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Studies on the Sulfur-containing Chelating Agents. XXXVIII.[1] Reaction of Platinum(II), Rhodium(III) and Mercury(II) Ion with Monothio-β-diketones and Their Disulfides

Shosuke Kawanishi, Akira Yokoyama and Hisashi Tanaka

Faculty of Pharmaceutical Sciences, Kyoto University[2]

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In platinum (II) dithioacetylacetonate which was obtained from monothioacetylacetone and platinum (II) ion in acidic medium by the replacement reaction of the ligand atom, considerable π-delocalization of the chelate ring is presumed by the spectroscopic data. Platinum (IV) monothioacetylacetonate which was obtained from monothioacetylacetone and platinum (II) ion in neutral medium did not produce dithio chelate with hydrogen sulfide unlike the case of palladium chelate. In the reaction of monothioacetylacetone with rhodium similar chelate formations were observed to the case of platinum chelate. In the reaction of monothioacetylacetone with mercury (II) ion, the product was a polymeric complex, which is considered to be produced from unstable complex through a intermolecular replacement of the ligand atom. From disulfide of monothiodibenzoylmethane, platinum, rhodium and mercury ions produced respective metal chelates or complexes. These features of the complex formations are attributed to b-character of these metals, namely particularly high affinity of these metals to sulfur.

In the previous paper,[3] we reported that the reaction of monothioacetylacetone with palladium ion yields palladium dithioacetylacetonate together with palladium monothioacetylacetonate, and palladium monothio-β-diketonate were obtained from dilsufide of monothio-β-diketones and palladium ion. If these novel reactions are due to the high affinity between palladium and sulfur, and the high stability of the palladium chelate formed, the similar reactions are also expected in other b-character metal ions, which have stronger affinity towards sulfur than oxygen. The present paper deals with the chelate formation of some monothio-β-diketones and their disulfides with other b-character metal ions, such as platinum, rhodium and mercury. In this report, the following abbreviations are used for various ligands; acetylacetone (AA), benzoylacetone (BA), monothioacetylacetone (SAA), monothioacetylbenzophenone (SAB), monothiobenzoylacetone (SBA), monothiodibenzoylmethane (SBB), dithioacetylacetone (SSAA).

Experimental

Isolation of Two Kinds of Platinum Chelates——(a) To a solution of K_2PtCl_4 (166 mg, 4×10^{-4} mole in 20 ml H_2O), a solution of NaOH (20 ml of 0.1N) and a solution of SAA (232 mg, 2×10^{-3} mole in 20 ml of EtOH) were added successively. After heating under reflux for 30 min, the reaction mixture was cooled, extracted with $CHCl_3$ and washed with water. The $CHCl_3$ solution was dried with anhydrous Na_2SO_4, and $CHCl_3$ was removed. Pt $(SAA)_4$ was recrystallized from MeOH–$CHCl_3$. Yield 34 mg. mp 202° (decomp). *Anal.* Calcd. for $C_{20}H_{28}O_4S_4Pt$: C, 36.63; H, 4.27. Found: C, 36.71; H, 4.30.

(b) To a solution of K_2PtCl_4 (166 mg, 4×10^{-4} mole in 20 ml H_2O), a solution of HCl (20 ml of 0.1N) and a solution of SAA (232 mg, 2×10^{-3} mole in 20 ml of EtOH) were added successively. After the reaction mixture was allowed to stand overnight at room temperature, it was extracted with $CHCl_3$ and washed with water. The $CHCl_3$ solution was dried with anhydrous Na_2SO_4, and $CHCl_3$ was removed. The product was purified over dry column chromatography and recrystallized from acetone. Yield 5 mg. mp 250°. *Anal.* Calcd. for $C_{10}H_{14}S_4Pt$: C, 26.25; H, 3.06. Found: C, 26.31; H, 2.78.

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[1] Part XXXVII: S. Kawanishi, A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 21, 2617 (1973).

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

[3] S. Kawanishi, A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 20, 262 (1972).

