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A Novel Method of Preparation of Bis(dithiobenzoylacetonato)Zn(II)

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When methyliodide and water were added to sodium phenylpropiolthioanilide suspended in ether, C-methylation and C–N bond rupture occurred at the thioamido group. S-[1-Phenyl-2-(thioacetyl)vinyl]isothiuronium *p*-toluenesulfonate was obtained by adding thiourea and *p*-toluenesulfonic acid to the ether phase. This salt did not give a free ligand, dithiobenzoylacetone, but produced a zinc chelate, bis(dithiobenzoylacetonato)-Zn (II) by adding aqueous Zn^{2+} to the aqueous alkaline solution of the salt.

Keywords——bis(dithiobenzoylacetonato)Zn(II); C-methylation; C–N bond rupture; isothiuronium salt; NMR spectra; infrared spectra

Only a few metal complexes of dithio-β-diketones have been reported because of their synthetical difficulties mainly caused by the reactive character of sulfur atom. The most popular ligand, dithioacetylacetone was tried to prepare as a free ligand but proved to be unsuccessful,[2–4] although the dimer of the ligand and its metal chelates were isolated.[5–9] These metal chelates, however, are limited to those Co(II), Ni(II), Pd(II) and Pt(II) because of the limited synthetic method of these complexes.

We have been studying the synthesis of new dithio chelating agents containing mainly mercapto and thioamido group. In the study, a new synthetic route to the metal chelates of dithio-β-diketone derivatives has been found successfully and the method of preparation of bis(dithiobenzoylacetonato)Zn(II) has been reported.

Experimental

Materials——S-[1-Phenyl-2-(thioacetyl)vinyl]isothiuronium *p*-toluenesulfonate (III): 0.5 mol of methyliodide and 100 ml of water were added to 0.1 mol of sodium phenylpropiolthioanilide[10] suspended in ether. To the solution 0.2 mol of *p*-toluenesulfonic acid and thiourea were added. After this solution was allowed to stand overnight, needle crystals separated were collected and recrystallized from aqueous ethanol. White fine needles were obtained, mp 226°. Yield 65%. *Anal.* Calcd. for $C_{18}H_{20}N_2O_3S_3$: C, 52.94; H, 4.90; N, 6.86; S, 23.53. Found: C, 52.72; H, 4.65; N, 6.58; S, 21.61.

Bis(dithiobenzoylacetonato)Zn(II) (V): 1.7 g of S-[1-phenyl-2-(thioaceto)vinyl]isothiuronium *p*-toluenesulfonate was hydrolyzed in 100 ml of 10% aqueous NaOH solution. To the solution an aqueous solution of 0.5 g zinc acetate was added. Yellow needles were recrystallized from pyridine, mp 186°. Yield 80%. *Anal.* Calcd. for $C_{20}H_{18}S_4Zn$: C, 53.22; H, 3.99. Found: C, 53.20; H, 4.17.

Apparatus——Ultraviolet and visible absorption spectra were recorded on a Shimadzu Multiconvertible spectrometer Model Double-40. Infrared absorption measurement was carried out as potassium bromide disks in the range 4000—650 cm^{-1} with a Hitachi Infrared spectrophotometer Model EPI-S2. Nuclear magnetic resonance (NMR) spectra were measured on a Varian A-60 spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

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1) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*
2) E. Frommand and P. Ziersch, *Chem. Ber.*, 39, 3599 (1906).
3) A. Fredga and A. Brandstrom, *Arkiv. Kemi Mineral. Geol.*, **26B**, 1 (1948).
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5) R.L. Martin, I.M. Stewart, *Nature* (London), **210**, 522 (1966).
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7) C.G. Barraclough, R.L. Martin, and I.M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).
8) G.A. Heath and R.L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).
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Results and Discussion

We prepared S-[1-phenyl-2-(phenylthiocarbamoyl)vinyl]isothiuronium *p*-toluenesulfonate (I) by the method shown in Chart 1 and reported.[11] (I) is a useful stock intermediate from which N-phenyl-β-mercaptothiocinnamamido metal chelates (II) are prepared with ease. In these reactions S-[1-phenyl-2-(thioacetyl)vinyl] isothiuronium *p*-toluenesulfonate (III) was obtained by adding methyliodide and water to sodium phenylpropiolthioanilide suspended in absolute ether and then *p*-toluenesulfonic acid and thiourea to the ether phase as shown in Chart 2.

