[Chem. Pharm. Bull. 18(2) 356–362 (1970)]

UDC 547.448.04-386

Studies on the Sulfur-containing Chelating Agents. XXII.[1] Some Metal Chelates of Thio-β-diketones and Bromination of Cobalt (III) Thio-β-diketonates

Akira Yokoyama, Shosuke Kawanishi
and Hisashi Tanaka

Faculty of Pharmaceutical Sciences, Kyoto University[2]

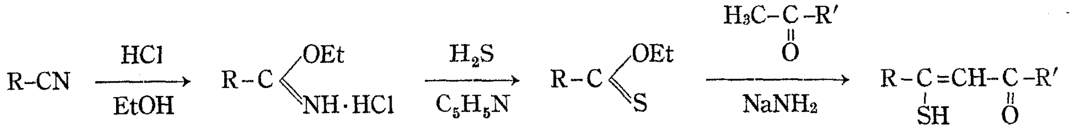
(Received October 6, 1969)

Four kinds of thio derivatives of β-diketone and their nickel, cobalt, zinc, palladium, copper, lead, rhodium and iron chelates were prepared. The ratio of metal to ligand was 1:3 in cobalt, rhodium and iron chelates and 1:2 in other metal chelates. Bromination of cobalt chelates by N-bromosuccinimide or bromine were successful in some cases to give tribrominated chelates. Comparison of cobalt thio-β-diketonates with their tribrominated chelates in infrared and nuclear magnetic resonance spectra indicated that the bromination took place at γ-carbon of chelate ring. The success of the bromination can be considered as a kind of support for quasiaromaticity of the chelate to some extent.

It is a problem of great interest to vary the ligand atom of previously known chelating agents keeping their basic structures, because it will cause a great change of property in the chelate formation. Especially, replacing the oxygen atom by the sulfur atom would give rise to the great change of the selectivity of the chelating agents and the stability of the metal chelates, the character of the sulfur as the ligand atom being considered.

From this point of view, thio derivatives of β-diketones were prepared, in an attempt to investigate their properties and those of their metal chelates, as a part of the systematic studies[3] on the chelating agents containing mercapto group, which we have conducted.

We reported briefly our results on their syntheses and the electrophilic substitution reaction of the chelates as a short communication.[4] This paper deals with its full details. Four kinds of thio-β-diketones (abbreviated as SAA, SAB, SBA and SBB hereafter) listed in Chart 1 were synthesized by the method outlined previously.[4]



$$\text{R-CN} \xrightarrow[\text{EtOH}]{\text{HCl}} \text{R-C}\begin{smallmatrix}\text{OEt}\\ \text{NH}\cdot\text{HCl}\end{smallmatrix} \xrightarrow[C_5H_5N]{H_2S} \text{R-C}\begin{smallmatrix}\text{OEt}\\ \text{S}\end{smallmatrix} \xrightarrow[\text{NaNH}_2]{H_3C\text{-}\overset{\displaystyle O}{\text{C}}\text{-R}'} \text{R-}\underset{\text{SH}}{\text{C}}\text{=CH-}\underset{\text{O}}{\text{C}}\text{-R}'$$

	R	R′
SAA	CH_3	CH_3
SAB	CH_3	C_6H_5
SBA	C_6H_5	CH_3
SBB	C_6H_5	C_6H_5

Chart 1

The reactivities of these ligands with various metal ions were found to be almost similar to those of sulfur-containing ligands reported before.[3] Several kinds of metal chelates listed in Table II were prepared. We have reported that some of the mercapto ketones were found

---

1) Part XXI: A. Yokoyama, M. Chikuma, H. Hayashi and H. Tanaka, *Bunseki Kagaku*, **18**, 24 (1969).
2) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*
3) *a*) A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **12**, 683 (1964); *b*) A. Yokoyama, K. Ashida and H. Tanaka, *ibid.*, **12**, 690 (1964); *c*) A. Yokoyama and H. Tanaka, *ibid.*, **17**, 290 (1967).
4) A. Yokoyama, S. Kawanishi, M. Chikuma and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **15**, 540 (1967).

to form cuprous chelates, in the reaction with cupric ion as the result of the oxidation–reduction between the ligand and cupric ion. However, in this case, the chelate obtained was considered to be cupric chelate and molar ratio of the metal–to–ligand was 1:2. As to the cobalt chelates, the chelate of the metal–to–ligand ratio 1:3 was easily obtained unlike the case of β-diketones. In the case of β-diketone, 1:2 cobaltous chelate was obtained usually, and 1:3 chelate could be prepared only when cobaltic carbonate complex was reacted with β-diketone or hydrogen peroxide was used as the oxidizing agent.[5] In the case of thio-β-diketones oxidization occurred promptly and 1:2 chelates was difficult to be isolated.

