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Metal Nitrate Complexes with Trimethylstibine Sulfide

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Recently metal complexes with tertiary phosphine[1-8] and arsine[9-12] sulfides have been studied extensively. On the other hand very few studies on metal complexes with tertiary stibine sulfide have been reported.[6,13] In the preceding paper,[14] we have described that trimethylstibine sulfide (TMSS) forms 2:1 and/or 1:1 complexes with cobalt(II), zinc(II), cadmium(II), and mercury(II) halides, and the sulfur–halogen exchange reaction is observed in the case of the interaction of TMSS with mercuric chloride.

In this paper, we will report treatments of TMSS with those four metal nitrates, and the properties of the complexes thus formed will be discussed since behaviors of the nitrate groups are easily clarified with the infrared spectra.

Experimental Section

Preparation of TMSS is described elsewhere.[13] All of the hydrated metal nitrates employed are commercially available.

Preparation of the Complexes.—All operations were carried out under anhydrous conditions and ethyl orthoformate was used as a dehydrating reagent.[15] The complexes were obtained by mixing methanol solutions of TMSS and metal nitrates in an appropriate stoichiometric molar ratio and the precipitates obtained by evaporating methanol were recrystallized quickly from dichloromethane. The complexes are hygroscopic and decompose in solution by standing overnight. The physical properties and analytical data of the complexes obtained are summarized in Table I.

When methanol solutions of TMSS and zinc or cadmium nitrate were combined in the 2:1 molar ratio, viscous oily materials resulted. Crystallization and identification of these materials were unsuccessful.

Attempts for Preparation of $[(C_6H_5)_3PO]_4M(NO_3)_2$ (M = Co, Zn).—Cobalt nitrate (0.29 g, 1 mmol) and triphenylphosphine oxide (1.25 g, 4.5 mmol) were allowed to react for 5 hr at room temperature. From the precipitates obtained by evaporating the solvent, unreacted triphenylphosphine oxide (0.70 g, 2.5 mmol) was extracted with benzene. Insoluble precipitates were confirmed to be $[(C_6H_5)_3PO]_2Co(NO_3)_2$ (0.70 g, 0.95 mmol) by its infrared spectrum.[16] Analogous results were obtained in the case of zinc nitrate.

Exchange Reaction between Sulfur and Nitrate Group.—A methanol solution of an equimolar amount of TMSS and mercuric nitrate was stirred for 1 hr at room temperature. Mercuric sulfide was precipitated and filtered off. From the filtrate was obtained trimethylantimony dinitrate; yield 80%; mp 148–149° (lit.[17] mp 149°).

Physical Measurements.—Infrared spectra were measured with Hitachi 225 and Hitachi EPI-L grating spectrophotometers and the results are presented in Table II. Electronic spectra were recorded on a Hitachi EPS-3 spectrophotometer equipped with 1-cm quartz cells for solutions and with a reflectance attachment for solid samples, and their results are shown in Table III and Figures 1 and 2. Molar conductances given in Table IV were obtained using a conventional universal bridge at 20°.

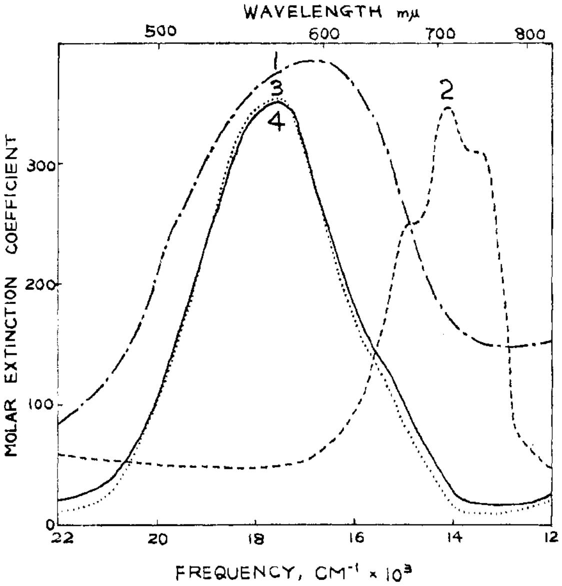

Figure 1.—Electronic spectra of the cobalt(II) nitrate complexes: 1, $(TMSS)_2Co(NO_3)_2$ (reflectance); 2, $(TMSS)_4Co(NO_3)_2$ (reflectance); 3, $(TMSS)_2Co(NO_3)_2$ (in CH_2Cl_2); 4, $(TMSS)_4Co(NO_3)_2$ (in CH_2Cl_2).

