Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 335–341. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 367–374.

Reaction of Sulfur Chlorides with Metal β-Diketonates

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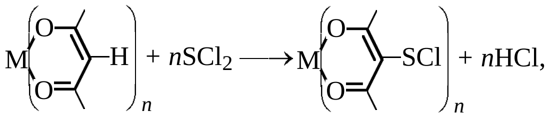
Received August 1, 2003

Abstract—Metal β-diketonates react with sulfur dichloride to form sulfenyl chlorides irrespective of β-substituent. Bulky phenyl and *tert*-butyl groups do not prevent formation of fully substituted complexes. The possibility of preparing sulfenyl chloride derivatives of rhodium, ruthenium, and vanadium β-diketonates was demonstrated. A new procedure was suggested for preparing chlorosulfenyl-substituted β-diketonates. Disulfur dichloride reacts with metal chelates with the substitution of both chlorine atoms and formation of polynuclear complexes in which the diketonate groups are linked by disulfide bridges.

It was shown previously that sulfur dichloride reacts with metal acetylacetonates with the substitution of one chlorine atom and formation of sulfenyl chloride derivatives [1]:


(1)

I–**IV**

M = Cr (**I**), Co (**II**), Al (**III**), $n = 3$; M = Be (**IV**), $n = 2$.

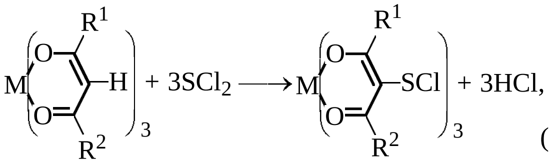
Sulfur dichloride was added to a suspension of acetylacetonate in pentane. The reactant ratio chelate : SCl_2 : pentane (g/ml/ml) was 1 : 1 : 10, which corresponded to a 1.8-fold excess of SCl_2. After stirring for 10 min, the product was filtered off.

The procedure is simple and convenient. However, it is applicable to only a limited range of metal complexes, namely, to those exhibiting high kinetic stability. Iron(III) and copper(II) acetylacetonates decompose under the conditions of reaction (1). Among compounds **I**–**IV**, the chromium complex **I** is the most stable. It can be stored for an unlimited time and can be purified by recrystallization. The cobalt (**II**) and aluminum (**III**) chelates decompose during storage or recrystallization.

Collman *et al*. [2] prepared an SCl-substituted acetylacetonate by reaction (1) starting from dichlorosubstituted chromium acetylacetonate.

The high reactivity of the SCl group was used to prepare chromium and cobalt acetylacetonates containing at the central carbon atom the thiophosphate [1, 3], thioamide [3], vinylthio [4], or chloroethylthio [5] group, and also siloxane polymers containing metal chelate groups [6].

Our goal was to apply reaction (1) to complexes of other β-diketones and to extend the range of metals whose complexes can be brought into this reaction. We obtained the SCl derivatives of the following metal chelates:


(2)

V–**XV**

M = Cr, $R^1 = R^2$ = Ph (**V**); M = Co, $R^1 = R^2$ = Ph (**VI**); M = Al, $R^1 = R^2$ = Ph (**VII**); M = Cr, $R^1 = CH_3$, R^2 = Ph (**VIII**); M = Cr, R^1 = *t*-Bu, $R^2 = CH_3$ (**IX**); M = Cr, $R^1 = CH_3$, R^2 = H (**X**); M = Co, $R^1 = CH_3$, R^2 = H (**XI**); M = Cr, $R^1 = R^2$ = H (**XII**); M = Rh, $R^1 = CH_3$, $R^2 = CH_3$ (**XIII**); M = Ru, $R^1 = CH_3$, $R^2 = CH_3$ (**XIV**); M = V, $R^1 = CH_3$, $R^2 = CH_3$ (**XV**).

β-Phenyl substituents drastically decrease the reactivity of the chelate ring. In the reaction of chromium dibenzoylmethanate [Cr(*dbm*H)$_3$] with sulfur dichloride under the conditions described in [1], the conversion of the starting chelate was incomplete (TLC monitoring). The decreased reactivity of dibenzoylmethanates in halogenation and nitration was reported previously [7, 8].

