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Studies on Some Metal Monothiobenzoates

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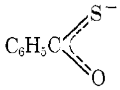
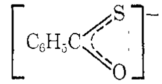
Monothiobenzoate (MTB)



complexes with the molecular formulas $Cr(MTB)_3$, $[Ni(MTB)_2]_n$, $[Zn(MTB)_2]_n$, $[Cd(MTB)_2]_n$, $[Hg(MTB)_2]_n$, $[Cu(MTB)]_n$, and $[Ag(MTB)]_n$ have been prepared and studied. All the complexes are nonionic in acetonitrile. Only the chromium complex is soluble in nitrobenzene and found to be monomeric cryoscopically. The thiobenzoate ligand appears to be asymmetrically chelated in Cr(III) and Cd(II) complexes, with stronger oxygen and sulfur coordination, respectively, while practically symmetrically coordinated in Ni(II) and Zn(II) complexes. These four complexes are assigned distorted octahedral structures around the metal ion. The coordination in Hg(II), Cu(I), and Ag(I) complexes is mainly through sulfur indicating the monodentate nature of the thiobenzoate ligand in these complexes. The coordination of monothiobenzoate ion in the complexes has been rationalized in terms of "hard" and "soft" acid–base concept.

Introduction

Recently, considerable interest has been aroused in the study of the complexes with ligands having sulfur as a donor atom.[1-3] However, studies on ligands which contain both sulfur and oxygen donors are relatively few.[4,5] The monothiobenzoate ion (MTB)



which possesses both sulfur and oxygen donor atoms, has not been investigated except for a report about the preparation of its lead, nickel, and cadmium complexes[6,7] for use as plasticizing agents for natural rubber. When the present work was in progress, Furlani, *et al.*,[8] published a note on the electronic spectrum of chromium(III) monothiobenzoate. In the present paper, the preparation and some physicochemical properties of monothiobenzoates of Cr(III), Ni(II), Zn(II), Cd(II), Hg(II), Cu(I), and Ag(I) are reported.

Experimental Section

Materials.—Thiobenzoic acid of 98.4% purity was obtained through the courtesy of Evans Chemetics, Inc., New York, N. Y. The reagent was used without further purification. Acetonitrile and nitrobenzene were purified by repeated distillation over phosphorus pentoxide. All other chemicals used were of the reagent grade.

Preparation of the Complexes.—Sodium thiobenzoate was prepared by allowing 1:2 mole proportions of sodium carbonate and thiobenzoic acid to react in water at room temperature. When a concentrated solution of sodium thiobenzoate was added to aqueous solutions of metal chlorides or nitrates, the precipitates of the corresponding metal thiobenzoates were obtained. Zn(II), Cd(II), Hg(II), and Ag(I) complexes precipitated in almost quantitative yields, while the Cr(III) complex was produced in about 20% yield. The yield of Ni(II) and Cu(I) complexes was over 50%. The reaction of thiobenzoate with Fe(III) and Co(II) salts was complicated and products with constant composition were not obtained. With Cu(II) salts, only the Cu(I) complex was obtained, as evidenced by its chemical analysis and diamagnetic character. All the complexes are insoluble in water, benzene, and carbon tetrachloride and sparingly soluble in acetonitrile. Only the Cr(III) complex is soluble in nitrobenzene.

Analyses.—The metal content in the complexes was determined by the usual analytical methods.[9] Sulfur was determined as $BaSO_4$, after heating the complexes with Eshka's mixture (2:1 $MgO–Na_2CO_3$). The analytical results along with the color of the complexes are given in Table I.