Isolation of Two Kinds of Rhodium Chelates——To a solution of SAA (1.16 g, 10^{-2} mole in 100 ml of EtOH), a solution of $RhCl_3$ (1 g, in 100 ml of 0.1 N HCl) was added. Then 40 ml of 0.2 N NaOH was added to adjust pH to about 2.5. After the reaction mixture was allowed to stand for 5 hr at room temperature, it was extracted with $CHCl_3$ and washed with water. The $CHCl_3$ solution was dried with anhydrous Na_2SO_4, and $CHCl_3$ was removed. The product was chromatographed on a column packed with dry silica gel which was dipped in benzene. From the respective bands, yellow (15 mg, mp 250°) and red (32 mg, mp>255°) chelates were isolated by the extraction with CH_2Cl_2 and the evaporation, and were recrystallized from acetone. Data of the elemental analyses of these chelates are shown in Table IV.

Reaction of SAA with $HgCl_2$——To a solution of $HgCl_2$ (272 mg, 10^{-3} mole in 20 ml H_2O), a solution of SAA (232 mg, 2×10^{-3} mole in 20 ml EtOH) was added. The reaction mixture was allowed to stand for 5 hr at room temperature. When 10 ml of H_2O was added the pale yellow precipitate appeared. The product was filtered off, washed with H_2O and EtOH and dried.

a) Nuclear magnetic resonance (NMR) measurement was performed in saturated $CHCl_3$ solution after drying for 30 min.

b) NMR measurement was performed in saturated $CHCl_3$ solution and d_6-DMSO solution after drying for 3 days.

Reaction of Disulfide of Monothio-β-diketone with Pt^{2+}, Rh^{3+} and Hg^{2+}——a) Formation of Platinum Chelate from Disulfide of Monothio-β-diketones: To a solution of disulfide of SBB (47.8 mg, 10^{-4} mole) in 20 ml of acetone, K_2PtCl_4 (41.5 mg, 10^{-4} mole) in 5 ml of H_2O was added (about pH 5), and then 1 ml of 0.2 N H_2SO_4 was added (about pH 2.5). The reaction mixture was allowed to stand over night at room temperature. The precipitate (platinum chelate) was collected and recrystallized from acetone. mp 222°, yield 19 mg.

b) Formation of Rhodium Chelate from Disulfide of Monothio-β-diketone: To a solution of disulfide of SBB (47.8 mg, 10^{-4} mole) in 20 ml of acetone, $RhCl_3$ (24.5 mg, 10^{-4} mole) in 5 ml of H_2O was added, and then 1 ml of 0.2 N H_2SO_4 was added. The reaction mixture was allowed to stand for a week at room temperature. The precipitate was chromatographed over nylon column packed with dry silicagel which was dipped in benzene. From the yellow band, rhodium chelate was extracted with benzene and recrystallized from acetone. mp>255° yield 6 mg.

c) Formation of Mercury Complex from Disulfide of Monothio-β-diketone: To a solution of disulfide of SBB (47.8 mg, 10^{-4} mole) in 30 ml of acetone, $HgCl_2$ (27.2 mg, 10^{-4} mole) in 20 ml of H_2O was added. The reaction mixture was allowed to stand for several days at room temperature. The precipitate (mercury complex) was collected and recrystallized from ethanol. mp 240°, yield 10 mg.

d) Formation of Platinum Chelate from Disulfide of Monothio-β-diketone: Solutions of disulfide with various concentrations (ranging from 10^{-5} M to 2×10^{-4} M) were mixed with 6×10^{-5} M $KPtCl_4$ in 50% EtOH which contain 6×10^{-4} M HCl and the reaction mixture was allowed to stand for 1 hr or 5 hr at room temperature. The absorbance of platinum chelate was measured at 400 mμ.

Apparatus——The electronic spectra were measured on a Hitachi recording spectrophotometer model EPS-2 and the absorbances were determined with a Shimadzu Spectrophotometer model QV-50. NMR spectra were measured by a Varian A-60 spectrometer at 60 Mc. with tetramethylsilane as internal standard. The infrared absorption spectra were measured as potassium bromide disks in the range 4000—400 cm^{-1} on Koken DS-301 spectrophotometer.