The fully substituted complex was obtained at increased concentration of SCl_2. The optimal reactant ratio (g/ml/ml) is Cr(*dbm*H)$_3$: SCl_2 : hexane = 1 : 2 : 5, which corresponds to a 7.5-fold excess of SCl_2. The optimal reaction time is 15 min. Further, even

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slight, increase in the SCl_2 concentration results in decomposition of Cr(*dbm*H)$_3$.

The fully substituted complex can also be obtained at a lower SCl_2 concentration, but the reaction time in this case should be as long as several hours. In this case, side decomposition reactions become more pronounced, decreasing the yield and quality of the product.

Compound **V** is quite stable, and it can be readily recrystallized. As shown by the analysis for S, Cl, and C, this is a trisubstituted complex. The IR spectrum of this compound in the range 1600–1500 cm^{-1} contains a strong band at 1508 cm^{-1} assignable to the chelating C=O groups [9] and two weak bands at 1597 and 1582 cm^{-1}, apparently belonging to phenyl groups. The spectrum of Cr(*dbm*H)$_3$ in the same range contains two strong bands at 1533 and 1524 cm^{-1} (C=O chelate, C=C) and a medium-intensity band at 1591 cm^{-1}. It is believed that the presence of a single band of chelated C=O is characteristic of complexes substituted at the central C atom [9].

Attempts to prepare Co(*dbm*SCl)$_3$ and Al(*dbm*SCl)$_3$ under the conditions described above failed. Cobalt and aluminum dibenzoylmethanates decomposed under the action of a large excess of SCl_2.

When the reaction is performed in solution, large excess of SCl_2 becomes unnecessary. The reactions of Cr(*acac*H)$_3$ and Cr(*dbm*H)$_3$ with a small excess of SCl_2 yielded fully substituted complexes similar to those prepared under heterogeneous conditions.

The reaction is performed at a low temperature (0–10°C) in chloroform or THF. THF is preferable, because the product in this case, according to elemental analysis, does not require additional purification. From chloroform, the product is isolated as a crystal solvate decomposing upon recrystallization.

SCl-Substituted cobalt (**VI**) and aluminum (**VII**) dibenzoylmethanates were prepared by the reaction in solution. The IR spectra of these compounds are similar to that of (**V**). The elemental analysis of the cobalt complex is reasonably consistent. However, the compound obtained from the Al complex shows strong deviations in the content of elements, apparently because the Al complex is less stable and decomposes to a greater extent.

Cr(*bzac*SCl)$_3$ (**VIII**) can be prepared in hexane at the reactant ratio used in [1] [chelate : SCl_2 : hexane = 1 : 1 : 10 (g/ml/ml)], which corresponds to a 2.8-fold excess of SCl_2. The yield of the product obtained by this procedure is 70–80%. When the reaction is performed in THF, the yield of **VIII** reaches 94–97%.

Since the reaction in solution yields a purer product (according to elemental analysis), it is preferable to perform the synthesis of **VIII** in solution.

Complex **VIII** is quite stable (it does not decompose noticeably during storage for several days), but, in contrast to the related acetylacetonate and dibenzoylmethanate derivatives, its attempted recrystallization failed. Therefore, the crude product was purified by precipitation from a benzene solution with hexane.

The IR spectrum of **VIII** in the range 1600–1500 cm^{-1} contains a strong band of chelated C=O (1530 cm^{-1}) and a weak band originating from vibrations of phenyl groups (1581 cm^{-1}). The spectrum of the unsubstituted complex in this range contains two strong bands at 1553 and 1515 cm^{-1} (C=O chelate, C=C) and two medium-intensity bands at 1588 and 1487 cm^{-1}.