TABLE I

COLOR AND ANALYTICAL DATA OF METAL MONOTHIOBENZOATES

Compound		Analysis, %			
		Metal		Sulfur	
(MTBC$_6$ = H$_5$COS)	Color	Found	Calcd	Found	Calcd
$Cr(MTB)_3$	Green	11.14	11.23	20.51	20.73
$Ni(MTB)_2$	Dark red	17.32	17.65	19.02	19.24
$Zn(MTB)_2$	White	19.06	19.27	18.63	18.86
$Cd(MTB)_2$	Cream	28.73	29.08	16.44	16.56
$Hg(MTB)_2$	Gray	41.95	42.27	13.08	13.49
Cu(MTB)	Red	31.29	31.70	16.12	15.96
Ag(MTB)	Light yellow	43.54	44.08	12.80	13.06

Apparatus.—The conductivity measurements were carried out in acetonitrile at room temperature, using Siemen's conductivity bridge. The molecular weight of the Cr(III) complex was determined cryoscopically in nitrobenzene. The magnetic susceptibilities of the solid complexes were determined by a standard Gouy apparatus at room temperature, using $Hg[Co(NCS)_4]$ as the standard. The infrared spectra of the complexes in KBr pellets were recorded by a Carl-Zeiss UR 10 automatic spectrophotometer using LiF, NaCl, and KBr optics. The electronic spectra of the complexes in chloroform were recorded on a Unicam recording spectrophotometer, 700 A, using 1-cm matched quartz cells.

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(1) S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

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TABLE II
ELECTRICAL CONDUCTANCE IN ACETONITRILE AND MAGNETIC MOMENTS OF THE COMPLEXES

	Electrical conductance		
Compound	Concn × 10^3, M	Molar conductance, ohm^{-1} cm^2 mol^{-1}	Magnetic moment, μ_{eff}, BM
Cr(MTB)$_3$	1.04	2.59	3.72
Ni(MTB)$_2$	1.00	5.04	3.31
Zn(MTB)$_2$	1.11	4.43	Diamag
Cd(MTB)$_2$	1.08	6.34	Diamag
Hg(MTB)$_2$	1.43	2.56	Diamag
Cu(MTB)	1.00	8.19	Diamag
Ag(MTB)	1.13	1.72	Diamag

Results and Discussion

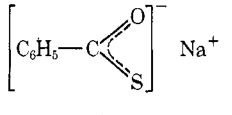
The molar conductivities of the complexes in acetonitrile at room temperature, given in Table II, are too low to account for any of their dissociation. The complexes are, therefore, nonelectrolytes in acetonitrile. The molecular weight of the Cr(III) complex determined cryoscopically in nitrobenzene is 452 while that calculated for Cr(MTB)$_3$ is 463, indicating that the complex exists as a monomer. The molecular weight of the other complexes could not be determined because of their poor solubility in nitrobenzene.

The magnetic moments of the Cr(III) and Ni(II) complexes, calculated from the respective corrected magnetic susceptibility at 25°, are 3.72 and 3.31 BM, respectively. The former value corresponds to the spin-only contribution for an octahedral Cr(III) complex while the latter is typical of an octahedral or a distorted octahedral Ni(II) complex which has an orbital contribution.[10] All the other complexes are found to be diamagnetic.

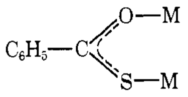
Infrared Spectra and the Nature of Bonding between the Metal and the Ligand.—The infrared spectra of thiobenzoate complexes have not been studied before. The ir frequencies together with their probable assignments are given in Table III. The assignments of C$\overset{\cdots}{-}$O, phenyl—C, and C$\overset{\cdots}{-}$S stretching frequencies have been made by comparison with the spectral bands of thiobenzoic acid[11] and alkali metal benzoates.[12]

The bands due to C=C, C—C=C, and C—H either remain unchanged or get shifted slightly when the acid is converted into its metal complexes. The thiobenzoic acid produces strong absorption bands at 1690, 1210, and 950 cm^{-1} which are assigned to ν(C=O), ν(phenyl—C), and ν(C—S), respectively. These are the bands which are mainly affected on complex formation.

