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Syntheses and Properties of Some Dithio-β-diketonato Complexes[*1]

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Some compounds of type $M(L_{SS})_2$, where M is Ni(II) or Co(II) and HL_{SS} is some dithio derivative of β-diketones (benzoylacetone, trifluoroacetylacetone, trifluorobenzoylacetone or dibenzoylmethane), were obtained by passing hydrogen chloride and hydrogen sulfide into ethanol solutions containing β-diketone and metal chloride. Such compounds seem to be isostructural to the bis(dithioacetylacetonato) complexes and are stable. They are all deeply colored and their solutions show a characteristic absorption in the visible region, 16700 cm^{-1} for bis(dithiobenzoylacetonato)nickel(II) and 15200 cm^{-1} for bis(dithiodibenzoylmethanato)nickel(II). On the other hand, infrared spectra of these complexes show ν(C=S) bands at 1220—1240, 1170—1180 and 840 cm^{-1}. $M(L_{SS})_2Cl_4$ type complexes (where M=Fe(II) or Co(II) and HL_{SS}=dithiobenzoylacetone) were also obtained and they seem to be isostructural to $Fe(C_5H_7S_2)_2Cl_4$. Their magnetic susceptibilities and electronic and infrared spectra are shown and discussed.

The dithio-derivatives of acetylacetonato complexes were previously synthesized[1-5] and they seem to have very interesting properties. Recently, the present authors reported the syntheses of the dithioacetylacetonato complexes of various metals and found that (1) there are two kinds of dithioacetylacetonato complexes the $M(L_{SS})_2$ type and the $M(L_{SS})_2Cl_4$ type,[4] (2) in the case of nickel complexes of thio-derivatives of acetylacetonates, there is a regular change in the wave numbers of infrared and visible spectra from $Ni(C_5H_7SO)_2$ *via* $Ni(C_5H_7S_2)(C_5H_7SO)$ to $Ni(C_5H_7S_2)_2$.[3] As these compounds have characteristic absorption bands in infrared spectra as well as in electronic spectra owing to the metal-sulfur bond and the pseudo-aromaticity of their chelate ring, an investigation of the same type of complexes of other dithio-β-diketones, comparing them with the dithioacetylacetonates, should be interesting.

The dithio-β-diketonato complexes of nickel(II) were obtained using benzoylacetone, trifluoroacetylacetone, trifluorobenzoylaceton and dibenzoylmethane in the same manner as the synthesis of dithioacetylacetonates from acetylacetonates. However, the dithio-derivatives of hexafluoroacetylacetone, ethylacetoacetate and methylacetoacetate could not be obtained by the same method, being too unstable. In the case of monothio-β-diketonato complexes of nickel(II), the wavelength of the visible absorption spectral band of thioethylacetoacetate is longer than that of the monothio-derivative of acetylacetonate, although both can be synthesized.[6] In the case of the nickel complexes of dithio-β-diketones, the longer the wavelength of the above band, the less stable the complex. Perhaps this fact is related to the instability of these complexes.

[*1] This peper was presented at the 17th Symposium on Coordination Chemistry, Hiroshima, December, 1967.

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4) A. Furuhashi, K. Watanuki and A. Ouchi, *ibid.*, **46**, 110 (1968).

5) R. Beckett and B. F. Hoskins, *Chem. Commun.*, **1967**, 909.

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Experimental

Materials and Instruments. Starting materials of GR grade were used without further purification. Infrared spectra were obtained with a potassium disc using Japan Spectroscopic Co., Ltd.'s, DS 403 G infrared spectrophotometer. Electronic spectra were obtained with a Hitachi EPS-2 automatic recording spectrophotometer. Magnetic moments were measured with a Gouy balance at room temperature (15°C).

Synthesis of Bis(dithiotrifluoroacetylacetonato)nickel(II). One and three tenth grams (0.01 mol) of anhydrous nickel(II) chloride and 3.1 g (0.02 mol) of trifluoroacetylacetone were dissolved in 20 m*l* of absolute ethanol. Into the clean, green solution, hydrogen chloride gas was bubbled for 30 min, then hydrogen sulfide for one hour. The solution was allowed to stand for one day at about 0°C. The black precipitate obtained was recrystallized from benzene and dried in vacuum. The yield was about 2.1 g (25% calculated for nickel(II) chloride).