The possibility of the substitution in complexes containing *tert*-butyl groups was checked with chromium pivaloylacetonate [Cr(*pvac*H)$_3$] as example. Treatment of a solution of Cr(*pvac*H)$_3$ in hexane with a small excess of SCl_2 gave complex **IX** in almost quantitative yield. Cr(*pvac*H)$_3$ is readily soluble in hexane; therefore, it is impossible to perform the reaction in a suspension. For analysis we took the crude complex, because its solubility in all inert organic solvents is too high to perform recrystallization.

The heaviest ion observed in the mass spectrum of **IX** is the molecular ion. Its isotopic pattern corresponds to the presence of three chlorine atoms.

Kluiber [1] noted that the formation of sulfenyl chlorides, and not sulfides, in reaction (1) was unexpected. This feature was due to the steric effect of β-methyl groups preventing the SCl group of the sulfenyl chloride to react with the molecule of unsubstituted acetylacetonate. Therefore, it was of particular interest to study the reaction of SCl_2 with chelates containing no β-substituents. As substrates for such a reaction we chose chromium and cobalt formylacetonates [Cr(*frac*H)$_3$, **X**; Co(*frac*H)$_3$, **XI**] and chromium malondialdehydate Cr(*mda*H)$_3$ (**XII**).

In the reaction with SCl_2, Cr(*frac*H)$_3$ and Co(*frac*H)$_3$ behave similarly to acetylacetonates. The reaction products were obtained by the traditional procedure [1] in high yields. The results of analysis for S, Cl, and C are consistent with the composition of the SCl-substituted chelates.

Complex **XI** is similar to Co(*acac*SCl)$_3$ in properties. It decomposes upon recrystallization or storage for 1–2 days, losing the solubility in organic solvents (benzene, chloroform). Complex **X** is less stable than its acetylacetonate analog. It decomposes upon recrystallization or storage for several weeks.

An unexpected result was obtained with the complex containing no substituents at the β-carbon atoms. On adding SCl_2 to a suspension of Cr(*mda*H)$_3$ in hexane, the crystals of the chelate changed the color from violet to beige, characteristic of **I** and **X**, but the IR spectrum of the reaction product was identical to that of the starting malondialdehydate. A TLC examination also revealed only the starting complex. Due to difficult availability of Cr(*mda*H)$_3$, we did not study the influence of the reaction time and SCl_2 concentration on the course of the substitution.

When performed in solution, the reaction yielded a complex whose IR spectrum in the range 1600–1500 cm^{-1} contained a single absorption band, characteristic of substituted metal chelates. The elemental analysis was approximately consistent with the formula of the trisubstituted complex. Apparently, the reaction yielded Cr(*mda*SCl)$_3$ contaminated with decompositions tion products. We failed to obtain the pure complex, as it decomposed during attempted recrystallization.

Thus, SCl_2 reacts with metal chelates containing one or no β-substituents similarly to the reaction with acetylacetonates. Hence, the shielding effect of β-substituents is not responsible for the fact that only one SCl group is involved in the reaction. The presence of phenyl or *tert*-butyl substituents does not prevent the reaction of the metal chelates with SCl_2. The SCl derivatives of acetylacetonates and formylacetonates are better prepared in suspension, whereas with the benzoylacetonate, dibenzoylmethanate, pivaloylacetonate, and malondialdehydate derivatives the synthesis in solution is preferable. Chlorosulfenyl derivatives of diketonates containing no β-substituents show decreased stability, which complicates their isolation and identification.

To extend the range of metals whose complexes can be converted into SCl derivatives, we studied the reaction of SCl_2 with Rh(III), Ru(III), Ga(III), V(III), and vanadyl(IV) acetylacetonates. The reactions were performed under the conditions described in [1]. We obtained previously unknown chlorosulfenyl derivatives of Rh(III) (**XIII**), Ru(III) (**XIV**), and V(III) (**XV**) acetylacetonates.

Taking into account the decreased reactivity of Rh(*acac*H)$_3$ in electrophilic substitutions [2], to prepare Rh(*acac*SCl)$_3$ we took the reactants in the following ratio (g/ml/ml): chelate : SCl_2 : hexane = 1 : 2 : 10, corresponding to a fourfold excess of SCl_2. Since Rh(*acac*H)$_3$ is more stable than Cr(III) and Co(III) acetylacetonates [2], increased concentration of SCl_2 does not cause decomposition of the complex.

