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# Transition Metal Complexes with Sulfur Ligands. 97.[1] Coordinatively and Electronically Unsaturated and Saturated Cr$^0$, Mo$^0$, and W$^0$ Dithiolate Complexes of the Type $[M(CO)_3('S_2')]^{2-}$ and $[M_2(CO)_7('S_2')]^{2-}$ $\{'S_2'^{2-} = S_2C_6R_4^{2-}$ (R = H, Cl, Me); $S_2C_2H_4^{2-}\}$

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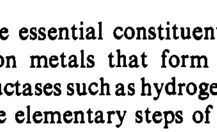
Reactions of $[Cr(CO)_3(MeCN)_3]$ with $S_2C_6R_4^{2-}$ (R = Cl, Me) yielded coordinatively and electronically unsaturated $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$, $[\mathbf{1}]^{2-}$, and $[Cr(CO)_3(S_2C_6Me_4)]^{2-}$, $[\mathbf{2}]^{2-}$. X-ray structure determination proved the Cr$^0$ center of $[\mathbf{1}]^{2-}$ to be five-coordinate and surrounded in a distorted trigonal bipyramid by three carbon and two sulfur donors. The distances indicate the double-bond character of the Cr–S bonds (231.8 pm) suggesting that the $S_2C_6Cl_4^{2-}$ ligand acts as $\sigma$–$\pi$ donor such that the Cr$^0$ center achieves a formal 18 e$^-$ configuration. The reaction of $CrCl_2$ with $S_2C_6H_4^{2-}$ led to $[Cr(S_2C_6H_4)_2]^{2-}$, $[\mathbf{12}]^{2-}$, which is shown by X-ray structure determination to have a four-coordinate Cr$^{II}$ center, the short Cr–S bonds (236.2 pm) exhibiting partial double-bond character. When reacted with CO, $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^{2-}$ yielded coordinatively and electronically saturated $[Cr(CO)_4(S_2C_6R_4)]^{2-}$ (R = Cl, $[\mathbf{3}]^{2-}$; R = Me, $[\mathbf{4}]^{2-}$). The X-ray structure determination of $[\mathbf{3}]^{2-}$ showed that the Cr center is six-coordinate and surrounded pseudooctahedrally by four carbon and two cis sulfur donors. The average Cr–S distance (242.0 pm) is significantly longer than that in $[\mathbf{1}]^{2-}$. Reactions of $[M(CO)_3('S_2')]^{2-}$ (M = Cr, Mo, W; 'S$_2$' = $S_2C_2H_4$, $S_2C_6R_4$) with $[M(CO)_4]$ complexes (M = Cr, Mo, W) yielded the dinuclear $[Cr_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{5}]^{2-}$, $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$, $[\mathbf{6}]^{2-}$, $[Mo_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{7}]^{2-}$, $[W_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{8}]^{2-}$, and $[Cr_2(CO)_7(S_2C_6R_4)]^{2-}$ (R = H, $[\mathbf{9}]^{2-}$; R = Cl, $[\mathbf{10}]^{2-}$; R = Me, $[\mathbf{11}]^{2-}$). X-ray structure determinations of $[\mathbf{5}]^{2-}$, $[\mathbf{6}]^{2-}$, $[\mathbf{7}]^{2-}$, and $[\mathbf{10}]^{2-}$ revealed that the metal centers each are surrounded pseudooctahedrally by four carbon and two sulfur donors, the sulfur donors, and one CO group bridging two $[M(CO)_3]$ fragments. In addition, the metal centers are connected by M–M single bonds and reach 18 e$^-$ configurations. Accordingly, the M–S bonds exhibit single-bond character ($[\mathbf{5}]^{2-}$, $d_{Cr-S}$ = 241.9 pm; $[\mathbf{6}]^{2-}$, $d_{Cr-S}$ = 242.9 pm; $[\mathbf{7}]^{2-}$, $d_{Mo-S}$ = 256.5 pm; $[\mathbf{10}]^{2-}$, $d_{Cr-S}$ = 243.5 pm). Crystal data for $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$: monoclinic space group $P2_1/c$, $a$ = 1518.5(15) pm, $b$ = 1355.8(8) pm, $c$ = 1564.2(11) pm, $\beta$ = 100.41(7) °, $Z$ = 4, $R/R_w$ = 6.6/5.1%. Crystal data for $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$: orthorhombic space group $Pca2_1$, $a$ = 1520.2(4) pm, $b$ = 2830.2(5) pm, $c$ = 1505.4(4) pm, $Z$ = 8, $R/R_w$ = 4.0/4.0%. Crystal data for $(NEt_4)_2[Cr(S_2C_6H_4)_2]$: monoclinic space group $P2_1/n$, $a$ = 1746.6(6) pm, $b$ = 1203.4(5) pm, $c$ = 1748.3(6) pm, $\beta$ = 119.82(3) °, $Z$ = 4, $R/R_w$ = 6.8/4.8%. Crystal data for $(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$: monoclinic space group $C2/c$, $a$ = 1887.0(9) pm, $b$ = 1118.4(3) pm, $c$ = 2534.6(1) pm, $\beta$ = 110.67(3) °, $Z$ = 4, $R/R_w$ = 8.3/6.4%. Crystal data for $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$: monoclinic space group $C2/c$, $a$ = 2384.0(7) pm, $b$ = 893.2(3) pm, $c$ = 3421.0(15) pm, $\beta$ = 93.91(3) °, $Z$ = 8, $R/R_w$ = 8.0/6.5%. Crystal data for $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$: trigonal space group $P3_1$, $a = b$ = 1103.4(1) pm, $c$ = 3949.5(11) pm, $Z$ = 3, $R/R_w$ = 6.5/4.5%. Crystal data for $(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$: monoclinic space group $P2_1/c$, $a$ = 1666.2(8) pm, $b$ = 1597.6(10) pm, $c$ = 2263.4(10) pm, $\beta$ = 90.22(4) °, $Z$ = 4, $R/R_w$ = 5.5/4.3%.

## Introduction

Sulfur donors are essential constituents of the coordination spheres of transition metals that form the active centers of numerous oxidoreductases such as hydrogenases or nitrogenases.[2] At these centers the elementary steps of the overall enzymatic reactions take place, which include addition and release of substrates. These two reactions require the intermediate existence of vacant coordination sites, and it is of interest to elucidate in which way sulfur donors influence the generation and stabilization of such vacant sites in comparison to other ligands such as amines or phosphines. In this context, the anion of $(NEt_4)_2[Cr(CO)_3(S_2C_6H_4)]$[3] is of particular interest.



It exhibits a coordinatively unsaturated Cr$^0$ center which has a 16 e$^-$ configuration only but is nevertheless stable at room temperature. In this respect, it remarkably differs from other complexes with five-coordinate and 16 e$^-$ Cr$^0$ centers such as $[Cr(CO)_5]$.[4] Because of its instability $[Cr(CO)_5]$ can be observed only at low temperatures in inert gas matrices. $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ salts also differ from $[M(CO)_3(PCy_3)_2]$ complexes, M = Cr,[5] Mo, and W,[6] that likewise possess formally five-coordinate 16 e$^-$ M$^0$ centers. These complexes, however, exhibit agostic M··H–C interactions which protect the vacant sixth coordination site and are so strong that 3c–2e [M··H–C] bonds leading to 18 e$^-$ configurations of the M$^0$ centers can be discussed.[6]

In contrast, the stability of the $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ anion must be attributed to the thiolate donors of the $S_2C_6H_4^{2-}$ ligand. The relatively short Cr–S distances (229.5 pm) indicate S→Cr $\pi$-donor bonds, which reduce the electron deficiency of the Cr$^0$ center. The vacant site, however, is not blocked completely as

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can be deduced from the reversible coordination of CO according to eq 1. Stabilization of coordinatively and electronically

$$[Cr(CO)_3(S_2C_6H_4)]^{2-} \underset{-CO}{\overset{+CO}{\rightleftarrows}} [Cr(CO)_4(S_2C_6H_4)]^{2-} \quad (1)$$

unsaturated metal centers by thiolate ligands was recently also observed in the Fe(IV) compounds $[Fe(S_2C_6H_4)_2]$.[7] The analysis of C–S and C–C distances in these complexes revealed that $\pi$-donation from thiolate sulfur donors to iron is responsible for the stabilization of the high valent Fe(IV) centers, and not the potentially "noninnocent" character of $S_2C_6H_4^{2-}$ ligands.