The electrophilic substitutions such as halogenation and nitration have been investigated on some of the metal chelates of β-diketones, and their quasiaromaticity have been discussed from the results.[6] The brominations of metal thio-β-diketonates were attempted in this connection. The brominations were carried out under various conditions, on the cobalt chelates, because they were found to be more stable than other metal chelates listed in Table II, under the reaction conditions studied.

The reactions of $Co(SAA)_3$ with stoichiometric amounts of brominating agents such as N-bromosuccinimide or bromine were carried out under mild conditions in chloroform or acetic acid, as described in experimental part. The substitution reaction at γ-carbon proceeded very rapidly without any apparent cleavage of the chelate ring and tribrominated chelate was obtained with comparatively good yield. In Method 2 in Experimental, the bromination proceeded not so rapidly and process of the reaction could be easily traced by thin–layer chromatography. The reaction solution was chromatographed on silica gel at regular time intervals. As shown in Fig. 1, four spots were observed in accordance with the proceeding of the reaction and the lowest and the highest spots were identified with those of the unsubstituted chelate and tribrominated chelate, respectively, by the comparison with the authentic samples. These chromatographic observations suggested that the substitution reaction took place stepwise in order of mono, di and tribromination. The decrease of the rate of the reaction in Method 2 is considered to be caused by the low solubility of N-bromosuccinimide into chloroform. The mechanism of this reaction is being investigated in detail. When chloroform was used as the reaction solvent or the recrystallization solvent, tribrominated $Co(SAA)_3$ was separated as the clathrate which contains one mole of chloroform per one mole of the chelate, as well as the case of tribrominated acetylacetonates.[7]

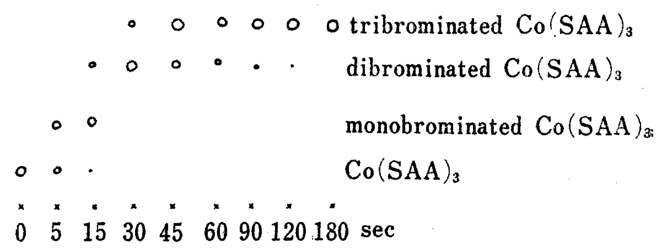


Fig. 1. Trace of Bromination Process by Thin–Layer Chromatography

The infrared and nuclear magnetic resonance spectra of $Co(SAA)_3$ and those of tribrominated chelate are comparatively shown in Fig. 2 and 3 . Infrared spectrum of $Co(SAA)_3$ showed two absorption bands ta 1573 cm^{-1} and 1468 cm^{-1}, and they are assigned to $\nu(C{=}O)$ and $\nu(C{=}C)$, respectively, recent assignments[8] in metal β-diketonates being referred. Whereas in tribrominated chelate, only one band which is considered to be assigned to those modes

---

[5] *a*) H.F. Bauer and W.C. Drikard, *J. Am. Chem. Soc.*, **82**, 5031 (1960); *b*) B.E. Bryant and W.C. Fernelius, "Inorganic Syntheses," Vol. V, McGraw–Hill, New York, N. Y., 1957, p. 188.

[6] J.P. Collman, *Angew. Chem.*, **77**, 154 (1965).

[7] R.W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

[8] *a*) S. Pinchas, B.L. Silver and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967); *b*) G.T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6** ,433 (1967); *c*) H. Musso and H. Junge, *Tetrahedron Letters*, **1966** 4003