Result and Discussion

Formation of Platinum(IV) Monothioacetylacetonate and Platinum(II) Dithioacetylacetonate

In the reaction of SAA with platinum ion, the formation of dark violet chelate was observed in acidic reaction medium, whereas yellow chelate was obtained when the reaction medium was neutral. From the results of elemental analyses, and infrared (IR) and NMR spectra, the yellow chelate was considered to be platinum(IV) monothioacetylacetonate, whereas the dark violet chelate was found to be identical to platinum(II) dithioacetylacetonate, which was reported by O. Sümann, *et al.*[4] Formation of platinum(II) dithioacetylacetonate was considered similarly to that of palladium(II) dithioacetylacetonate.[3]

The formation of platinum(IV) monothioacetylacetonate from platinum(II) ion is not unusual reaction, being referred the following examples. Sometimes the reaction of the ligand involving mercapto group with a metal ion in low oxidation state gives a metal complex of a higher oxidation state. From reaction of cobalt(II) ion with monothio-β-diketones,

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[4] O. Sümann and J. Fresco, *Inorg. Chem.*, 8, 1846 (1969).

1: 2 cobalt(II) chelates were not isolated and the oxidation took place promptly to form 1: 3 cobalt(III) chelates.[5] Similar oxidation from iron(II) to iron(III) occurs readily.[5] Moreover, reaction of titanium(III) chloride with monothiodibenzoylmethane gives a titanium(IV) compound with violent release of hydrogen sulfide.[6] The following experimental results may support the structure of 1: 4 platinum monothioacetylacetonate. Platinum(IV) monothioacetylacetonate is very stable and does not give platium(II) dithioacetylacetonate by the reaction with excess of hydrogen sulfide or sodium sulfide, unlike to the case of palladium monothioacetylacetonate. In the NMR spectrum of platinum(IV) monothioacetylacetonate, the chemical shifts of the proton of methine and methyl groups were found to be higher than expected and the chemical shifts of two methyl groups split into doublet to great extent.

TABLE I. Chemical Shifts of Platinum, Palladium and Nikel Chelates of Acetylacetone, Its Monothio- and Dithio- Derivatives in $CDCl_3$

	AA		SAA			SSAA	
	=CH–(τ)	–CH_3(τ)	=CH–(τ)	–CH_3(τ)	$\Delta\tau$	=CH–(τ)	–CH_3(τ)
Pt	4.48	8.05	3.74	7.82 8.13	0.31	2.34	7.88
($J_{\text{Pt-H}}$)	(10)	(5.4)	(5)	(8.1) (3.4)		(~2)	(8.6)
Pd	4.58	7.93	3.72	7.70 7.80	0.10	2.80	7.49
Ni			3.62	7.83 7.97	0.14	2.87	7.66

( ): spin coupling constant between ^{195}Pt and ^{1}H
$\Delta\tau$; difference in the chemical shifts between two methyl groups

In Table I, the results of the measurements of NMR spectra of platinum, palladium and nickel chelates of acetylacetone, its monothio- and dithio-derivatives[3,5] are summarized. On the whole, the lower field shift is observed by the introduction of sulfur atom. These observation on the NMR spectra may be explained by the long range deshielding effect due to the presence of the sulfur containing group.[3] In addition, the protons of the chelate ring and the methyl groups of platinum(II) dithioacetylacetonate show the chemical shifts at 2.34 and 7.88 ppm respectively. The former value is lower than that of benzene, and the latter value is close to that of methyl group of toluene. The possibility of the ring current must be taken into account for this observation. The lower shift of the chemical shift of methine proton in platinum, palladium and nickel chelates increases its degree in accord with the order in the affinity toward sulfur. The order consequently indicates that the degree of aromaticity of the chelate ring increases in the order, nickel chelate<palladium chelate<platinum chelate.

In two methyl groups of $Pt(SAA)_4$, marked difference was observed in their chemical shifts. The difference ($\Delta\tau$ 0.31) may be related to the difference between the affinity of platinum to sulfur and that to oxygen. In addition, since platinum contains 34% of the isotope ^{195}Pt with a nuclear spin of 1/2, each signal of proton should be split into a triplet of 1: 4: 1. For the methine proton in $Pt(AA)_2$ large coupling constants is observed ($J_{\text{Pt-H}}$—10), while for that in $Pt(SSAA)_2$, small coupling constant is observed ($J_{\text{Pt-H}}$—2) and for that in $Pt(SAA)_4$, intermediate coupling constant is observed ($J_{\text{Pt-H}}$—5). On the contrary, for the methyl group in $Pt(AA)_2$, small coupling constant is observed ($J_{\text{Pt-H}}$—5.4), while for that in $Pt(SSAA)_2$ large coupling constant is observed ($J_{\text{Pt-H}}$—8.6), and for that in $Pt(SAA)_4$, the band at 7.82 ppm is split into triplet with $J_{\text{Pt-H}}$—8.1, while the absorption at 8.13 ppm is split