Results and Discussion

As shown in Table I, treatments of TMSS with cobalt(II), zinc(II), and cadmium(II) nitrates result in the formation of the 4:1 complexes $(TMSS)_4M(NO_3)_2$ (M = Co, Zn, Cd) and the 2:1 cobalt complex $(TMSS)_2Co(NO_3)_2$. The infrared spectra presented in Table II indicate the coordination of TMSS through sulfur in all of these complexes, because the Sb–S stretching frequency in the free ligand (433 cm^{-1}) is shifted to lower energy by about 30 cm^{-1}.

It is to be noted that treatments of an excess of triphenylphosphine oxide with cobalt and zinc nitrates result in the formation of 2:1 complexes alone. This difference may be due to the more basic character of the sulfur atom in the Sb–S bond than that of the oxygen atom in the P–O bond.[18]

Complexes in the Solid State.—In the infrared spectrum of the 2:1 cobalt complex $(TMSS)_2Co(NO_3)_2$, in

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TABLE I

PROPERTIES AND ANALYSES OF TMSS–METAL(II) NITRATE COMPLEXES

Complex	Color	Mp, °C	% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found
$(TMSS)_2Co(NO_3)_2$	Bluish violet	112–113	12.41	12.35	3.12	3.20	4.82	4.84
$(TMSS)_4Co(NO_3)_2$	Greenish blue	154–155	14.73	14.66	3.71	3.90	2.86	2.86
$(TMSS)_4Zn(NO_3)_2$	White	168–169	14.62	14.53	3.66	3.82	2.84	2.87
$(TMSS)_4Cd(NO_3)_2$	White	175–176	13.97	13.98	3.52	3.59	2.71	2.74

TABLE II

INFRARED FREQUENCIES (CM^{-1}) OF THE METAL(II) NITRATE COMPLEXES[a]

$(TMSS)_2Co(NO_3)_2$		$(TMSS)_4Co(NO_3)_2$		$(TMSS)_4Zn(NO_3)_2$		$(TMSS)_4Cd(NO_3)_2$		
Solid	Soln	Solid	Soln	Solid	Soln[b]	Solid	Soln[b,c]	Assignment
1495 s[d]	1486 s, b		1490 s, b		1480 s, b		1480	$\nu(N{=}O)$
		1409 sh		1409 sh		1410 sh		
		1363 s		1355 s		1355 s		$\nu_{asym}(NO_3)$
		1330 s		1335 s		1334 s		
1298 s	1284 s, b		1283 s, b		1285 s, b		1285	$\nu_{asym}(NO_2)$
1275 s	1245 s		1244 s		1245 s		1243	
		1039 vw		1048 vw		1046 vw		$\nu(N{-}O)$
1028 m	1019 m		1020 m		1018 m, b		1025	$\nu_{sym}(NO_2)$
1022 m								
808 w	807 w	830 w	807 w	827 w	833 w	826 w	833	$\pi(NO_3)$ or $\pi(O_2N{=}O)$
561 m	559 m	564 m	559 m	562 m	560 m	562 m	559	$\nu_{asym}(Sb{-}C)$
532 m	532 m	532 m	532 m[e]	532 m	531 m[e]	531 m	531[e]	$\nu_{sym}(Sb{-}C)$
409 s	405 s, b	404 s	405 s, b	401 s	406 s, b	399 s	405	
398 s		395 s		385 s		385 s		$\nu(Sb{-}S)$
		389 sh						
			551 m		550 m		550	$\nu_{asym}(Sb{-}C)$[f]
			436 s		436 s		436	$\nu(Sb{-}S)$[f]

[a] Solid indicates mull in Nujol or hexachlorobutadiene; solutions were in dichloromethane. [b] Although it is not certain whether the nitrate groups act as monodentate or bidentate ligands, the assignments were made according to the latter case for convenience. [c] On account of limited solubility, the data seem not so reliable as those of other solution spectra. [d] Abbreviations: s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder. [e] Bands due to coordinated and uncoordinated TMSS are overlapping. [f] Bands due to uncoordinated TMSS.

