups and no absorptions attributable to an oxidized form of the ligands. For example, the $\text{P}=\text{O}$, $\text{As}=\text{O}$, and $\text{Sb}=\text{O}$ groups, if present, would have strong infrared absorptions in reasonably clear and accessible regions of the spectra.

Electronic Spectral Trends. The first excited electronic state (${}^1\text{T}_{1g}$ in Oh symmetry) should be split into three components in these complexes of C_s symmetry. The three bands overlap extensively, so no Gaussian analysis of the spectra was undertaken. However, from the position of the observed maxima it is evident that the normal spectrochemical series, $-\text{NCS} > \text{Cl} > \text{Br} > \text{I}$ is followed in the $[\text{CoLX}_2]\text{ClO}_4$ complexes (Table II). In addition, the spectrochemical effect of the apex atom is $\text{P} > \text{As} > \text{Sb}$ (Table II); this same spectrochemical series has been observed recently in complexes of monodentate ligands and in a series of trigonal-bipyramidal nickel complexes.¹⁹ The electronic spectra of these $[\text{CoLX}_2]^+$ complexes compare quite favorably with those of *cis*- $[\text{Co}(\text{diars})_2\text{X}_2]^+$, where diars = *o*-phenylenebis(dimethylarsine) (Table III).

The position of thiocyanate in the spectrochemical series depends upon its mode of bonding. The following series $\text{M}-\text{SCN} \approx \text{M}-\text{Cl} < \text{M}-\text{NCS}$ has been given by several workers.^{24,25} In the $[\text{Co}(\text{lig})\text{X}_2]^+$ complexes under discussion, the first maxima for a given thio-

Table II. Electronic Spectral Data for the Lowest Energy Band of the $[\text{CoLX}_2]^+$ and $[\text{CoLXY}]^{1+ \text{ or } 2+}$ Complexes, L = tap, tta, or tasb.

X ₂ or XY	Tetradentate Ligand					
	tap	log ε	tta	log ε	tasb	log ε
NCS	20,830 cm ⁻¹	3.35	19,760 cm ⁻¹	3.39	19,320 cm ⁻¹	3.33
Cl	19,600	2.92	18,420	2.87	17,730	2.91
Br	19,000	2.90	17,510	2.75	16,880	2.90
I	16,530	3.10	15,630sh	~3.00	15,630sh	~3.06
Cl, NCS	20,080	3.00				
Cl, H ₂ O	20,200	3.13				
Cl, DMF	20,400	2.92				

Table III. Data for the First Maximum of Some Cobalt(III) Chloride Complexes.

Complex	cm ⁻¹	log ε	Reference
<i>cis</i> -[Co(diars) ₂ Cl ₂] ⁺	20,400	2.80	7
<i>cis</i> -[Co(en) ₂ Cl ₂] ⁺	18,600	1.95	7
[Co(tap)Cl ₂] ⁺	19,600	2.92	20
[Co(tta)Cl ₂] ⁺	18,400	2.87	21
[Co(tasb)Cl ₂] ⁺	17,730	2.91	22
<i>trans</i> -[Co(diars) ₂ Cl ₂] ⁺	16,400	1.85	7
<i>trans</i> -[Co(en) ₂ Cl ₂] ⁺	16,100	1.61	7

Table IV. Infrared Data in the C≡N Stretching Region for the [CoL(NCS)₂]ClO₄ Complexes.

Ligand	1st band ^a cm ⁻¹	2nd band ^a cm ⁻¹	Integrated Intensity ^{b,c} (A/SCN) (M ⁻¹ cm ⁻²)
tap	2102	2093	10.99 × 10 ⁴
tta	2101	2092	13.01 × 10 ⁴
tasb	2096	2090	11.14 × 10 ⁴

^a Peak positions were obtained on a Beckman IR-9 spectrophotometer and are accurate to ± 1 cm⁻¹. ^b The solvent is nitromethane. ^c The experimental procedure has been described previously.^{25,27}

cyanate complex appears 1400-1000 cm⁻¹ higher than the first maxima of the respective chloride complex, strongly suggesting that both thiocyanates are bonded to cobalt *via* the nitrogen atom. Additional evidence for isothiocyanato coordination results from a determination of the integrated intensities of the thiocyanate bands in the 2100 cm⁻¹ region. The two overlapping peaks give integrated absorption values of 11-13 × 10⁴ M⁻¹cm⁻², indicative of N-bonded thiocyanate groups.^{25,26} The electronic spectrum of the chloro-thiocyanato complex [Co(tap)(NCS)Cl]ClO₄ is between the spectra of the [Co(tap)(NCS)₂]⁺ and [Co(tap)Cl₂]⁺ complexes, as expected for the mixed complex.

The tasb complexes provide the first reported examples of Co^{III}-SbR₃ coordination compounds. The nature of the chelating ligand tasb forces the antimony atom into a favorable coordination site and may contribute significantly to the stability of the Co^{III}-Sb bond. These tasb complexes appear to be stable indefinitely in the solid state; however, a dichloromethane solution of [Co(tasb)₂]ClO₄ decomposed over a 2-3 month period.

Cis and Trans Effects in Co^{III} Complexes. In recent years there has been a large increase in the knowledge

of *cis* and *trans* effects in Co^{III} chemistry as witnessed by a recent review article.²⁸ The article cites evidence that the effects of a given group appear to be non-directional, *i.e.* a given group will affect both the *cis* and *trans* positions.

The tap, tta and tasb complexes appear to be potentially useful for studying the *cis* and *trans* effects in cobalt(III) complexes. As shown in Figure 1, the monodentate X ligands are in different electronic and steric environments.

Infrared studies on the Co^{III} dicyanide complexes of tap, tta and tasb appeared attractive; however, the complexes could not be isolated. Therefore, the C≡N stretching frequencies of the thiocyanate complexes were carefully studied. Two closely spaced infrared bands are observed, in agreement with predictions for the *cis*-structures. A small decrease in the stretching frequency is apparent as the polarizability of the bridgehead atom increases, *i.e.*, Sb > As > P. It is interesting to note that the shift is greater for the peak at higher energy (Table IV). Perhaps this could be taken as evidence for the directional influence of the apex atom. However, the data are inconclusive since at this stage a) the changes in stretching frequencies are quite small and the sensitivity of the thiocyanate stretch to environmental changes has not been syste-

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matically studied, and b) the changes in the steric effects of the ligands with changes in the apex donor atom are not known.

The preparation of the $[\text{Co}(\text{tap})(\text{H}_2\text{O})\text{Cl}](\text{ClO}_4)_2$ complex was followed by attempts to separate the two possible isomeric products by cellulose thinlayer chromatography. There was no noticeable separation,

indicating either that only one product was obtained or that the two possible products are not separable by this method.

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