Ruthenium complex **XIV** was prepared under similar conditions.

Compounds **XIII** and **XIV** are similar to the Cr complex in the stability. Their analytical data are reasonably consistent with the formulas of the trisubstituted chelates. The IR spectra are typical of substituted acetylacetonates. They contain a single band in the range 1600–1500 cm^{-1} (instead of two bands in the spectra of unsubstituted complexes), assignable to vibrations of the chelated C=O group [9]; weak bands of C^{α}–H bending vibrations at 1200 and 800 cm^{-1} [9] disappear. The mass spectra of these compounds contain molecular peaks; their isotopic pattern corresponds to the presence of three Cl atoms.

V(*acac*SCl)$_3$ was prepared by the traditional procedure [1]. Complex **XV** decomposes within a day. It was characterized by the IR spectrum, typical of a substituted acetylacetonate, and by elemental analysis. The content of C and Cl is approximately consistent with the formula of the trisubstituted chelate. The observed deviations are due to partial oxidation of the product and impossibility of its purification.

Gallium and vanadyl acetylacetonates decompose under the action of SCl_2 and the released HCl.

A mass-spectrometric study of **I**–**IX**, **XIII**, and **XIV** revealed the presence of molecular peaks in the spectra of SCl-substituted chromium, aluminum, beryllium, rhodium, and ruthenium acetylacetonates and in the spectrum of Cr(*pvac*SCl)$_3$. The spectra of the other complexes contain no heavy ions and are of no interest. Apparently, compounds **II** and **V**–**VIII** cannot be heated without decomposition to a temperature required for vaporization in the ionization chamber. Cobalt complex **II** decomposes even on slight heating; phenyl-substituted complexes **V**–**VIII** are insufficiently volatile.

In the series of SCl-substituted acetylacetonates, the molecular peaks decrease in intensity with an increase in the molecular weight of the complexes. The most common fragmentation pathway is successive removal of atoms of one of substituents and then of the ligand as a whole (*dik* = *acac* or *pvac*) (Table 1).

$$[M(dik\mathrm{SCl})_3]^{\cdot+} \longrightarrow [M(dik\mathrm{SCl})_2(acac\mathrm{S})]^+, \quad (3)$$

$$[M(dik\mathrm{SCl})_2(acac\mathrm{S})]^+ \longrightarrow [M(dik\mathrm{SCl})_2(acac)]^+, \quad (4)$$

$$[M(dik\mathrm{SCl})_3]^{\cdot+} \longrightarrow [M(dik\mathrm{SCl})_2]. \quad (5)$$

The ligand removal is the major fragmentation pathway for the aluminum and beryllium complexes.

Further fragmentation depends on the metal ion.

Table 1. Relative intensity of peaks (%) in the mass spectra of **I, III, IV, IX, XIII**, and **XIV**

Ion	**I**	**III**	**IV**	**IX**	**XIII**	**XIV**
$[\mathrm{M}(\textit{dik}\mathrm{SCl})_3]^+$	34	30		18	8	10
$[\mathrm{M}(\textit{dik}\mathrm{SCl})_2(\textit{dik}\mathrm{S})]^+$	14	11		9	2	7
$[\mathrm{M}(\textit{dik}\mathrm{SCl})_2(\textit{dik})]^+$	3	5		12	4	6
$[\mathrm{M}(\textit{dik}\mathrm{SCl})_2\mathrm{Cl}]^+$	19			27		
$[\mathrm{M}(\textit{dik}\mathrm{SCl})_2]^+$	20	100	35	39	3	
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\textit{dik}\mathrm{S})]^+$			60			
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\textit{dik})]^+$			27			
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\mathrm{OC}(\mathrm{CH}_3)\mathrm{C{=}S})\mathrm{Cl}]^+$	29			55		
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\mathrm{OC}(\mathrm{CH}_3)\mathrm{C{=}S})]^+$	16			75	13	
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\textit{dik})(\mathrm{Cl})]^+$		41		41	5	
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\textit{dik})]^+$		32			8	
$[\mathrm{M}(\textit{dik}\mathrm{SCl})(\mathrm{Cl})]^+$		12				
$[\mathrm{M}(\textit{dik}\mathrm{SCl})]^+$	6	6	55	32	3	

