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Manganese(II) and Mercury(II) Complexes Containing a Thio Derivative of Acetylacetone*[1]

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New compounds of the type $M(C_5H_7S_2)_2Cl_4$, where M is Mn(II) or Hg(II), were obtained by passing hydrogen chloride and hydrogen sulfide through ethanol solutions containing acetylacetone and metal chlorides. Such adducts seem to be isostructural to iron compounds, and are stable in the solid state. They seem to decompose when brought into contact with such solvents as water, methanol and dimethylformamide. Their magnetic susceptibilities show that these compounds are all bivalent. The infrared spectra and electronic spectra resemble those of the dithioacetylacetonato iron compound.

The dithio derivatives of acetylacetonato complexes are expected to have many interesting properties, but their syntheses were not successful until only recently.

Martin and Stewart[1] have succeeded in synthesizing dithioacetylacetonate of nickel(II), cobalt(II), palladium(II) and platinum(II).

The present authors have investigated the syntheses of the dithioacetylacetonato complex of various other metals, and have come to synthesize

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[1] L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966).

a series of $M(C_5H_7S_2)_2Cl_4$ type complexes where M is manganese(II), mercury(II) or iron(II). These compounds are mutually very similar in properties as well as in IR spectra but are a little different from the group of $M(C_5H_7S_2)_2$ complexes where M is nickel(II) or cobalt(II).

Recently Knauer, Hemerich and Van Voorst have published[2] a note about the synthesis of $Fe(C_5H_7S_2)_2Cl_4$. Although we have accomplished our synthesis of the iron complex independently, the compound is exactly the same properties as the one reported by Knauer and others. In this paper, therefore, the syntheses and the properties of the manganese(II) and mercury(II) complexes are mainly reported.

Knauer and others reported in their paper[2] that iron complexes dissociated in aqueous solution into dithiolium ion, ferrous ion and chloride ion. In fact, it is only by assuming the presence of dithiolium unit ($C_5H_7S_2^+$), instead of the usual dithioacetylacetonato unit ($C_5H_7S_2^-$), that the bivalency of iron and the above formula can be reconciled. The merucry and manganese compounds reported in this paper are considered to have similar constitutions.

Experimental

Materials and Instruments. The starting materials were of GR grade and were used without further purification. IR spectra were obtained by the KBr disc procedure using a DS 403G infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. Electronic spectra were obtained with an Hitachi EPS-2 type automatic spectrophotometer.

Syntheses of Dithioacetylacetonato Manganese(II). Three grams of manganese(II) dichloride tetrahydrate (0.015 mol) was dehydrized by direct heating. The anhydrous salt and 3.1 *ml* of acetylacetone (0.030 mol) were dissolved into 30.0 *ml* of absolute ethanol. Hydrogen chloride and then hydrogen sulfide were passed through it. The solution thus obtained was mixed with an equivolume of petroleum ether and kept overnight. Fine yellow crystals were obtained. Yield was about 30%.

The same method as for manganese(II) compounds was effective for the synthesis of the mercury(II) compound from mercury(II) chloride, and for the synthesis of the iron(II) compound from iron(III) chloride hexahydrate. Yields were about 25% and 45% respectively.

All these three compounds are only very slightly soluble in usual organic solvents such as benzene, chloroform and acetone. On the other hand, they are soluble in water, methanol dimethylformamide and dimethylsulfoxide, with probable decomposition. Because of this, their recrystallization has not yet been successful.

Results and Discussion

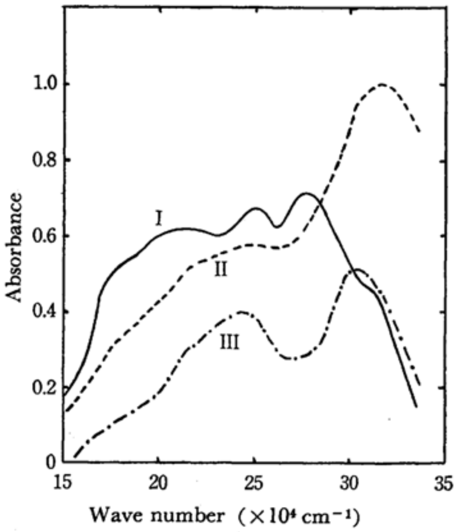

Fig. 1. Reflection spectra of the complexes.