The sodium salt of the monothiobenzoic acid gives ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) at 1500 and 960 cm^{-1}, respectively (Table III). The decrease of ν(C$\overset{\cdots}{-}$O) and a slight increase in ν(C$\overset{\cdots}{-}$S) as compared to the corresponding frequencies of the thiobenzoic acid indicate that the sodium salt has the ionic structure



The coordination of monothiobenzoate anion to metal ions can occur in any one of the types



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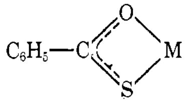

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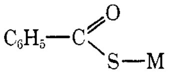
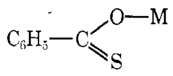


III

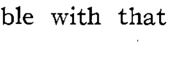


IV

A comparison of ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) of the complexes with those of the sodium salt can help in distinguishing the type of bonding between the metal ion and the thiobenzoate ion. If the bonding is of type I, both ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) are expected to decrease appreciably as compared to those of the sodium salt. The band positions of ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) of the complexes rule out the possibility of this type of bonding in any of the complexes studied.

If the bonding in M—O and M—S is, more or less, symmetrical as in II, both ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) are expected to remain almost unaffected. The Ni(II) complex shows this type of symmetric chelation, as the bands occur, respectively, at 1508 and 958 cm^{-1} with very little shift from the corresponding bands of the sodium salt. In the Zn(II) complex, ν(C$\overset{\cdots}{-}$S) occurs as a split band at 955 and 928 cm^{-1} while ν(C$\overset{\cdots}{-}$O) is at 1545 cm^{-1}, thus indicating an increased bond strength between the metal and the sulfur. The positions of ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$S) of the Cd(II) complex around 1590 and 930 cm^{-1}, respectively, show greater asymmetric chelation, the stronger bond arising between the metal and the sulfur. On the other hand, in the Cr(III) complex, ν(C$\overset{\cdots}{-}$S) is raised to 982 cm^{-1} while ν(C$\overset{\cdots}{-}$O) is lowered to 1465 cm^{-1}. These changes clearly indicate an asymmetric chelation of the thiobenzoate ion to Cr(III), the stronger bond being between chromium and oxygen.

In the Hg(II) complex, an appreciable lowering of ν(C$\overset{\cdots}{-}$S) to 912 cm^{-1} and raising of ν(C$\overset{\cdots}{-}$O) to 1630 cm^{-1} suggest coordination of thiobenzoate mainly through sulfur as indicated in type III. The same type of monodentate bonding through sulfur can be inferred in Cu(I) and Ag(I) complexes from the shifts of the ν(C$\overset{\cdots}{-}$S) and ν(C$\overset{\cdots}{-}$O) frequencies. The behavior of thiobenzoate as a monodentate sulfur-coordinating ligand in Hg(II), Cu(I), and Ag(I) complexes is comparable with that of diethylmonothiophosphate



which acts as a unidentate ligand coordinating through sulfur in its Hg(II) and Ag(I) complexes.[13]

From the results given in Table III, it is evident that the ν(C$\overset{\cdots}{-}$O) frequency is progressively raised while the ν(C$\overset{\cdots}{-}$S) is lowered in the complexes of d^{10} metal ions from Zn(II) through Hg(II). This trend

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(11) J. H. S. Green, W. Kynaston, and A. S. Lindsey, *Spectrochim. Acta*, **17**, 486 (1961).

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TABLE III

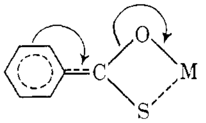
INFRARED SPECTRAL BANDS OF METAL MONOTHIOBENZOATES AND THEIR PROBABLE ASSIGNMENTS[a]