The fragmentation of chromium complexes **I** and **IX** can be described by Eq. (6):

$$[\mathrm{Cr}(\textit{dik}\mathrm{SCl})_2]^+ \xrightarrow[-\mathrm{RC(O)Cl}]{} [\mathrm{Cr}(\textit{dik}\mathrm{SCl})(\mathrm{OC}(\mathrm{CH}_3){=}\mathrm{C}{=}\mathrm{S})]^+, \quad (6)$$

$$\mathrm{R} = \mathrm{CH}_3,\ t\text{-Bu}.$$

It is interesting that, in the case of **IX**, from which two ions with different substituents can form according to Eq. (6), only the ion formed by the loss of pivaloyl chloride is formed.

The ruthenium compound showed the most complex fragmentation pattern. We were able to identify only several peaks. Identification of the other peaks was prevented by their large number, low intensity, and complex isotopic patterns (ruthenium has six major isotopes).

Table 2. Spectral characteristics of chlorosulfenyl derivatives of metal β-diketonates **I–VI, VIII–XI, XIII**, and **XIV**

Comp. no.	Compound	^{1}H NMR spectrum, δ, ppm	Absorption spectrum, λ, nm (log ε)
I	$\mathrm{Cr}(\textit{acac}\mathrm{SCl})_3$		292 (4.19), 550 (2.11)
II	$\mathrm{Co}(\textit{acac}\mathrm{SCl})_3$		291 (4.50), 576 (2.31)
III	$\mathrm{Al}(\textit{acac}\mathrm{SCl})_3$	2.66, 2.70	284 (4.31)
IV	$\mathrm{Be}(\textit{acac}\mathrm{SCl})_2$	2.66, 2.70	
V	$\mathrm{Cr}(\textit{dbm}\mathrm{SCl})_3$		291 (4.70), 559 (2.29)
VI	$\mathrm{Co}(\textit{dbm}\mathrm{SCl})_3$		277 (4.77), 590 (2.60)
VIII	$\mathrm{Cr}(\textit{bzac}\mathrm{SCl})_3$		271 (4.55), 552 (2.21)
IX	$\mathrm{Cr}(\textit{pvac}\mathrm{SCl})_3$		298 (4.37), 538 (2.10)
X	$\mathrm{Cr}(\textit{frac}\mathrm{SCl})_3$		276 (4.30), 552 (1.86)
XI	$\mathrm{Co}(\textit{frac}\mathrm{SCl})_3$		278 (4.33), 580 (2.06)
XIII	$\mathrm{Rh}(\textit{acac}\mathrm{SCl})_3$	2.76, 2.82	292 (4.56)
XIV	$\mathrm{Ru}(\textit{acac}\mathrm{SCl})_3$		265 (4.32), 345 (–), 535 (3.43)

We have measured the ^{1}H NMR spectra of complexes **III**, **IV**, and **XIII** (Table 2). In all these cases, the methyl groups give two separate signals of equal intensity, which suggests their nonequivalence. To account for this fact, we can assume the bent structure of the SCl group with its arrangement in the chelate ring plane and braked rotation around the C^α–S bond. In this case, the methyl groups differ in the distance from the chlorine atom.

We failed to obtain the ^{1}H NMR spectrum of **II**. All the samples of this compound contained an impurity of paramagnetic Co compounds whose formation was caused by impurities formed in the synthesis of sulfenyl chloride.