Solid samples were diluted ten times with calcium carbonate (in weight). Reference was calcium carbonate.

I: $FeCl_4(L_{SS})_2$, II: $MnCl_4(L_{SS})_2$, III: $HgCl_4(L_{SS})_2$

TABLE 1. ANALYTICAL RESULTS OF THE COMPLEXES (Figures are shown in %)

		$FeCl_4$ $(C_5H_7S_2)_2$	$MnCl_4$ $(C_5H_7S_2)_2$	$HgCl_4$ $(C_5H_7S_2)_2$
Metal	Calcd	12.14	11.97	33.15
	Found	12.10	12.11	33.30
C	Calcd	26.10	26.19	19.90
	Found	26.79	26.23	20.97
H	Calcd	3.05	3.05	2.32
	Found	3.13	3.34	2.36
S	Calcd	27.85	27.92	21.20
	Found	27.80	26.92	20.05
Cl	Calcd	30.90	31.00	23.50
	Found	30.40	31.40	23.66

* The oxydation of sulfur in this compound is very difficult and alway smaller values were obtained.

Analytical data of these compounds are summarized in Table 1. Significant features of the infrared spectra are shown in Table 2, and those of the visible reflection spectra in Fig. 1, both including the data on the iron compound for comparison.

The magnetic moment of the manganese compound measured by Gouy's balance is 5.92 B. M. per one mole of metal indicating the existence of 5 unpaired electrons, while the mercury compound is diamagnetic, indicating the absence of any unpaired electron. The iron(II) compound seems to have 4 unpaired electrons, as it shows 4.99 B. M.

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[2] K. Knauer, P. Hemmerich and J. D. W. Van Voorst, *Angew. Chem. Intern. Ed. Engl.*, **6**, 262 (1967).

TABLE 2. INFRARED SPECTRA OF THE COMPLEXES
Figures are given in cm^{-1}. L_{SS} means ($C_5H_7S_2$).

$FeCl_4(L_{SS})_2$	$MnCl_4(L_{SS})_2$	$HgCl_4(L_{SS})_2$	$Ni(L_{SS})_2$	$Ni(L_{OO})_2$	Tentative assignment
				1598	ν(C=O)
1470 s	1485 s	1480 s	1495 s	1514	ν(C=C)+δ
1420—1430	1432 m	1430 m	1433 w	1453	
1375 s	1378 w	1375 m		1398	δ(CH_3)
1353 s	1357 m	1355 m	1353 m	1367	
			1314 m		ν(C–CH_3)+
			1290 m	1261	ν(C=C)
1230 m	1234 m	1230 m			ρ(CH_3),
1200 s	1208 s	1205 s		1198	ν(C=S)
			1159 s		
1093 w	1095 w	1095 w			
1007 m	1022 w	1020 w	1013 m	1020	ρ(CH_3)
	1010 m	1008 m			
997 m	1000 w	1000 w			
982 w	985 w	982 w			ν(C–CH_3),
				929	ν(C=O)
860 s	865 s	862 s	841 s		ν(C=S)
			749 m	764	π(C–H)
710 w	717 w	715 w	705 w		
696 s	703 w	700 s			
				666	δRing+
					ν(M–O)
573 w	578 w	575 w		579	
557 s	559 s	557 s	558 s	563	π
523 w	527 w	525 w			
459 w	460 w	458 w			
436 s	439 s	438 s	422 w	427	π
422 w	422 w	420 w			

per iron atom. These facts show that these compounds have high spin octahedral or tetrahedral structures and not planar or distorted tetragonal ones. This supports the assumption proposed by Knauer and others.2)

The infrared spectra data for the above compounds are summarized in Table 2 together with those of acetylacetonato-3) and dithioacetylacetonatonickel(II)4). The general feature of the former resembles those of acetylacetonates except some additional special bands. The tentative assignments of many bands were given from the comparison with the acetylacetonates as shown in Table 2.

