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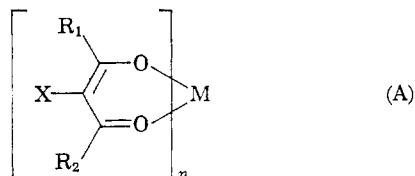
## Inner Complexes. IV. Chelate Sulfenyl Chlorides and Thiocyanates

BY RUDOLPH W. KLUIBER

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Chelate sulfenyl chlorides have been prepared by the reaction of the less labile metal 2,4-pentanedionates with sulfur dichloride. Further reaction with cyanide ion produced chelate thiocyanates independently synthesized by the action of thiocyanogen on the metal 2,4-pentanedionates.

Reactions of metal chelates in which the metal containing rings retain their integrity can be classified into three categories: (a) addition to the central metal atom or the chelate molecule as a whole, (b) reaction at functional groups and reactive sites pendent to the chelate ring and (c) substitution of hydrogens or other groups attached directly to the ring. Of particular interest are those reactions (c) involving substitutions on the ring as they provide information on the electronic structure of the ring as well as yield new chelate compounds. The synthetic aspect assumes importance in such readily available materials as the metal  $\beta$ -dicarbonyl chelates A ( $X = H$ ) where substitution of reactive functional groups for the hydrogen atom attached directly to the ring would give rise to polyfunctional chelates. These, in addition to any other utility, could prove useful in the preparation of chelate polymers.



Until recently few substitution reactions of metal  $\beta$ -dicarbonyl chelates have been recorded. Halides of structure A ( $X = \text{halogen}$ ) have been prepared in varying generality by apparent substitution on the chelate ring A ( $X = H$ ) using such reagents as bromine,<sup>1-3</sup> iodine,<sup>2</sup> iodine and mercuric oxide,<sup>4</sup> iodine monochloride,<sup>2</sup> sulfuryl chloride,<sup>4</sup> N-chlorosuccinimide,<sup>2,4</sup> N-bromosuccinimide<sup>2,5</sup> and N-iodosuccinimide.<sup>2,4</sup> Some nitro derivatives A ( $X = \text{NO}_2$ )<sup>6,7</sup> and acyl derivatives<sup>7,8</sup> A ( $X = \text{RCO}-$ ) also have been reportedly obtained directly from reactions which appear to involve substitution of the chelate ring. Although some of these reactions may be found to proceed through a ring cleavage step with subsequent recombination, at least one example, the bromination of chromium III (2,4-pentanedionate), A ( $M = \text{Cr}$ ,  $X = \text{H}$ ,  $R_1 = R_2 = \text{CH}_3$ ,  $n = 3$ ) with N-bromosuccinimide, has been shown to proceed without any intermediate ring cleavage.<sup>5</sup>

- (1) H. Reihlen, R. Ilig and R. Wittig, *Ber.*, **58**, 12 (1925).
- (2) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).
- (3) A. Becker, *Helv. Chim. Acta*, **32**, 1584 (1949).
- (4) R. W. Kluiber, unpublished results.
- (5) R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).
- (6) C. Djordjevic, J. Lewis and R. S. Nyholm, *Chem. and Ind. (London)*, 122 (1959).
- (7) J. P. Collman, R. A. Moss, S. D. Goldby and V. S. Trahanousky, *ibid.*, 1213 (1960).
- (8) W. F. Barry, *J. Chem. Soc.*, 670 (1960).

The chelate halides, the only group of these products on which reactivity studies have been made, were found to be inert toward further reactions in which the chelate ring remained intact.<sup>2</sup> Thus, although their formation is of theoretical interest, these derivatives are of no synthetic utility. The present work describes the preparation of some chelate sulfenyl chlorides A ( $X = -\text{SCl}$ ). Unlike the previously prepared derivatives, these new  $\beta$ -dicarbonyl chelates are capable of further conversion. A general synthesis of chelate thiocyanates A ( $X = \text{SCN}$ ) and the reaction of cyanogen bromide to give the halide A ( $X = \text{Br}$ ) are also described.