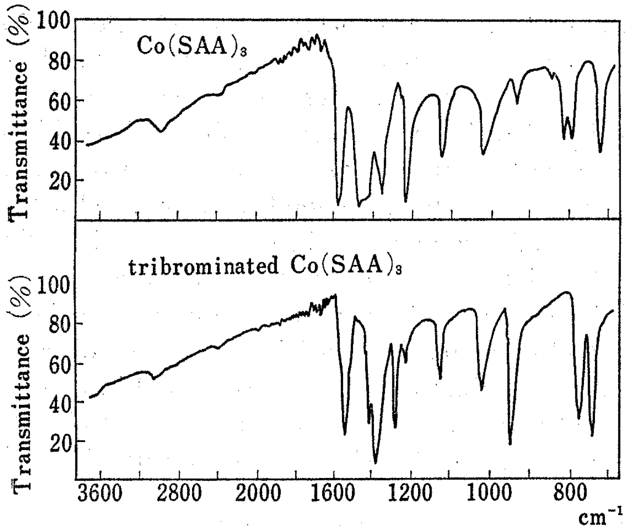


Fig. 2. Infrared Spectra of Co(SAA)$_3$ and the Bromination Product in KBr Disk

of vibrations was observed at 1543 cm^{-1}. The spectral change on the bromination is similar to the case of the metal acetylacetonates.[9] The disappearance of one band upon substitution on the chelate ring was supposed to be caused by the mass effect of bromine atom.[10]

In nuclear magnetic resonance spectra,[11] the disappearance of the signal ($\tau=3.76$) of the proton in Co(SAA)$_3$ upon substitution of the chelate ring indicates clearly that bromination took place at the chelate ring. In addition, in the case of Co(SAA)$_3$, a singlet was observed as a signal of the methyl groups ($\tau=7.79$), whereas in the case of tribrominated Co(SAA)$_3$, the signal of the methyl groups splits into doublet ($\tau=7.36$ and 7.60). The splitting of the signal of the methyl group upon bromination is supposed to be due to the localization of π-electrons in the chelate ring, caused by introducing such a electron–negative atom as bromine.

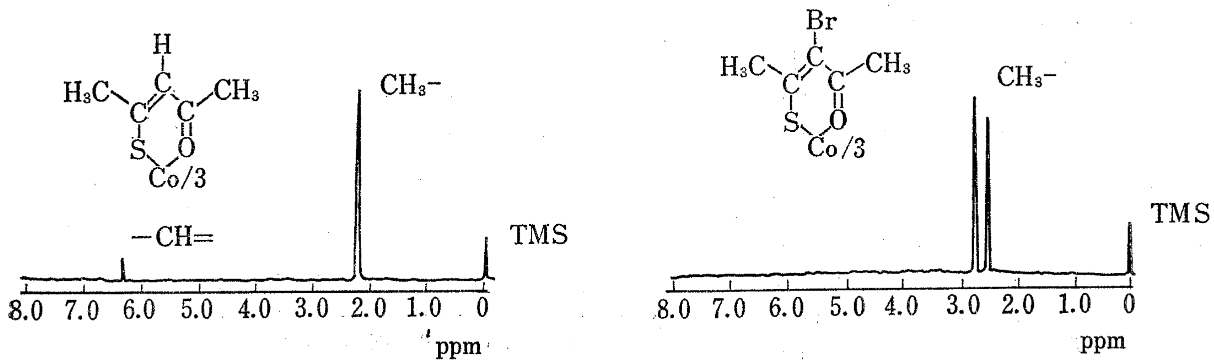


Fig. 3. Nuclear Magnetic Resonance Spectra of Co(SAA)$_3$ and the Bromination Product

The bromination was also conducted on the cobalt chelates of SAB, SBA and SBB in chloroform under the same condition as in the case of Co(SAA)$_3$, because these chelates are not very soluble in acetic acid. Co(SBA)$_3$ was brominated smoothly and the tribrominated chelate was separated from the reaction mixture as the chloroform clathrate, whereas, in the case of Co(SAB)$_3$, only the formation of the monobrominated chelate was approved by the thin–layer chromatography, and enlonging of the reaction time caused the gradual cleavage of the chelate ring. On the other hand, in the case of Co(SBB)$_3$, bromination did not take place at all and the cleavage of the chelate ring was recognized. These results may possibly be explained from the effect of the steric hindrance of the phenyl group to the bromination in the following way. Introducing a bulky substituent as bromine to the chelate ring will result the steric hindrance, and the phenyl group and the chelate ring will be made impossible to be present on the same plane, and hence the bonding axis between cobalt and oxygen or sulfur will deviate from the plane of the chelate ring. These effects will result to facilitate the cleavage of the chelate ring. The cleavage of the chelate ring of Co(SBB)$_3$ will be emphasized

---

9) P.R. Singh and R. Sahai, *Australian J. Chem.*, **20**, 639 (1967).
10) J.P. Collman, R.A. Moss, H. Maltz and C.C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).
11) The nuclear magnetic resonance spectra were obtained with carbon tetrachloride solution on a Varian model A-60 spectrometer with tetramethylsilane as internal standard.

by steric hindrance by two phenyl groups. On the other hand, when the phenyl group is present on Co–S bonding site of the chelate ring as in case of Co(SBA)$_3$, the resonance structure shown in Chart 2 may possibly be considered, similarly to the resonance structure of benzoylacetonate.[12] The bonding of Co–S in Co(SBA)$_3$ may be stronger compared with that of other chelates because of the resonance effect, and the effect is considered to contribute to the success of the bromination. On the other hand, in the case of Co(SAB)$_3$, this type of resonance can hardly be considered and steric hindrance may easily lead to the cleavage of the chelate ring.