Synthesis of Bis(dithiotrifluoroacetylacetonato)cobalt(II). This complex was obtained by almost the same method as the corresponding nickel(II) complex. As it is fairly soluble in ethanol, 5 m*l* of ethanol was enough par 0.01 mol of cobalt chloride. The yield was only about 15%.

Synthesis of Bis(dithiotrifluorobenzoylacetonato)nickel(II). The crude compound, obtained by the same method as was used for dithiotrifluoroacetylacetonates, contains by-products. The main impurity seems to be the dimer of dithio-β-diketone, but dithiolate salts may also be present. Repeated recrystallization was carried out with a mixture of chloroform and petroleum ether. The chromatographic method may also be applied to purification. The yield was about 30% or less due to loss in the recrystallization process.

Synthesis of Bis(dithiobenzoylacetonato)nickel(II). The crude complex, prepared in a manner similar to the above, was purified by the column chromatography. Alumina column chromatography, using benzene as the eluent, was effective. The yield was about 30%. Bis(dithiodibenzoylmethanato)nickel(II) was also synthesized by the same method as was used in the synthesis of dithiobenzoylacetonate. The yield was less, about 20%.

Synthesis of Bis(dithiobenzoylacetonato)cobalt(II) Tetrachloride and Bis(dithiobenzoylacetonato)iron(II) Tetrachloride. The method of synthesizing the dithio-β-diketonato complex was applicable, using anhydrous cobalt(II) chloride or ferric chloride as the source of metal salts, respectively. Analytically pure products precipitated from the mother liquor, and chromatographic separation was not necessary. The yield was 30% and 42%, respectively (calculated for the metal salts).

Results and Discussion

Analytical data and the magnetic moments of these compounds are summarized in Tables 1 and

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

		Metal	C	H	S	Cl
$Ni(sbzsac)_2$	Calcd	13.18	53.94	4.07	28.80	
	Found	12.75	53.97	4.19	29.10	
$Co(sbzsac)_2Cl_4$	Calcd	10.03	40.90	3.09	21.84	24.14
	Found	10.36	40.96	3.37	22.50	24.50
$Fe(sbzsac)_2Cl_4$	Calcd	9.56	41.11	3.11	21.95	24.27
	Found	9.95	40.73	3.15	22.40	24.70
$Ni(sbzsbz)_2$	Calcd	10.31	63.27	3.89	22.52	
	Found	10.10	62.39	4.54	22.60	
$Ni(sfasac)_2$	Calcd	13.68	27.99	1.88	29.89	
	Found	12.90	27.98	1.37	30.07	
$Co(sfasac)_2$	Calcd	13.73	27.98	1.88	29.87	
	Found	13.50	27.72	1.72	30.10	
$Ni(sfasbz)_2$	Calcd	10.61	43.42	2.18	23.18	
	Found	10.56	43.15	2.20	23.50	

sbzsac=dithiobenzoylacetone ($C_{10}H_9S_2$)
sbzsbz=dithiodibenzoylmethane ($C_{15}H_{11}S_2$)
sfasac=dithiotrifluoroacetylaetone ($C_5F_3H_4S_2$)
sfasbz=dithiotrifluorobenzoylacetone ($C_{10}F_3H_6S_2$)

Table 2. Magnetic moment of complexes (Figures are given in B. M. per 1 mol of metal.)

$Ni(sbzsac)_2$	diamagnetic	$Co(sfasac)_2$	1.34
$Ni(sbzsbz)_2$	diamagnetic	$Co(sbzsac)_2Cl$	4.12
$Ni(sfasac)_2$	diamagnetic	$Fe(sbzsac)_2Cl_4$	5.10
$Ni(sfasbz)_2$	diamagnetic		

* Refer to Table 1 about the abbreviations in this table.

