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Studies on the Sulfur-containing Chelating Agents.[1] XXXVII. Solvent Effect on Nuclear Magnetic Resonance Spectra of Cobalt(III) Monothioacetylacetonate and Its Brominated Products

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Mono-, di and tribrominated chelates were prepared by direct bromination of cobalt (III) monothioacetylacetonate (I). From Infrared and/or nuclear magnetic resonance spectra, it was assumed that I exists as cis (facial) isomer and in brominated chelates, each chelate ring is independent fundamentally. Linear relationship was observed between chemical shift of methine proton and dielectric function with respect to various solvents in I. In some solvents, such as benzene and pyridine, particular interactions are assumed for the explanation of the nuclear magnetic resonance spectra of I and the brominated chelates.

Effect of the solvent has been extensively studied on the metal chelates of β-diketones with various spectroscopic method and many kinds of solvate or adduct compound containing water, alcohols, haloalkanes, acetone, dioxane or amines as adduct molecule have been studied.[3] In addition, synergic effect due to the formation of adduct compound has been widely applied for the solvent extractions of metals with β-diketones.[4] On the contrary, effect of the solvent in the metal chelates of thio-β-diketones has not been studied extensively.

We have reported the preparation and the property of cobalt(III) chelates of some monothio-β-diketones and their brominated chelates.[5] Mono-, di- and tri-brominated cobalt chelates were isolated, by the direct bromination of tris(monothioacetylacetonato) cobalt-(III) (abreviated as CoSAA hereafter). These brominated chelates are abreviated as CoSAA-Br(1), CoSAABr(2) and CoSAABr(3) hereafter. The effect of various solvents upon the nuclear magnetic resonance spectra of these chelates were investigated and the interactions between the chelates and the solvents are discussed in the present paper.

Experimental

Materials——(i) Cobalt (III) chelates of 4-mercapto-3-penten-2-one (thioacetylacetone) was prepared by the method reported previously.[5] (ii) Brominated cobalt chelates of thioacetylacetone; N-bromosuccinimide (356 mg, 2×10^{-3} mole) was added with stirring to the solution of CoSAA (404 mg, 10^{-3} mole) in 100 ml of $CHCl_3$, and after two minutes the reaction mixture was washed with water. The $CHCl_3$ solution was dried and $CHCl_3$ was removed. The reaction mixture was chromatographed over nylon column packed with dry silicagel which was dipped in benzene. Four bands corresponding to CoSAA, mono, di, and tribrominated cobalt chelates were cut off and were extracted with MeOH respectively. After the MeOH was removed, the product was recrystallized from MeOH or $CHCl_3$. The yields of CoSAABr (1), CoSAABr (2) and CoSAABr (3) were 100 mg, 100 mg and 40 mg, respectively. CoSAABr (1); mp 180°. *Anal.* Calcd. for $C_{15}H_{20}O_3BrCoS_3$: C, 37.28; H, 4.16; Co, 12.20. Found: C, 37.45; H, 4.16; Co, 12.26. CoSAABr (2); mp 167°. *Anal.* Calcd. for $C_{15}H_{19}O_3Br_2CoS_3$: C, 32.33; H, 3.57; Co, 10.55. Found: C, 32.04; H, 3.38; Co, 10.47. CoSAABr (3); mp 174°. When $CHCl_3$ was used as the recrystallization solvent, CoSAABr (2) was

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1) Part XXXVI: S. Kawanishi, A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **21**, 2613 (1973).

2) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*

3) *a*) T.S. Davis and J.P. Fackler, Jr., *Inorg. Chem.*, **5**, 242 (1966); *b*) F.R. Clarke, J.F. Steinbach and W.F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964) and references therein.

4) L. Newman and P. Klotz, *J. Phys. Chem.*, **67**, 204 (1963) and reference therein.

5) A. Yokoyama, S. Kawanishi and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 356 (1970).

separated as the clathrate which contains one mole of $CHCl_3$ per one mole of the chelate, as well as the case of CoSAABr (3).[5]

Infrared (IR) Spectra——The spectra were measured as potassium bromide disks in the range 4000—400 cm^{-1} on Koken DS 301 spectrophotometer.

Nuclear Magnetic Resonance (NMR) Spectra——The spectra were measured by Varian A-60 spectro meter at 60 Mc with tetramethylsilane as internal standard.