### Experimental

Samples of the 2,4-pentanedionates of copper (II), chromium (III) and cobalt (III) were obtained from the Union Carbide Metals Company, Niagara Falls, New York. Analyses were by Drs. Weiler and Strauss, Oxford, England, and the Union Carbide Plastics Company's Analytical Laboratory under the direction of Mr. J. V. Atkinson. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected.

**Sulfenyl Chloride of Chromium Tris-(2,4-pentanedionate).**—To a suspension of chromium tris-(2,4-pentanedionate), 10 g. (0.028 mole), in 100 ml. of olefin-free pentane was added slowly with stirring 10 ml. (0.15 mole) of sulfur dichloride. After stirring an additional five minutes, the mixture was filtered to yield 12.8 g. of insoluble crude sulfenyl chloride. This material was recrystallized from benzene-pentane (olefin-free) to give material, m.p. 185 dec. In pure form this material was quite stable at room temperature. The infrared spectrum showed only a single absorption ( $6.4 \mu$ ) in the  $6.25-6.75 \mu$  region and no absorption at  $8.25 \mu$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_6\text{S}_2\text{Cl}_2\text{Cr}$ : C, 32.82; H, 3.30; S, 17.52; Cl, 19.38; mol. wt., 549. Found: C, 33.14; H, 3.51; S, 17.94; Cl, 19.60; mol. wt. (cryoscopic, benzene), 576.

**Sulfenyl Chlorides of Aluminum (III) and Cobalt (III) 2,4-Pentanedionates.**—To 2.0 g. (0.0062 mole) of aluminum tris-(2,4-pentanedionate) suspended in 25 ml. of petroleum ether was added with stirring 20 ml. (0.30 mole) of sulfur dichloride. The resulting yellow precipitate, 2.6 g., was collected by filtration, m.p. dec.  $160-165^\circ$ . The product slowly decomposed upon standing at room temperature, liberating hydrogen chloride.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_6\text{S}_2\text{Cl}_2\text{Al}$ : S, 19.1. Found: S, 18.8.

The analogous cobalt compound, green, m.p. dec.  $100^\circ$ , was similarly obtained. This material was quite unstable and was identified best through its infrared spectrum which was similar to that of the chromium and aluminum chelates.

**Sulfenyl Chloride of Beryllium Bis-(2,4-pentanedionates).**—Beryllium bis-(2,4-pentanedionate), 2 g. (0.009 mole), was suspended in 25 ml. of pentane and 2 ml. (0.030 mole) of sulfur dichloride added with stirring. The reaction mixture was concentrated to 10 ml. and kept in the refrigerator at  $-20^\circ$  for one week. Yellow crystals, 1.2 g., were obtained by filtration, m.p.  $85-93^\circ$ .

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}_2\text{Cl}_2\text{Be}$ : S, 18.8; Cl, 20.8. Found: S, 19.7; Cl, 18.2. The material decomposed rapidly at about  $155^\circ$ .

**Reaction of Triethyl Phosphite with Chelate Sulfenyl Chlorides.**<sup>9</sup>—The sulfenyl chloride of chromium (III) tris-(2,4-pentanedionate), 3.02 g. (0.0165 eq.), was dissolved in 20 ml. of dry toluene and cooled to  $-30^{\circ}$ , whereupon 2.74 g. (0.0165 eq.) of triethyl phosphite in 10 ml. of toluene was added. The reaction was allowed to warm to room temperature with stirring, washed with sodium bicarbonate and water and dried over magnesium sulfate. Removal of the solvent (finally at 1.0 mm.,  $60^{\circ}$ ) produced 3.1 g. of a viscous oily material which was chloride free according to the Beilstein test. In addition to the chelate bands, the infrared spectrum contained absorptions at 8.60, 9.13, 9.60 and 10.34 microns, indicating the presence of a thiophosphate residue.

*Anal.* Calcd. for  $C_{27}H_{43}O_{15}P_3S_3Cr$ : S, 11.26; P, 10.88. Found (on the crude oil): S, 10.8; P, 10.1.