$Na(C_6H_5COS)H_2O$	$Cr(C_6H_5COS)_3$	$Ni(C_6H_5COS)_2$	$Zn(C_6H_5COS)_2$	$Cd(C_6H_5COS)_2$	$Hg(C_6H_5COS)_2$	$Cu(C_6H_5COS)$	$Ag(C_6H_5COS)$	Assignments
3400 s, br								ν(OH) of H_2O
		3088 w		3090 w	3090 w	3085 w		γ(C—H)
	3065 w	3070 w	3060 w	3065 w	3065 w	3056 w	3058 w	
2170 w	2170 w	2170 w	2170 m	2170 m	2170 m	2170 w	2170 w	
1635 w	1635 w	1690 w	1640 w		1705 w	1640 w		ν(C—C)
1605 w	1605 w	1602 w	1602 w			1590 w		
1592 w	1550 w	1590 w	1590 w					
1500 vs	1465 s	1508 vs	1545 vs	1597 s	1640 vs		1612 vs	$\nu(\mathrm{C}\underline{\cdots}\mathrm{O})$
				1580 s	1630 vs	1570 vs	1583 vs	
1450 m	1420 s	1495 w	1452 m	1492 w		1452 m	1455 m	
1422 w	1345 w	1452 m	1406 w	1455 m	1452 m	1402 w		ν(C—C)
1310 m	1318 s	1312 m	1320 w	1312 m	1342 w	1318 m	1318 m	
					1318 m			
1210 vs	1235 vs	1225 vs	1225 vs	1215 vs	1210 vs	1210 vs	1210 vs	ν(phenyl—C)
1175 s	1178 s	1180 s	1180 s	1180 s	1180 s	1180 s	1180 s	
1083 m	1080 w	1080 w	1085 w	1080 w	1080 w	1080 w	1080 w	ρ(C—H)
1030 m	1030 w	1032 w	1032 m	1032 w	1030 w	1028 w	1030 w	
1005 w	1005 m	1005 m	1005 m	1005 w	1005 w	1005 w	1005 w	Ring breathing
960 vs	982 vs	958 vs	955 s	948 s		935 s	924 vs	$\nu(\mathrm{C}\underline{\cdots}\mathrm{S})$
			928 s	920 s	912 vs	910 vs	910 s	
782 s	780 vs	778 s	780 s	778 s	772 vs	775 vs	773 vs	π(C—H) of monosubstituted benzene ring
695 s	715 s	717 s	708 s	690 s	690 vs	686 vs	687 vs	
	685 s	690 s	695 s					
665 m	650 m	648 m	660 m	652 m	646 s	648 m	649 m	δ(O—C—S)
618 w	618 w	620 w	615 w	618 w	635 w	635 w		α(C—C—C)
	577 s	570 m	560 m					ν(M—O)
550 w				540 w	545 w	535 w		
450 w, br	460 w			470 w	465 w	460 w	445 w	π(phenyl ring)
	440 w	435 w	490 w	450 w	430 w	425 w		

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; br, broad; ρ, in-plane bending, π, out-of-plane bending; δ deformation.

implies that the strength of oxygen coordination decreases while that of sulfur increases from Zn(II) through Hg(II) in the monothiobenzoate complexes of the zinc group of metals.

The phenyl–C band occurring at 1210 cm^{-1} in the sodium salt shifts to higher frequencies in Cr(III), Ni(II), and Zn(II) complexes, while it is not altered in Hg(II), Cu(I), and Ag(I) complexes, in which strong sulfur coordination occurs. The increase in the frequency of the former set of complexes may be explained by the following type of electron drift which increases phenyl–C bond order



When the coordination through sulfur is strong, a similar electron drift is not evidenced, probably due to back-bonding from the d-filled metal ion to the vacant d orbitals of the sulfur, which in turn retards the electron drift from the phenyl–C group.

The medium-intensity bands at 577, 570, and 560 cm^{-1} in Cr(III), Ni(II), and Zn(II) complexes, respectively, may be assigned to the metal–oxygen stretching vibration. In monothio-β-diketone complexes, in which nickel is chelated to both oxygen and sulfur, ν(Ni—O) is observed around 500 cm^{-1}.[14] From the position of ν(M—O) band in the complexes, the following decreasing order for the metal–oxygen bond strength can be arrived at: Cr(III) > Ni(II) > Zn(II). The order is the same as that indicated by the $\nu(\mathrm{C}\dot{=}\mathrm{O})$ frequency.