The aim of this work was to investigate the influence of the sulfur substituents in bidentate 1,2-dithiolates with respect to properties and stabilities of $[M(CO)_3('S_2')]^{2-}$ and $[M(CO)_4('S_2')]^{2-}$ complexes (M = Cr, Mo, W). Substituted benzenedithiolates and aliphatic 1,2-dithiolates were used as ligands.

## Experimental Section

**General Data.** Unless noted otherwise, all reactions and operations were carried out under nitrogen at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments. IR ($CaF_2$ cuvettes or KBr pellets): Zeiss IMR 16 and Perkin-Elmer 983. NMR: Jeol JNM-GX 270. $[Cr(CO)_3(MeCN)_3]$,[8] $[M(CO)_3(EtCN)_3]$ (M = Mo, W),[9] $[M(CO)_4(nor)]$ (M = Cr, Mo; nor = norbornadiene),[10] $[W(CO)_4(MeCN)_2]$,[11] $CrCl_2$,[12] cyclohexane-*trans*-1,2-dithiol,[13] benzene-1,2-dithiol,[14] and tetrachlorobenzene-1,2-dithiol[15] were prepared by literature methods. Tetramethylbenzene-1,2-dithiol was obtained by modification of the synthesis described in ref 16.

**Syntheses and Reactions. $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[1].** Under argon, a yellow solution of $[(Cr(CO)_3(MeCN)_3]$ (140 mg, 0.54 mmol) in 8 mL of THF was combined with a solution of $S_2C_6Cl_4H_2$ (150 mg, 0.54 mmol) and LiOMe (41 mg, 1.08 mmol) in 4 mL of MeOH. The resulting wine-red reaction mixture was treated with $NEt_4Cl$ (1.08 mmol, 1.08 mL of a 1.0 M MeOH solution) and filtered. The solvents were removed in vacuo, and the residue was suspended in 8 mL of THF and treated with MeOH (ca. 2.5 mL) to give a clear solution. Cooling to −30 °C yielded dark-red thin plates which were separated, washed with 10 mL of THF, and dried in vacuo. Yield: 230 mg (63%). Anal. Calcd for $C_{25}Cl_4CrH_{40}N_2O_3S_2$ ($M_r$ 674.53): C, 44.52; H, 5.98; N, 4.15; S, 9.51. Found: C, 44.43; H, 6.20; N, 4.01; S, 9.77. IR (MeCN, $cm^{-1}$): 1760, 1882 (s, $\nu_{CO}$). $^1H$ NMR ($CD_3CN$, $\delta$ [ppm]): 2.95 (s, 16 H, $N(CH_2CH_3)_4$); 1.10 (s, 24 H, $N(CH_2CH_3)_4$). $^{13}C\{^1H\}$ NMR ($CD_3CN$, $\delta$ [ppm]): 249.0 (CO); 156.0, 130.0, 120.5 ($S_2C_6Cl_4$); 57.0 ($N(CH_2CH_3)_4$); 10.5 ($N(CH_2CH_3)_4$).

**$(NEt_4)_2[Cr(CO)_3(S_2C_6Me_4)]$, $(NEt_4)_2$[2].** This compound was prepared in the same way as $(NEt_4)_2$ [1]. Setup: Solutions of $[Cr(CO)_3(MeCN)_3]$ (260 mg, 1.0 mmol) in 12 mL of THF, $S_2C_6Me_4H_2$ (200 mg, 1.0 mmol) and LiOMe (76 mg, 2.0 mmol) in 5 mL of MeOH, and $NEt_4Cl$ (2.0 mmol, 2.0 mL of a 1.0 M MeOH solution). The residue was dissolved in 15 mL of THF and ca. 4 mL of MeOH. Yield: 330 mg (56%) dark-red thin plates. Anal. Calcd for $C_{29}CrH_{52}N_2O_3S_2$ ($M_r$ 592.86): C, 58.75; H, 8.84; N, 4.73; S, 10.82. Found: C, 58.43; H, 9.16; N, 4.72; S, 10.63. IR (MeCN, $cm^{-1}$): 1740, 1865 (s, $\nu_{CO}$). $^1H$ NMR ($CD_3CN$, $\delta$ [ppm]): 2.70 (s, broad, 16 H, $N(CH_2CH_3)_4$); 0.95 (s, 24 H, $N(CH_2CH_3)_4$); 2.65 (s, 6 H, $S_2C_6Me_4$); 2.20 (s, 6 H, $S_2C_6Me_4$). $^{13}C\{^1H\}$ NMR ($CD_3CN$, $\delta$ [ppm]): 250.4 (CO); 151.5, 131.8, 125.3 ($S_2C_6Me_4$); 56.2 ($N(CH_2CH_3)_4$); 10.0 ($N(CH_2CH_3)_4$); 20.8, 17.2 ($S_2C_6Me_4$).

**$(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[3].** A yellow solution of $[Cr(CO)_3(MeCN)_3]$ (170 mg, 0.66 mmol) in 10 mL of THF was combined with a solution of $S_2C_6Cl_4H_2$ (185 mg, 0.66 mmol) and LiOMe (50 mg, 1.32 mmol) in 4 mL of MeOH. $NEt_4Cl$ (1.32 mmol, 1.32 mL of a 1.0 M MeOH solution) was added. CO was bubbled through the solution for ca. 2 min, whereupon the color of the reaction mixture changed from wine-red to orange. When the solution was layered with 5 mL of hexane under CO orange crystals precipitated, which were collected after 2 d, washed with 3 mL of THF, and dried in vacuo. Yield: 345 mg (74%). Anal. Calcd for $C_{26}Cl_4CrH_{40}N_2O_4S_2$ ($M_r$ 702.54): C, 44.45; H, 5.74; N, 3.99; S, 9.13. Found: C, 44.53; H, 5.88; N, 4.01; S, 9.11. IR (MeCN, $cm^{-1}$): 1980 (m, $\nu_{CO}$); 1865, 1830, 1780 (s, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.15 (s, 16 H, $N(CH_2CH_3)_4$); 1.15 (s, 24 H, $N(CH_2CH_3)_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 233.7, 220.7 (CO); 158.2, 128.6, 117.0 ($S_2C_6Cl_4$); 52.2 ($N(CH_2CH_3)_4$); 7.6 ($N(CH_2CH_3)_4$).

**$(NEt_4)_2[Cr(CO)_4(S_2C_6Me_4)]$, $(NEt_4)_2$[4].** This compound was prepared in the same way as $(NEt_4)_2$[3]. Setup: Solutions of $[Cr(CO)_3(MeCN)_3]$ (260 mg, 1.0 mmol) in 12 mL of THF, $S_2C_6Me_4H_2$ (200 mg, 1.0 mmol) and LiOMe (76 mg, 2.0 mmol) in 4 mL of MeOH and $NEt_4Cl$ (2.0 mmol, 2.0 mL of a 1.0 M MeOH solution). The resulting solution was layered with 8 mL of hexane. Because $(NEt_4)_2$[4] rapidly loses CO in vacuo, it was dried in a stream of CO and stored under CO. Yield: 290 mg (48%) yellow needles. Anal. Calcd for $C_{30}CrH_{52}N_2O_4S_2$ ($M_r$ 620.87): C, 58.04; H, 8.44; N, 4.51; S, 10.33. Found: C, 57.96; H, 8.68; N, 4.56; S, 10.35. IR (MeCN, $cm^{-1}$): 1965 (m, $\nu_{CO}$), 1850, 1810, 1755 (s, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.07 (s, 16 H, $N(CH_2CH_3)_4$); 1.06 (s, 24 H, $N(CH_2CH_3)_4$); 2.36 (s, 6 H, $S_2C_6Me_4$); 2.03 (s, 6 H, $S_2C_6Me_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 237.0, 222.6 (CO); 150.8, 130.3, 122.6 ($S_2C_6Me_4$); 52.6 ($N(CH_2CH_3)_4$); 7.8 ($N(CH_2CH_3)_4$); 20.3, 16.6 ($S_2C_6Me_4$).