**Chromium Tris-(3-thiocyanato-2,4-pentanedionate).**—Using 10 g. (0.10 mole) of potassium thiocyanate, 8 g. (0.10 mole) of bromine and 5.8 g. (0.0165 mole) of chromium tris-2,4-pentanedionate, an essentially quantitative yield of chelate thiocyanate was obtained by the procedure of Grant and Snyder.<sup>10</sup> Recrystallization from benzene-petroleum ether gave pure thiocyanate, m.p.  $198.5-200^{\circ}$ . Like the corresponding chloride, but unlike the bromide and iodide, it did not form an insoluble solvate with chloroform. It absorbed in the infrared at  $4.64 \mu$ , characteristic of the thiocyanate group<sup>10</sup> and showed only a single absorption at  $6.40 \mu$  in the  $6.25-6.75 \mu$  region and no peak at  $8.25 \mu$ .

*Anal.* Calcd. for  $C_{18}H_{18}O_6N_3S_3Cr$ : C, 41.53; H, 3.48; N, 8.07. Found: C, 42.02; H, 3.83; N, 7.94.

Similarly prepared was cobalt tris-(3-thiocyanato-2,4-pentanedionate), green, m.p. dec.  $185^{\circ}$ . Recrystallized from benzene, it formed a 1:1 solvate which was quite stable.

*Anal.* Calcd. for  $C_{18}H_{18}O_6N_3S_3Co \cdot C_6H_6$ : C, 47.59; H, 3.99; N, 6.94; S, 15.88. Found: C, 47.25; H, 4.19; N, 6.74; S, 15.7. Recrystallization from methanol-water solution gave solvent-free thiocyanate.

*Anal.* Calcd. for  $C_{18}H_{18}O_6N_3S_3Co$ : C, 40.98; H, 3.44. Found: C, 40.87; H, 3.34.

In lower yield was obtained the white aluminum tris-(3-thiocyanato-2,4-pentanedionate), m.p.  $197-199^{\circ}$ , identified by its infrared spectrum.

**Preparation of Copper Bis-(3-thiocyanato-2,4-pentanedionate).**—The reaction was run as above except 4.0 g. of sodium bicarbonate was added along with the copper bis-(2,4-pentanedionate). The product was recrystallized from a large volume of benzene to give a blue precipitate, dec.  $170^{\circ}$ .

*Anal.* Calcd. for  $C_{12}H_{12}O_4N_2S_2Cu$ : C, 38.34; H, 3.22; N, 7.45. Found: C, 39.66; H, 3.45; N, 6.96.

In the absence of sodium bicarbonate, a copper-free compound was isolated, m.p.  $78-81^{\circ}$ . This material was very volatile and decomposed upon standing. Analysis and infrared data (absorption at 4.53, 5.75 and 6.30 microns) indicate it to be 3-thiocyanato-2,4-pentanedione.

*Anal.* Calcd. for  $C_8H_7O_2NS$ : C, 45.84; H, 4.49; N, 8.91. Found: C, 45.24; H, 4.79; N, 9.33.

**Conversion of the Chelate Sulfenyl Chloride to the Thiocyanate.**<sup>11</sup>—A mixture of 2 g. (0.03 mole) of potassium cyanide and 2 g. (0.0035 mole) of chromium tris-(3-sulfenyl chloride-2,4-pentanedionate) in 20 ml. of acetic acid was stirred for 1 hr. and poured into water. The crude thiocyanate was isolated by filtration in essentially quantitative yield. It proved identical with that prepared by thiocyanolysis by both mixed melting point and infrared spectra.

**Bromination with Cyanogen Bromide.**<sup>12</sup>—Into a flask containing 2.8 g. of cyanogen bromide in 40 ml. of carbon tetrachloride was added 2.3 g. of chromium tris-(2,4-pentanedionate). After 1 hr., only starting chelate was recovered by extracting with ether, washing with water and concentrating. After standing 24 hr., 3.3 g. of chromium tris-(3-bromo-2,4-pentanedionate) (chloroform 1:1 adduct)<sup>6</sup> was isolated. An experiment carried out as above but to which was added 4.0 g. of boron trifluoride etherate

yielded after 45 minutes 2.0 g. of the bromochelate chloroform solvate.

