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Syntheses and Properties of Some Tetrabromobis(dithioacetylacetonato) Complexes

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Some compounds of type $M(L_{SS})_2Br_4$, where M is Mn(II), Fe(II), Co(II), Cu(II), Zn(II) and Cd(II) and HL_{SS} are dithioacetylacetone, were obtained by passing hydrogen bromide, adding bromine and passing hydrogen sulfide through an ethanolic solution containing an anhydrous metal bromide and acetylacetone. Such compounds, which seem to be isostructural with tetrachlorobis-(dithioacetylacetonato)iron(II), are stable. They are all of high spin, and their infrared spectra show characteristic bands at about 1200, 1000 and 860 cm^{-1}. $Cu^I(L_{SS})_2Br_3$ was also obtained from cupric bromide by the same method without using bromine, but from cupric chloride, an isostructural complex was not obtained but $[Cu(C_5H_8S_2)Cl]_n$. Electronic spectra are also shown and discussed.

The tetrachlorobis(acetylacetonato) complexes of iron(II),[1)] manganese(II)[2)] and mercury(II)[2)] have already been synthesized and discussed. The present authors investigated the syntheses of the homologue of the complex, but chloro-complexes of other metals were hardly obtained. This seems due to the fact that, 1) the chloro complexes are relatively unstable and especially sensitive to water and alcohol, and the products may be decomposed by the solvent during synthesis; 2) in these complexes, dithioacetylacetone is probably in the form of dithiolium ion of unipositive charge; then some oxidant must be added during synthesis.

In the case of $Fe^{II}(L_{SS})_2Cl_4$, ferric chloride was used as the starting material and a tervalent ferric salt works as the oxidant. Manganese and mercury have another relatively stable oxidation state other than the bivalent state, and they may act as a kind of autooxidation catalyst in the process. On the other hand, zinc and cadmium, for example, have a very stable bivalent state and no oxidation ability nor oxidation catalytic effects are expected.

Consequently, an improved synthetic method for the $M^{II}(L_{SS})_2X_4$ (where HL_{SS} is dithioacetylacetone, X is Cl or Br) has been investigated in our laboratory and the complexes of many metals are newly obtained.

The $M^{II}(L_{SS})_2Br_4$ type complexes thus obtained are all of high spin, and show almost the same infrared spectra as that of $Fe^{II}(L_{SS})_2Cl_4$, and not that of $Co(L_{SS})_2$.[3)]

When cupric bromid was used as the starting material and bromine not added, the cuprous complex $Cu^I(L_{SS})_2Br_3$ was obtained; but if bromine was added, the cupric complex precipitates. From cupric chloride, however, an isostructural complex was not obtained but $[Cu(C_5H_8S_2)Cl]_n$.

Experimental

Materials and Instruments. The starting materials were of GR grade and were used without further purification. Infrared spectra were obtained by the KBr

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

[2)] A. Furuhashi K. Watanuki and A. Ouchi, This Bulletin, **41**, 110 (1968).

[3)] A. Ouchi, M. Hyodo and Y. Takahashi, *ibid.*, **40**, 2819 (1967).

disc procedure using a Type DS 403 G infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. Electronic spectra were obtained with a Hitachi EPS-2 type automatic recording spectrophotometer. Reflectance spectra were obtained with an Ito Model QV-3 spectrophotometer, using a reflectance attachment and a magnesium oxide standard. Magnetic moments were measured with a Gouy balance at room temperature (15°C).

Syntheses of Tetrabromobis(dithioacetylacetonato)manganese(II). Three and three tenth grams (0.015 m*l*) of anhydrous manganese(II) bromide and 3.00 g (0.030 mol) of acetylacetone were mixed with 20.0 m*l* of absolute ethanol, and all solid materials*[2] dissolved. To the solution cooled on ice, were added first dry hydrogen bromide for 30 min, then 1.1 m*l* (0.042 mol) of bromine dropwise while shaking and finally hydrogen sulfide for 5 min until a some precipitate appeared. The precipitate was filtered off and the filtrate kept in an ice bath for about one hour. The yellow precipitate thus obtained was filtered off and washed with carbon disulfide, ethyl alcohol, chloroform and petroleum ether in succession. The product was dried in a vacuum desiccator. The yield was about 4.0 g (42.0%). Though the product is soluble in water or polar organic solvents, it reacts with them and it is insoluble in non-polar organic solvents. For this reason recrystallization has not yet succeeded.