**$A_2[Cr_2(CO)_7(S_2C_2H_4)]$, $A_2$[5] (A = $NEt_4$, $PPh_4$). Method a. A = $NEt_4$.** A filtered solution of $[Cr(CO)_3(MeCN)_3]$ (130 mg, 0.5 mmol) in 12 mL of THF was added dropwise to a solution of $Na_2S_2C_2H_4$ (69 mg, 0.5 mmol) in 2 mL of MeOH, whereupon the color of the reaction mixture immediately changed from orange to red-violet. The solution was successively layered with 10 mL of MeOH and a solution of $NEt_4Cl$ (165 mg, 1.0 mmol) in 7 mL of MeOH. Within the course of 7 d, the color of the solution slowly changed from red-violet to red-brown and longish crystals precipitated, which were separated, washed with 6 mL of THF, and dried in vacuo for 5 h. Yield: 100 mg (61% related to $Na_2S_2C_2H_2$). Anal. Calcd for $C_{25}Cr_2H_{44}N_2O_7S_2$ ($M_r$ 652.74): C, 46.00; H, 6.79; N, 4.29; S, 9.82. Found: C, 45.89; H, 7.08; N, 4.10; S, 9.59. IR (MeCN, $cm^{-1}$): 1950 (m, $\nu_{CO}$); 1885, 1800 (s, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]: 3.20 (s, 16 H, $N(CH_2CH_3)_4$); 1.16 (s, 24 H, $N(CH_2CH_3)_4$); 2.21 (s, 4 H, $S_2C_2H_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 252.9 ($\mu$-CO); 232.2, 230.6 (CO); 51.6 ($N(CH_2CH_3)_4$); 7.3 ($N(CH_2CH_3)_4$); 31.4 ($S_2C_2H_4$).

**A = $PPh_4$.** Single crystals of the $PPh_4$ analogue were obtained in the same way by using a solution of $PPh_4Cl$ (375 mg, 1.0 mmol) in 7 mL of MeOH.

**Method b. A = $NEt_4$.** Under argon an orange suspension of $[Cr(CO)_3(MeCN)_3]$ (310 mg, 1.2 mmol) in 12 mL of THF was combined with a solution of $Li_2S_2C_2H_4$ (130 mg, 1.2 mmol) in 3 mL of MeOH, whereupon the color turned red-violet. A solution of $[Cr(CO)_4(nor)]$ (305 mg, 1.2 mmol) in 5 mL of THF was added, and the reaction mixture was stirred for 3 h. The resulting red-brown solution was filtered and combined with a solution of $NEt_4Cl$ (395 mg, 2.4 mmol) in 3 mL of MeOH. When the resulting mixture was reduced in volume to ca. 7 mL, a microcrystalline solid precipitated. It was separated and redissolved in a mixture of 5 mL of MeOH and ca. 3 mL of MeCN, which was cooled to −30 °C. Red-brown crystals precipitated, which were separated, washed with 6 mL of THF, and dried in vacuo for 8 h. Yield: 590 mg (75%).

**$(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]$, $(NEt_4)_2$[6].** A filtered orange solution of $[Cr(CO)_3(MeCN)_3]$ (130 mg, 0.5 mmol) in 12 mL of THF was added dropwise to a solution of $Na_2S_2C_6H_{10}$ (95 mg, 0.5 mmol) in 2 mL of MeOH, whereupon the color immediately changed to red-violet. The resulting solution was layered with 10 mL of MeOH and a solution of $NEt_4Cl$ (165 mg, 1.0 mmol) in 7 mL of MeOH. In the course of 7 d, the color of the mixture slowly changed to red-brown, and red-brown crystals precipitated, which were collected and washed with 6 mL of THF. Suitable crystals for X-ray analysis were separated; the remaining material was pulverized and dried in vacuo for 10 h. Yield: 95 mg (54%). Anal. Calcd for $C_{29}Cr_2H_{50}N_2O_7S_2$ ($M_r$ 706.84): C, 49.28; H, 7.13; N, 3.96; S, 9.07. Found: C, 49.50; H, 7.39; N, 3.80; S, 8.87. IR (DMSO, $cm^{-1}$): 1945 (m, $\nu_{CO}$); 1880, 1795 (s, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.21 (s, 16 H, $N(CH_2CH_3)_4$); 1.17 (s, 24 H, $N(CH_2CH_3)_4$);

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2.02, 1.63, 1.10 (m, 10 H, $S_2C_6\mathit{H}_{10}$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 254.8 ($\mu$-$\mathit{C}O$); 232.9, 231.6, 230.5 ($\mathit{C}O$); 51.4 ($N(\mathit{C}H_2CH_3)_4$); 7.3 ($N(CH_2\mathit{C}H_3)_4$); 54.8, 37.8, 27.3 ($S_2\mathit{C}_6H_{10}$).

**$A_2[Mo_2(CO)_7(S_2C_2H_4)]$, $A_2$[7] (A = $NEt_4$, $PPh_4$). A = $NEt_4$.** A yellow solution of $[Mo(CO)_3(EtCN)_3]$ (645 mg, 1.87 mmol) in 10 mL of MeCN was combined with a solution of $Na_2S_2C_2H_4$ (258 mg, 1.87 mmol) in 4 mL of MeOH. To the resulting red-brown mixture a yellow solution of $[Mo(CO)_4(nor)]$ (560 mg, 1.87 mmol) in 8 mL of MeCN was added dropwise and stirred for 10 h. A solution of $NEt_4Cl$ (620 mg, 3.74 mmol) in 4 mL of MeOH was added; the resulting mixture was filtered over cellulose pulps and reduced in volume to ca. 5 mL. An orange powder precipitated, which was separated and redissolved in a mixture of 10 mL of MeOH and ca. 10 mL of MeCN. Cooling of the resulting solution to −30 °C afforded orange-red crystals, which were collected, washed with 10 mL of THF, and dried in vacuo for 20 h. Yield: 1.14 g (82%). Anal. Calcd for $C_{25}H_{44}Mo_2N_2O_7S_2$ ($M_r$ 740.63): C, 40.54; H, 5.99; N, 3.78; S, 8.66. Found: C, 40.46; H, 6.20; N, 3.61; S, 8.63. IR (MeCN, $cm^{-1}$): 1975 (w, $\nu_{CO}$), 1890 (vs, $\nu_{CO}$), 1815 (s, $\nu_{CO}$), 1770 (m, $\nu_{\mu\text{-}CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.24 (q, 16 H, $N(C\mathit{H}_2CH_3)_4$); 1.18 (t, 24 H, $N(CH_2C\mathit{H}_3)_4$); 2.38 (s, 4 H, $S_2C_2\mathit{H}_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 232.2 ($\mu$-$\mathit{C}O$); 223.3, 218.4 (broad, $\mathit{C}O$); 51.4 ($N(\mathit{C}H_2CH_3)_4$); 7.0 ($N(CH_2\mathit{C}H_3)_4$); 32.9 ($S_2\mathit{C}_2H_4$).

