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Syntheses and Properties of Some Thio Derivatives of Acetylacetonato-nickel(II)*[1]

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Derivatives of acetylacetonato-nickel(II) in which the coordinating oxygen is replaced by sulfur to various extents have been isolated by the reaction between nickel(II) acetylacetonate and hydrogen sulfide in an ethanolic solution, using hydrogen chloride as the catalyst. These compounds are soluble in organic solvents, such as benzene, acetone, or carbon tetrachloride, but can hardly be dissolved in water. The proton magnetic resonance spectra indicate that the proton of the methyl group attached to the C=S carbon gives greater chemical shifts than that of the methyl group attached to the C=O carbon. The infrared spectra of these compounds are discussed with particular reference to the C=S stretching bands. The electronic spectra of these compounds and the Hückel LCAO-MO calculation of bis dithio compounds are also compared.

Although the syntheses of bis-monothio derivatives[1)] and bis-dithio derivatives[2)] of nickel(II) acetylacetonate have already been described, little information on the properties of such thioacetylacetonates has been published. It seemed very interesting to the present authors to study how the properties change when the oxygen atoms of the ligands are replaced with sulfur. The electronegativity of sulfur is less than that of oxygen, being almost equal to that of carbon; the thio derivatives may thus have properties such as those of organometallic compounds. The nickel(II) acetylacetonate has a trimeric structure[3)] and is paramagnetic, but the thio derivatives are diamagnetic and seem to have square planar structures. To study the effect of the replacement of oxygen by sulfur, a mixed complex, monothioacetylacetonatodithioacetylacetonatonickel(II), has been synthesized, besides bis(monothioacetylacetonato) nickel(II) and bis(dithioacetylacetonato) nickel(II), The comparison of the properties of these compounds gave a considerable amount of information as to the properties of the sulfur-containing ligands described below.

Experimental

Materials. The chemicals were of GR quality and were used without further purification. Hydrogen sulfide was obtained by the reaction of CP-grade iron sulfide and CP-grade hydrochloric acid, washed with water, and dried with calcium chloride. Hydrogen chloride was obtained by the reaction of sodium chloride and sulfuric acid and was dried with concentrated sulfuric acid.

Instruments. The infrared spectra were obtained by the KBr disc procedure, using a DS 403G type infrared spectrophotometer of Japan Spectroscopic Co., Ltd. The proton magnetic resonance spectra were obtained by a Varian model HA 100 instrument. The electronic spectra were obtained by a Hitachi EPS-2 Automatic Spectrophotometer.

Syntheses of Compounds. *Bis(monothioacetylacetonato)nickel(II).* Three and six-tenths grams (0.0152 mol) of nickel(II) chloride hexahydrate were dehydrated by direct heating. The anhydrous chloride and 2.40 m*l* (0.0235 mol) of acetylacetone were then mixed with 100 m*l* of absolute ethanol and refluxed for 1 hr. The clean green solution thus obtained was used as the starting solution for the syntheses of the three compounds; it will be named "solution A" in this paper.

To "solution A" were added first hydrogen chloride for one minute; then, slowly, hydrogen sulfide for 30 min, and finally hydrogen chloride for one more minute.

The solution thus obtained gave no precipitate immediately after the operation, but after the solution had stood for one day at room temperature, a dark brown precipitate appeared. The product was washed with petroleum ether to remove any impurities and then dried in a vacuum. The yield was about 20% (calculated from nickel(II) chloride). Recrystallization was carried out by using a mixture of petroleum-ether and acetone. This product gave the same infrared spectra as that obtained by Lockyer's method using monothioacetylacetone and nickel(II) acetate.[1)]

Monothioacetylacetonatodithioacetylacetonato Nickel(II). Hydrogen chloride was passed through "solution A" for 3 min. A pale green precipitate (perhaps bisacetylacetonato nickel(II)) appeared. Hydrogen sulfide was then passed for 1.5—2 hr through the stirred mixture obtained above. A black crystalline precipitate was thus obtained. The product was washed with ethanol to remove the monothio derivative

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*[1] This paper was presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967.

1) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer and V. A. Pickles, *Aust. J. Chem.*, **18**, 1927 (1965).

2) L. Martin and I. M. Stewart, *Nature*, **210** (5065), 522 (1966).

3) G. J. Bullen, R. Mason and P. Pauling, *ibid.*, **189**, 291 (1961); *Inorg. Chem.*, **4**, 456 (1965).

and other impurities, and dried in a vacuum. The yield was about 55% (calculated from nickel(II) chloride). It was recrystallized with benzene.

Bis(dithioacetylacetonato)nickel(II). When hydrogen chloride was passed through "solution A" for 2 hr, a yellow precipitate was produced. Hydrogen sulfide was passed through a stirred mixture of the precipitate and the mother liquor for 2—4 hr (or longer, if necessary). The product thus obtained was washed with water, and the insoluble black powder was dried. The dried material was washed with ethanol and then with petroleum ether. The product was finally dried in a vacuum; the yield was about 35% of nickel(II) chloride. It was recrystallized from benzene or chloroform.

Results and Discussion

The analytical data for these compounds are given in Table 1, the proton magnetic resonance data, in Table 2 and some significant features of the infrared and electronic spectra, in Tables 3 and 4.

TABLE 1. ANALYSIS OF COMPLEXES
(Figures are given in %.)

		$Ni(C_5H_7SO)_2$	$Ni(C_5H_7SO)\cdot(C_5H_7S_2)$	$Ni(C_5H_7S_2)_2$
Ni	Calcd	20.31	19.27	18.28
	Found	20.09	19.16	18.14
C	Calcd	41.55	39.36	37.40
	Found	41.06	39.48	37.35
H	Calcd	4.88	4.62	4.39
	Found	4.79	4.76	4.50
S	Calcd	22.19	31.52	39.93
	Found	23.20	31.53	39.68
O	Calcd	11.07	5.24	0.00
	Found	—	—.	—

TABLE 2. PROTON MAGNETIC RESONANCE SPECTRA OF COMPLEXES

	Signals, ppm				Ratio of the areas of signals
	1st group		2nd group		
$Ni(C_5H_7SO)_2$	1.94	2.06	6.18		3 : 3 : 1
$Ni(C_5H_7SO)\cdot(C_5H_7S_2)$	2.03	2.27	6.33	7.30	3 : 9 : 1 : 1
$Ni(C_5H_7S_2)_2$		2.37		7.22	6 : 1
Tentative assignment	Methyl protons		Vinyl protons		

The magnetic susceptibility was measured by Gouy's balance at room temperature (15°C). All of the three compounds are diamagnetic, although the acetylacetonato nickel(II) is paramagnetic. This fact suggests that our three thio compounds all have planar structures.

The proton magnetic resonance spectra of these compounds are shown in Table 2. The assignments were obtained from the values of the chemical shifts and the areas of the peaks.

The peak at about 7 ppm is that of the vinyl proton; the existence of this peak shows that the chelate of these thio-derivatives is also in the enol form; if it were in the keto form, the chemical shift would be smaller and the area would be larger.

The peak at about 2 ppm is that of the methyl proton. This peak splits into two in the cases of the bismonothioacetylacetonate and the monothioacetylacetonatodithioacetylacetonate; the ratio of the areas of the two peaks is 1 : 1 in the former case and 3 : 1 in the latter. These facts show that the split of the peak is due to the effect of the

TABLE 3. INFRARED SPECTRA OF COMPLEXES
Figures are given in cm^{-1}.
$L_{SS}=(C_5H_7S_2)$, $L_{SO}=(C_5H_7SO)$
s=strong, m=medium, w=weak and sh=shoulder