The syntheses of cobalt(II), zinc(II), cadmium(II) and copper(II) complexes were carried out by almost the same method; the yields were about 30—50%.

The iron(II) complex was obtained from ferric bromide without using bromine, as ferric ion itself worked as the oxidizing agent. The copper(I) complex was obtained from cupric bromide without bromine.

Synthesis of Chlorodithioacetylacetonatocopper(I). One and seven tenth grams of cupric chloride (0.010 mol) and 2.0 g (0.020 mol) of acetylacetone were dissolved in 30 m*l* of absolute ethanol, and the solution refluxed for 2 hr. The clean solution thus obtained was cooled on an ice bath and hydrogen chloride was bubbled in, then hydrogen sulfide. Yellow precipitate appeared immediately. The precipitated product was very unstable, but when washed with absolute ethanol repeatedly, a pale brownish white product was obtained which was very stable even in air. The yield was about 2.1 g (91.5%).

The attempt to synthesize $Zn(L_{SS})_2Cl_4$ or $Cu(L_{SS})_2Cl_4$ from the bivalent metal chloride using chlorine as an oxidant was not successful; perhaps the product is not stable to the solvent during synthesis. On the other hand, the bromo-complexes of these metals are sufficiently stable, and moreover, bromine is easier to handle quantitatively than chlorine; as the addition of a large exess of halogen should be avoided to minimize the side reaction. The syntheses of the iodo-complexes were also attempted, but iodine did not react easily, and the bonding was not very stable; consequently, stable iodo-complexes were not obtained. When ferric bromide was used as the starting material and bromine added, the iron(III) complex did not precipitate. Perhaps tervalent iron complex is not stable, as the formula of the iron(III) complex should be $Fe(L_{SS})_2Cl_5$ from the valence equilibrium, and the central metal ion should be hepta-coordinated; it is probably not a stable state.

The attempt to synthesize the isostructural nickel complex was not successful by the same method, perhaps this is due to the fact that the dithioacetylacetonato complex is very stable.

Results and Discussion

Analytical data for these compounds are summarized in Table 1. Their magnetic moments are given in Table 2.

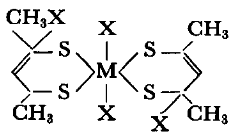
From the magnetic data, the $M(L_{SS})_2Br_4$ type complexes are all high spin types. Though their exact structures have not been determined yet, it may be octahedral.[1,2] $Co(L_{SS})_2Br_5$, for example, seems to have three unpaired electrons, though the observed value is higher than the calculated value, 3.8, as is commonly recognized for many cobalt(II) octahedral complexes.[4] On the other hand, bis-(dithioacetylacetonato)cobalt(II), which has a planer structure,[5] is a low spin type and has only one unpaired electron.

Consequently, there are two types of dithioacetylacetonato complexes of the same metal; one is $M(L_{SS})_2$ and the other $M(L_{SS})_2X_4$ (general formulae).

The infrared spectral data for the complexes are summarized in Tables 3 and 4 together with those of some related compounds.[2,3] The general features of the infrared spectra of these complexes rather resemble that of $Fe(L_{SS})_2Cl_4$ and not that of $Co(L_{SS})_2$.

The wave numbers of the main peaks of $Fe(L_{SS})_2Cl_4$ and $Fe(L_{SS})_2Br_4$ are very similar in the 2000—400 cm^{-1} region, indicating that these two complexes are almost isostructural and chlorine or bromine does not affect the vibrational frequencies in that region seriously. This fact seems to suggest that the halogen atoms do not bond directly to the carbon atom in these complexes.[6]

Then one of the formulae proposed by Knauer,[1] (I), is not probable.



(I)

The characteristic bands which seem to be $\nu(C=S)$ bands or mixed bands containing $\nu(C=S)$[7] appear

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[*2] After the dissolution some crystal may appear, which is redissolved into the solvent when hydrogen bromide is passed.

4) F. A. Cotton and G. Wilkison, "Advanced Inorganic Chemistry," 2nd ed., Interscience Publ. (Div. of Wiley and Son Co.) New York, N.Y. (1966), p. 870.