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5) A. Yokoyama, S. Kawanishi and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 356 (1970).
6) M. Cox and J. Darken, *Coord. Chem. Rev.*, **7**, 29 (1971).

with $J_{\text{Pt-H}}$—3.4. As the number of intermediate atoms between the interacting nuclei, which effects mainly the magnitude of the splitting by ^{195}Pt, is equal, other facters, namely the effect of π-electrons[7] and zig-zag coupling[8] may be taken into account in the influence of platinum to methine and two methyl groups. Above-mentioned observations may be explained reasonably when the following hypothesis is provided. The effect of π-electron is dominant for the Pt(AA)$_2$ in which π-electron is localized in three carbon relative to Pt(SSAA)$_2$, while zig-zag coupling is dominant for the Pt(SSAA)$_2$ with strong bond Pt–S and delocalization of π-electron.

Wave numbers and the possible assignments of the main absorption bands in IR spectra of platinum, palladium and nickel chelates of acetylacetone, its monothio- and dithio-derivatives are listed in Table II. On the whole, in the case of dithioacetylacetonate, the absorption band of ν(C=C) was observed at lower wave number than in the case of acetylacetonate, especially in platinum chelate. On the whole, the observations in NMR and IR spectra support the delocalization of π-electrons shown in Chart 1, although the relation between Pt(SAA)$_4$ and Pt(SSAA)$_2$ is not clearly interpreted from the observations in wave numbers of ν(C=C) bands.

TABLE II. Infrared Spectral Bands of Platinum, Palladium and Nickel Chelates of Acetylacetotone, Its Monothio- and Dithio- derivatives in KBr Disks

	AA		SAA		SSAA	
	ν(C=O)	ν(C=C)	ν(C=O)	ν(C=C)	ν(C=O)	ν(C=C)
Pt	1562	1532	1538	1465		1467
Pd	1565	1520	1570	1470		1485
		1545		1490		
Ni	1598	1514	1562	1473		1488

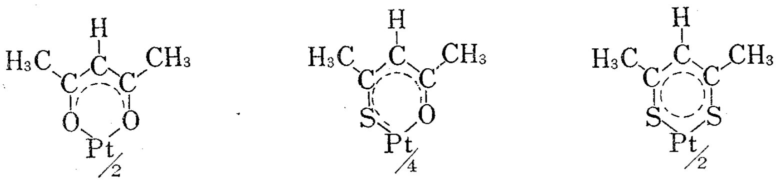

Chart 1

In the reaction of platinum ion with other thio-β-diketones than SAA in acid solution, very small amounts of platinum chelates of dithio derivative of SAB was obtained and identified by IR spectra, whereas the chelates of dithio derivatives of SBA and SBB were not obtained. These observations may be related to the fact that SAA is readily hydrolysed to acetylacetone and hydrogen sulfide whereas SBA and SBB are stable and relatively resistant to hydrolysis.

Rhodium Monothio-β-diketonates

In Table III, the results of the measurements of IR and NMR spectra of rhodium monothio-β-diketonates[5] are summarized.

In the rhodium(III) thio-β-diketonates of four different ligands, considerable differences were observed between thioacetylacetonate and other chelates involving phenyl group as in the case of cobalt(III) chelates.[9] The absorption bands of ν(C=C) of chelates involving

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7) S. Sternhell, *Rev. Pure. Appl. Chem.*, **14**, 15 (1964).
8) T. Schaefer, *J. Chem. Phys.*, **36**, 2235 (1962).
9) A. Yokoyama, S. Kawanishi and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 363 (1970).