TABLE IV

ELECTRONIC SPECTRAL DATA FOR CHROMIUM(III) AND NICKEL(II) MONOTHIOBENZOATES

Band positions cm^{-1}	Log ϵ_{max}	Probable assignments
	$Cr(C_6H_5COS)_3$	
38,170	4.75	$\pi \rightarrow \pi^*$ of benzene + ${}^4A_2 \rightarrow {}^4T_1(P)$
34,480 sh	4.53	$\pi \rightarrow \pi^*$ of $\mathrm{C}\dot{=}\mathrm{S}$
30,310	4.30	Charge-transfer band
22,980 sh	2.61	${}^4A_2 \rightarrow {}^4T_1(F)$
16,260	2.07	${}^4A_2 \rightarrow {}^4T_2(F)$
14,080 sh	1.65	${}^4A_2 \rightarrow {}^2E$
	$Ni(C_6H_5COS)_2$	
40,800	4.28	$\pi \rightarrow \pi^*$ of benzene
35,100 sh	3.98	$\pi \rightarrow \pi^*$ of $\mathrm{C}\dot{=}\mathrm{S}$
31,250	3.88	Charge-transfer band
26,700 sh	3.63	${}^3A_2 \rightarrow {}^3T_1(P)$
19,610	*a*	${}^3A_2 \rightarrow {}^1A_1(G)$
13,380	*a*	${}^3A_2 \rightarrow {}^3T_1(F)$
9,010	*a*	${}^3A_2 \rightarrow {}^3T_2(F)$

[a] ϵ could not be calculated since the spectrum was recorded in mull below 20,000 cm^{-1}.

The coordination tendency of thiobenzoate ion in its complexes can be rationalized by the concept of "hard" and "soft" donors and acceptors.[15,16] According to this concept, sulfur is a soft donor, while oxygen is a hard one. Usually the soft donors coordinate strongly to the soft acceptors while the hard donors coordinate to the hard acceptors. Among the metal ions investigated here, Cr(III) is a hard acceptor, Ni(II) and Zn(II) are intermediates, and Cd(II), Hg(II), Cu(I), and Ag(I) are soft acceptors. This classification

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[14] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Australian J. Chem.*, **18**, 673 (1965).

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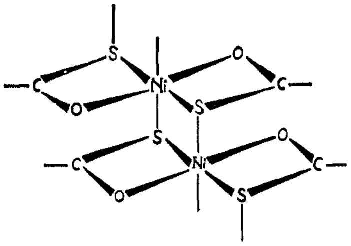
[16] R. G. Pearson, *Chem. Brit.*, **3**, 103 (1967).

explains the strong oxygen coordination in the Cr(III) complex, the nearly symmetric chelation in Ni(II) and Zn(II) complexes, and the strong sulfur bonding in Cd(II), Hg(II), Cu(I), and Ag(I) complexes.

Electronic Spectra and Probable Configurations of the Complexes.—The electronic spectral data together with their probable assignments for Cr(III) and Ni(II) complexes are given in Table IV. The Cr(III) complex gives two broad d–d transitions centered at 22,980 and 16,260 cm^{-1}. The broadening of these bands suggests a composite nature of the transitions concomitant with the lowering of the octahedral symmetry. The third d–d band, $^4A_2 \rightarrow {}^4T_1(P)$, expected around 37,000 cm^{-1} seems to have merged with the strong $\pi \rightarrow \pi^*$ transition at 38,170 cm^{-1}.