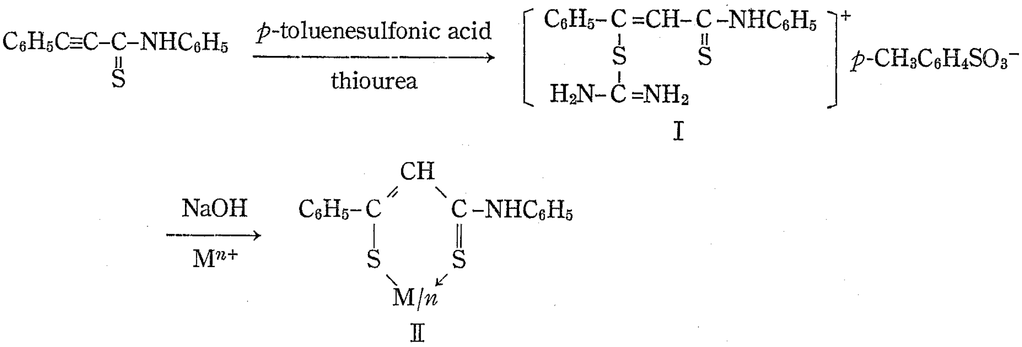

Chart 1

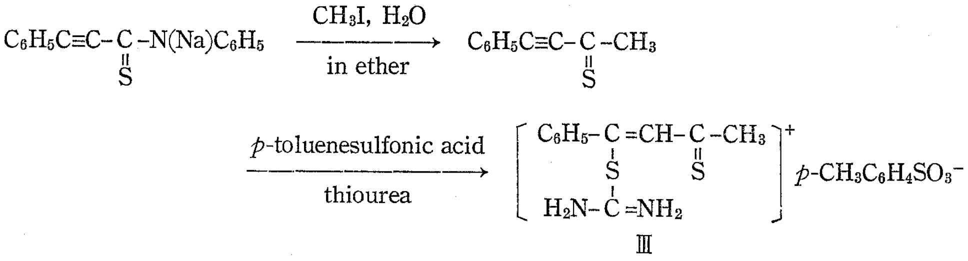

Chart 2

The C-methylathion was supposed to proceed by the following mechanism. Methyliodide initially attacks the negative charge on the nitrogen atom, which causes the cleavage of the C–N bond of thioamido group. This bond cleavage may give negative charge to the carbon atom to which methyliodide attacks again as shown in Chart 3.

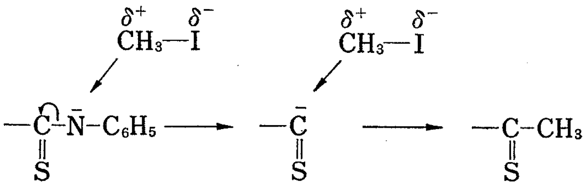

Chart 3

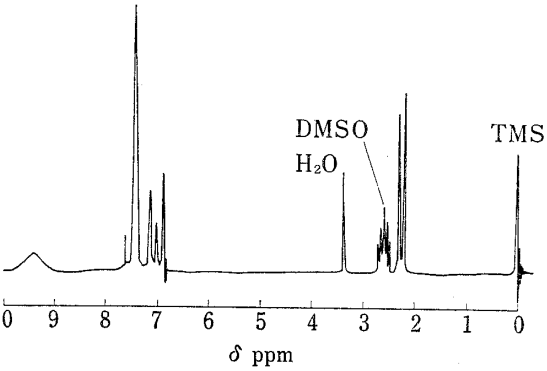

Fig. 1. NMR Spectrum of the Compound (III) in DMSO-d_6

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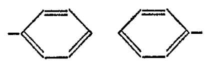
[11] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1021 (1978).

The NMR spectrum of the obtained isothiuronium salt (III) is shown in Fig. 1 and the data were presented in Table I compared with those of I. These signals of both compounds are in good accordance except the lack of NH signal and an additional CH_3 signal in the compound (III). This disappearance of NH signal shows that the cleavage of the C–N bond has been attained completely. On the other hand, an additional signal of CH_3 implies that the introduction of methyl group has proceeded.

TABLE I. The NMR Data of the Compounds (I) and (III) in DMSO-d_6 (δ ppm)

Compound	Proton					
	-NH-	$-NH_2$		=CH-	$-CH_3$	
I	11.65	9.22	7.73—7.13	7.07	2.30	
III	n.o.	9.35	7.57—6.98	6.92	2.29	2.23

n.o.: not observed.

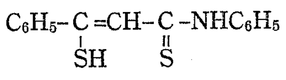
TABLE II. The Infrared Spectra of the Compounds (I) and (III) (cm^{-1})

Compound	Absorption band				
	-NH- $-NH_2$	C=C	NCS I	NCS II	NCS III or C=S
I	3250	1650	1550	1400	1200
III	3150	1670	n.o.	n.o.	1220

n.o.: not observed.