**A = $PPh_4$.** For X-ray analysis, single crystals of $(PPh_4)_2$[7] were obtained in the same way as $(PPh_4)_2$[**5**]. Combining solutions of $[Mo(CO)_3(MeCN)_3]$ (152 mg, 0.5 mmol) in 12 mL of THF and $Li_2S_2C_2H_4$ (53 mg, 0.5 mmol) in 3 mL of MeOH yielded a brown mixture that was successively layered with 5 mL of MeOH and a solution of $PPh_4Cl$ (375 mg, 1.0 mmol) in 8 mL of MeOH. In the course of 4 weeks, orange-red prisms of $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot$THF precipitated.

**$(NEt_4)_2[W_2(CO)_7(S_2C_2H_4)]$, $(NEt_4)_2$[8].** A yellow-brown solution of $[W(CO)_3(EtCN)_3]$ (1.82 g, 4.2 mmol) in 40 mL of MeCN was combined with $Na_2S_2C_2H_4$ (580 mg, 4.2 mmol) in 5 mL of MeOH. To the resulting red-brown mixture, a solution of $[W(CO)_4(MeCN)_2]$ (1.59 g, 4.2 mmol) in 50 mL of MeOH was added and stirred for 10 h. Addition of $NEt_4Cl$ (1.39 g, 8.4 mmol) in 8 mL of MeOH, filtration over pulps and reducing the filtrate in volume to ca. 10 mL yielded an orange-red powder. It was separated and redissolved in 20 mL of MeOH and ca. 25 mL of MeCN. At −30 °C red crystals precipitated, which were collected, washed with 10 mL of THF, and dried in vacuo for 20 h. Yield: 3.09 g (80%). Anal. Calcd for $C_{25}H_{44}N_2O_7S_2W_2$ ($M_r$ 916.45): C, 32.76; H, 4.84; N, 3.06; S, 7.00. Found: C, 32.55; H, 5.05; N, 2.90; S, 7.22. IR (MeCN, $cm^{-1}$): 1970 (w, $\nu_{CO}$), 1880 (vs, $\nu_{CO}$), 1810 (s, $\nu_{CO}$), 1760 (m, $\nu_{\mu\text{-}CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.21 (q, 16 H, $N(C\mathit{H}_2CH_3)_4$); 1.18 (tt, 24 H, $N(CH_2C\mathit{H}_3)_4$); 2.40 (s, 4 H, $S_2C_2\mathit{H}_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$), $\delta$ [ppm]): 221.3 ($\mu$-$\mathit{C}O$); 216.4 ($\mathit{C}O$); 210.2 (broad, $\mathit{C}O$), 51.4 ($N(\mathit{C}H_2CH_3)_4$); 7.0 ($N(CH_2\mathit{C}H_3)_4$); 34.2 ($S_2\mathit{C}_2H_4$).

**$A_2[Cr_2(CO)_7(S_2C_6R_4)]$. General Method of Preparation for Complexes with A = $NEt_4$ and R = H and Me and A = $PPh_4$ and R = Cl.** A suspension or solution of $[Cr(CO)_3(MeCN)_3]$ in THF was combined with a solution of $S_2C_6R_4$-$H_2$ and LiOMe in MeOH, whereupon the color immediately changed from orange to wine-red. A solution of $[Cr(CO)_4(nor)]$ in THF was added, and the reaction mixture was stirred for 20 h. Successive layering of the resulting red-brown solution with MeOH and with a solution of ACl (A = $NEt_4$, $PPh_4$) in MeOH yielded red-brown thin plates, which were collected and recrystallized from mixtures of MeOH and MeCN at −30 °C. The precipitating red crystals were separated, washed with MeOH, and dried in vacuo.

**$(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_4)]$, $(NEt_4)_2$[9].** Setup: Suspension of $[Cr(CO)_3(MeCN)_3]$ (520 mg, 2.0 mmol) in 10 mL of THF; solutions of $S_2C_6H_4$-$H_2$ (0.23 mL, 2.0 mmol) and LiOMe (152 mg, 4.0 mmol) in 5 mL of MeOH, $[Cr(CO)_4(nor)]$ (510 mg, 2.0 mmol) in 10 mL of THF, and $NEt_4Cl$ (660 mg, 4.0 mmol) in 4 mL of MeOH; recrystallization from 10 mL of MeOH and 15 mL of MeCN. Yield: 1.19 g (85%) red crystals. Anal. Calcd for $C_{29}Cr_2H_{44}N_2O_7S_2$ ($M_r$ 700.79): C, 49.70; H, 6.33; N, 4.00; S, 9.15. Found: C, 49.46; H, 6.49; N, 3.81; S, 9.28. IR (MeCN, $cm^{-1}$): 1955 (w, $\nu_{CO}$); 1895, 1805 (s, $\nu_{CO}$); 1850 (sh, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.21 (q, 16 H, $N(C\mathit{H}_2CH_3)_4$); 1.16 (t, 24 H, $N(CH_2C\mathit{H}_3)_4$); 6.93, 6.22 (m, 4 H, $S_2C_6\mathit{H}_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 255.8 ($\mu$-$\mathit{C}O$); 230.4 ($\mathit{C}O$); 160.2, 126.4, 120.1 ($S_2\mathit{C}_6H_4$); 51.4 ($N(\mathit{C}H_2CH_3)_4$); 7.0 ($N(CH_2\mathit{C}H_3)_4$).

**$(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot$MeCN, $(PPh_4)_2$[10]$\cdot$MeCN.** Setup: Solutions of $[Cr(CO)_3(MeCN)_3]$ (130 mg, 0.5 mmol) in 5 mL of THF, $S_2C_6Cl_4H_2$ (140 mg, 0.5 mmol) and LiOMe (38 mg, 1.0 mmol) in 3 mL of MeOH, $[Cr(CO)_4(nor)]$ (128 mg, 0.5 mmol) in 3 mL of THF, and $PPh_4Cl$ (375 mg, 1.0 mmol) in 2 mL of MeOH. Recrystallization from 3 mL of MeOH and 5 mL of MeCN gave $(PPh_4)_2$[**10**]$\cdot$MeCN. Yield: 365 mg (56%) dark red crystals. Anal. Calcd for $C_{63}Cl_4Cr_2H_{43}NO_7P_2S_2$ ($M_r$ 1297.91): C, 58.30; H, 3.34; N, 1.08; S, 4.94. Found: C, 58.39; H, 3.64; N, 1.02; S, 4.82%. IR (MeCN, $cm^{-1}$): 1965 (w, $\nu_{CO}$); 1905, 1820 (s, $\nu_{CO}$); 1855 (sh, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 8.04–7.68 (m, 40 H, $P(C_6\mathit{H}_5)_4$); 2.10 (s, 3 H, $C\mathit{H}_3CN$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 254.7 ($\mu$-$\mathit{C}O$); 230.0, 228.6 ($\mathit{C}O$); 164.8, 128.8, 121.4 ($S_2\mathit{C}_6Cl_4$); 135.2 (s, broad, $P(\mathit{C}_6H_5)_4$); 134.2, 130.3, 117.6 (d, $P(\mathit{C}_6H_5)_4$); 117.9 ($CH_3\mathit{C}N$); 1.1 ($\mathit{C}H_3CN$).