These compounds show no ν(C=O) band near 1570 cm^{-1} and this fact shows that they do not have any carbonyl oxygens. The ν(C=S) bands of these compounds, containing two dithioacetylacetonate ligand per one metal ion, appear near 1200 and 862 cm^{-1}, but on the other hand those of bisdithioacetylacetonate of nickel(II) and cobalt(II) appear near 1160 and 844 cm^{-1}. In other words, ν(C=S) has about 40—20cm^{-1} higher wave numbers in these tetrachloro compounds. This fact seems to indicate that the C–S bond in these tetrachloro compounds has a more covalent character and the metal-sulfur bond may not be as strong as in nickel or cobalt bisdithioacetylacetonate.

Reflection spectra of these compounds are shown in Fig. 1. Since usual Hg(II), Mn(II), as well as Fe(II) compounds have no marked d–d absorption in this region, the peaks in these spectra should be due to charge transfer, or to π–π transfer bands.

When these compounds are dissolved, they seem to be decomposed, and the spectra of the solutions are not the same as those in the solid state. But the solutions of these compounds, after staying about one hour at room temperature (20°C),

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3) K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

4) A. Ouchi, M. Hyodo and Y. Takahashi, This Bulletin, **40**, 2819 (1967).

Table 3. Electronic spectra of the complexes dissolved in some solvents*
(After 1 hr at 20°C, 10^{-3}—10^{-5} mol/l)
Figures are given in cm^{-1} for wave numbers and log ε for intensities (in palentheses).

Methanol solution					
$\mathrm{FeCl_4(L_{SS})_2}$	37700	34500	27400	21720	16650
	(4.13)	(4.19)	(2.19)	(2.07)	(1.71)
$\mathrm{MnCl_4(L_{SS})_2}$	38500	34650		22800	16660
	(3.86)	(3.85)		(2.49)	(0.70)
$\mathrm{HgCl_4(L_{SS})_2}$	37000	34100		23600	17550
	(4.15)	(4.24)		(3.52)	(2.92)
Aqueous solution					
$\mathrm{FeCl_4(L_{SS})_2}$	38300	34600		23200	
	(4.18)	(4.31)		(1.35)	
$\mathrm{MnCl_4(L_{SS})_2}$	37600	34650	27800	23300	
	(3.96)	(4.09)	(1.37)	(1.12)	
$\mathrm{HgCl_4(L_{SS})_2}$	37700	34500	30600	23710	18200
	(4.09)	(4.20)	(3.92)	(4.54)	(2.37)
Dimethyl formamide solution					
$\mathrm{FeCl_4(L_{SS})_2}$	36400		30300	22800	17550
	(4.51)		(4.02)	(4.10)	(2.33)
$\mathrm{MnCl_4(L_{SS})_2}$	35500		28200	23300	16700
	(3.38)		(3.74)	(3.48)	(2.30)
$\mathrm{HgCl_4(L_{SS})_2}$	36750	33300	28200	21720	16700 sh
	(4.12)	(4.07)	(3.98)	(3.30)	(2.50)

* These spectra should be those of some reaction products of complexes with solvents and may not be the spectra of the complex itself.

show reproducible spectra; the ε in appearance almost follows Beer's law in the concentration region of 10^{-3}—10^{-4} mol/l in the case of visible spectra, and 10^{-4}—10^{-5} mol/l in the case of ultraviolet region. From this fact, decomposition seems to be almost complete in solutions. The maxima and ε's (in appearance) of the main peaks are shown in Table 3.

In aqueous solution these complexes seems to be decomposed into M^{2+}, $(\mathrm{C_5H_7S_2})^+$ and Cl^- (where $\mathrm{M}^{2+}=\mathrm{Fe}^{2+}$, Mn^{2+} or Hg^{2+}). The color of the aqueous solution is weaker than that of solid or dimethylformamide solution. In the case of the iron complex, the existence of Fe^{2+} was recognized by the formation of bipyridine complex by Knauer and others,[2] and by the formation of *O*-phenanthroline complex in our study. The existence of Cl^- was found by the immediate precipitation of silver chloride by the addition of silver nitrate in our research. The existence of $[\mathrm{C_5H_7S_2}]^+$ was proved by Knauer *et al.*[2] by the formation of picrate $\mathrm{C_{11}H_9O_7N_3S_2}$. They also assigned the 280 mμ and 265 mμ peaks in aqueous solution to the π-π transition in the dithiolium ring.