Table III. Infrared Spectral Bands and Chemical Shifts of Rhodium Chelates of Thio-β-diketones

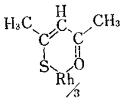
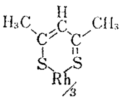
Ligand	IR(cm^{-1})		NMR(τ)	
	ν(C=O)	ν(C=C)	=CH-	-CH_3
SAA	1567	1465	3.75	7.75 7.80
SAB	1535	1462	2.75	7.58
SBA	1560	1453	3.33	7.66
SBB	1530	1460	~2.66	

phenyl group were observed at lower wave number than that of thioacetylacetonate. Also, in the case of the chelates involving phenyl group the signal of methine proton was observed in lower field than that of thioacetylacetonate. As to the reasons of this observation, two factors, namely, the deshielding effect and mesomeric effect of the phenyl group, can be taken into account, as discussed in cobalt(III) chelates.[9] In the NMR spectra, the signal of methyl group was observed as a doublet in Rh$(SAA)_3$, whereas a singlet in Co$(SAA)_3$ in chloroform. This observation may be explained by the difference to that in the affinity to sulfur between rhodium and cobalt, namely both metal ions are regarded to be provided with both a-character and b-character, and the extent of b-character is greater in rhodium than in cobalt.

Formation of Rhodium Dithioacetylacetonate

In the reaction of SAA with rhodium ion, the formation of violet chelate was observed in strong acidic medium, whereas yellow chelate was obtained when the reaction medium was neutral. From the results of elemental analyses, the IR and NMR spectra, the yellow chelate was found to be identical to Rh$(SAA)_3$, whereas the violet chelate was considered to be Rh$(SSAA)_3$ as shown in Table IV. In the case of the reaction of rhodium ion with thio-β-diketones other than SAA, the formation of rhodium dithio-β-diketonate was not observed. As previously reported, in the reaction of SAA with cobalt ion, the formation of dithiochelate was not observed. The occurance of the replacement of the ligand atom in rhodium monothioacetylacetonate indicates that occurrance of this reaction mainly is effected by the extent of the affinity of the metal ion to sulfur. Structure of the chelates may not be related to this reaction, structure of the chelates of palladium, rhodium and cobalt being considered. Palladium which forms dithio chelate generally forms square planar chelate whereas both rhodium and cobalt form octahedral chelate.

Table IV. Two Kinds of Rhodium Chelates obtained from Monothioacetylacetone with Rhodium Ion

						
Color		yellow			reddish violet	
mp (°C)		250			>255	
	H	C	Rh	H	C	Rh
Anal. Calcd.	4.68	40.18	22.99	4.23	36.29	20.77
Found	4.86	39.96	23.68	4.26	36.16	19.27
IR	ν(C=O)		ν(C=C)	ν(C=O)		ν(C=C)
(cm^{-1})	1567		1465			1465
NMR	=CH-		-CH_3	=CH-		-CH_3
(τ)	3.75		7.75 7.80	3.02		7.65

Reaction of SAA with $HgCl_2$

Mercury(II) complex with β-diketones are insoluble in most of the organic solvent and considered to have ploymeric structure. Although they have not been fully characterized, the existence of mercury-carbon bonds in the molecule seems highly probable.$^{10)}$ SAA forms a complex of metal-to-ligand ratio 1: 2 first, and this labile complex decomposes gradually. The NMR spectrum of the product of the reaction of SAA with $HgCl_2$, indicated the formation of Hg complex. The spectrum changes with time to show the formation of keto tautomer of acetylacetone, and at the same time, the intensity of the signal of water which exists in chloroform decreased, and the precipitation of black mercuric sulfide was observed. This change is explained by the hydrolysis of SAA mercury complex with a little amount of water in chloroform.

In the reaction of SAA with mercuric chloride, the formation of the similar complex of acetylacetone may possibly be considered through the decomposition of SAA complex. As shown in Chart 2, on the other hand, pale yellow SAA mercury complex was converted into brown powder even when it was dried *in vacuo* for a few days. The NMR spectrum of pale yellow SAA complex showed the spectrum of enol form of acetylacetone in deuterochloroform. Brown powder is insoluble in chloroform but soluble in dimethylsulfoxide to yield red solution. The NMR spectrum of this red solution in d_6-dimethylsulfoxide showed very broad signal of methyl group, which suggests a polymeric structure as shown in Chart 3.