5) R. Becket and B. F. Itokins, *Chem. Commun.*, **1967**, 909.

6) D. Gibson, C. Oldham, J. Lewis, D. Lawton, R. Mason and G. B. Robertson, *Nature*, **208** (**5010**), 580 (1965).

7) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

Table 1. Analysis of complexes (Figures are given in %.)

		Metal	C	H	S	X
$Mn(L_{SS})_2Br_4$	Calcd	8.62	18.85	2.22	20.13	50.17
	Found	9.45	19.71	2.40	19.90	50.02
$Fe(L_{SS})Br_4$	Calcd	8.74	18.83	2.21	20.11	50.10
	Found	9.02	19.01	2.55	20.58	50.05
$Co(L_{SS})_2Br_4$	Calcd	9.19	18.74	2.20	20.01	49.86
	Found	10.00	19.67	2.61	20.78	50.03
$Cu^{I}(L_{SS})_2Br_3$	Calcd	11.23	21.23	2.49	22.67	42.37
	Found	11.25	21.65	2.52	21.18	42.30
$Cu^{II}(L_{SS})_2Br_4$	Calcd	9.84	18.60	2.19	19.86	49.51
	Found	9.80	19.73	2.29	20.56	49.70
$Zn(L_{SS})_2Br_4$	Calcd	10.10	18.55	2.18	19.81	49.37
	Found	10.78	18.21	2.48	20.50	50.40
$Cd(L_{SS})_2Br_4$	Calcd	16.18	17.29	2.03	18.47	46.02
	Found	17.05	17.42	1.95	19.21	47.00
$Cu(C_5H_8S_2)Cl$	Calcd	27.48	25.95	3.49	27.73	15.33
	Found	27.54	25.76	3.30	27.58	15.43

L_{SS} = dithioacetylacetone; $(C_5H_7S_2)^+$
X = Cl or Br

Table 2. Magnetic moments of complexes (at 15°C)

Compound	Magnetic moment* (B.M.)	Number of unpaired electrons	Oxidation number of the central metal
$Mn(L_{SS})_2Br_4$	6.02	5	+2
$Fe(L_{SS})_2Br_4$	5.51	4	+2
$Co(L_{SS})_2Br_4$	4.82	3	+2
$Cu^{II}(L_{SS})_2Br_4$	1.84	1	+2
$Cu^{I}(L_{SS})_2Br_3$	diamagnetic	0	+1
$Zn(L_{SS})_2Br_4$	diamagnetic	0	+2
$Cd(L_{SS})_2Br_4$	diamagnetic	0	+2
$Cu(C_5H_8S_2)Cl$	diamagnetic	0	+1

* per one mol of metal

near 1230 and 860 cm^{-1}. The exact assignment of these bands has not yet been made; those written in Table 3 are only tentative. But the general features of the infrared spectra of these complexes resemble those of potassium dichloroacetylacetonatoplatinate(II) and related complexes.[8,9] In the latter compounds, there is a ring structure of acetylacetone, which is bonded to the central metal atom by γ-carbon atom or by the π-electrons of the C=C double bond. Strong 1200, 1000 and 860 cm^{-1} bands are also recognized in the spectra of the platinum complexes, but the band at 800 cm^{-1} is absent. However, this fact should not be taken as evidence of the existence of a γ-carbon bonding structure, since the thio- and dithioacetylacetonato chelate rings seem to have an electronic structure different from that of acetylacetonato chelate. The final decision should be arrived from an X-ray crystallographic analysis. But we can expect at least that the halogenobis(dithioacetylacetonato) complexes do not have usual MS_4 type coordination which is found in the $Co(L_{SS})_2$ complex. The dithioacetylacetonato ligands of these compounds seem to form rings themselves, unipositive dithiolium ion for example, and this is the reason that the infrared spectra of these compounds and that of γ-carbon bonding acetylacetonate coincide with each other. The ring form ligand may be a unidentate in these complexes, although it is not yet clear by which atom it bonds to the central metal.