## Discussion

Sulfur dichloride reacts exothermically with the 2,4-pentanedionates of aluminum (III), beryllium (II), chromium (III) and cobalt (III) A ( $R_1 = R_2 = CH_3$ ,  $X = H$ ) to produce chelate sulfenyl chlorides A ( $X = -SCl$ ). The normal reaction product of sulfur dichloride with an olefin or an enolic compound such as 2,4-pentanedione<sup>13</sup> is a sulfide presumably formed by the reaction of the intermediate sulfenyl chloride with additional olefin or enol. Reported attempts to prepare pure sulfenyl chlorides of olefins by the addition of only one mole of sulfur dichloride across a double bond have proven relatively unsuccessful.<sup>14</sup> However, sulfenyl chlorides have been reported to be prepared by the interaction of sulfur dichloride with methylmalonamide or malonamide.<sup>15</sup> In addition to the utilization of favorable stoichiometry and solubility, the isolation of sulfenyl chlorides in the present case seems also due to steric shielding of the 3-position by the adjacent methyl groups. Steric hindrance at this position previously has been observed to account for the non-conjugation of a phenyl group in the 3-position with the resonance stabilized ring as evidenced by ultraviolet spectra. It is also possible to attribute the inertness of the chelate halides A ( $X = \text{halogen}$ ) not only to deactivation of the halogen by the resonance stabilized ring system but also to this steric shielding.

The reaction to form chelate sulfenyl chlorides proceeds only with the less labile chelates. Labile metal 2,4-pentanedionates such as those of copper (II) and iron (III) are cleaved readily in the presence of sulfur dichloride to a mixture of the corresponding inorganic sulfides and chlorides. The inner orbital complexes of chromium (III) and cobalt (III) are recognized for their inertness. The ability of the outer orbital chelates of aluminum (III) and beryllium (II) to survive the reaction conditions without apparent ring cleavage may also be explained by the relative inertness of these chelates due to the large charge radius ratios of the metal atoms and the absence of any empty low energy level orbitals. This degree of inertness has previously been observed in exchange reactions between aluminum or beryllium 2,4-pentanedionate and radioactive 2,4-pentanedione in chloroform.<sup>5</sup> Alternately the chelate ring could be cleaved in this reaction by the liberated hydrogen chloride and the by-product metal chloride subsequently recombined with the substituted ligand to give the appearance that no cleavage occurred. Such a sequence is not considered to be as likely, as in this process appreciable amounts of sulfide should be formed. This was not observed.

Unlike the previously prepared halides, these chelate sulfenyl chlorides react readily with diverse reagents such as amines, phenols, thiocyanates and

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(9) D. C. Morrison, *J. Am. Chem. Soc.*, **77**, 181 (1955).

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(11) T. Zincke and K. Eismayer, *Ber.*, **51**, 751 (1918).

(12) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publ. Corp., New York, N. Y., 1947, pp. 115-116.

olefins to form the anticipated derivatives,<sup>16</sup> roughly characterized by infrared spectra, the presence or absence of halogen and elemental analysis of the crude product. [Because of the trifunctionality of these chelates and less than quantitative yields in these reactions, most of the crude products could not be purified.] As an example, the reaction of the chelate sulfonyl chlorides with triethyl phosphite produced a material presumed to be the thiophosphate A ( $X = -SPO(\dot{O}C_2H_5)_2$ ). The parent  $\beta$ -diketone previously had been prepared by a different route, but its chelates were not reported.<sup>17</sup> In addition to these typical reactions and analytical data, the structures of these chelate sulfonyl chlorides were confirmed by infrared spectra which showed only single peaks in the 6.25–6.75  $\mu$  region and no peak at 8.2  $\mu$ . This is characteristic of 3-substituted metal 2,4-pentanedionates in which the substituent does not conjugate strongly with the ring.<sup>6,7,18</sup> Also, the sulfonyl chlorides of the normally colorless beryllium and aluminum chelates were yellow in color due to the  $-SCl$  chromophore. This color disappeared upon reaction with reagents such as cyclohexene, again a characteristic of sulfonyl chlorides. Chromium tris-(3-bromo-2,4-pentanedionate) was unreactive toward sulfur dichloride, emphasizing the importance of an unsubstituted 3-position and supporting the direct substitution of the 3-position rather than an initial radical attack on a side chain methyl group followed by an allylic migration to the ring.

