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Halogenation Reaction of Bis(dithioacetylacetonato) Complexes of Cobalt(II) and Nickel(II)[*1]

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Reactions of halogenation reagents with acetylacetonato complexes have already been studied,[1,2] with the successful halogenation of the chelate ring. This reaction is one proof of the aromaticity of the acetylacetonato chelate ring. Thus, the halogenation of dithioacetylacetonato complexes is very interesting, and the chlorination or bromination of $M(L_{SS})_2$ type compounds (where M is Ni(II) or Co(II), HL_{SS} is dithioacetylacetone) prepared by a method given in a previous paper[3] was examined. However, in these cases the products obtained were another type of dithioacetylacetonato complex; *i. e.* $M(L_{SS})_2X_n$.[4,5] The chloro complexes thus obtained were green $M(L_{SS})_2Cl_4$, and the bromo complexes yellow $M(L_{SS})_2Br_6$. All are new compounds. Anlayses and the magnetic moments of these compounds are given in Table 1, IR spectral data between 1800 and 600 cm^{-1} in Table 2 and UV spectra of the methanolic solutions in Table 3. Assignments of the IR spectra are only tentative.[4,8)]

The magnetic moments of these chloro compounds are a little higher than those calculated from the formula $\sqrt{n(n+2)}$. In the case of cobalt(II) complexes, these higher values are rather common for octahedral configurations. Although these higher values are not common in the case of nickel(II) octahedral complexes,[6,7] it is not probable that only the nickel complex has a structure different from the other $M(L_{SS})_2Cl_4$ type complexes.[8] As the general properties of complexes having the same general formula, including IR spectral data, are very similar, the structure of the Ni(II) and Co(II) complexes are as follows (shown in a previous paper[8]): four chlorine atoms are directly bonded to the central metal atom, and two dithiolium[9] ions to the metal as a mono-dentate. Their infrared spectra are very similar to those of usual $M(L_{SS})_2X_4$ type complexes. Although methanol decomposes these complexes into the metal, dithiolium and halogen ions, their methanol solution shows two characteristic peaks in the ultraviolet range due to dithiolium ion produced by solvolysis. The wave

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Table 1. Analyses and magnetic moments of complexes (HL_{SS} means dithioacetylacetone)

	Magnetic moments (B.M.)		Analyses (%)				
			M	C	H	S	X
$Co(L_{SS})_2Cl_4$	4.51	Calc.	12.73	25.92	3.02	27.07	30.69
		Obs.	12.59	25.36	3.05	26.60	29.93
$Co(L_{SS})_2Br_6$	4.40	Calc.	7.36	15.00	1.75	16.00	59.90
		Obs.	7.85	15.40	2.08	17.04	59.50
$Ni(L_{SS})_2Cl_4$	3.81	Calc.	12.72	25.93	3.03	27.07	30.70
		Obs.	13.09	25.50	3.34	26.68	30.22
$Ni(L_{SS})_2Br_6$	3.16	Calc.	7.35	15.00	1.75	16.00	59.91
		Obs.	7.38	14.77	2.02	15.43	59.50

Table 2. Infrared spectra of the complexes

Figures are given in cm^{-1}, HL_{SS} means dithioacetylacetone.

$Fe(L_{SS})_2Cl_4$[4]	$Co(L_{SS})_2Cl_4$	$Co(L_{SS})_2Br_6$	$Ni(L_{SS})_2Cl_4$	$Ni(L_{SS})_2Br_6$	Tentative Assignments
		1600m		1595 s	
1470 s	1480 s	1480 s 1440w	1480 1470 s	1480 s	ν(C=C) + δ(C–H)
1443 1420 m	1410w	1410w	1410w	1410w	$\delta(CH_3)$
1375 1353 s	1365m	1370m	1368m	1370m	$\delta(CH_3)$
1230m	1230w	1237w	1230w	1226w	δ(C–H), ν(C=S)
1200 s	1206 s	1207 s	1203 s	1203 s	$\nu(C{-}CH_3)$ or mixture of them
1093w	1095w	1080w	1073w	1075w	$\rho(CH_3)$
	1015w	1015w	1015w		
1007m	1008 s	1008 s	1010m	1016m	
997m	1000w	995w	1000w	990w	$\nu(C{-}CH_3)$
982w	983w	980w	977w	975w	
	983w	890w	878w	885w	$\nu(C{-}CH_3)$, ν(C=S) or the mixture of them
860 s	863 s	860 s	862 s	865 s	
710w					ring deformation or others
696 s	703m	702m	705m	710m	

δ: bending ν: stretching ρ: rocking s: strong m: medium w: weak

Table 3. Ultraviolet spectra of the complexes dissolved in methanol

(After 30 min at 15°C, 10^{-8}—10^{-5} mol/l)
Figures are given in cm^{-1} for wave numbers and log ε for intensities (in parentheses). HL_{SS} is dithioacetylacetone.