Result and Discussion

Infrared Spectra

Wave numbers and the possible assignments[6] of the main absorption bands of CoSAA and the brominated chelates are listed in Table I. In the infrared absorption spectrum of CoSAA, two absorption bands assigned for ν(C=O) and ν(C=C) were observed. Whereas, in CoSAABr(1), CoSAABr(2) and CoSAABr(3), the number of the absorption bands assigned to these modes of vibrations were three, three and one, respectively. As seen in Table I, remarkable differences were observed between the brominated and non-brominated chelates, namely in the region 1540—1560 cm^{-1} a band was observed in all brominated chelates, whereas in CoSAA no band was observed in this region. The mass effect by bromine atom was clearly observed in the brominated chelates. These observations in IR absorption spectra suggest that each chelate ring is considered to be independent fundamentally.

Table I. Infrared Spectral Bands of Cobalt(III) Monothioacetylacetonate and the Brominated Products in KBr Disks

Compounds	Bands (cm^{-1}) ν(C=O)	ν(C=O)+ν(C=C)	ν(C=C)
CoSAA	s 1573		s 1468
CoSAABr(1)	m 1575	m 1560	s 1470
CoSAABr(2)	m 1582	s 1550	s 1468
CoSAABr(3)		s 1543	

Nuclear Magnetic Resonance Spectra

In Table II, the results of the measurements of the nuclear magnetic resonance spectra in $CDCl_3$ are summarized. In the case of CoSAA, a singlet was observed as a signal of methyl group. It can therefore be presumed that CoSAA exists exclusively as *cis* isomer as shown in Chart 1, although in tris-chelate of unsymmetrical bidentate ligand, two geometrical isomers, namely *cis* (facial) and *trans* (meridianal) can be considered.

Table II. Chemical Shifts of Co(III) Monothioacetylacetonate and Its Brominated Products in $CDCl_3$

Compounds	Br	H	H (τ)	CH_3 (τ) Brominated chelate ring		CH_3 (τ) Not brominated chelate ring
CoSAA	0	3	3.63			7.75
CoSAABr(1)	1	2	3.62	7.38	7.60	7.75
CoSAABr(2)	2	1	3.60	7.35	7.58	7.72
				7.37	7.59	7.73
CoSAABr(3)	3	0		7.35	7.59	

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6) A. Yokoyama, S. Kawanishi and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 363 (1970).

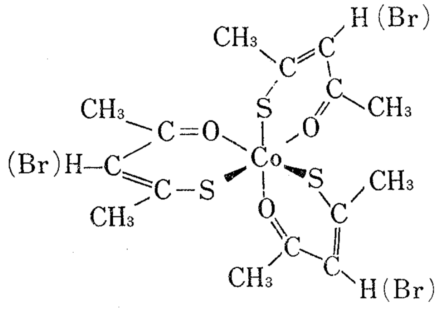

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Chart 1

Table III. Chemical Shifts of Co(III) Monothioacetylacetonate in Various Solvents

Solvent	H (τ)	CH_3 (τ)		Δ (τ)
CCl_4	3.75	7.78		0
$CDCl_3$	3.63	7.75		0
CH_2Cl_2	3.61	7.78		0
CS_2	3.80	7.87	7.90	0.03
Dioxane	3.65	7.84	7.86	0.02
d_6-acetone	3.56	7.83 7.84	7.86	0.025
CD_3OD	3.54	7.80	7.82	0.02
CD_3CN	3.53	7.80 7.81	7.83	0.025
d_6-benzene	3.95	7.98	8.11	0.13
d_5-pyridine	3.58	7.78	7.88	0.10

Eddy, *et al.*,[7] reported that nickel, palladium and platinum chelates of monothiodibenzoylmethane exist only in *cis* form. In consideration of great ability to form π-bonding between metal and sulfur, the preferential stability of *cis* form which permits the double bond character between cobalt and sulfur to large extent, may be reasonably accepted in the case of CoSAA. In addition, the preferential *cis* stability may arise also partly from the interaction among nonbonded three sulfur atoms in *cis* form, as Holm, *et al.*[8] pointed out. In the cases of the brominated chelates, the signal of methyl group splits into doublet and is observed in lower field than in the case of CoSAA. The values of the chemical shifts of the protons of methyl groups of CoSAABr(1), CoSAABr(2) and CoSAABr(3) do not differ each other so much. It can therefore be presumed that bromine atom does not affect the chemical shifts of the methyl groups of other chelate rings, and each chelate ring is independent from other chelate rings. Collman, *et al.*,[9] have also pointed out that in tris rhodium chelate of β-diketone, each chelate ring is considered to be independent from others.