TABLE III

ELECTRONIC SPECTRA (CM^{-1}) OF THE COBALT(II) NITRATE COMPLEXES

Reflectance	In CH_2Cl_2[a]	In CH_3NO_2[b]
	$(TMSS)_2Co(NO_3)_2$	
16,700	17,700 (351)	17,100 (76.8)
	15,000 (23)	15,100 (9.5)
		14,300 (· · ·)
	$(TMSS)_4Co(NO_3)_2$	
15,000	17,700 (349)	16,600 (76.1)
14,100	15,000 (32)	15,000 (29.0)
13,300		14,100 (19.6)
		13,100 (· · ·)

[a] At concentrations ~10^{-3} M. Molar extinction coefficients are given in parentheses. [b] At concentrations 2.0×10^{-3} M. Absorbances in per cent are given in parentheses.

TABLE IV

MOLAR CONDUCTANCES OF THE METAL(II) NITRATE COMPLEXES

Complex	Λ,[a] cm²/ohm mol	
	CH_2Cl_2	CH_3NO_2
$(TMSS)_2Co(NO_3)_2$	<1	18.0 (84.4)[b]
$(TMSS)_4Co(NO_3)_2$	<1	42.1 (87.0)
$(TMSS)_4Zn(NO_3)_2$	1.9	68.3 (114.3)
$(TMSS)_4Cd(NO_3)_2$	2.5	78.0 (136.7)

[a] At concentrations ~10^{-3} M. [b] Values in parentheses are those when an excess of TMSS (10:1 TMSS:complex molar ratio) was added.

the solid state, bands characteristic of a nonionic nitrate group are observed. The reflectance spectrum of this complex given in Table III and Figure 1 is quite similar to those of $(R_3EO)_2Co(NO_3)_2$[16] (E = P, As), which possess six-coordinated cobalt with a very irregular arrangement of the ligand atoms involving bidentate nitrate groups.[19] Thus $(TMSS)_2Co(NO_3)_2$ is likely to

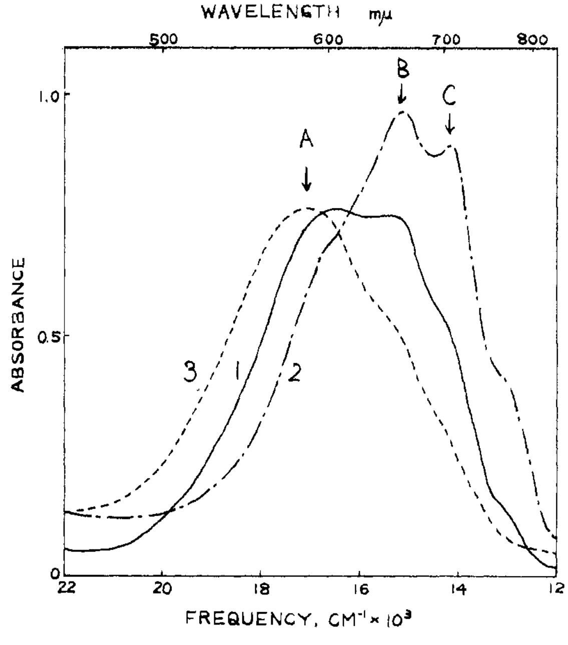

Figure 2.—Electronic spectra of the cobalt(II) nitrate complexes in CH_3NO_2 (2.0×10^{-3} M): 1, $(TMSS)_4Co(NO_3)_2$; 2, $(TMSS)_4Co(NO_3)_2$ + 10TMSS; 3, $(TMSS)_2Co(NO_3)_2$.

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[19] This structure is confirmed for $[(CH_3)_3PO]_2Co(NO_3)_2$ by an X-ray diffraction study: F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, **85**, 2402 (1963).

have an analogous configuration. As for the infrared spectrum of a bidentate nitrate group, the assignments given in Table II were made with reference to that of the bidentate carbonate group.[20–22]

It is evident from the infrared spectra that all of the 4:1 complexes have uncoordinated nitrate anions[23] in the solid state. Accordingly these complexes seem to be formulated as $[(TMSS)_4M]^{2+}(NO_3^-)_2$ (M = Co, Zn, Cd). Certainly this formulation is strongly supported for the cobalt complex by the reflectance spectrum (Table III and Figure 1) which exhibits the structured band around 14,000 cm^{-1} typical of a tetrahedral cobalt(II) ion.

Complexes in Solution.—Since the infrared and electronic spectra of $(TMSS)_2Co(NO_3)_2$ in dichloromethane are essentially similar to those of the solid, the configuration is possibly the same in the two states. This conclusion is also confirmed by its low molar conductance in this solution (Table IV).