This reflection spectra between 28000 and 13500 cm^{-1} are shown in Table 5. Cabalt(II) complex has an intense band at about 15900 cm^{-1}, and this peak seems to be not only the d–d band but a mixture of d–d and d–π bands. Iron(II) and copper(II) complexes also have an intense color, but their peaks are not clear; shoulders at about 20000—19000 cm^{-1} seem to correspond to them. The intense color of these compounds disappears when they are dissolved in water or methanol. Although weak bands are recognized in this absorption spectra, log ε is only about 2 in both cases; in other words, only about one tenth that of bis(dithioacetylacetonato)cobalt(II).[3] This intense color of these solid complexes seems to indicate that there is a kind of bonding between the central metal and the ligands. They are not the MX_4^{2-}-$(L_{SS}^+)_2$ type simple ionic bonding compounds, though, because the metal ion, as well as the dithiolium ion,

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[8] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433, 440 (1967), **7**, 330 (1968).

[9] D. Gibson, J. Lewis and C. Oldham. *J. Chem. Soc.* (*A*), **1967**, 72

TABLE 3. INFRARED SPECTRA OF COMPLEXES (Figures are given in cm^{-1}.)
s=strong, m=medium, w=weak, $L_{SS}=(C_5H_7S_2)$

$Ni(L_{SS})_2$*	$Fe(L_{SS})_2Cl_4$**	$Mn(L_{SS})_2Br_4$	$Fe(L_{SS})_2Br_4$	$Co(L_{SS})_2Br_4$	$Cu^I(L_{SS})_2Br_3$	$Cu^{II}(L_{SS})_2Br_4$	$Zn(L_{SS})_2Br_4$	$Cd(L_{SS})_2Br_4$	$Cu(C_5H_8S_2)Cl$	Tentative assignments
1490 s	1470 s	1480 s	1478 s	1475 s	1475 s	1475 s	1478 s	1480 s		ν(C=C)
								$\left.\begin{matrix}1438\\1425\end{matrix}\right\}$m	1452 sh	δ(C-H)
1433 w	1430 s	1425 m	1428 m	1425 m	1415 m	1425 m	1425 m		1445 s	
									1415 w	
	1420 s	1400 w	1400 w	1400 w	1400 w		1398 w		1405 m	
	1375 s	1380 m	1380 m	1375 m	1370 m	1360 m	1375 m	1370 s	1385 s	
1353 m	1353 s	1356 m	1355 m	1353 m			1355 m		1375 w	
1314 m										
1290 m										$\delta_S(CH_3)$
	1230 m	1230 m	1231 m	1230 m	1233 m	1232 m	1230 m	1236 m	1151 s	ν(C=C)
	1200 s	1205 s	1205 s	1204 s	1205 s	1204 s	1205 s	1200 s		ν(C=S)
1154 s										or the mixture of them
	1073 w	1095 w	1095 w	1095 w	1100 w	1098 w	1095 m	1100 w	1100 vs	δ(C-H) or ν(C-C)
1013 m	1007 m	1020 w	1020 w	1020 w	1018 s	1010 s	1020 w	1020 s	1035 s	$\rho(CH_3)$
	997 m	1010 s	1010 s	1008 s	998 w	998 w	1010 s	1000 w	990 w	$\nu(C-CH_3)$
	982 w	1000 w	998 w	998 w			997 w		955 w	
		982 w	983 w	980 w			980 w		945 m	
									940 m	
841 s	860 s	862 s	865 s	861 s	883 w	881 m	860 s	876 m		$\nu(C-CH_3)$
					845 s	840 s		886 s		ν(C=S)
										or the mixture of them
749 m	710 w	702 m	715 w	700 s	700 m	700 m	700 m	705 m	670 s	π(C-H)
705 w	696 s		702 m							

* See Ref. 2, ** See Ref. 3, δ_S: symmetric bending, π( ): out-of-plane bending

TABLE 4. FAR INFRARED SPECTRA OF COMPLEXES (Figures are given in cm^{-1}.)

