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Syntheses and Properties of Some Metal Bromo-Dithiolium Complexes*[1]

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The bromo-3-methyl-5-phenyl-1,2-dithiol-1-ium complexes were obtained from metal benzoylacetonate, using hydrogen sulfide and bromine with a catalyst of hydrogen bromide. These complexes resemble bromo-bis(3,5-dimethyl-1,2-dithiol-1-ium) complexes and many of them are of the high-spin type. The Zn(II) and Cd(II) complexes are of the ML_2Br_4 type (where M = metal and L = 3-methyl-5-phenyl-1,2-dithiol-1-ium), like 3,5-dimethyl-1,2-dithiol-1-ium complexes, while Cu(I) is of the $MLBr_2$ type. However the analytical results shows that the Mn(II), Fe(II) and Co(II) complexes are of the ML_2Br_3 type. Infrared spectra as well as electronic spectra are shown and discussed.

The tetrachloro-[1,2] and tetrabromo-[3] bis(3,5-dimethyl-1,2-dithiol-1-ium) complexes have already been synthesized and discussed, and the cobalt(II) and iron(II) tetrachlorobis(3,5-dimethyl-1,2-dithiol-1-ium) complexes were also reported on recently.[4] As the tetrabromobis(3,5-dimethyl-1,2-dithiol-1-ium) complexes are synthesized from many kinds of metal acetylacetonates without difficulty, it seemed that it would be very interesting to apply this synthesis technique in an attempt to obtain other bromo-dithiolium complexes. Consequently, the present authors have examined syntheses using many kinds of β-diketonates, including cobalt(II), nickel(II), zinc(II) complexes of benzoylacetone, trifluoroacetylacetone, dibenzylmethane, trifluorobenzoylacetone, methyl acetoacetate, and ethyl acetoacetate. However, the expected products were obtained only from the benzoylacetonates; the syntheses using other β-diketonates have not yet been successful.

Attempts to synthesize chloro(3-methyl-5-phenyl-1,2-dithiol-1-ium) complexes using hydrogen chloride and chlorine in place of hydrogen bromide and bromine were all unsuccessful. This seems due to the facts that: 1) the dithiolium ring is not easily formed from these β-diketones under the experimental condition presented above; 2) some β-diketones are more easily destroyed by free chlorine or bromine than is acetylacetone, and some side-reaction occurs predominantly; 3) steric hindrance owing to the introduced radicals on 2- or 4- carbons seriously affects the formation of complexes.

From the syntheses, two types of complexes of bivalent metals were obtained; ML_2Br_4 (where M = Zn(II) or Cd(II)) and ML_2Br_3 (where M = Mn(II), Fe(II) and Co(II)). The former seems to be isostructural to tetrabromo-bis(3,5-dimethyl-1,2-dithiol-1-ium) complexes. However, the latter compounds are of the new type. The cuprous salt has the $CuLBr_2$ formula and not the CuL_2Br_3 formula; the compound of the latter type was obtained from acetylacetonate.

Recently in our laboratory we have been successful in synthesizing some halogeno(3-methyl-5-phenyl-1,2-dithiol-1-ium) complexes by means of the reaction of metal halide and dithiolium perchlorate.[5] The products are ML_2X_4 or MLX_3-type complexes for bivalent metals and MLX_4-type complexes for tervalent metals. From manganese(II) and cobalt(II) bromides, regular ML_2X_4-type complexes and not ML_2X_3-type complexes were obtained. The colors of these two types of complexes are a little different; the ML_2X_4-type manganese(II) complex is light yellow, while the ML_2X_3-type one is deeper yellow; the former type of cobalt(II) complex is yellowish green, and the latter type is grass green. From ferric bromide a MLX_4-type complex was obtained, while a ML_2X_4-type complex was obtained from cupric bromide, as the redox reaction does not occur in the synthetic process using dithiolium salt. On the other hand, the direct synthesis of the halogeno-(dithiolium)-complex may include some different reactions because of the use of an excess of strong

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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. Furuhashi, T. Takeuchi and A. Ouchi, *ibid.*, **41**, 2049 (1968).

4) A. Ouchi, M. Nakatani and Y. Takahashi, *ibid.*, **41**, 2044 (1968).