The infrared spectra of all 4:1 complexes in dichloromethane show bands due to nonionic coordinated nitrate groups and, in addition, bands attributable to the uncoordinated TMSS, as listed in Table II. It appears from these results that all of the 4:1 complexes dissociate completely into 2:1 complexes and free TMSS.

$$(TMSS)_4M(NO_3)_2 \rightleftharpoons (TMSS)_2M(NO_3)_2 + 2TMSS \quad (M = Co, Zn, Cd) \quad (1)$$

This is consistent with the fact that the electronic spectrum of the 4:1 cobalt complex in dichloromethane is superimposable with that of the 2:1 complex (Figure 1). For the zinc and cadmium complexes, the low molar conductances in dichloromethane suggest that the 2:1 complexes formed according to eq 1 are nonelectrolytes, but it is not clear whether nitrate groups act as monodentate or bidentate groups.

In a more polar solvent such as nitromethane, an unexpected low value, which seems to be too small for the ionic formulation mentioned above, is obtained for the molar conductance of the 4:1 cobalt complex $(TMSS)_4Co(NO_3)_2$. The electronic spectrum of this complex in nitromethane (Table III and Figure 2) gives rise to a band at 15,100 cm^{-1} (B band) and a shoulder band at 14,300 cm^{-1} (C band), both of which may be attributable to $(TMSS)_4Co(NO_3)_2$, in addition to an absorption maximum at 16,600 cm^{-1} (A band) due to $(TMSS)_2Co(NO_3)_2$. Therefore it is apparent that $(TMSS)_4Co(NO_3)_2$ is involved in equilibrium 1 in this solution. This is confirmed by addition of an excess of TMSS to this system, which results in weakening of the A band and strengthening of the B and C bands. In accordance with this conclusion, addition of TMSS also leads to a large increase in the molar conductance (Table IV). The electronic spectrum of $(TMSS)_2Co(NO_3)_2$ in nitromethane exhibits the B band as a very weak shoulder, and thus a somewhat large molar conductance may be derived from $(TMSS)_4Co(NO_3)_2$. The 4:1 zinc and cadmium complexes in nitromethane are also involved in equilibrium 1 and some contribution of the 2:1 species encountered in the absence of an excess of the ligand is negligible when an excess of TMSS is present, since the molar conductances give sufficiently large values to assume 1:2 electrolytes. In summary, all 4:1 complexes are involved in equilibrium 1 in solution. The equilibrium is shifted completely to the right-hand side in dichloromethane, whereas a contribution of the ionic 4:1 species is increased in a polar solvent such as nitromethane.

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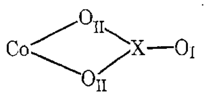
[21] On the basis of infrared spectra alone, it is not in general possible to distinguish between monodentate and bidentate nitrate groups although possible in the case of the carbonate group.[16] This difference may be explained by comparing the structures of the two groups.



I, X = C or N

According to X-ray diffraction studies,[19,22] the C–O_I distance in the bidentate carbonate group is fairly shorter than the C–O_{II} distance, but the distance of the N–O_I bond in the nitrate group is comparable with that of the N–O_{II} bond. Therefore the C–O_I bond has a considerable double-bond character and exhibits its stretching band at high frequency (1560–1643 cm^{-1}),[20] whereas the band due to the N–O_I bond with a less double-bond character appears at lower frequency (1469–1517 cm^{-1}) where the monodentate nitrate group also gives rise to a characteristic band.

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Facile Interconversion of Arene- and Cyanocyclohexadienylmanganese Complexes

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The reaction of cyanide ion with cationic complexes of the type $(arene)Mn(CO)_3^+$, where the arene is benzene, xylene, mesitylene, etc., has been reported[1,2] to yield the neutral complexes $(arene)Mn(CO)_2CN$. In some cases an intermediate, formulated as the ionic compound $[(arene)Mn(CO)_3]CN$, could be isolated.[1]

As part of a general survey of substitution on coordinated arenes, we have investigated the reaction of complexes $(arene)Mn(CO)_3^+$ with a range of nucleophiles. This communication deals specifically with the reaction with cyanide ion, indicating that the ionic formulation of the intermediate is incorrect.

Experimental Section

Reactions were performed under nitrogen using oxygen-free solvents. Products were stored under nitrogen and kept away from light.

Preparation of 1-Cyano-2,4,6-trimethylcyclohexadienyltricar-

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[2] T. H. Coffield and R. D. Closson, *Chem. Abstr.*, **59**, 11558*d* (1963); U. S. Patent 3,042,693 (July 3, 1962).