The electronic absorption spectra of **I**–**XIV** show that the SCl group appreciably alters the spectra of all the metal chelates. Instead of a set of separate bands of d–π_4 and π_3–π_4 transitions, all the spectra contain a single broad band exceeding in the intensity the bands of the unsubstituted complex (Table 2). This result is unusual, since the spectra of the other thio-substituted complexes $\{\mathrm{Cr}(\textit{acac}\mathrm{SC_2H_4Cl})_3$, $\mathrm{Cr}[\textit{acac}\cdot\mathrm{SPO(OEt)_2}]_3$, $\mathrm{Cr}(\textit{acac}\mathrm{SCN})_3$ [10]$\}$ are similar to the spectrum of the unsubstituted complex.

It appeared impossible to make an empirical assignment of the band observed in the spectra of the SCl-substituted complexes, since it does no coincide in the position and shape with any of the bands of the unsubstituted complex.

Our next goal was to study for comparison the reaction of the metal chelates with the closest analog of SCl_2, S_2Cl_2.

Treatment of a suspension of Cr(*acac*H)$_3$ in hexane with S_2Cl_2 under the conditions described in [1] resulted in the formation of a sticky rubbery mass blocking the stirrer even before adding the whole volume of S_2Cl_2. The reaction product was not studied in detail.

The reaction of S_2Cl_2 with excess Cr(*acac*H)$_3$ yielded several products that could be chromatographed, which indicates that these products contained no SCl groups. Along with the unchanged acetylacetonate, we isolated from the reaction mixture a product giving in the mass spectrum the peak at *m/z* 760 as the heaviest ion. This peak corresponds to a compound in which two acetylacetonate fragments are linked with a disulfide bridge: (H*acac*)$_2$Cr(*acac*S–S*acac*)Cr(*acac*H)$_2$. The presence of strong peaks of [(H*acac*)$_2$Cr(*acac*S)]$^+$ and [(H*acac*)$_2$Cr(*acac*)]$^+$ (relative intensity 100% each) confirms this formula. The IR spectrum of this compound in the range 1700–1600 cm^{-1} shows a superposition of two bands corresponding to the vibrations of four unsubstituted rings and a band of two substituted rings. Thus, the reaction of S_2Cl_2 with Cr(*acac*H)$_3$ involves both SCl groups, in accordance with Eq. (7):

$$\mathrm{Cr}(acac\mathrm{H})_3 + \mathrm{S_2Cl_2} \longrightarrow \underset{\mathbf{XVI}}{(\mathrm{H}acac)_2\mathrm{Cr}(acac\mathrm{S{-}S}acac)\mathrm{Cr}(acac\mathrm{H})_2}. \tag{7}$$

The other spots in the chromatogram apparently belong to oligomers consisting of three, four, or more metal chelate fragments.

With the aim to prepare the monochlorosulfenyl derivative, we treated compound **XVI** with 1 equiv of SO_2Cl_2.

The reaction yielded three chromatographically mobile products. No compounds with zero chromatographic mobility were obtained. Since chlorosulfenyl derivatives of all the diketonates studied show zero mobility on silica gel (probably because of the reaction of SCl groups with silanol groups), we can conclude that the chlorosulfenyl derivative was not obtained. The IR spectra of the three complexes formed by the reaction are indicative of successive substitution of the chelate rings with chlorine atoms.

Sulfuryl chloride was not used previously as a chlorinating agent for metal diketonates. To check this possibility, we treated Cr(*acac*H)$_3$ with sulfuryl chloride. We obtained Cr(*acac*Cl)$_3$, which was identified by TLC and IR spectroscopy. Thus, sulfuryl chloride reacts with unsubstituted chelates and can be used as a chlorinating agent.

Treatment of **XVI** with a large excess of SO_2Cl_2 yielded a single product, which showed chromatographic mobility and hence was not a chlorosulfenyl derivative. Apparently, the reaction stops at the step of formation of the fully chlorinated dimer [Cr(*acac*·Cl)$_2$(*acac*S–)]$_2$. The β-methyl groups probably limit the penetration of sulfuryl chloride molecules to the disulfide group and thus prevent its cleavage.