5) Y. Takahashi, M. Nakatani and A. Ouchi, *ibid.*, **42**, 274 (1969).

reagents, such as hydrogen sulfide or bromine.

The infrared spectra and electronic spectra of the complexes of all these types, *i. e.*, ML_2X_4, ML_2X_3, MLX_2, and MLX_4, are almost identical, and so their structures are probably not very different from one another.

Experimental

Materials and Instruments. The starting materials were of a G. R. grade and were used without purification. The infrared spectra were obtained by a nujol and hexachloro-1,3-butadiene mull procedure using a DS-301-type infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. Electronic spectra were obtained with a Hitachi EPS-2-type automatic recording spectrophotometer. The reflectance spectra were obtained with an Ito Model QU-3 spectrophotometer using a reflectance attachment and a magnesium oxide standard. The magnetic moments were measured with a Gouy balance at room temperature (21°C).

Synthesis of Tetrabromo-bis(3-methyl-5-phenyl-1,2-dithiol-1-ium)cadmium(II). Two and seven-tenths grams (0.010 mol) of anhydrous cadmium(II) bromide and three grams (0.018 mol)[*3] (or less) of benzoylacetone were mixed with 30 m*l* of absolute ethanol. After the dissolution, a precipitate appeared. To the mixture cooled on ice dry hydrogen bromide was added over a 1 hr period; the precipitate was completely dissolved during this procedure. Then about 1.0 m*l* (0.04 mol) of bromine[*4] was stirred in, drop by drop. Finally hydrogen sulfide was passed through for about 5 min until a little precipitate appeared.[*5] The precipitate was filtered off and the filtrate was mixed with a half volume of petroleum ether and kept in a cold room (−about 5°C) overnight. The needle-like yellow precipitate thus obtained was filtered off, and the product was washed with ethanol, carbon disufide, chloroform, and diethyl ether (in that order) to remove the mother liquor, sulfur, the dimer of the dithiobenzoylacetone, and the washing solvents respectively. The product was then dried in a vacuum desiccator at room temperature. The yield was about 2.1 g (36.0% calculated from the quantity of benzoylacetone used).

Though the product is soluble in such polar solvents as water or alcohol, it reacts with them; on the other hand it is hardly soluble in non-polar solvents. For this reason recrystallization has not yet been successful.

The syntheses of the zinc(II) complex and of ML_2Br_3-type complexes of manganese(II) and cobalt(II) were carried out by almost the same method. The yields are shown in Table 1.

The iron(II) complex, FeL_2Br_3, was obtained from iron(III) bromide without using bromine as the ferric ion itself worked as the oxidizing agent. The copper(I) complex, $CuLBr_2$, was obtained from copper(II) bromide by the same process without bromine. In both cases no product was isolated if bromine was added during the process.

The Analyses of Bromine in Complexes. The analysis of the bromine in these complexes was difficult; the Volhard method and the iodometry, both to be described below, were examined.

i) Volhard Method. The solid sample was stirred with a silver nitrate-nitric acid aqueous solution for about 10 min and the excess silver ion was titrated with a thiocyanate solution.

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

		Metal	C	H	S	Br	Yield
MnL_2Br_3	Calcd	8.06	35.26	2.66	18.83	35.19	19
	Found	8.16	35.30	2.70	19.08	33.00	
FeL_2Br_3	Calcd	8.19	35.21	2.66	18.80	35.14	19
	Found	7.75	35.39	2.62	18.08	33.41	
CoL_2Br_3	Calcd	8.60	35.05	2.65	18.72	34.98	19
	Found	8.86	35.02	2.72	19.15	34.90	
ZnL_2Br_4	Calcd	8.47	31.13	2.33	16.63	41.43	16
	Found	8.27	31.99	2.72	16.48	42.60	
CdL_2Br_4	Calcd	13.73	29.34	2.22	15.67	39.04	36
	Found	14.14	29.22	2.29	15.84	39.20	
$CuLBr_2$	Calcd	15.25	28.83	2.18	15.39	38.35	20
	Found	15.30	29.11	2.53	16.36	38.30	

HL = dithiobenzoylacetone ($C_{10}H_{10}S_2$)

[*3] In these syntheses metal salt should be present in excess, as: i) the trapping effect of the dithio-chelate is better; ii) the dimerization reaction is minimized, and iii) the excess of metal halide is easily washed out by ethanol after the reaction.