**$(NEt_4)_2[Cr_2(CO)_7(S_2C_6Me_4)]$, $(NEt_4)_2$[11].** Setup: Suspension of $[Cr(CO)_3(MeCN)_3]$ (260 mg, 1.0 mmol) in 5 mL of THF; solutions of $S_2C_6Me_4H_2$ (200 mg, 1.0 mmol) and LiOMe (76 mg, 2.0 mmol) in 3 mL of MeOH, $[Cr(CO)_4(nor)]$ (255 mg, 1.0 mmol) in 5 mL of THF, and $NEt_4Cl$ (330 mg, 2.0 mmol) in 2 mL of MeOH; recrystallization from 6 mL of MeOH and 10 mL of MeCN. Yield: 495 mg (65%) red-brown crystals. Anal. Calcd for $C_{33}Cr_2H_{52}N_2O_7S_2$ (756.90): C, 52.37; H, 6.92; N, 3.70; S, 8.47. Found: C, 52.62; H, 7.21; N, 4.47; S, 8.56. IR (MeCN, $cm^{-1}$): 1955 (w, $\nu_{CO}$); 1895, 1805 (s, $\nu_{CO}$); 1840 (sh, $\nu_{CO}$). $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 3.20 (s, 16 H, $N(C\mathit{H}_2CH_3)_4$); 1.17 (s, 24 H, $N(CH_2C\mathit{H}_3)_4$); 2.24 (s, 6 H, $S_2C_6\mathit{Me}_4$); 1.90 (s, 6 H, $S_2C_6\mathit{Me}_4$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 256.9 ($\mu$-$\mathit{C}O$); 230.6 ($\mathit{C}O$); 155.0, 131.0, 126.1 ($S_2\mathit{C}_6\mathit{Me}_4$); 19.6, 16.1 ($S_2C_6\mathit{Me}_4$); 52.1 ($N(\mathit{C}H_2CH_3)_4$); 7.6 ($N(CH_2\mathit{C}H_3)_4$).

**$(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[12].** Dropwise addition of a solution of $Li_2S_2C_6H_4$ (1.80 g, 11.7 mmol) in 25 mL of MeOH to a light-blue solution of $CrCl_2$ (720 mg, 5.86 mmol) in 50 mL of MeOH gave a blue-violet solution, which was layered with a solution of $NEt_4Cl$ (1.94 g, 11.7 mmol) in 12 mL of MeOH. Violet-brown crystals precipitated, which were separated after 2 d, washed with 10 mL of THF, and dried in vacuo. When the mother liquor was reduced in volume to ca. one-third and layered with ether, crystals precipitated which were suitable for X-ray analysis. Yield: 2.03 g (58%). Anal. Calcd for $C_{28}CrH_{48}N_2S_4$ ($M_r$ 592.94): C, 56.72; H, 8.16; N, 4.72; S, 21.63. Found: C, 56.96; H, 8.51; N, 4.52; S, 21.54%. $^1H$ NMR (DMSO-$d_6$, $\delta$ [ppm]): 7.4 (s, 4 H, $S_2C_6\mathit{H}_4$); 6.6 (s, 4 H, $S_2C_6\mathit{H}_4$); 3.1 (s, broad, 16 H, $N(\mathit{C}H_2CH_3)_4$); 1.25 (s, 24 H, $N(CH_2C\mathit{H}_3)_4$).

**Decomposition of $(NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$ by HX ($X^-$ = $Cl^-$, $BF_4^-$, $CF_3SO_3^-$).** A solution of $(NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$ (100 mg, 0.15 mmol) in 5 mL of MeCN was treated with HCl in THF (0.45 mL, 0.3 mmol of a 0.66 M solution), $HBF_4$ in $Et_2O$ (0,04 mL, 0.3 mmol of a 54% solution), or $CF_3SO_3H$ (0.027 mL, 0.3 mmol), whereupon the color of the reaction mixture changed from red-brown to orange. $[Cr(CO)_3(MeCN)_3]$ and $[Cr(CO)_4(MeCN)_2]$ were identified by IR spectroscopy; the free $S_2C_2H_4H_2$ ligand was identified by $^1H$ NMR-spectroscopy via a shift of the $S_2C_2H_4$ signal from 2.34 ppm to 2.65 ppm.

**X-ray Structure Determinations.** Single crystals of $(NEt_4)_2$[**3**], $(PPh_4)_2$[**5**], $(NEt_4)_2$[**6**]$\cdot$0.55MeOH, $(PPh_4)_2$[7]$\cdot$THF, $(PPh_4)_2$[**10**]$\cdot$MeCN, and $(NEt_4)_2$[**12**] were obtained as described above, and single crystals of $(NEt_4)_2$[**1**] were obtained from a saturated MeOH solution which was stored for some days at room temperature.

Suitable crystals were sealed in glass capillaries under $N_2$ and mounted on a Siemens P4 or a Nicolet R3m/V diffractometer. Corrections for absorption were not applied. The structures were solved by direct methods (SHELXTL-PLUS). Unless otherwise noted, non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined with common isotropic temperature factors. The aromatic hydrogen atoms were calculated for ideal geometry and restricted during refinement. Methyl and methylene hydrogen atoms were calculated for ideal tetrahedra and allowed to rotate around the central carbon atom during refinement.

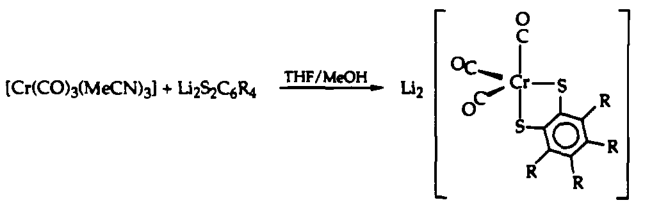
$(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$ contains two independent anions in the asymmetric unit. The structure was solved in the noncentrosymmetric space group $Pca2_1$. Structure solution in the appropriate higher centrosymmetric space group *Pbcm* was tested but failed. The hydrogen atoms of the methyl and methylene groups were located from difference Fourier maps and fixed. Two of the four $NEt_4^+$ cations exhibit disorder, which was successfully modeled in terms of two sites with 0.59/0.41 and 0.55/0.45 occupancies for the methylene carbon atoms. The disordered carbon atoms were refined isotropically only. The hydrogen atoms of these cations could not be localized.

The asymmetric unit of $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot$0.55MeOH contains one complex anion, one cation, and two half-cations, which are completed by the symmetry of the crystal. One of the cations is disordered. The site occupation factor of the MeOH molecule contained in the crystal converged at 55(5)%. The disordered cation and the MeOH molecule were refined isotropically and without hydrogen atoms.

The asymmetric unit of $(NEt_4)_2[Cr(S_2C_6H_4)_2]$ contains two independent anions. Tables I and II summarize selected crystallographic data; Tables III–IX give fractional atomic coordinates and equivalent thermal parameters.

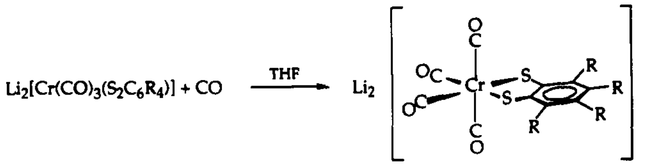
## Results and Discussion

**Syntheses and IR Spectroscopic Characterization of the Complexes.** The mononuclear complex anions $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ with five-coordinate $Cr^0$ centers were formed by reaction of $[Cr(CO)_3(MeCN)_3]$ with substituted benzene-1,2-dithiolates $S_2C_6R_4^{2-}$ (R = Cl, Me) according to eq 2.



$[1]^{2-}$, R = Cl; $[2]^{2-}$, R = Me (2)

They could be precipitated with $NEt_4Cl$ in MeOH and were isolated as $(NEt_4)_2$[**1**] (R = Cl) and $(NEt_4)_2$[**2**] (R = Me). According to eq 3, further reaction with CO yielded the $[Cr(CO)_4(S_2C_6R_4)]^{2-}$ ions with six-coordinate $Cr^0$ centers which were also isolated as $NEt_4^+$ salts $(NEt_4)_2$[**3**] (R = Cl) and $(NEt_4)_2$[**4**] (R = Me).