EXPERIMENTAL

The IR spectra in the range 4000–400 cm^{-1} were recorded on an Impact-400 spectrometer (KBr pellets). The UV spectra were taken on Hitachi-220A and Specord μ-40 spectrometers in chloroform in 1-cm cells (solution concentration 10^{-3} M for the visible range and 10^{-5} M for the UV range). The mass spectra were taken on an LKB-9000 device at an ionizing voltage of 70 eV. The ^{1}H NMR spectra were recorded on a Bruker WH-250 spectrometer (250 MHz, $CDCl_3$) relative to TMS. The TLC analysis was performed with Sorbfil PTSKh-P-V plates, with benzene or benzene–acetone (10 : 1) as eluent. The analytical data for the compounds obtained are given in Table 3.

Preparation of tris(2-chlorosulfenyl-1,3-diphenyl-1,3-propanedionato)chromium(III) V in a suspension. A 2-ml portion of SCl_2 was added dropwise to a stirred suspension of 12 ml of finely ground chromium dibenzoylmethanate in 5 ml of hexane. After stirring for 15 min, the precipitate was filtered off, washed with hexane, vacuum-dried, and recrystallized from benzene–hexane. Yield 0.81 g (63%); brown crystalline substance, mp 160–163°C.

Preparation of tris(2-chlorosulfenyl-1,3-diphenyl-1,3-propanedionato)chromium(III) V in solution. A solution of 1.9 ml of SCl_2 in 5 ml of THF was added dropwise at –10°C to a stirred solution of 3.6 g of chromium dibenzoylmethanate in 100 ml of THF. After stirring for 40 min, the solvent was distilled off in a vacuum at room temperature. The residue was recrystallized from benzene–hexane. Yield 3.25 g (70%); brown crystalline substance, mp 162–164°C.

Tris(2-chlorosulfenyl-1,3-diphenyl-1,3-propanedionato)cobalt(III) VI was prepared similarly from 2 g of cobalt dibenzoylmethanate, 50 ml of THF, and 1.0 ml of SCl_2. The residue after distilling off the solvent was washed with hexane. Yield 98%. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-1,3-diphenyl-1,3-propane-

Table 3. Analytical data for **V**–**XVI**

Comp. no.	Found, %			Formula	Calculated, %		
	C	Cl	S		C	Cl	S
V[a]	58.47	11.50	10.31	$C_{45}H_{30}Cl_3CrO_6S_3$	58.67	11.54	10.44
V[b]	58.50	11.60	10.97	$C_{45}H_{30}Cl_3CrO_6S_3$	58.67	11.54	10.44
VI	58.04	11.06	10.37	$C_{45}H_{30}Cl_3CoO_6S_3$	58.23	11.46	10.36
VII	61.27	10.45	8.82	$C_{45}H_{30}AlCl_3O_6S_3$	60.31	11.87	10.73
VIII[a]	50.31	14.01	12.35	$C_{30}H_{24}Cl_3CrO_6S_3$	49.02	14.47	13.09
VIII[b]	48.74	14.83	13.42	$C_{30}H_{24}Cl_3CrO_6S_3$	49.02	14.47	13.09
IX	40.60	15.52	–	$C_{24}H_{36}Cl_3CrO_6S_3$	42.70	15.75	14.25
X	28.20	21.12	19.31	$C_{12}H_{12}Cl_3CrO_6S_3$	28.44	20.99	18.98
XI	28.44	20.30	19.12	$C_{12}H_{12}Cl_3CoO_6S_3$	28.06	20.70	18.72
XII	24.85	23.45	21.49	$C_9H_6Cl_3CrO_6S_3$	23.26	22.89	20.70
XIII	31.71	17.23	16.74	$C_{15}H_{18}Cl_3O_6RhS_3$	30.04	17.73	16.04
XIV	30.71	17.80	16.23	$C_{15}H_{18}Cl_3O_6RuS_3$	30.13	17.79	16.09
XV[c]	31.16	–	–	$C_{15}H_{18}Cl_3O_6S_3V$	32.89	19.42	17.56
XVI[d]	–	–	8.80	$C_{30}H_{40}Cr_2O_{12}S_2$	47.36	–	8.43