$Ni(L_{SS})_2$	$Ni(L_{SS})(L_{SO})$	$Ni(L_{SO})_2$	$Ni(L_{OO})_2$	Tentative assignments
	1558(s)	1567(s)	1598	ν(C=O)
1495(s)	1490(s)	1480(s)	1514	ν(C=C)+δ
		1476(s)		
		1445(m)	1453	ν(C=C)+δ
		1440(m)		
1433(w)	1425(m)	1430(m)		
	1415(m)	1420(m)		
1353(m)	1360(m)	1375(m)	1398	$\delta(CH_3)$
	1340(m)	1340(m)	1367	
1314(m)	1312(w)	—	1261	ν(C=C)+δ
1290(m)	1294(w)	—		$\nu(C-CH_3)$
	1232(s)	1235(s)	—	ν(C=S), δ(C-H)
1159(s)	1162(s)		1198	
	1125(w)	1120(m)		
	1115(w)			
1013(m)	1015(m)	1017(m)	1020	$\rho(CH_3)$
		987(w)		
	937(w)	937(w)	927	$\nu(C-CH_3)$ ν(C=O)
841(s)	831(s)	815(s)	—	ν(C=S)
	802(s)	810(s)		
749(m)	748(m)		764	π(C-H)
	727(m)	723(s)		
705(w)	712(w)			
	656(m)	667(m)	666	Ring δ+ ν(M=O)
		647(m)		
558(s)	553(m)		579	
			563	π
	522(w)	501(m)		
	498(m)	494(m)		
422(w)	422(w)	420(w)	427	π

sulfur or the oxygen atom bonded to the carbon to which the methyl group is attached. If it were the effect of the vinyl proton, the pair of peaks would always have the same area.

The more sulfur atoms are introduced in the compounds, the greater are the chemical shifts which appear for both vinyl proton and methyl proton peaks. This seems to indicate that the thio derivatives have more reactive hydrogen than acetylacetonate attached to 3-carbon.

The infrared spectra of these compounds are shown in Table 3. They are similar to that of the acetylacetonate in many points; tentative assignments are, therefore, given with reference to those of the acetylacetonate given by Nakamoto *et al.*[4]

The ν stretching bands (C=S) have a tendency to mix with other vibrations.[5] It is not, therefore, easy to assign ν(S=C) bands. Livingstone *et al.* assigned the bands at 1235(S) and 815(S) cm^{-1} to the ν(C=S) for the monothioacetylacetonates.[1] If this is correct, the ones at 1162(S) and 841(S) cm^{-1} should be the ν(C=S) bands of bisdithioacetylacetonate. In fact, both kinds of peaks can be recognized in the spectra of monothioacetylacetonate and dithioacetylacetonate. The difference in the wave number is very extensive; this is because these peaks are not those of pure ν(C=S) vibrations, but are mixtures, and because the grade of mixing is not the same in both cases.

The peak near 1600 cm^{-1} disappeared in the case of bisdithioacetylacetonate, but that near 1500 cm^{-1} did not. On the other hand, the existence of a C=C double bond can be assumed from the proton magnetic resonance data. Therefore, the 1600 cm^{-1} peak should be ν(C=O), and the one near 1500 cm^{-1}, ν(C=C), although both of them may be mixed with other vibrations. The ν(M-O) bands of acetylacetonato nickel(II) or oxygen-containing thio derivatives appear at about 666 cm^{-1}, but this band disappears in the case of the bis dithio derivative.

The data on the electronic spectra are shown in Table 4. The intensities of the bands in the visible region of these compounds are very strong compared with that of acetylacetonato nickel(II), as in the case of thio-thenoyltrifluoroacetone chelates.[6]

TABLE 4. ELECTRONIC SPECTRA OF COMPLEXES IN METHANOL SOLUTION

Figures are given in cm^{-1} for wave numbers and log ε for intensities (in parantheses).