TABLE 3. INFRARED FREQUENCIES OF THE DITHIO-β-DIKETONATO COMPLEXES (cm^{-1})

s=strong, m=medium, w=weak, sh=shoulder, L$_{SO}$=(C$_5$H$_7$SO), L$_{SS}$=(C$_5$H$_7$S$_2$). Refer to Table 1 for the abbreviations of the names of the complexes.

Ni(L$_{SO}$)$_2$	Ni(L$_{SO}$)(L$_{SS}$)	Ni(L$_{SS}$)$_2$	Ni(sbzsac)$_2$	Ni(sbzsbz)	Ni(sfasac)$_2$	Co(sfasac)$_2$	Ni(sfasbz)$_2$	Fe(L$_{SS}$)$_2$Cl$_4$	Fe(sbzsac)$_2$Cl$_4$	Co(sbzsac)$_2$Cl$_4$	Tentative assignments
1567(s)*	1558 s*						1595 w		1593 w	1593 w	aryl, *=ν(C=O)
$\left.\begin{matrix}1480\\1476\end{matrix}\right\}$ s	1490 s	1495 s	1470 s 1465 s	1471 s 1448 s	1505 s 1490 s	1490 s	1490 s	1470 s	1500 w 1475 s	1500 w 1475 s	ν(C=C), δ(C-H)
$\left.\begin{matrix}1445\\1440\\1430\end{matrix}\right\}$ m	$\left.\begin{matrix}1425\\1415\end{matrix}\right\}$ m	1433 w	1445 s			1440 w	1450 s	$\left.\begin{matrix}1430\\1420\end{matrix}\right\}$ s	1455 w		δ(CH$_3$)
1375m 1340m	1360m 1340m	1353m	1360m 1350 s	1347m	1363m 1340w	1363m 1340w	1390m	1375 s 1353 s	1372w 1340m	1350w 1340m	δ(CH$_3$) and others
	1312w 1294w	1314m 1290m	1298 s 1273m	1295 s 1282m	1302 s	1303 s	1295 s		1312w	1303m	ν(C=C), ν(C-R)
1235 s	1232 s 1162 s	1154 s	1219m 1209w 1180m	1223 s 1175m	1237 s 1170 s	1234 s 1170 s	1240 s 1212w 1170 s	1230m 1200 s	1258 s 1218w	1257 s 1220m	ν(C=S), δ(C-H) ν(C-C) or the mix. of them
1120m	1125w 1115w		1155w 1108w 1073w	1155w 1100w 1074m	1142 s 1135 s 1118 s	1138 s 1120 s	1145 s 1110 s	1073w	1145m 1098m	1145m 1110w 1100m	ν(C-F) and others
1170m 987w 937w*	1015m 937w*	1013m	1025m 1018m 998m** 908m	1028w 999m** 965w 945m 922w 905m	1010w 928 s	1015w 928 s	1030m 1000m** 965 s 920w	1007m 997m 982w	1018m 998 s** 923 s	1013m 988 s** 922 s	ρ(CH$_3$) and others; *, ν(C-CH$_3$); **, aryl
815 s 810 s	831 s 810 s	841 s	840m	840m	848 s	845 s	850 s 825w	860 s	877 s 865 s	878 s 860m	ν(C=S)
723 s 667m 647m $\left.\begin{matrix}501\\494\end{matrix}\right\}$ m 420w	748m 727m 712w 656m 553m 522m 498m 422w	749m 705w 558 s 422w	763 s 736 s 690 s 677m 633m 525m 458w	753 s 730w 692 s 655m 618w 560w 493w 420w	765 s 712w 695 s 650m 565w 538w 481m	763 s 695 s 648m 565w 539w 490m	750 s 695 s 646m 618w 602w 592m 563w 548 s 478w 447w	710w 696 s 573w 557 s 523w 459w 431 s 422w	760 s 708m 675 s 638w 600w 559w 508m	760 s 708m 676 s 637m 600w 560m 508m 444m	π, aryl ring and others

Table 4. Electronic spectra of the dithio-β-diketonato complexes (cm^{-1} (log ε))
br=broad, sh=shoulder. Refer also to Table 1 for the abbreviations of the names of the complexes.