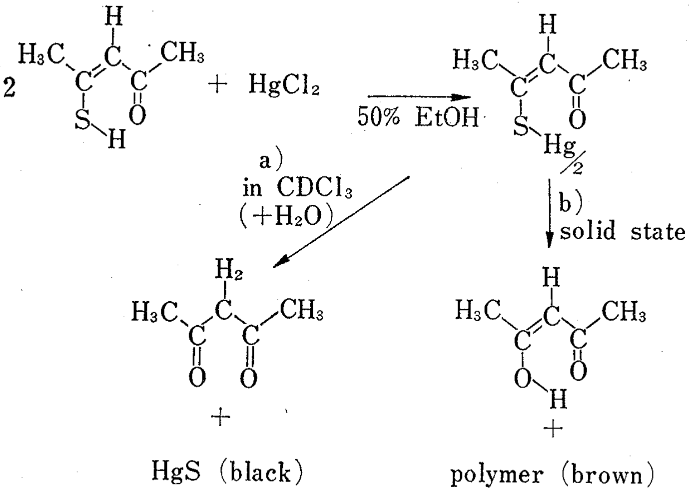


Chart 2

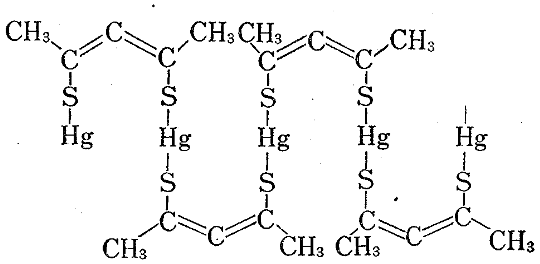


Chart 3

SBB forms the most stable mercury complex among four monothio-β-diketones tested. Mercury complex of SAB seems to be stable in $CDCl_3$ but the color turns from pale yellow to brown, and brown complex was converted to black substance through green complex, with

Table V. Three Kinds of Novel Reaction of SAA with Palladium, Platinum, Rhodium and Mercury

Type	Metal	
I	Pd	a) $Pd^{++} + SAA \longrightarrow Pd(SSAA)_2$
		b) $Pd(SAA)_2 + Na_2S \longrightarrow Pd(SSAA)_2$
II	Pt	a) $Pt^{++} + SAA \longrightarrow Pt(SSAA)_2$
	Rh	a) $Rh^{+++} + SAA \longrightarrow Rh(SSAA)_3$
III	Hg	c) $Hg^{++} + SAA \longrightarrow AA + [Hg(SSAA)]_n$

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10) D. Gibson, *Coordin. Chem. Rev.*, 4, 225 (1969).

the formation of BA. Mercury complex of SBA decomposed to BA and unknown red complex. The high stability of $Hg(SBB)_2$ can be ascribled to its resonance system. The replacement of the methyl group by phenyl group in sulfur side of the ligand molecule stabilizes the complex probably due to the back-donation of electron from d filled metal ion to the vacant d orbitals of the sulfur, which in turn retards the electron drift from phenyl group.[11]

The results of the reaction of SAA with platinum, rhodium, mercury and palladium ion can be compiled as shown in Table V. The attitude of these b-character metal ions in the replacement reaction of the ligand atom is classified into three types. In the reaction of palladium, SAA in acid solution yielded palladium dithioacetylacetonate and at the same time the reaction of the palladium monothioacetylacetone with sulfide ion yielded palladium dithioacetylacetone. In platinum and rhodium, the reaction of SAA in acid solution yielded the metal chelates of dithioacetylacetone but the metal chelates of monothioacetyl-