The structure was confirmed further by the reaction of the sulfonyl chloride A ( $M = Cr, n = 3, X = -SCl, R_1 = R_2 = CH_3$ ) with cyanide ion to form the thiocyanate A ( $M = Cr, n = 3, X = -SCN, R_1 = R_2 = CH_3$ ). This was independently synthesized by the action of thiocyanogen on chromium tris-(2,4-pentanedionate) A ( $M = Cr, n = 3, X = H, R_1 = R_2 = CH_3$ ). As a pseudohalogen, thiocyanogen reacted in a manner similar to bro-

mine which substitutes the 3-position. This substitution reaction of thiocyanogen was found to be relatively general for this class of chelates with the cobalt (III) and aluminum (III) thiocyanates being analogously prepared. The labile copper (II) bis-(2,4-pentanedionate) was cleaved in the presence of thiocyanogen to give an organic material believed to be 3-thiocyanato-2,4-pentanedione. This ring cleavage could be eliminated by adding to the reaction mixture an excess of solid sodium bicarbonate to scavenge the liberated acid. In this manner copper (II) bis-(3-thiocyanato-2,4-pentanedionate) A ( $M = Cu, n = 2, X = -SCN, R_1 = R_2 = CH_3$ ) was obtained. Under these conditions, thiocyanolation appears to be a general reaction of these chelates.

The nature of the reagents used in ring substitution of these chelates does not allow the mechanism of these reactions to be unambiguously assigned. Thus, reagents such as N-bromosuccinimide or bromine can produce the halide by either a radical or ionic mechanism. In support of electrophilic substitution, chromium tris-(2,4-pentanedionate) has been acetylated in the 3-position under mild Friedel-Crafts conditions.<sup>7</sup> However, oxidative degradation of these chelates, presumably a radical process, also has been found to be favored by an unsubstituted 3-position.<sup>19</sup> In the course of attempts to prepare other derivatives of the 2,4-pentanedione chelates, it was observed that cyanogen bromide brominates chromium tris-(2,4-pentanedionate) slowly in the 3-position in the absence of any added catalyst. This reaction finds analogy in the ring bromination of other resonance stabilized systems such as phenols and the  $\alpha$  bromination of ketones.<sup>12</sup> Attempts to change the course of this reaction with chelates by use of Friedel-Crafts catalysts only markedly accelerated the rate of ring bromination. In the absence of an exact mechanistic study, firm conclusions cannot be made, but, superficially, it appears that this reaction is an additional example of electrophilic substitution of the chelate ring.

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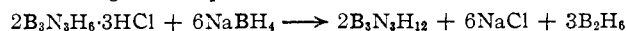
[CONTRIBUTION NO. 973 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

## Studies of Boron-Nitrogen Compounds. III.<sup>1</sup> Preparation and Properties of Hexahydroborazole, $B_3N_3H_{12}$

BY GERD H. DAHL AND RILEY SCHAEFFER

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The compound  $B_3N_3H_{12}$  has been prepared by addition of hydrogen chloride to borazole followed by reduction with sodium borohydride in diglyme according to the equation



Studies of its physical and chemical properties confirm that it is a six membered ring system composed of alternate  $BH_2$  and  $NH_2$  groups. The substance is a slightly volatile solid forming well defined crystals on sublimation in high vacuum and shows generally the physical properties of a moderately polar compound.

Since the discovery of borazole in 1926 many investigators have studied this molecule and numerous derivatives have been prepared.<sup>2</sup> The

fact that borazole is isoelectronic with benzene has attracted much attention and it is perhaps not unfair to say that the analogy between the two

(1) For paper II of this series see G. L. Brennan, G. H. Dahl and R. Schaeffer, *J. Am. Chem. Soc.*, **82**, 6248 (1960).

(2) For a general review of borazole chemistry see J. C. Sheldon and B. C. Smith, *Quart. Rev.*, **14**, 200 (1960).