$[3]^{2-}$, R = Cl; $[4]^{2-}$, R = Me (3)

As in the case of the couple $[Cr(CO)_3(S_2C_6H_4)]^{2-}$/$[Cr(CO)_4(S_2C_6H_4)]^{2-}$ containing the parent ligand $S_2C_6H_4^{2-}$, the addition of CO to $[1]^{2-}$ and $[2]^{2-}$ is reversible. For this reason salts of $[4]^{2-}$ must be precipitated and stored under CO atmosphere, and only solid $(NEt_4)_2$[**3**] is stable enough to be handled at standard conditions.

Because of the sensitivity of the resulting compounds, the reactions according to eqs 2 and 3 were monitored by IR spectroscopy. In the syntheses of $[1]^{2-}$ and $[2]^{2-}$, it was observed that the reaction solutions (THF/MeOH) showed three $\nu_{CO}$-bands indicating the formation of *fac*-$[Cr(CO)_3(S_2C_6R_4)]^{2-}$ ions with $C_S$ symmetry. When the anions had been precipitated, however, the isolated $NEt_4^+$ salts exhibited only two $\nu_{CO}$ bands in KBr and in solution, displaying an intensity pattern being typical of $[Cr(CO)_3]$ complexes with local $C_{3v}$ symmetry. The reaction mixtures of the $[Cr(CO)_4(S_2C_6R_4)]^{2-}$ complexes showed four $\nu_{CO}$ absorptions whose pattern was characteristic of $[Cr(CO)_4]$ complexes with local $C_{2v}$ symmetry. Additionally, low intensity $\nu_{CO}$ bands of uncharacterized CO species were observed which were not precipitated.

Table X shows that the $\nu_{CO}$ frequencies of $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ and $[Cr(CO)_4(S_2C_6R_4)]^{2-}$ decrease in the direction R = Cl > H > Me, but that this decrease is only small. This indicates that the substituents R do influence the electron density at the metal centers and the $\pi$-back-bonding to the CO ligands but that this influence is not very strong.

The corresponding molybdenum and tungsten complexes $(NEt_4)_2[Mo(CO)_n(S_2C_6H_4)]$ ($n$ = 3, 4)[17] and $(NMe_4)_2[W(CO)_n(S_2C_6H_4)$ ($n$ = 3, 4)[18] were reported previously, when we discussed also dimeric structures for the $[M(CO)_3]$ complexes. Because the Mo and W complexes exhibit properties quite analogous to those of the $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ complexes reported here, they might also be mononuclear and contain 16 $e^-$ metal centers. Among the $[M(CO)_3(S_2C_6H_4)]^{2-}$ ions with M = Cr, Mo and W, the tungsten complex shows the highest stability at standard conditions. Furthermore, the Mo and W derivatives of the $[M(CO)_4(S_2C_6H_4)]^{2-}$ ions are considerably more stable than the $[Cr(CO)_4(S_2C_6H_4)]^{2-}$ ion and do not split off CO at standard conditions.

**Table I.** Selected Crystallographic Data for $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[**1**], $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**], and $(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**]

| | $(NEt_4)_2$[**1**] | $(NEt_4)_2$[**3**] | $(NEt_4)_2$[**12**] |
|---|---|---|---|
| formula | $C_{25}Cl_4CrH_{40}$-$N_2O_3S_2$ | $C_{26}Cl_4CrH_{40}$-$N_2O_4S_2$ | $C_{28}CrH_{48}$-$N_2S_4$ |
| $M_r$ | 674.53 | 702.54 | 592.94 |
| space group | $P2_1/c$ | $Pca2_1$ | $P2_1/n$ |
| $a$ (pm) | 1518.5(15) | 1520.2(4) | 1746.6(6) |
| $b$ (pm) | 1355.8(8) | 2830.2(5) | 1203.4(5) |
| $c$ (pm) | 1564.2(11) | 1505.4(4) | 1748.3(6) |
| $\beta$ (deg) | 100.41(7) | | 119.82(3) |
| $V$ (nm$^3$) | 3.167(4) | 6.477(3) | 3.188(2) |
| $Z$ | 4 | 8 | 4 |
| $d_{calc}$ (g/cm$^3$) | 1.41 | 1.44 | 1.24 |
| $\mu$ (cm$^{-1}$) | 8.5 | 8.4 | 6.2 |
| radiation Mo K$\alpha$, $\lambda$ (pm) | 71.073 | 71.073 | 71.073 |
| measd temp (K) | 293 | 200 | 293 |
| $R/R_w$ (%)[a] | 6.6/5.1 | 4.0/4.0 | 6.8/4.8 |

[a] $R = \sum(\mathrm{del})/\sum(F(\mathrm{obs}))$; $R_w = \sum[\mathrm{del}(w)^{1/2}]/\sum[F(\mathrm{obs})(w)^{1/2}]$; del = $|[F(\mathrm{obs}) - F(\mathrm{calc})]|$; $w = 1/\sigma^2$.

The thiolate donors of the $S_2C_6R_4^{2-}$ ligands occupy ortho positions of the benzene rings such that $S_2C_6R_4^{2-}$ ligands are related to dithiolene ligands that are regarded as typical "noninnocent" ligands. In order to examine whether the formation of $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ complexes with five-coordinate $Cr^0$ centers depends on the potential dithiolene character of the $S_2C_6R_4^{2-}$ ligands, we also investigated aliphatic 1,2-dithiolates.

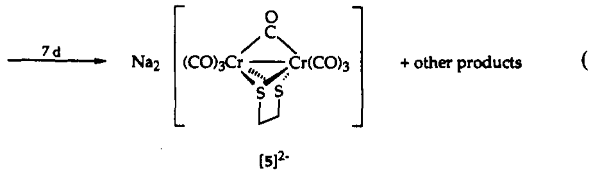
Consistent with our previous findings[19,3] the ethanedithiolate complexes $[M(CO)_3(S_2C_2H_4)]^{2-}$ formed according to eq 4. They

$$[M(CO)_3(MeCN)_3] + Li_2S_2C_2H_4 \xrightarrow{MeCN} Li_2[M(CO)_3(S_2C_2H_4)] \quad (4)$$

$$M = Cr, Mo, W$$

could be precipitated as $NMe_4^+$ salts and characterized spectroscopically as well as by elemental analyses, but proved to be considerably more labile than the $[M(CO)_3(S_2C_6R_4)]^{2-}$ complexes and failed to yield single crystals.

In repeated attempts to obtain such crystals of $[Cr(CO)_3(S_2C_2H_4)]^{2-}$ salts, we now observed that the anions slowly undergo CO transfer reactions and form the dinuclear $[\mu_2$-$(S_2C_2H_4)$-$\mu$-$(CO)\{Cr(CO)_3\}_2]^{2-}$ ions, $[5]^{2-}$, according to eq 5. Single



$[5]^{2-}$ (5)

crystals of $NEt_4^+$ or $PPh_4^+$ salts could be separated from the solution. The cyclohexane-1,2-dithiolate complex formed in an exactly analogous reaction according to eq 6. Monitoring the reaction by IR spectroscopy indicated the primary formation of $Na_2[Cr(CO)_3(S_2C_2H_4)]$ or $Na_2[Cr(CO)_3(S_2C_6H_{10})]$. In the