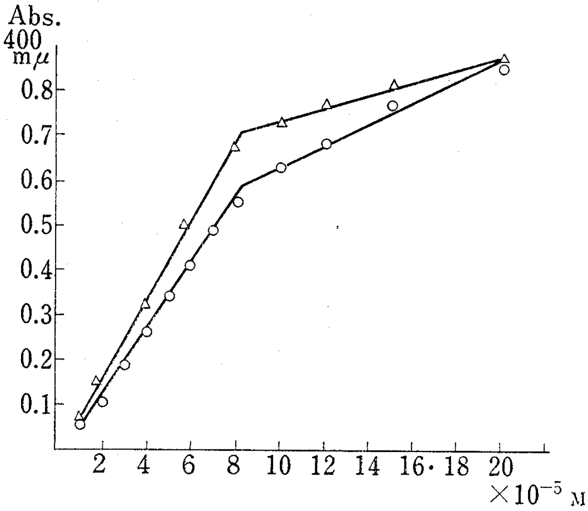

Fig. 1. Change in Absorbance with Ratio of $(SBB)_2$ to Pt Ion Concentration of K_2PtCl_4 6.0×10^{-5}M

△: 5 hr after mixing
○: 1 hr after mixing

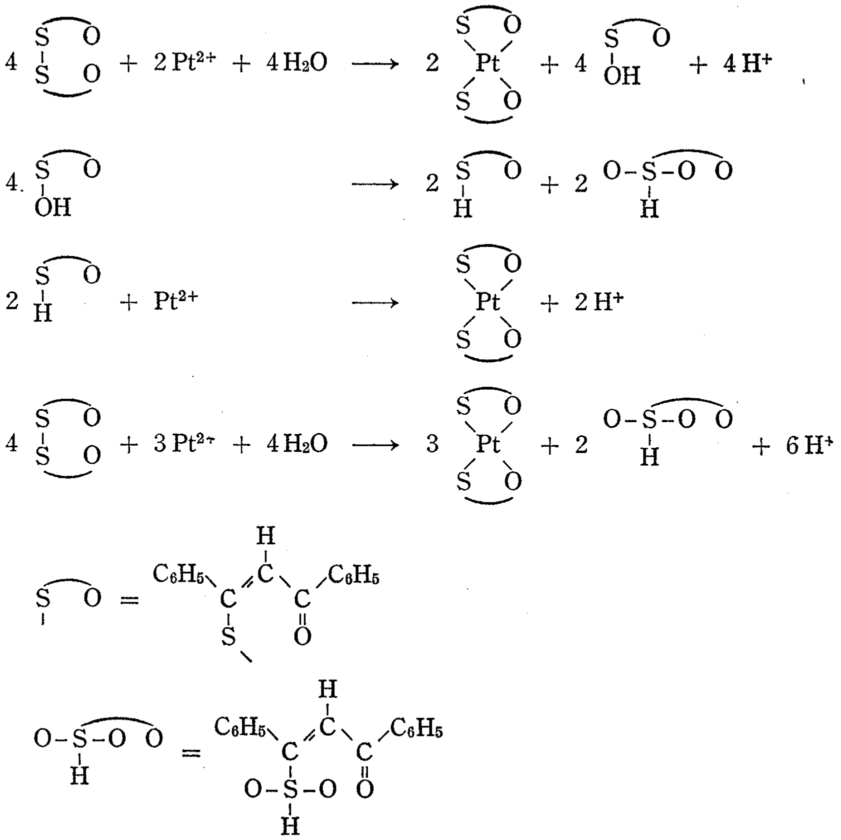

Chart 4

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[11] V.V. Savant, J. Gopalakrishnan and C.C. Patel, *Inorg. Chem.*, **9**, 748 (1970).

acetone does not react with sulfide ion. Mercury reacts in considerably different way from the cases of palladium, platinum and rhodium. In the case of mercury complex, homo-intramolecular replacement reaction occurs in solid state.

Reaction of Disulfide of Monothio-β-diketones with b-Character Metal Ions

From disulfide of SBB and platinum ion, rhodium ion or mercury ion, chelates of SBB of respective metal ions were obtained, similarly to the case of the reaction with palladium.3) Similar experiments were carried out for the reaction with platinum to the case of the reaction with palladium previously described.3) From the result shown in Fig. 1 the reaction may be described as Chart 4, namely 3 moles of platinum chelate is produced from 4 moles of disulfide of SBB and 3 moles of platinum. The occurrance of this reaction is attributed to the high affinity between the metal ion and sulfur, namely b-character of the metal ion and also to the high stability of the chelate formed.

Acknowledgement The authors are indebted to Dr. T. Shingu for the measurements of nuclear magnetic resonance spectra and the member of the Micro Analytical Center of Kyoto University for elemental analyses.