[*4] A little excess is necessary as the reaction solution contains a great excess of hydrogen sulfide. The bromine added reacts first with hydrogen sulfide to produce sulfur; then the sulfur bromine and hydrogen sulfide seem to undergo a complicated reaction (polysulfide may be produced on the way), and finally the complexes are obtained. To add too much bromine destroys the product, and the yield is not good either.

[*5] If hydrogen sulfide was passed through too long, the complex precipitate on the step, the impurities, and the yield were seriously lowered.

ii) Iodometry. The solid sample was dissolved into water and oxidized with potassium permanganate in the presence of phosphoric acid at room temperature. The isolated bromine was extracted with carbon tetrachloride, the organic solvent layer was shaken and introduced into the aqueous solution of potassium iodide, and the freed iodine was titrated with a standard sodium thiosulfate solution.

Both analytical techniques were applicable to ML_2Br_4-type complexes. However, for ML_2Br_3-type complexes the Volhard method gave too high values, about 30% higher than the expected values; on the other hand, the iodometry gave us too low values, about 30—50% lower than the calculated values.

The results of the bromine analyses of ML_2Br_3 complexes given in Table 1 were obtained by the usual elemental analysis technique for organic compounds-measuring as silver bromide after other interfering substances had been removed. This method is not very suitable, either, and considerable error is inevitable. However, the results of the analyses of the other elements, metal, sulfur, carbon, and hydrogen of these complexes coincide with the expected values within the range of experimental error, thus confirming the formulae shown here.

Results and Discussion

The analytical data as well as the yields of the synthesis process are shown in Table 1. Their magnetic moments are given in Table 2.

TABLE 2. MAGNETIC MOMENTS OF COMPLEXES
(Figures are given in B. M. per 1 mol of metal.)

	B. M.	Valence of the central metal
MnL_2Br_3	5.95	II
FeL_2Br_3	5.35	II
CoL_2Br_3	4.68	II
ZnL_2Br_4	diamagnetic	II
CdL_2Br_4	diamagnetic	II
$CuLBr_2$	diamagnetic	I

From the magnetic data, the manganese(II), iron(II), and cobalt(II) complexes all seem to be high-spin complexes. ML_2Br_4-type complexes of zinc(II) and cadmium(II) are diamagnetic and bivalent. The copper complex is also diamagnetic and univalent.

The colors of the solids and the reflectance spectra between 12500 and 28500 cm^{-1} are shown in Table 3. The manganese(II), zinc(II), and cadmium(II) complexes are yellow, and very little absorption is recognized in the 12500—22000 cm^{-1} region. On the other hand, iron(II) and copper(I) complexes have a deep color and have considerable absorption in this region, although the band is too broad and the wave numbers of the maximum points are not clear. The cobalt(II) complex has an absorption maximum at 14300 cm^{-1} which is probably a d–d band.

All of these complexes have the intense band at about 24000—25000 cm^{-1} which is characteristic of all of this type of compound, but it is not seen in their absorption spectra in ethanol, probably because of the dissociation of the complexes in the solution.

The absorption spectra of the ethanol solution of these complexes are shown in Table 4. The absorptions in the visible region are very weak; the absorption peaks are seen almost only in the ultraviolet region.

The wavelengths and the molar absorption coefficients of the absorption maxima of the solutions coincide with those of 3-methyl-5-phenyl-1,2-dithiol-1-ium perchlorate, which is synthesized by the method of Schmidt and Schulz.⁶⁾ Judging from these facts, the complex seems to dissociate completely into ions in the solution.

If the pure ethanol which does not contain perchloric acid was used as the solvent, the color of the solution gradually turned red at room temperature; this is due to the decomposition of the dithiolium ion, because the same color change is also seen in the solution of pure dithiolium salt.