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**Table II.** Selected Crystallographic Data for $(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$, $(PPh_4)_2$**[5]**, $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$, $(NEt_4)_2$**[6]**·0.55MeOH, $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$, $(PPh_4)_2$**[7]**·THF, and $(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$, $(PPh_4)_2$**[7]**·MeCN

| compound | $(PPh_4)_2$**[5]** | $(NEt_4)_2$**[6]**·0.55 MeOH | $(PPh_4)_2$**[7]**·THF | $(PPh_4)_2$**[10]**·MeCN |
|---|---|---|---|---|
| formula | $C_{57}Cr_2H_{44}O_7P_2S_2$ | $C_{29.55}Cr_2H_{52.2}N_2O_{7.55}S_2$ | $C_{61}H_{52}Mo_2O_8P_2S_2$ | $C_{63}Cl_4Cr_2H_{43}NO_7P_2S_2$ |
| $M_r$ | 1071.03 | 724.46 | 1231.02 | 1297.91 |
| space group | $C2/c$ | $C2/c$ | $P3_1$ | $P2_1/c$ |
| $a$ (pm) | 1887.0(9) | 2384.0(7) | 1103.4(1) | 1666.2(8) |
| $b$ (pm) | 1118.4(3) | 893.2(3) | 1103.4(1) | 1597.6(10) |
| $c$ (pm) | 2534.6(1) | 3421.0(15) | 3949.5(11) | 2263.4(10) |
| $\beta$ (deg) | 110.67(3) | 93.91(3) |  | 90.22(4) |
| $V$ (nm$^3$) | 5.002(4) | 7.267(5) | 4.163(2) | 6.025(5) |
| $Z$ | 4 | 8 | 3 | 4 |
| $d_{calc}$ (g/cm$^3$) | 1.42 | 1.35 | 1.47 | 1.43 |
| $\mu$, cm$^{-1}$ | 6.2 | 4.4 | 6.2 | 7.1 |
| radiation Mo K$\alpha$, $\lambda$ [pm] | 71.073 | 71.073 | 71.073 | 71.073 |
| measd temp (K) | 200 | 200 | 293 | 293 |
| $R/R_w$ (%)[a] | 8.3/6.4 | 8.0/6.5 | 6.5/4.5 | 5.5/4.3 |

[a] See footnote *a* in Table I.

**Table III.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2$ × $10^{-1}$) for the anion of $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$**[1]**

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 2716(1) | 777(1) | 6575(1) | 44(1) |
| S(1) | 2537(1) | −879(1) | 6879(1) | 47(1) |
| S(2) | 2694(1) | 1034(1) | 8035(1) | 52(1) |
| C(1) | 2932(4) | 509(5) | 5497(4) | 54(3) |
| C(2) | 3328(4) | 1901(6) | 6532(4) | 54(3) |
| C(3) | 1790(5) | 1429(5) | 6020(4) | 57(3) |
| C(15) | 2456(3) | −90(4) | 8471(3) | 37(2) |
| C(10) | 2392(3) | −954(4) | 7962(3) | 37(2) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table IV.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2$ × $10^{-1}$) for the Two Independent Anions of $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[3]

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 9586(1) | 1282(1) | 0 | 30(1) |
| S(1) | 11069(2) | 1372(1) | 54(2) | 34(1) |
| S(2) | 9254(2) | 1036(1) | 1510(2) | 35(1) |
| C(1) | 9883(7) | 1495(3) | −1123(7) | 32(3) |
| C(2) | 8468(7) | 1174(4) | −393(7) | 39(4) |
| C(3) | 9357(7) | 1910(4) | 399(7) | 37(3) |
| C(4) | 9859(8) | 657(4) | −350(8) | 46(4) |
| C(15) | 10242(6) | 1080(3) | 2092(7) | 27(3) |
| C(10) | 11045(7) | 1218(3) | 1662(7) | 30(3) |
| Cr(2) | 5449(1) | 3656(1) | 349(1) | 27(1) |
| S(3) | 5740(2) | 3885(1) | 1872(2) | 32(1) |
| S(4) | 3923(2) | 3682(1) | 780(2) | 32(1) |
| C(5) | 5203(6) | 3449(3) | −777(7) | 31(3) |
| C(6) | 5465(6) | 3028(4) | 799(7) | 34(3) |
| C(7) | 5310(7) | 4299(4) | −24(8) | 41(4) |
| C(8) | 6625(7) | 3674(3) | 81(7) | 32(3) |
| C(25) | 3919(6) | 3831(3) | 1889(7) | 25(3) |
| C(20) | 4704(6) | 3925(3) | 2382(7) | 27(3) |

[a] See footnote *a* in Table III.

**Table V.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2$ × $10^{-1}$) for the Two Independent Anions of $(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$**[12]**

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 0 | 0 | 5000 | 69(1) |
| S(1) | −1201(2) | 595(3) | 3653(2) | 94(2) |
| S(2) | 107(2) | 1847(2) | 5506(1) | 80(1) |
| C(15) | −659(6) | 2576(12) | 4583(7) | 76(7) |
| C(10) | −1225(7) | 2035(10) | 3775(9) | 81(6) |
| Cr(2) | 0 | 0 | 0 | 73(1) |
| S(3) | −519(1) | 1844(2) | −130(2) | 81(1) |
| S(4) | 1352(2) | 636(3) | 1183(2) | 97(2) |
| C(25) | 1199(9) | 2065(10) | 1199(7) | 82(6) |
| C(20) | 391(7) | 2585(12) | 633(6) | 77(7) |

[a] See footnote *a* in Table III.

**Table VI.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2$ × $10^{-1}$) for the Anion of $(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]\cdot(PPh_4)_2$**[5]**

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 4763(1) | 2446(1) | 1932(1) | 38(1) |
| S(1) | 5818(1) | 3615(2) | 2524(1) | 51(1) |
| C(1) | 3929(4) | 1554(7) | 1587(3) | 46(3) |
| C(2) | 5321(5) | 1556(7) | 1631(4) | 57(4) |
| C(3) | 4454(4) | 3271(7) | 1256(3) | 49(3) |
| C(4) | 5000 | 1017(11) | 2500 | 64(6) |
| O(4) | 5000 | 0(7) | 2500 | 96(5) |
| C(5) | 5424(4) | 5080(7) | 2482(4) | 83(5) |

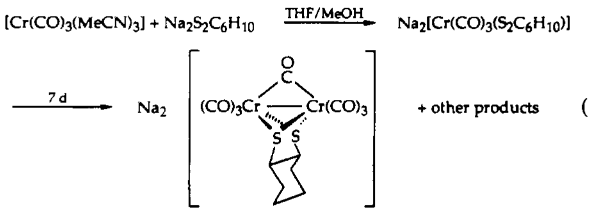
[a] See footnote *a* in Table III.

**Table VII.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2$ × $10^{-1}$) for the Anion of $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$, $(NEt_4)_2$**[6]**·0.55MeOH

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 1335(1) | 5879(1) | 1575(1) | 24(1) |
| Cr(2) | 333(1) | 5739(1) | 1155(1) | 27(1) |
| S(1) | 1108(1) | 7341(2) | 983(1) | 31(1) |
| S(2) | 1093(1) | 3964(2) | 1097(1) | 29(1) |
| C(15) | 1416(5) | 4660(9) | 663(3) | 56(3) |
| C(10) | 1463(6) | 6213(10) | 634(3) | 67(4) |
| C(1) | 1438(3) | 7411(8) | 1920(2) | 28(2) |
| C(2) | 2101(3) | 5814(9) | 1580(2) | 32(2) |
| C(3) | 1394(3) | 4520(7) | 1971(2) | 26(2) |
| C(4) | −43(3) | 5394(9) | 669(3) | 40(3) |
| C(5) | −159(3) | 4389(9) | 1328(2) | 33(2) |
| C(6) | −152(3) | 7262(9) | 1224(2) | 32(2) |
| C(7) | 495(3) | 6094(10) | 1746(3) | 41(3) |
| O(7) | 275(2) | 6330(9) | 2033(2) | 67(3) |

[a] See footnote *a* in Table III.

reaction with $S_2C_2H_4^{2-}$, for instance, three $\nu_{CO}$ bands were observed at 1885, 1765, and 1730 cm$^{-1}$ (Figure 1a), which can be assigned to the mononuclear ion $[Cr(CO)_3(S_2C_2H_4)]^{2-}$ due to the appropriate region, intensity, and characteristic pattern. They cannot be observed any longer in the isolated dinuclear $(NEt_4)_2$**[5]** which shows $\nu_{CO}$ absorptions at 1950, 1885, and 1800 cm$^{-1}$ in MeCN (Figure 1b).