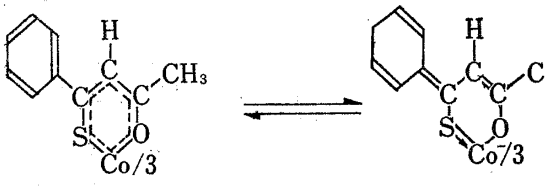


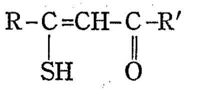
Chart 2

The success of the bromination in some of the metal chelates of thio-β-diketones can be considered as a kind of support for their quasiaromaticity to some extent, as in the metal chelates of β-diketones. The quasiaromaticity of the metal chelates of thio-β-diketones will be discussed by the use of physico-chemical methods in the succeeding paper.

Experimental

Preparation of Thio-β-diketones——General Procedure: Dehydrated methyl ketone (0.4 mole) was added slowly to NaNH$_2$ (0.4 mole) suspended in 200 ml of ether with continuous stirring. The mixture was allowed to stand at room temperature until NH$_3$ gas became no longer detectable. The solution of thionic acid ester (0.2 mole) in 50 ml of ether was added dropwise over a 90-minute period to the solution under refluxing. After the solution was maintained at room temperature for 1 hr, the reaction mixture was poured over ice and diluted with water to 200 ml. The aqueous phase was neutralized with dryice and acetic acid. SBB which precipitated was collected and recrystallized from EtOH. SAA, SAB and SBA which separated were extracted with ether. The ether solution was dried with anhydrous Na$_2$SO$_4$, and ether was removed. SBA was recrystallized from EtOH. SAA and SAB were distilled *in vacuo*. Thio-β-diketones obtained are listed in Table I. Properties of these compounds were almost identical to those reported by Chaston[13] and Uhlemann.[14]

TABLE I. Thio-β-diketones



$$\underset{\displaystyle \mathrm{SH}}{\mathrm{R{-}\underset{|}{C}{=}CH{-}}}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}R'}$$

Compound	R	R′	Appearance	mp (°C) (bp (°C/mmHg))	Yield (%)
SAA	CH$_3$	CH$_3$	orange liquid	(54/14)	56
SAB	CH$_3$	C$_6$H$_5$	orange crystals	28 (112/9)	50
SBA	C$_6$H$_5$	CH$_3$	orange-red crystals	61	62
SBB	C$_6$H$_5$	C$_6$H$_5$	red-crystals	85	70

Preparation of the Metal Chelates of Thio-β-diketones——General Procedure: The following metal salt solutions were prepared. Ni(OAc)$_2$, Co(OAc)$_2$, Pb(OAc)$_2$ and Zn(OAc)$_2$ were dissolved in distilled water. Cu(OAc)$_2$ and FeCl$_3$ were dissolved in EtOH. PdCl$_2$ was dissolved in dil. HCl. RhCl$_3$ was dissolved in dil. HNO$_3$. The solution of metal salt was added to the EtOH solution of the ligand. The chelate precipitated immediately was filtered. After drying the chelate was recrystallized from acetone. In the case of the rhodium chelates, the acetone solutions were chromatographed on silica gel and the yellow chelates

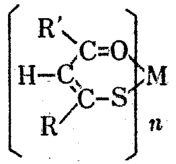
---

[12] K. Nakamoto, P.J. McCarthy, A. Ruby and A.E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

[13] *a*) S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer and V.A. Pickles, *Australian J. Chem.*, **18**, 673 (1965); *b*) *Idem, ibid.*, **20**, 1065 (1967).

[14] *a*) E. Uhlemann, G. Klose and H. Müller, *Z. Naturforsch*, **19b**, 962 (1964); *b*) E. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966); *c*) *Idem, Z. Anorg. Allg. Chem.*, **356**, 71 (1968).