The existence of the free dithiolium ion in aqueous solutions of the complex is very interesting, although the dithiolium ions were already reported in many papers.[5-8] They are the planar, benzenoid, heterocyclic, monopositive ions. Such salts as perchlorate or chloride are colorless and stable.

The aqueous solution of Mn(II) and Hg(II) compounds also reacts with silver nitrate and precipitates silver chloride immediately. Moreover, the wave numbers and ε's of the absorption in maxima in the ultraviolet region are very similar to that of the Fe(II) compounds. This fact shows that the aqueous solution of Mn(II) and Hg(II) compounds also contains dithiolium ion.

A complicated solvation phenomenon was found when Mn(II), Hg(II) and Fe(II) complexes are dissolved in dimethylformamide; the solution was violet immediately after the dissolution, but in a few minutes, the color turned yellow at room temperature. If the fresh yellow solution is diluted by more dimethylformamide the color turns blue, but the blue color is very unstable, turning yellow after a while. The old yellow solution does not change its color upon dilution. The values given in Table 3 are those of the final yellow solution.

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5) E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).
6) E. Klingsberg, *J. Org. Chem.*, **31**, 3489 (1966).
7) G. Barinkow and H. Kunzeh, *Z. Chem.*, **6**, 343 (1966).
8) D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, **1960**, 252.

The kinetic approach of the above change has not yet been successful. The mean molecular weight of the species in the dimethylformamide solution of the iron complex was 110 as found by vapor pressure depression measurement, and this fact shows that the iron complex should be split into four or more parts in the solution. By analogy, the Mn(II) and Hg(II) complexes should also be split into several pieces in the solution.

The ultraviolet spectra of all of these compounds in water, methanol and dimethylformamide show two characteristic peaks (Table 3), and they are assigned to the $\pi-\pi$ transition of the dithiolium ion ring as in the case of dithiolium derivatives.5-8)

In the case of the dimethylformamide solution, the maxima of the two peaks in the ultraviolet region shift to lower wave number; 36000, and 28000 cm^{-1}, respectively. This fact may show that in dimethylformamide solution a part of the metal-sulfur bonding structure is kept, although it is not the same as that in the solid state.

It should be noted that a dimer of dithioacetylacetone is also very easily produced when acetylacetone is treated with hydrogen sulfide. This dimer is very stable, not decomposing easily. However, the infrared spectra of the dimer is very different from those of the complexes mentioned above.

In the case of dithioacetylacetonato nickel(II), or cobalt(II), the complexes are easily soluble in a non-polar solvent, but not in water. On the other hand, the complexes of iron, manganese and mercury are hardly soluble in non-polar solvents, and soluble in water (though accompanied by some decomposition). Infrared spectra of complexes of these two types are also different from each other.

From these data it is concluded that the dithioacetylacetone in these complexes does not exist in dimer form, nor in the usual dithioacetylacetonato $[C_5H_7S_2]^-$ form (as found in the nickel complex). Knauer and other's assumption2) of the existence of dithiolium ion in it thus seems to be the most reasonable one. They have suggested two hypothetical formulae; (a) $FeCl_2(C_5H_7S_2)^{2+}Cl_2^-$, (b) $FeCl_2[CH_3(Cl)CS\ CH\ CS\ CH_3(Cl)]_2^0$ to explain the intense color of the solid iron complex. However, there seems to be still several other possibilities. The X-ray study which is going on by the present authors is expected to clarify this point. The manganese, and mercury complexes probably have the same type of structure.

The authors wish to thank to the Analytical Division of the Department of Pharmacy, The University of Tokyo for their elemental analyses of these compounds as well as for the measurement of infrared spectra; we also acknowledge Professor Yukichi Yoshino and the colleagues of our laboratory for helpful discussions.

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