$\mathrm{Ni(L_{SO})_2}$	$\mathrm{Ni(L_{SO})(L_{SS})}$	$\mathrm{Ni(L_{SS})_2}$	$\mathrm{Ni(sbzsac)_2}$	$\mathrm{Ni(sbzsbz)_2}$	$\mathrm{Ni(sfasbz)_2}$	$\mathrm{Ni(sfasac)_2}$	$\mathrm{Co(sfasac)_2}$	$\mathrm{Fe(L_{SS})_2Cl_4}$		$\mathrm{Fe(sbzsac)_2Cl_4}$	$\mathrm{Co(sbzsac)_2Cl_4}$		
Methanol	Methanol	Methanol	Methanol	Benzene	Benzene	Methanol	Methanol	(Reflectance)	Methanol	Methanol	Benzene	Methanl	Solvent
	49000 (4.38)												Tentative assign-ment
	41600 (4.14)	41300 (4.18)	39060 (4.28)						37700 (4.13)	39700 (4.60)		39700 (4.27)	π-π
39700 (4.29)	38500 (4.40)					37040 (4.71)	37040 (4.65)						
37100(sh) (4.03)	37300 (4.40)	36900 (4.53)	33550 (4.34)	31530 (4.40)	32800 (4.42)				34500 (4.19)	34500 (3.93)	33200 (3.62)	34900 (3.92)	
32300 (4.03)	30400 (4.23)	29700 (4.30)	28740 (4.34)	27400 (4.62)	27200 (5.57)	29600 (4.03)	29600 (4.31)	30300					π-π or d-π
26800 (3.53)								27700	27400 (2.19)	28260 (3.72)	28590 (3.35)	28360 (4.30)	
								25300					
22500 (3.37)	22600 (3.34)	23800(sh) (3.55)	23000 (3.62)			23250(sh) (3.37)	23250(sh) (3.37)	21000(br)	21720(br) (2.07)	20000(br) (2.64)	22720(sh) (2.59)	20210(br) (2.69)	
18900 (2.94)	21300 (3.35)	20900 (2.92)		21360(sh) (3.91)	21730(sh) (3.52)								
		17850 (3.54)						17850(vw)					d-d or d-π or mix. of them
	16380 (2.82)		16660 (3.02)			16800 (3.17)	16800 (3.19)		16650(sh) (1.71)		16660 (2.08)		
15400 (2.29)				15200 (3.30)	15110 (3.28)								

2, respectively. The relevant infrared frequencies of these complexes are shown in Table 3, and the wave numbers of their electronic spectra in Table 4 together with those of some related compounds.

From the magnetic moment data, the $M(L_{SS})_2$ type compounds are all low spin types; the nickel(II) complexes are all diamagnetic and the cobalt(II) complex has about one unpaired electron. This result is the same as that for the bis(dithioacetylacetonato) complexes, and these compounds would also have a planar structure as was the case of bis(dithioacetylacetonato)cobalt (II), which was found through X-ray crystallographic analysis.[5] The $M(L_{SS})_2Cl_4$ complexes are high spin octahedral types, as bis(dithioacetylacetonato)iron(II) tetrachloride, although the exact structure has not yet been determined.[2,4]

The general features of the spectra of these complexes resemble those of the acetylacetonates and dithioacetylacetonates, except for many additional bands due to the introduction of a phenyl or trifluoromethyl group. The tentative assignments given in Table 3 were made by referring to the acetylacetonates.

Sometimes, the compounds containing phenyl groups show a sharp weak band near 1590 cm^{-1}, but the band is different in shape from the ν(C=O) band; perhaps it is a skeletal inplane vibration band of the benzene ring.

The ν(C=S) bands of these compounds appear near 1220—1240; 1170 and 840—850 cm^{-1} in the case of $M(L_{SS})_2$ type compounds.