Table II. Metal Chelates of Thio-β-diketones



Ligand	R	R′	M	n	Colour	mp (°C)	Analysis (%) Calcd. C	Calcd. H	Calcd. S	Calcd. M	Found C	Found H	Found S	Found M
(SAA)	CH_3	CH_3	Ni	2	brown	170 (167)[a]	41.57	4.85			41.76	5.11		
(SAA)	CH_3	CH_3	Co	3	dark green	180 (185)[b]	44.55	5.20	23.76		44.58	5.15	22.31	
(SAA)	CH_3	CH_3	Zn	2	pale yellow	179	40.62	4.73	21.66		40.32	4.84	19.61	
(SAA)	CH_3	CH_3	Pd	2	yellow	183	35.67	4.16	19.02	31.62	35.40	4.16	18.81	31.69
(SAA)	CH_3	CH_3	Cu	2	brown	130	40.89	4.77	21.81	21.64	40.71	4.90	19.94	21.79
(SAA)	CH_3	CH_3	Pb	2	yellow	141	27.45	3.20	14.64		27.75	3.43	12.32	
(SAA)	CH_3	CH_3	Rh	3	yellow	250	40.18	4.68		22.99	39.96	4.86		23.68
(SAB)	CH_3	C_6H_5	Ni	2	reddish brown	228 (225)[a] (223—224)[d]	58.15	4.36		14.22	58.22	4.65		13.90
(SAB)	CH_3	C_6H_5	Co	3	dark brown	234	61.03	4.58		9.98	61.00	4.79		10.00
(SAB)	CH_3	C_6H_5	Zn	2	yellow	159	57.21	4.21	15.26		57.48	4.39	14.53	
(SAB)	CH_3	C_6H_5	Pd	2	orange	210	52.13	3.91	13.91	23.11	52.05	3.94	13.35	24.57
(SAB)	CH_3	C_6H_5	Cu	2	brown	151	58.13	4.36	15.50	14.26	58.00	4.61	13.39	14.41
(SAB)	CH_3	C_6H_5	Pb	2	brown	148	42.77	3.21	11.40		42.75	3.20	9.68	
(SBA)	C_6H_5	CH_3	Ni	2	reddish brown	223 (220—224)[d]	58.15	4.36		14.22	57.89	4.33		14.10
(SBA)	C_6H_5	CH_3	Co	3	dark green	206	61.03	4.58		9.98	61.25	4.88		10.85
(SBA)	C_6H_5	CH_3	Zn	2	pale yellow	180	57.21	4.29	15.26		57.93	4.33	14.80	
(SBA)	C_6H_5	CH_3	Pd	2	brown	230	52.13	3.91	13.91	23.11	51.87	3.93	13.37	24.10
(SBA)	C_6H_5	CH_3	Cu	2	brown	147					e)			
(SBA)	C_6H_5	CH_3	Pb	2	orange	149	42.77	3.21	11.40	36.92	42.88	3.46	9.19	35.93
(SBA)	C_6H_5	CH_3	Rh	3	yellow	230	56.78	4.25			56.96	4.49		
(SBB)	C_6H_5	C_6H_5	Ni	2	brown	180 (184)[a] (183—185)[c]	67.06	4.10		10.95	66.77	4.40		11.03
(SBB)	C_6H_5	C_6H_5	Co	3	dark brown	241 (245)[b] (229—231)[c]	69.61	4.25		7.58	69.78	4.49		7.18
(SBB)	C_6H_5	C_6H_5	Zn	2	yellow	173 (172)[b] (175—176)[c]	66.25	4.05		12.04	66.63	4.40		10.49
(SBB)	C_6H_5	C_6H_5	Pd	2	red	240 (133)[b] (236—238)[c]	61.60	3.76		18.21	61.90	3.84		18.55
(SBB)	C_6H_5	C_6H_5	Cu	2	brown	162 (156)[b] (162—163)[c]					e)			
(SBB)	C_6H_5	C_6H_5	Pb	2	orange	198	52.54	3.21			52.47	3.42		
(SBB)	C_6H_5	C_6H_5	Fe	3	black	155 (151)[b]	69.88	4.27		7.22	69.57	4.38		8.00

a) lit.[12a)] b) lit.[12b)] c) lit.[13a)] d) lit.[13b)] e) These chelates were very difficult to be completely purified.

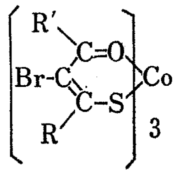
were separated from the byproducts. The chelates obtained are listed in Table II. Some of the chelates were reported by Chaston[13)] and Uhlemann,[14)] and our results on them were almost identical to their results as shown in Table II.