In Table III, the results of the measurements of nuclear magnetic resonance spectra of CoSAA in various solvents are summarized. The signal of the methyl group is observed as a singlet in non-polar solvent such as carbon tetrachloride, (deuterio) chloroform, and (deuterio) dichloromethane, whereas it splits into doublet in other solvents. Particularly, the chemical shifts of two methyl groups are greatly different each other in benzene and pyridine. The fact that a singlet was observed as the signal of methyl group in non-polar solvent is explained by assuming that two methyl groups are equivalent through the delocalization of π-electron of the chelate ring. For the explanation of the nuclear magnetic resonance spectra in benzene and pyridine, some particular interaction[10] between the chelate and the solvent should be taken into account. Buckingham, *et al.*,[11] have defined the screening contribution of the solvent to the solute as follows. $\alpha(\text{solvent}) = \alpha B + \alpha \mathrm{W} + \alpha A + \alpha E$

In this equation, αB is the screening contribution arising from the medium bulk susceptibility, $\alpha\mathrm{W}$ is that due to Van der Waals or dispersion forces between the solute and the solvent molecules, αA is that arising from the magnetic anisotropy of the medium and αE is that produced by the electric field induced in the medium by the polar solute. Among these factors, αB can be discounted because internal reference was used in the measurement

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[7] L.P. Eddy, J.W. Hayes, S.E. Livingstone, H.L. Nigam and D.V. Radford, *Australian J. Chem.*, **24**, 1071 (1971).

[8] R.H. Holm, D.H. Gerlach, J.G. Gordon, II and M.G. McNamee, *J. Amer. Chem. Soc.*, **90**, 4184 (1968).

[9] J.P. Collman, R.L. Marshall and W.L. Yound (III), *Chem. Ind.* (London), **1962**, 1380.

[10] *a*) T. Schaefer and W.H. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960); *b*) *Idem*, *ibid.*, **32**, 1224 (1960).

[11] A.D. Buckingham, T. Schaefer and W.G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

and αW is considered to be within experimental error. Accordingly, two factors, namely the electric field and the neighbor anisotropy effect in solute-solvent interaction should be taken into account for the interpretation of the observations in benzene and pyridine. The formation of the complexes by means of local dipole–induced dipole interactions has been observed in nuclear magnetic resonance spectra in some instances.12) The disturbance of the π-cloud system which is caused by the interaction between the permanent dipole moment of the solute and the dipole moment in the aromatic molecule (solvent) induced by the polarization of the aromatic molecule through the electric field arising from the permanent dipole moment of the solute, has been detected in the nuclear magnetic resonance spectra. In the case of the interaction between CoSAA and the solvent (benzene and pyridine), the dipole moment is induced on aromatic molecule by methyl group and the electric field caused by this interaction may cause the delocalization of π-electrons to some extent, and consequently the signal of the methyl group splits into doublet. In order to discuss on this interaction further, the relationship between τ values of methine protons and the dielectric function of the various solvents ($\varepsilon - 1/2\,\varepsilon + n^2$) is presented in Fig. 1. With respect to the solvents except for benzene, dioxane and carbon disulfide, linear relationship is observed in Fig. 1. The fact that chemical shifts of methine protons in pyridine, acetone, methanol and acetonitril which are able to interact with the solute by hydrogen bond were observed in lower field may be explained by the electric field effect of the polarization. The anisotropic effect must be considered for the marked deviation from the straight line in benzene. In Tables IV, V and VI, data of the nuclear magnetic resonance spectra of CoSAA and the brominated chelates are summarized. It has been known that the aromatic solvents tend to cause some shift to higher field in the nuclear magnetic resonance spectra of the solute. This effect has been

TABLE IV. Chemical Shifts of Co(III) Monothioacetylacetonate and Its Brominated Products in d_6-Benzene

				CH_3 (τ)			
Compounds	Br	H	H (τ)	Brominated chelate ring		Not brominated chelate ring	
CoSAA	0	3	3.95			7.98	8.11
CoSAABr(1)	1	2	3.97	7.63	7.73	8.01	8.10 8.12
CoSAABr(2)	2	1	4.01	7.63 7.65	7.77	8.05	8.13
CoSAABr(3)	3	0		7.66	7.81		