The infrared spectra data of the complexes and the 3-methyl-5-phenyl-1,2-dithiol-1-ium perchlorate are summarized in Table 5, together with those of some related compounds.⁴⁾ The general features of the infrared spectra of these complexes, both ML_2Br_4 and ML_2Br_3-type complexes, resemble those of tetrachloro-bis(3-methyl-5-phenyl-1,2-dithiol-1-ium)iron(II) and not those

TABLE 3. REFLECTANCE SPECTRA OF COMPLEXES
(Figures are given in cm^{-1}. s: strong, m: medium, w: weak, sh: shoulder, br: broad)

	Color				
MnL_2Br_3	light yellow	25000 s, sh	22400 w, sh		
FeL_2Br_3	greenish brown	24400 s, sh			18200 br 15350 m
CoL_2Br_3	light green	24400 s, sh	22210 w, sh	21200 m, sh	14300 s
ZnL_2Br_4	light yellow	24400 s, sh	21730 w, sh		15750 w, sh
CdL_2Br_4	light green	24100 s, sh			
$CuLBr_2$	dark reddish brown	24400 s, sh	22200 br 18850 m		16100 br, m, sh

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6) M. Schmidt and H. Schulz, *Chem. Ber.*, **101**, 277 (1968).

TABLE 4. ELECTRONIC SPECTRA OF COMPLEXES (Figures are given in cm^{-1} for wave numbers and log ε for intensities (in parenthese).)

	Broad	Shoulder	Peak	Sharp peak
$LClO_4$	45200 (3.92)	41200 (3.66)	34100 (3.80)	28300 (4.29)
MnL_2Br_3	45200 (4.15)	41200 (3.96)	34100 (4.05)	28250 (4.56)
FeL_2Br_3	44900 (4.38)	41300 (4.20)	34100 (4.20)	28250 (4.66)
CoL_2Br_3	45100 (4.26)	41200 (4.04)	34100 (4.14)	28250 (4.61)
ZnL_2Br_4	45100 (4.26)	41200 (4.05)	34100 (4.16)	28250 (4.61)
CdL_2Br_4	45100 (4.24)	41200 (4.07)	34100 (4.13)	28300 (4.58)
$CuLBr_2$	45100 (3.88)	41200 (3.68)	34100 (3.69)	28300 (4.14)

$L=C_{10}H_9S_2$
Solvent: 35%(volume) ethanol solution of 60% perchloric acid

of bis-(dithiobenzoylacetonato)nickel(II). Moreover, the 3-phenyl-5-methyl-1,2-dithiol-1-ium perchlorate shows a very similar pattern as well, though the absorption in the 1050—1130 cm^{-1} region is not clear because of the overlapped absorption of the perchlorate ion.

From these facts, it can be said that in ML_2X_4-type complexes halogen atoms do not seriously effect the infrared spectra of the dithiolium ion. Therefore, their structure should be isostructural to tetrabromo-bis(3,5-dimethyl-1,2-dithiol-1-ium) complexes,[3] though an X-ray crystallographic study of them is necessary to clarify the structure in detail. By analogy, Cu(I)LBr_2 may have a $(-M-Br-)_n$ chain structure, where one more bromine and probably dithiolium ion bond to each tetracoordinated metal atom.

In the case of ML_2X_3-type complexes, as the central metal atom is bivalent and not abnormally charged, how the charge is distributed in the whole molecule is a problem. One dithiolium ion is

TABLE 5. INFRARED FREQUENCIES OF THE COMPLEXES (cm^{-1})

br=broad, s=strong, m=medium, w=weak, sh=shoulder, $L=C_{10}H_9S_2$. *=absorption by ClO_4^-