Bromination Procedure——Method 1: Solution of N-bromosuccinimide (134 mg, 7.5×10^{-4} mole) in 10 ml of acetic acid was added with stirring to a solution of $Co(SAA)_3$ (101 mg, 2.5×10^{-4} mole) in 10 ml of acetic acid at room temperature. The precipitate was filtered and recrystallized from methanol–chloroform.

Method 2: N-Bromosuccinimide (134 mg) was added with stirring to the solution of $Co(SAA)_3$ (101 mg) in 100 ml of chloroform, and after five minutes the reaction mixture was washed with water. The chloroform solution was dried, and chloroform was removed. The product was recrystallized from chloroform-methanol or acetone.

Method 3: Solution of N-bromosuccinimide (134 mg) in 10 ml of acetone was added with stirring to the solution of $Co(SAA)_3$ (101 mg) in 100 ml of acetone. After a few minutes, the solution was diluted with chloroform, and then washed with water several times. The chloroform solution was dried, and chloroform was removed. The product was recrystallized from chloroform–methanol or acetone.

TABLE III. Tribrominated Cobalt (III) Chelates of Thio-β-diketones

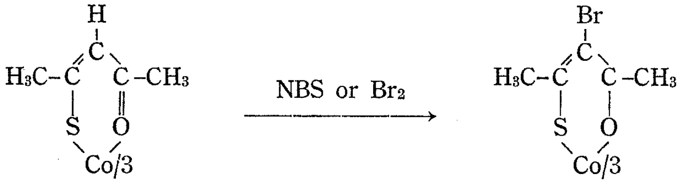


No.	Ligand	R	R′	Colour	mp (°C)	Formula
1	SAA	CH_3	CH_3	dark green	174	$C_{15}H_{18}Br_3CoO_3S_3$
2	SAA	CH_3	CH_3	dark green	174	$C_{15}H_{18}Br_3CoO_3S_3CHCl_3$[a)]
3	SBA	C_6H_5	CH_3	dark green	211	$C_{30}H_{24}Br_3CoO_3S_3CHCl_3$[a)]

	Analysis (%)									
No.	Calcd.					Found				
	C	H	S	Co	Br	C	H	S	Co	Br
1	28.08	2.81	14.97		37.44	28.34	3.09	14.13		37.55
2	25.24	2.49	12.62	7.76	63.11	25.71	2.76	12.48	7.59	63.18
3	39.31	2.64		6.22	50.18	39.80	3.03		5.72	49.45

a) chloroform clathrate

TABLE IV. Bromination of Cobalt (III) Chelates of Thio-β-diketones of Various Conditions



Methods	Brominating agents	Solvents	Reaction time required	Product (Yield) (%)
1	NBS	acetic acid	5 sec	tribromo- (50)
2	NBS	chloroform	2 min	tribromo- (78)
3	NBS	acetone	5 sec	mixture
4	Br_2	acetic acid	5 sec	tribromo- (32)
5	Br_2	chloroform	5 sec	tribromo- (52)

Method 4: Solution of bromine (78 mg, 7.5×10^{-4} mole) in 1 ml of acetic acid was added with stirring to the solution of $Co(SAA)_3$ (101 mg) in 10 ml of acetic acid containing potassium acetate (400 mg). After few minutes, the precipitate was filtered and washed with water several times. The product was recrystallized from chloroform–methanol or acetone.

Method 5: Solution of bromine (78 mg) and potassium acetate (400 mg) in 1 ml of acetic acid was added with stirring to the solution of $Co(SAA)_3$ (101 mg) in 100 ml of chloroform and after a few minutes the reaction mixture was washed with water. The chloroform solution was dried, and chloroform was removed and the product was recrystallized from chloroform–methanol or acetone. The brominated products are listed in Table III. The yield and the reaction time needed to complete the reaction are summarized in Table IV.

Thin–Layer Chromatography——A drop of the reaction mixture of the each method was taken and spotted on the plate of silicagel (Kiesel gel G nach Stahl) at regular time intervals (0, 5, 15, 30, 45, 60, 90, 120, 150, 180 sec). The end of the plate was dipped in benzene. Fig. 1 represents the chromatogram of the reaction by Method 2.

Acknowledgement The authors are indebted to Dr. T. Shingu and Miss M. Ohkawa, Kyoto University, for NMR measurements, Mr. S. Kojima, Kyoto University, for IR measurements, and to the members of the Micro Analytical Center of Kyoto University for elemental analyses.