TABLE V. Chemical Shifts of Co(III) Monothioacetylacetonate and Its Brominated Products in d_5-Pyridine

				CH_3 (τ)			
Compounds	Br	H	H (τ)	Brominated chelate ring		Not brominated chelate ring	
CoSAA	0	3	3.58			7.78	7.88
CoSAABr(1)	1	2	3.57	7.48	7.60	7.80	7.84 7.86
CoSAABr(2)	2	1	3.56	7.42 7.43 7.47	7.62	7.81	
CoSAABr(3)	3	0		7.42	7.63		

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12) *a*) W.G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962); *b*) J. Homer and P.J. Huck, *J. Chem. Soc.* (A), **1968**, 277.

Table VI. Chemical Shifts of Co(III) Monothioacetylacetonate and Its Brominated Product in d_6-Acetone

Compounds	Br	H	H (τ)	CH_3 (τ)			
				Brominated chelate ring		Not brominated chelate ring	
CoSAA	0	3	3.56			7.83	7.86
CoSAABr(1)	1	2	3.53	7.47	7.66	7.80	7.83
CoSAABr(2)	2	1	3.48	7.42 7.63	7.45 7.66	7.78	

interpreted in terms of the "disk" shape of the molecule of the aromatic solvent combined with their large diamagnetic anisotropies. Benzene rings have large induced magnetic moments only when the ring is present at right angle to the magnetic field. As seen in Tables IV, V and VI, the signals of methine and methyl groups were observed in higher field in benzene than in other solvents, and the signals of methyl groups split to some extent ($\Delta\tau=0.13$) and further, the shift of the signals of methyl groups to still higher field was observed by the bromination. These observations can not be accounted for simply on the basis of the effect of the ring current, which should give rise to averaged effect of the dilution shifts of benzene to all proton signals of the molecule of the solute. The observations seen in Tables IV, V and VI, must be explained by some specific interaction between the solute and benzene. Since benzene is regarded as a weak π-electron donor, the formation of the hydrogen bond between benzene and methyl group of CoSAA may be proposed as the interaction. The splitting of the signals of the methyl group may be explained by the difference in the strength of the π-hydrogen bond of benzene with one methyl group and that with other methyl group.

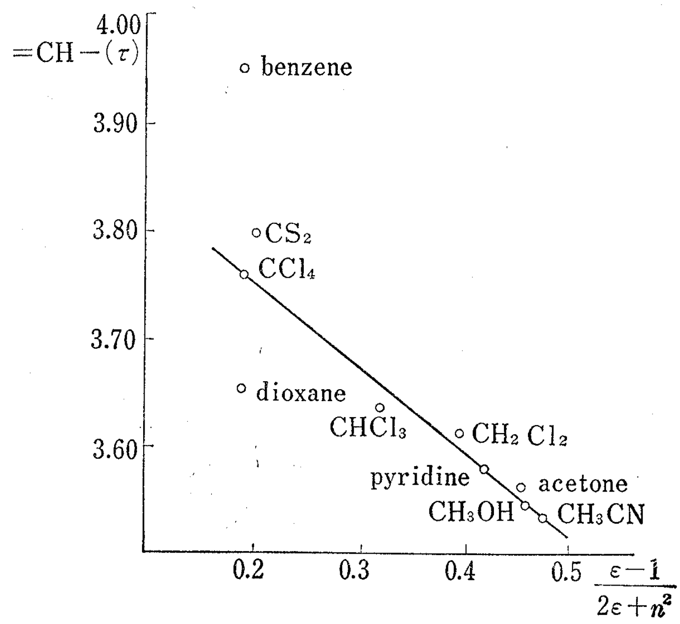

Fig. 1. Plot of τ(=CH-) vs. $\varepsilon-1/2\varepsilon+n^2$ for Co(III) Monothioacetylacetonate in various solvents.

In pyridine the signals of methyl groups were observed as a doublet in higher field, whereas a signal of methine group was observed in lower field than in chloroform. These observations may be reasonably interpreted by the π-hydrogen bond between pyridine ring and methyl group and also that between methine proton and nitrogen lone-pair electron. Further, the observation that the signal of methine was observed in lower field in acetone than in chloroform may be explained by the weak hydrogen bond between methine proton and oxygen lone-pair electron of acetone.

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