$LClO_4$	NiL_2	FeL_2Cl_4	MnL_2Br_3	FeL_2Br_3	CoL_2Br_3	ZnL_2Br_4	CdL_2Br_4	$CuLBr_2$	Tentative assignment
		1593w	1590w	1588w	1588w	1587w	1590w	1585w	aryl
1500w	1470 s	1500w	1495w	1498w	1495w	1490w	1500w		ν(C=C), δ(C-H)
1478 s	1465 s	1475 s	1478 s	1475 s	1475 s	1475w	1480 s	1478 s	
1452m	1445 s	1455w	1455w	1455w	1455w	1455w	1455w	1455 s	
1380w	1360m	1372w	1378w	1370w	1378w	1373w	1383w	1342 1333 br	$\delta(CH_3)$ and others
1340w	1350 s	1340w	1340w	1340w	1340w	1338 br	1338w		
1317w	1298 s	1312w			1305w	1300w	1315w	1311w	ν(C=C)
1255 s	1273m	1258 s	1256 s	1256 s	1257 s	1255 s	1255 s	1250 s	ν(C-R)
1190w	1219m								ν(C=S), or the mix. of them
1170w	1209w								
	1180m								
1150w	1155w	1145m	1148m	1147m	1145m	1146m	1163 1153 m 1145	1145m	aryl
1080 vs* br	1108w	1098w	1098w	1098w	1095w	1095w	1097w	1095w	δ(C-H), ν(C-C) or others
	1073w								
1005w	1025m		1025 br	1020 br	1020 br	1015 br	1020 br	1020w	$\rho(CH_3)$ $\nu(C-CH_3)$
	1018m	1018m							
995w	998m	998m	999m	998m	998m	996m	999m	996m	
			975w	972w	970w	968w	973w		aryl
933m	908m	923 s	927m	925m	925m	923m	927 920 w	921w	
860 s		877 s					880m		
	840m	865 s	865 s	862 s	865 s	860 s	850 835 m	860 s	$\nu(C{=}S)^+$ δ(C-H)
770 s	763 s	760 s	763 s	761 s	760 s	757 s	772 762 s	761 s	aryl or π
	736 s								
685m	690 s	708w	710w	708w	707w	703w	708w		π(C-H)
	677m	675 s	680 s	681 s	680 s	673 s	676 s	675 s	aryl

unipositive, so the other one should be zero valent. The monomer of the free dithio-β-diketone is unstable, and the dimer and the complex containing the dimers, $(Cu^{I}(C_5H_7S_2)Cl)_n$, for example,³⁾ show very different infrared spectra. Judging from this fact, this complex does not contain the dimer.

When the dithiolium complexes are synthesized directly from the dithiolium salt, the formulae of the products of the complexes of these metals are ML_2Br_4 and there is no difficulty in making a bromine analyses of them. Consequently, one dithiobenzoylacetone of the ML_2X_3-type complexes is not a usual dithiolium ion but is more easily hydrolyzed, and the sulfur atoms in it are apt to be isolated as sulfide ions.

As for benzoylacetone adducts, Rosenheim synthesized $SbCl_5(C_{10}H_{10}O_2)$;⁷⁾ the benzoylacetone is zero valent in it. Really the $MLCl_3$-type dithiolium compounds have already been synthesized;⁵⁾ these ML_2Br_3-type compounds may be the adducts of the zero valent dithiole to the $MLBr_3$-type complexes; then the dithiole-type ligand, which is less stable than the dithiolium type in the case of dithiobenzoylacetone, can easily be destroyed.

From these results, the other dithio-β-diketone is probably a 1,2-dithiole derivative, 3*H*-3-methyl-5-phenyl-1,2-dithiole, for example, although the evidence is not decisive. During the process of synthesis the coexistence of the Mn(II), Fe(II), or Co(II) ions in the solution may prevent the perfect oxidation of the ligand to the dithiolium cation.

However, the presence of a uni-negative-valent brominated dithiole ion, for example, cannot be denied completely. Really, such compounds may be easily produced as intermediates of the synthetic process.⁸⁾ The 3-methyl-4-bromo-5-phenyl-1,2-dithiole, for example, should be uni-negative, and its infrared spectra may be expected not to be very different from those of the usual dithiolium ion, as in the case of halogenated acetylacetonates.⁹⁾ On the other hand, if the bromine atom is attached to the 3- or 5-carbon of the ditholium ion, more serious deviations of the infrared spectra may be expected. These brominated dithiolium ions seem to be easily hydrolyzed by water or alcohol.¹⁰⁾ However, as our attempt to synthesize ML_2Br_2-type compounds failed, the presence of the LBr^- ion was not proved.

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7) A. Rosenheim, W. Loewenstamm and L. Singer, *Ber.*, **36**, 1833 (1903).

8) D. Leaver, D. M. McKinnon and W. A. H. Robertson, *J. Chem. Soc.*, **1962**, 5104; **1965**, 32.

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

10) J. Faust and R. Mayer, *Angew. Chem.*, **75**, 573 (1963).