$Fe(L_{SS})_2Cl_4$	$Fe(L_{SS})_2Br_4$	$Co(L_{SS})_2Br_4$	$Cu^I(L_{SS})_2Br_3$	$Cu^{II}(L_{SS})_2Br_4$
573 w	571 w	571 w	573 w	571 w
557 s	558 s	558 s	548 s	556 s 545 s
523 w	519 w	520 w	517 w	516 w
436 s	457 w	455 w	454 w	453 w
436 s	434 s	435 s	433 s	431 s

TABLE 5. ELECTRONIC SPECTRA OF COMPLEXES

(Figures are given in cm^{-1} for wave numbers and log ε for intensities (in parentheses).) (vs: very strong, s: strong, m: medium, w: weak, sh: shoulder) (absorption means the absorption spectra of the methanol solution.*)

$Mn(L_{SS})_2Br_4$	absorption		37300	34700		22750		
			(4.09)	(4.18)		(2.17)		
	reflectance					22700(m)		14280(vw)
$Fe(L_{SS})_2Br_4$	absorption		37500	34500	27200	23270	20300	16660
			(3.49)	(3.79)	(2.75)	(2.68)	(2.67)	(2.43)
	reflectance				27800(s)	24400(w)	20000(sh)	16950(sh)15150(w)
$Co(L_{SS})_2Br_4$	absorption		37600	34800	27500	22730		
			(4.12)	(4.14)	(2.48)	(2.39)		
	reflectance				27800(w)	22200(m)	18500(w)	15900(vs)
$Cu^I(L_{SS})_2Br_3$	absorption		37600	34500	26600	23280	19240	16670
			(3.76)	(3.89)	(2.61)	(2.51)	(2.40)	(2.33)
	reflectance				27000(w)	23300(s)	20900(w)	1638(sh)
$Cu^{II}(L_{SS})_2Br_4$	absorption	42900	37900	34900	26600	23580		17070
		(3.81)	(4.03)	(4.10)	(2.85)	(2.66)		(2.45)
	reflectance				27800(s)	23800(w)	19050(sh)	16250(sh)
$Zn(L_{SS})_2Br_4$	absorption	43700	37500	34800	27600	22720		
		(3.61)	(3.65)	(3.82)	(2.21)	(2.16)		
	reflectance					23800(s)	19650(w)	
$Cd(L_{SS})_2Br_4$	absorption		37600	34500		23300		
			(4.02)	(4.09)		(2.38)		
	reflectance					23000(s)	19420(w,sh)	

* These absorption spectra of the solutions should be those of some decomposition product of complexes with solvents and may not be the spectra of the complex itself.

do not have such intense color. Copper(I), manganese(II), zinc(II) and cadmium(II) complexes also have a less intense peak in this region in the solid state, but not in solution.

The absorptions near 23000 cm^{-1} and 28000 cm^{-1} are found both in their reflection and absorption spectra. These bands and the ones near 34500 and 37500 cm^{-1} of the methanolic solution can probably be assigned to π-π transitions of the dithiolium salts.[10,11] The latter two are also found for 3,5-dimethyl-1,2-dithiolium perchlorate too.[12] From this result, the dithiolium cation seems to exist without decomposition even if the metal-ligand bond is broken by dissolution of the compelexes in methanol, or other similar polar solvents. All of these $M_{SS}^{II}(L_{SS})_2X_4$ type complexes seem to dissociate almost completely into M^{++}, $(L_{SS})^+$ and X^-, as in the case of $Fe_{SS}^{II}(L_{SS})_2Cl_4$.[1] Although this fact was recognized previously, it is also recognized from the qualitative electric conductivity measurement of the aqueous and acetonitrilic solution of these compounds.

From these results, structure (III) is preferable to that proposed by Knauer,[1] which is shown in (II).

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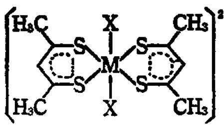
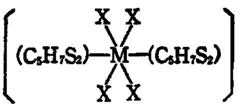
[10] E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

[11] E. Klingsberg, *ibid.*, **84**, 2941 (1962).

[12] M. Schmidt and H. Schulz, *Chem. Ber.*, **101**, 277 (1968).



(II)



(III)

An X-ray crystallographic study of these compounds, which is now in progress by the present authors, may clarify the detailed structure of these comples.

The infrared spectra of $[Cu(C_5H_8S_2)Cl]_n$ is very unique and resembles that of dithioacetylacetone dimer. But it is insoluble in nonpolar solvents and is stable. Though the exact structure is not yet clear, it may be a kind of adduct; a $(-Cu(C_5H_8S_2)-Cl-)_n$ type chain, in which dithioacetylacetone, $C_5H_8S_2$, molecules are bonded to each other copper atom as an unidentate is tentatively proposed.

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