The electronic spectral data together with the paramagnetic moment of 3.31 BM suggests a distorted octahedral configuration around Ni(II). Such a configuration can be satisfied by proposing the polymeric structure



The polymeric nature of the complex could not be substantiated further from molecular weight measurements, because of its insolubility or poor solubility in any suitable solvent. However, a suspension of the complex in petroleum ether (bp 40–50°), when treated with pyridine, yielded green crystals of a complex having the molecular formula Ni(MTB)$_2$(py)$_2$. The complex is monomeric, with a distorted octahedral symmetry as revealed by the d–d transitions and the magnetic moment. The formation of this complex from [Ni(MTB)$_2$]$_n$ can be explained by the rupture of the two weaker axial Ni–S bonds by the coordination of two pyridine molecules in their position. The Zn(II) and the Cd(II) complexes may also have the same type of distorted octahedral structure as that of the Ni(II) complex. However, the axial bonds in these complexes appear to be stronger as they are not affected by pyridine.

In the mercury(II) thiobenzoate complex, Hg(II) may be diagonally coordinated with the sulfur atoms from a pair of thiobenzoate groups and possibly also axially to an already coordinated thiobenzoate, thus conferring polymeric nature on the complex. Cu(I) and Ag(I) complexes may have polymeric chains, sulfur of thiobenzoate acting as a bridge between two metal ions. The present data are insufficient to assign an exact coordination to Hg(II), Cu(I), and Ag(I).

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Dissociative Mechanisms for Substitution of Sulfito Complexes

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Above pH 12, the substitution of *trans*-Co(en)$_2$SO$_3$OH by SO$_3^{2-}$ to form *trans*-Co(en)$_2$(SO$_3$)$_2^-$ is reversible with an equilibrium constant $K_I = 0.36_8$ at 25° and $\Delta H_I = 0.25 \pm 0.2$ kcal mol^{-1}. The rate law for sulfite substitution is consistent with a reversible two-step limiting SN1 mechanism. The rate parameters for formation of the intermediate Co(en)$_2$SO$_3$$^+$ from *trans*-Co(en)$_2$(SO$_3$)$_2^-$ are $k(25°) = 0.11_1$ sec^{-1}, $\Delta H^{\ddagger} = 20.5 \pm 0.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.9 \pm 3$ eu while formation of the same intermediate from *trans*-Co(en)$_2$SO$_3$OH is described by $k(25°) \geq 3$ sec^{-1}, $\Delta H^{\ddagger} = 21 \pm 2$ kcal mol^{-1}, and $\Delta S^{\ddagger} \geq 4$ eu. Hydroxide ion is at least 50 times more reactive than sulfite ion toward Co(en)$_2$SO$_3^+$. At pH 8.1, substitution of *trans*-Co(en)$_2$SO$_3$OH$_2^+$ by SO$_3^{2-}$ is virtually complete and the observed rate law is consistent with a limiting SN1 mechanism. The intermediate Co(en)$_2$SO$_3^+$ is formed from *trans*-Co(en)$_2$SO$_3$OH$_2^+$ with $k(25°) = 13.4$ sec^{-1}, $\Delta H^{\ddagger} = 15.9 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{+} = 0.2 \pm 2$ eu. Both N$_3^-$ and HSO$_3^-$ exhibit the same limiting rate for substitution as does SO$_3^{2-}$. The relative reactivity of sulfite and water (k_s/k_w) toward Co(en)$_2$SO$_3^+$ is $(9 \pm 5) \times 10^3$. The labilizing effect of the sulfito ligand arises from the unusually low $\Delta H^{\ddagger}$ values for dissociative release of the ligand *trans* to the sulfito ligand.

Introduction

The rates of substitution reactions of cobalt(III) complexes are accelerated markedly by the presence of a sulfito ligand.[1-3] The reaction half-times of seconds or less observed for these sulfito reactions at 25° are at least 10^3 times shorter than for typical substitution reactions of other diamagnetic cobalt(III) complexes.

In the case of the reactant complexes Co(NH$_3$)$_5$SO$_3^+$,

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