

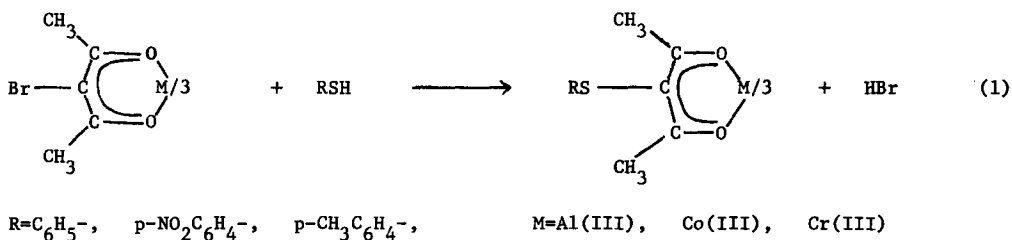
THE REACTION OF METAL (III) CHELATES OF 3-BROMO-2,4-PENTANEDIONE WITH THIOPHENOLS

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Although extensive works on electrophilic substitution reaction of metal acetylacetonates have been reported by J. P. Collman and his co-workers (1,2), successful examples of nucleophilic displacement on the chelate ring have never been found so far (3). We have succeeded in the first nucleophilic reaction on the metal-acetylacetonate chelate ring by the reaction of tris-(3-bromo-2,4-pentanediono) aluminum (III), cobalt (III) or chromium (III) with thiophenols, leading to yield tris-(3-arylthio-2,4-pentanediono)-metal (III). Some of these compounds have been obtained by the reaction of tris-(2,4-pentanediono)-metal (III) with phenylsulfenylchloride (sulfur electrophile) (4). We wish to report this interesting nucleophilic displacement of bromine of the brominated chelates with thiophenols shown in eq. 1.



The results of reactions are summarized in table 1. The structure of the products ($\text{I}_a \sim \text{III}_c$) was confirmed by their elemental analysis and spectral properties (Table 2).

For example, treatment of the brominated metal chelates with three times moles of thiophenol in CH_2Cl_2 at $-15 \sim -20^\circ\text{C}$ for aluminum (III) and cobalts (III) chelates and at $-5 \sim -10^\circ\text{C}$ for chromium (III) chelate afforded tris-(3-phenylthio-2,4-pentanediono)-metal (III).

For aluminum (III) chelate, the white precipitate from ethanol-water was found to be tri-substituted chelate (I_a). Thin layer chromatography showed the exclusive presence of

Table 1

	Metal	R	Yield(%)*	mp(°C)
I _a	Al(III)	C ₆ H ₅	13.3	89 ~ 92
I _b	Al(III)	p-CH ₃ C ₆ H ₄	39.6	162 ~ 164
I _c	Al(III)	p-NO ₂ C ₆ H ₄	18.6	135 ~ 137
II _a	Co(III)	C ₆ H ₅	45.3	104 ~ 106
II _b	Co(III)	p-CH ₃ C ₆ H ₄	44.8	170 ~ 171
II _c	Co(III)	p-NO ₂ C ₆ H ₄	43.5	163 ~ 165
III _a **	Cr(III)	C ₆ H ₅	90.0	105 ~ 107
III _b	Cr(III)	p-CH ₃ C ₆ H ₄	68.6	100 ~ 102
III _c	Cr(III)	p-NO ₂ C ₆ H ₄	88.6	148 ~ 150

* based on chelate. ** (lit. (3), 104 ~ 106°)

tri-phenylthio-substituted chelate for cobalt (III) chelate. In the case of chromium(III) chelate the column chromatography with benzene on Florisil gave tri-phenylthio-substituted chelate as a major product and small amounts of mixed-ligand chelate which was considered to be bis-(3-phenylthio-2,4-pentanediono)(2,4-pentanediono)-chromium(III) on the basis of IR and UV spectra.

Table 2 lists spectroscopic data (the nmr spectra in CCl₄ and CDCl₃, the IR spectra in KBr and the UV spectra in CH₂Cl₂). The proposed structures of the products are confirmed by the nmr spectra for aluminum(III) and cobalt(III) chelates. The characteristic IR absorptions of the phenyl ring appeared at around 1480 cm⁻¹ (ν_{C=C} of phenyl ring) and 800 cm⁻¹ (π (CH), out-of-plane vibration) show that the phenylthio group has been introduced to the chelate ring. The both absorptions have not been observed for the brominated chelates. Two bands appeared at around 850 cm⁻¹ for I_c, II_c and III_c having p-nitrophenylthio group are possibly assigned to π(CH) and the stretching vibration of C-N.

Table 2

	Chemical Shifts		τ in CCl_4		IR ^{****}		UV (in CH_2Cl_2)	
	CH_3^a , CH_3^b	R	$\nu(\text{C}=\text{C})$	$\pi(\text{CH})$, $\nu(\text{CN})$	λ_{max} (m μ)	(log ϵ)		
I _a	7.63 (18H)s*	2.90 ~ 3.05 (15H)m*	1480	805	252 (4.53)	291 (4.43)		
I _b	7.64 (18H)s	3.05 (12H)s, 7.76 (9H)s	1495	808	254 (4.56)	290 (4.49)		
I _c **	7.63 (18H)s	2.01 (6H)d* 2.82 (6H)d	1478	842	292 (4.54)	340 (4.56)		
II _a	7.46 (18H)s	2.92 ~ 3.05 (15H)m	1482	805	253 (4.77)			
II _b	7.50 (18H)s	3.06 (12H)s, 7.77 (9H)s	1495	807	255 (4.83)			
II _c **	7.40 (18H)s	1.90 (6H)s, 2.75 (6H)d	1477	842	255 (4.53)	341 (4.69)		
III _a ***			1481	806	252 (4.51)	335 (3.94)		
III _b ***			1495	806	254 (4.65)	334 (4.03)		
III _c ***			1477	841	340 (4.72)			

* s, d and m denote singlet, doublet and multiplet respectively.

** NMR spectra were measured in CDCl_3 with TMS as an internal reference.

*** No nmr spectra were observed due to the paramagnetic property of the chromium(III) chelates.

**** Only the characteristic new bands are listed.

UV spectra of (I_a), (I_b), (III_a) and (III_b) in CCl₄ showed new bands at 250 mμ assigned to a $\pi \rightarrow \pi^*$ local excitation of C₆H₅S and p-CH₃C₆H₄S. Unfortunately, these bands of (II_a) and (II_b) are overlapped with the intrinsic band of chelate ring of chromium (III) complex. The absorption at around 340 mμ of (I_c) and (II_c) is probably attributed to a $\pi \rightarrow \pi^*$ transition of p-NO₂C₆H₄S group.

The similar changes in IR and UV spectra of (III_a), (III_b) and (III_c) are good evidence to support that the three compounds also possess the tri-substituted p-nitrophenylthio group.

While an explanation for the reaction mechanism is not conclusive, the formation of the C-S linkage seems to involve the displacement of bromine from the chelate by attack of the sulfur nucleophile. In addition, the possibility of the radical reaction may be excluded by the occurrence of these reactions to the same extent under nitrogen atmosphere in dark. We are currently investigating the mechanism of reaction and attempting to find out another nucleophilic displacement. These results will be published elsewhere in near future.

References

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