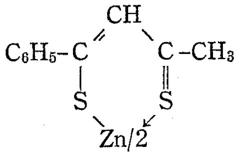
The infrared spectra of those two compounds were examined and some of these data were tentatively assigned and listed in Table II. Rao *et al.*[12] reported that in the compounds with $\rangle$N–C=S group, three strong bands due to the mixed vibration by ν_{C-N}, $\nu_{C=S}$ and δ_{N-H} appear in the regions 1395—1570, 1260—1420 and 960—1140 cm^{-1} which were tentatively designated as "NCS I, II and III band," respectively. In the compound (III), NCS I and II absorptions disappeared and NCS III absorption remained compared with the compound (I). Since NCS III band is supposed to be mainly due to $\nu_{C=S}$, these results signify that the C–N bond rupture has been completed.

The compound (I) was hydrolyzed in aqueous alkaline solution and produced N-phenyl-β-mercaptothiocinnamamide (IV) as a free dithio ligand by neutralization of the solution with aqueous acidic solution.[11] On the contrary, the compound (III) never gave its free ligand. Zinc(II) chelate (V), however, was prepared by adding aqueous Zn^{2+} solution to the aqueous alkaline solution of the compound (III).



$C_6H_5-\underset{SH}{C}=CH-\underset{\overset{\|}{S}}{C}-NHC_6H_5$

IV



V

The elemental analysis gave appropriate data supporting this complex only to carbon, hydrogen and nitrogen, while those of zinc and sulfur were not obtained because of the volatile property of zinc sulfide.

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12) C.N. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

The NMR spectrum of V is presented in Fig. 2. It shows three signals corresponding to phenyl, methine and methyl group whose integral ratio is 5:1:3. The NMR data for bis(O-ethylthioacetothioacetato)Zn(II)13) (VI) and bis(N-phenyl-β-mercaptothiocinnamamido)-Zn(II)14) are included in Table III for comparison with the present complex.

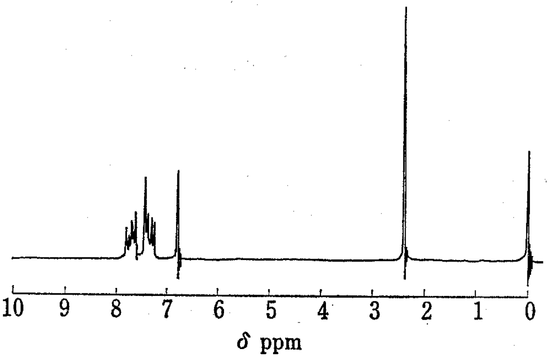
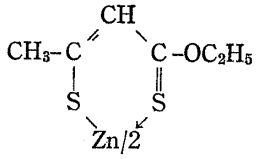
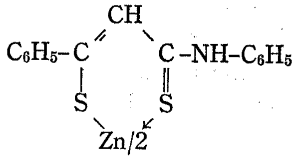


Fig. 2. NMR Spectrum of the Complex (V) in $CDCl_3$



VI



VII

Table III. Partial NMR Data for the Compounds (V), (VI) and (VII) in $CDCl_3$ (δ_{ppm})

Compound	Proton			
	-NH-	C_6H_5	=CH-	$-CH_3$
V		7.75—7.17	6.77	2.42
VI			6.78	2.45
VII	8.28	7.31	6.85	

The infrared spectrum of V was examined compared with those of the compounds (VI) and (VII). The C=C stretching mode of VI and VII appears at 1499 and 1500 cm^{-1}, respectively, while that of V appears at 1540 cm^{-1}. This higher frequency than VI and VII seems to be caused by electron donative property of CH_3 group. ν_{N-H} was not found in V as supposed. With respect to the assignment of C=S stretching mode, Ouchi *et al.*15) reported 1220—1240, 1170—1180 and 840 cm^{-1} for some dithio-β-diketonatometal chelates. On the other hand, Martin *et al.*16) described 745 and 700 cm^{-1} for bis(dithioacetylacetonato)Co(II). Although the zinc complex (V) shows strong bands at 1215, 1180 and 820 cm^{-1}, no bands are detected around 745 and 700 cm^{-1}.

The electronic spectrum of V was measured in chloroform and only two λ_{max} were detected as shown in Table IV, which are tentatively assigned by reference to Martin's report.13)

Table IV. Electronic Spectrum of V in $CHCl_3$

λ_{max}	log ε	Tentative assignment
380 nm	4.52	$L \longrightarrow L^*$ or $M \longrightarrow L^*$
289 nm	4.35	$L \longrightarrow L^*$

Although it seems very difficult to prepare dithio-β-diketonatometal chelates, thiuronium salt (III) mentioned above is very stable and easily reacts with metal ions forming various metal chelates. Therefore it can be used for a useful stock reagent.

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13) A.R. Hendrickson and R.L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).
14) S. Kitagawa and H. Tanaka, unpublished.
15) A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Jap.*, **41**, 2044 (1968).
16) G.A. Heath and R.L. Martin, *Aust. J. Chem.*, **24**, 2061 (1971).