Ni(L_{SS})$_2$	Ni(L_{SO})(L_{SS})	Ni(L_{SO})$_2$	Ni(L_{OO})$_2$	Cu(L_{OO})$_2$
	49000 (4.38)		49100 (3.38) 44200 (3.04)	49700 (4.20)
41300 (4.18)	41600 (4.14) 38500 (4.40)	39700 (4.29)	39300 (3.22)	40700 (4.22)
36900 (4.53)	37300 (4.40)	37100(sh) (4.03)	33800 (3.50)	33700 (4.37)
29700 (4.30)	30400 (4.23)	32300 (4.03) 26800 (3.53)	32700 (3.40) 25900(sh) (3.21)	32800(sh) (3.60)
23800 (3.55)	22600 (3.44)	22500 (3.37)		
20900 (2.92)	21300 (3.35)	18900 (2.94)		17900 (1.00)
17850 (3.54)	16380 (2.82)	15400 (2.29)	15600 (0.21)	14950 (1.15)
14300 (2.17)				

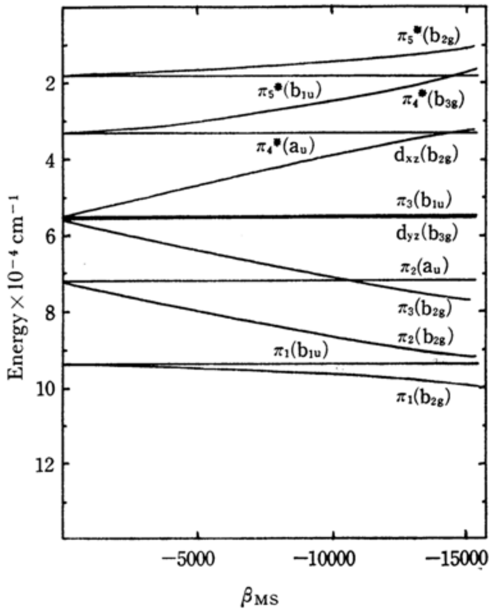

Fig. 1. Effect of metal-sulfur π-bonding on energy levels of Ni($C_5H_7S_2$)$_2$.

From the comparison of the spectra of these compounds with those of copper acetylacetonate and other acetylacetonates, these spectra were assigned as below. However, since the assignment of the spectra of the acetylacetonate still has some problems, the assignments given here must be regarded as only tentative ones. Thus, the bands at 33,000—36,000 cm^{-1} are assigned to $\pi \rightarrow \pi$ bands, and that at ~40,000 cm^{-1} seems to be a

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[4] K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y. (1963), p. 217.

[5] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curram and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

[6] E. W. Berg and K. P. Reac, *Anal. Chim. Acta*, **36**, 372 (1966).

$\pi\rightarrow d$[7], or a $\pi_3\rightarrow\pi_4{}^*$[8] charge transfer band. Although there have been many discussions about the 20,000—27,000 cm^{-1} bands, they are thought to be charge transfer bands of some kind. The band at 17,000 cm^{-1} is identified as a d-d band.

The Hückel LCAO-MO calculations were applied to bis(dithioacetylacetonato) nickel(II) using the method of J. P. Fachler, Jr. *et al.*[7] and adopting the value of $\chi_s=2.50$, $U(\text{C=S})=128$ kcal/mol, and $U(\text{C-S})=65$ kcal/mol.

The values of the parameters obtained are: $\alpha_M=-55{,}170$ cm^{-1}, $\alpha_A=-54.050$ cm^{-1}, $\alpha_B=-55{,}950$ cm^{-1}, $\alpha_C=-56{,}250$ cm^{-1}. $\beta_{CS}=-22{,}040$ cm^{-1}, $\beta_{CC}=-22{,}100$ cm^{-1}, where the symbols have the same meaning as in Ref. 7.

The energy levels calculated are shown in Fig. 1. From these figures the energy splittings are found to be: $\pi_3(b_{2g})\rightarrow\pi_4(a_u)$ 37,500 cm^{-1}, $\pi_3(b_{1u})\rightarrow\pi_4(b_{3g})$ 30,000 cm^{-1}, if $\beta_{MS}=10{,}000$ cm^{-1} is assumed. The bands observed at 36,900 cm^{-1} and at 29,700 cm^{-1} thus seem to correspond to the above two transitions.

To confirm the structure decisively, further investigation, especially using an X-ray technique is necessary; these further studies are now going on in our laboratory.

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7) J. P. Fackler, Jr., F. A. Cotton and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

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