$Fe(L_{SS})_2Cl_4$[4]	$Co(L_{SS})_2Cl_4$	$Co(L_{SS})_2Br_6$	$Ni(L_{SS})_2Cl_4$	$Ni(L_{SS})_2Br_6$	$(L_{SS})ClO_4$[9]
34500	34800	34700	34700	34700	34300
(4.19)	(4.08)	(4.31)	(3.96)	(4.18)	(3.91)
37700	37700	37800	38100	37750	37330
(4.13)	(4.05)	(4.22)	(3.90)	(4.11)	(3.76)

numbers and absorption coefficients of the absorption maxima are very similar to those of dithiolium perchlorate reported in Schmidt's paper.[9] In the visible region only a broad band and a d–d band of the metal ion produced are observed in each case, as is usual for $M(L_{SS})_2X_4$ complexes.[8]

The bromo-complexes thus obtained contain six bromine atoms per metal atom, but from electrovalence consideration,[5] two of them should not be ionic. But it is not a mixture of two compounds, as $M(L_{SS})_2Br_6$ (where M is Ni(II) or Co(II)) is yellow and the analyses and color do not change even after repeated washing with benzene or carbon tetrachloride; on the other hand, $Co(L_{SS})_2Br_4$ is green. All bromine is titrated by the Volhard method in an aqueous nitric acid solution. These compounds oxidize potassium iodide in aqueous acetic acid solution.

In the case of $Co(L_{SS})_2Br_6$, two atoms of bromine react very soon, but the reaction continues even after that and two more atoms of bromine react very slowly at room temperature. In the case of the nickel compound, the reaction is slow from the beginning but about four atoms of bromine per molecule react in a few hours at 20°C. The role of the dithiolium ion must be considered in the oxidation-reduction reaction too. Although dithiolium perchlorate does not liberate iodine from potassium iodide in aqueous acetic acid solution, the salt changes to orange yellow. Then the oxidation-reduction reaction of the complex is not simple, but at least the existence of labile bromine in it is recognized. $M(L_{SS})_2X_4$ complexes do not react with iodide under the same condition.[5)]

These hexabromo complexes decompose rapidly at about 100°C, and slowly even at room temperature. At room temperature, $Co(L_{SS})_2Br_6$ evolves bromine and changes into $Co(L_{SS})_2Br_4$ in several months, but at higher temperatures it loses more, probably due to a second step reaction by evolved bromine. The nickel compound decomposes into bromine and a black product both at room temperature and 100°C. On the other hand, the usual $M(L_{SS})_2X_4$ complexes are far more stable.

The magnetic moments of these hexabromo-complexes are a little lower than those of the corresponding chloro-complexes, as shown in Table 1.

The infrared spectra of these hexabromo-complexes show a sharp peak at about 1600 cm^{-1} but other than that their general features are almost the same as those of usual $M(L_{SS})_2X_4$ type complexes; the ν(C=C) band near 1480 cm^{-1} also appears. (In the case of acetylacetonates, the ν(C=C) band near 1500 cm^{-1} disappears through halogenation though other parts of the spectra do not change seriously.[2)]) The electronic spectra of their methanol solutions are almost the same as the usual tetrahalogeno complexes.

From these observations, although the two excess bromine atoms may bond to γ-carbon of the chelate or to β-carbon as proposed by Knauer in the case of $Fe(L_{SS})_2Cl_4$,[5)] the bonds are very weak. Then it is reasonable to assume that these compounds are adducts of Br_2 to $M(L_{SS})_2Br_n$.

Milder halogenation reactions using *N*-chlorosuccinimide or *N*-bromosuccinimide were also tried with nickel(II) or cobalt(II) dithioacetylacetonate. Some adducts containing these reagents precipitated immediately, and from the filtrate, tetrachlorobis(dithioacetylacetonato)-cobalt(II) was obtained. But from the cobalt(II) complex and NBS or from the nickel complex and NCS or NBS, the products obtained by the same process were contaminated with the adduct of NXS, and the pure product was hardly obtained.

When solid mixture of sodium borohydride and halogeno complexes were treated with a little water, the starting $M(L_{SS})_2$ type complexes (where M=Co(II) or Ni(II)) were obtained. The yield was about 30%. These products were identified through their analyses, IR spectra and UV spectra of the methanolic solutions. This method is a new convenient synthesis of dithio-β-diketonato complexes.

Experimental

IR spectra were obtained through the nujol and hexachloro-1,3-butadiene mull procedure, using a DS 301 type infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. Ultraviolet spectra were obtained with a Hitachi EPS-2 Spectrophotometer. Magnetic susceptibility measurements were carried out with a Gouy's balance at room temperature (15°C).

Synthesis of Tetrachlorobis (dithioacetylacetonato)nickel(II). Five hundred milligrams (1.56 mmol) of bis(dithioacetylacetonato) nickel(II) was suspended in 20 m*l* of carbon tetrachloride, and chlorine gas was bubbled in while stirring and cooling with ice. A green precipitate was obtained. The product was washed with carbon disulfide, chloroform, carbon tetrachloride and petroleum ether in that order. Recrystallization was not successful. The reaction was almost quantitative and the yield was 700 mg (1.52 mmol).

Other compounds were obtained by almost the same method.

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