[a] For the complex prepared in hexane. [b] For the complex prepared in solution. [c] V(*acac*SCl)$_3$. [d] [Cr(*acac*H)$_2$(*acac*S)]$_2$.

dionato)aluminum VII was prepared similarly from 2 g of aluminum dibenzoylmethanate, 50 ml of THF, and 1.1 ml of SCl_2. The residue after removing the solvent was washed with hexane. Yield 93%. The product was analyzed without additional purification.

Preparation of tris(2-chlorosulfenyl-1-phenyl-1,3-butanedionato)chromium(III) VIII in suspension. A 1.0-ml portion of SCl_2 was added dropwise to a stirred suspension of 1 g of finely ground chromium benzoylacetonate in 10 ml of hexane. After stirring for 15 min, the precipitate was filtered off, washed with hexane, and vacuum-dried. Yield 0.96 g (70%); brown powder. For analysis, the sample was reprecipitated from benzene with hexane.

Preparation of tris(2-chlorosulfenyl-1-phenyl-1,3-butanedionato)chromium(III) VIII in solution was performed similarly to Cr(*dbm*SCl)$_3$. The product was analyzed without additional purification; mp 130–135°C (dec.).

Tris(3-chlorosulfenyl-5,5-dimethyl-2,4-hexanedionato)chromium(III) IX was prepared similarly to Cr(*dbm*SCl)$_3$ from 0.5 g of Cr(*pvac*H)$_3$, 30 ml of hexane, and 0.4 ml of SCl_2. Yield 0.65 g (92%); brown resinous substance. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-1,3-butanedionato)chromium(III) X. A 0.5-ml portion of SCl_2 was added dropwise to a stirred suspension of 0.5 g of Cr(*frac*H)$_3$ in 5 ml of hexane. After stirring for 10 min, the precipitate was filtered off, washed with hexane, and vacuum-dried. Yield 0.73 g (90%); beige powder. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-1,3-butanedionato)cobalt(III) XI was prepared similarly. Yield 74%. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-1,3-propanedionato)chromium(III) XII was prepared similarly to Cr(*dbm*SCl)$_3$. Yield 63%. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-2,4-pentanedionato)rhodium(III) XIII. A 1-ml portion of SCl_2 was added dropwise to a stirred suspension of 0.5 g of Rh(*acac*H)$_3$ in 5 ml of hexane. After stirring for 10 min, the precipitate was filtered off, washed with hexane, and dried in air. Yield 0.69 g (92%); yellow powder. The product was recrystallized from benzene–hexane; decomposition point 120–130°C.

Tris(2-chlorosulfenyl-2,4-pentanedionato)ruthenium(III) XIV was prepared similarly. Yield 89%. The product was analyzed without additional purification.

Tris(2-chlorosulfenyl-2,4-pentanedionato)vanadium(III) XV was prepared similarly from 0.5 g of V(*acac*H)$_3$, 5 ml of hexane, and 0.5 ml of SCl_2. Yield 80%. The product was analyzed without additional purification.

[3,3'-Dithiobis(2,4-pentanedionato)]tetrakis(2,4-pentanedionato)dichromium(III) XVI. A solution of 0.4 ml of S_2Cl_2 in 10 ml of chloroform was added with stirring to a solution of 3.5 g of Cr(*acac*H)$_3$ in 50 ml of chloroform. After 5 min, 2 ml of triethylamine was added. The solvent was removed in a vacuum at room temperature. The reaction products were isolated chromatographically on silica gel, eluent benzene–acetone (stepwise elution, from 400 : 1 to 400 : 10). We recovered 0.5 g (14%) of unchanged Cr(*acac*H)$_3$, mp 209–212°C (published data: mp 214°C [11]) and isolated 2.4 g of violet crystalline complex **XVI** (yield 63%) after recrystallization from benzene–heptane.

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