Thioacetylacetonato complex, $Ni(L_{SS})(L_{SO})$, also exhibited three ν(C=S) at 1232, 1162 and 830 cm^{-1}. On the other hand, those of bis(dithioacetylacetonato)nickel(II) and cobalt(II) appear near 1160 and 840 cm^{-1} only. This fact seems to indicate that the C=S bond character of the $M(L_{SS})_2$ complexes resemble those of $M(L_{SS})(L_{SO})$ type compounds, and there are two kinds of C=S bonds in these complexes; one sulfur atom may at least be more weakly bonded to the central metal atom than the other. Thus the chelate ring of the complexes now investigated may be more or less deformed, although it has been reported from X-ray crystallographic analysis that bis(dithioacetylacetonato)cobalt(II) has four identical Co–S bonds.[5]

The infrared spectra of bis(dithiobenzoylacetonato)cobalt(II) (or iron(II)) tetrachloride have ν(C=S) bands near 1257 and 870 cm^{-1}, as bis(dithioacetylacetonato-iron(II) tetrachloride. Generally, the infrared spectra of these three complexes resemble one another, and they seem to be isostructural.

The intensities of the visible region bands of these compounds are very strong compared with those of the corresponding β-diketonato complexes, as in the case of the thio-derivatives of acetylacetonates. From a comparison of the spectra of these complexes with those of the acetylacetonates,[7,8] tentative assignments are given in Table 4. The band near 16000 cm^{-1} of $M(L_{SS})_2$ type complexes may be taken as the d-d band from the wave number, but as its intensity is too high, it seems to be d-π band or at least a mixture of d-d and d-π bands.

The wave number of this band of nickel complexes of dithiotrifluoroacetylacetone and dithiobenzoylacetone is about 16800 cm^{-1}, and that of the dithiodibenzoylmethanato and dithiotrifluorobenzoylacetonato complexes about 15200 cm^{-1}.

On the other hand, the wavelengths of the bands of the series of thioacetylacetonatonickel(II) complexes are as follows; 17850 for bis(dithioacetylacetonate), 16380 for monothioacetylacetonatodithioacetonate and 15400 for bis(monothioacetylacetonato) (cm^{-1}).

From a comparison of the spectra of these two series of complexes, it is deduced at least that the substitution of trifluoromethyl or phenyl groups into the dithioacetylacetone chelate in place of methyl groups has the same effect as the substitution of sulfur by oxygen. Although the intensity of the band is almost the same in these substituted dithio-β-diketonato complexes, that of the oxygen substituted complexes is lowered when the number of oxygen atoms is increased.

These facts may be explained as follows. The introduction of oxygen into the chelate decreases the electron density of the six membered ring to some extent since the oxygen atom bonds to the central metal atom in a pure coordination bond. Thus, the sulfur-metal bond of the chelate ring is weakned. In the same way, the substitution of the methyl group of the acetylacetonato chelate with a phenyl or trifluoromethyl group also decreases the electron density of the ring by withdrawing electrons to the group. As a result, the electronic energy levels of these two series of compounds, as well as the wave numbers of the d-π band, should resemble each other.

From the absorption coefficients of the complexes of both series, back donation seems to be possible only from the central metal to sulfur, and not to oxygen in these chelate rings.

A benzene solution of bis(dithiobenzoylacetonato)-cobalt(II) tetrachloride shows a similar spectrum as the $M(L_{SS})_2$ type complexes; a band at 16660 cm^{-1} appears, although the intensity of this band is only one tenth that of $M(L_{SS})_2$ type complexes. This band does not occur in an alcoholic solution of the same complex. This fact suggests that the compound does not have simple ionic bonding between the tetrachloroiron(II) anion and the dithiolium cation, but has a kind of coordination bond between them. In alcoholic solution, as well as in aqueous solution, this complex seems to decompose into a

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[8] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221; **22**, 183 (1961).

solvated metal ion and dithiolium ion, as is found from the absorption spectra.

To confirm the structure definitely, further investigation, especially X-ray analysis, is necessary, and is now going on in our laboratory.

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