(6)

**[6]**$^{2-}$

The formation of the dinuclear anions **[5]**$^{2-}$ and **[6]**$^{2-}$ from mononuclear $[Cr(CO)_3]$ complexes requires CO transfer and $[Cr(CO)_3]$ decomposition reactions, because the anions formally consist of $[Cr(CO)_3]$ and $[Cr(CO)_4]$ fragments. Accordingly,

**Table VIII.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) for the Anion of $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$,$(PPh_4)_2$[**7**]·THF

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Mo(1) | 1950(2) | –45(1) | 6667 | 42(1) |
| Mo(2) | 1997(1) | 45(1) | 5926(1) | 37(1) |
| S(1) | 2426(4) | –1643(4) | 6286(1) | 50(2) |
| S(2) | 4070(4) | 1638(4) | 6306(1) | 50(2) |
| C(1) | 2798(17) | –112(15) | 7099(4) | 42(8) |
| C(2) | 219(18) | –1583(17) | 6845(3) | 48(9) |
| C(3) | 1639(15) | 1375(17) | 6869(4) | 48(9) |
| C(4) | 285(17) | –1375(17) | 5726(4) | 43(9) |
| C(5) | 1770(15) | 1557(17) | 5754(4) | 50(9) |
| C(6) | 2920(15) | 115(15) | 5501(4) | 44(8) |
| C(7) | 430(16) | –19(18) | 6294(5) | 58(10) |
| O(7) | –604(11) | 12(16) | 6301(3) | 77(8) |
| C(8) | 4342(16) | –780(16) | 6305(5) | 68(11) |
| C(9) | 5097(18) | 785(19) | 6287(5) | 84(13) |

[a] See footnote *a* in Table III.

**Table IX.** Selected Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) for the anion of $(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$,$(PPh_4)_2$[**10**]·MeCN

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Cr(1) | 10400(1) | 6189(2) | 7566(1) | 51(1) |
| Cr(2) | 9058(2) | 5461(2) | 7945(1) | 54(1) |
| C(1) | 10724(9) | 7173(10) | 7906(7) | 54(7) |
| C(2) | 10958(9) | 6508(10) | 6908(7) | 52(7) |
| C(3) | 11301(9) | 5646(10) | 7810(7) | 59(8) |
| C(4) | 8121(10) | 4919(11) | 7705(9) | 80(9) |
| C(5) | 9253(10) | 4543(10) | 8412(6) | 60(7) |
| C(6) | 8470(10) | 5954(10) | 8525(7) | 68(8) |
| C(7) | 10023(10) | 5937(10) | 8429(7) | 59(7) |
| O(7) | 10250(7) | 6002(8) | 8917(4) | 91(6) |
| S(1) | 9056(2) | 6690(2) | 7299(2) | 57(2) |
| S(2) | 9809(2) | 4968(2) | 7103(2) | 53(2) |
| C(15) | 9287(9) | 5422(13) | 6513(9) | 52(8) |
| C(10) | 8941(10) | 6221(14) | 6606(7) | 53(8) |

[a] See footnote *a* in Table III.

**Table X.** $\nu_{CO}$ Data for $(NEt_4)_2[Cr(CO)_3(S_2C_6R_4)]$ and $A_2[Cr(CO)_4(S_2C_6R_4)$ (R = Cl, H, Me) (A = $NEt_4$, $NMe_4$)

| compound | $\nu_{CO}$ (MeCN) ($cm^{-1}$) |
|---|---|
| $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$ [**1**] | 1880, 1769 |
| $(NEt_4)_2[Cr(CO)_3(S_2C_6H_4)]$[3] | 1870, 1745 |
| $(NEt_4)_2[Cr(CO)_3(S_2C_6Me_4)]$, $(NEt_4)_2$ [**2**] | 1865, 1740 |
| $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**] | 1980, 1865, 1830, 1780[a] |
| $(NMe_4)_2[Cr(CO)_4(S_2C_6H_4)]$[3] | 1975, 1855, 1820, 1770[a] |
| $(NEt_4)_2[Cr(CO)_4(S_2C_6Me_4)]$, $(NEt_4)_2$[**4**] | 1965, 1850, 1810, 1760[a] |

[a] Solvent saturated with CO.

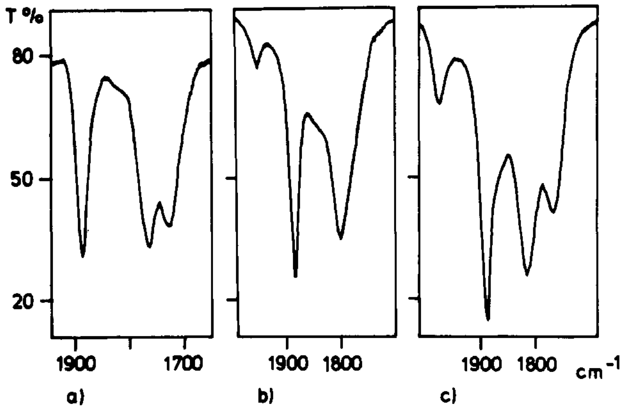


**Figure 1.** $\nu_{CO}$ region of the IR spectra of (a) $Na_2[Cr(CO)_3(S_2C_2H_4)]$ in THF/MeOH (b) $(NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$ in MeCN, and (c) $(NEt_4)_2[Mo_2(CO)_7(S_2C_2H_4)]$ in MeCN.

$(NEt_4)_2$[**5**] could be obtained in higher yields when $[Cr(CO)_3(S_2C_2H_4)]^{2-}$ was reacted with the labile $[Cr(CO)_4(nor)]$ (nor = norbornadiene) according to eq 7. The analogous molybdenum and tungsten complexes $(NEt_4)_2[Mo_2(CO)_7(S_2C_2H_4)]$, $(NEt_4)_2$[**7**],

$$Li_2[Cr(CO)_3(S_2C_2H_4)] + [Cr(CO)_4(nor)] \xrightarrow[+2\,NEt_4Cl]{THF/MeOH} (NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)] \quad (7)$$

$$(NEt_4)_2[\mathbf{5}]$$

and $(NEt_4)_2[W_2(CO)_7(S_2C_2H_4)]$, $(NEt_4)_2$[**8**], were obtained according to eqs 8a and 8b. $(NEt_4)_2$[**7**] ($\nu_{CO}$: 1975, 1888, 1815,

$$Na_2[Mo(CO)_3(S_2C_2H_4)] + [Mo(CO)_4(nor)] \xrightarrow[+2\,NEt_4Cl]{MeCN/MeOH} (NEt_4)_2[Mo_2(CO)_7(S_2C_2H_4)] \quad (8a)$$

$$(NEt_4)_2[\mathbf{7}]$$

$$Na_2[W(CO)_3(S_2C_2H_4)] + [W(CO)_4(MeCN)_2] \xrightarrow[+2\,NEt_4Cl]{MeCN/MeOH} (NEt_4)_2[W_2(CO)_7(S_2C_2H_4)] \quad (8b)$$

$$(NEt_4)_2[\mathbf{8}]$$

and 1770 $cm^{-1}$) (Figure 1c) and $(NEt_4)_2$[**8**] ($\nu_{CO}$: 1970, 1880, 1810, and 1760 $cm^{-1}$) exhibit four $\nu_{CO}$ bands in MeCN, of which the lowest band can be assigned to the $\mu$-CO group in both cases. This assignment was not possible in the case of $(NEt_4)_2$[**5**] and $(NEt_4)_2$[**6**] due to the overlapping of $\nu_{CO}$ bands of terminal and bridging CO ligands.

The formation of the dinuclear anions [**5**]$^{2-}$, [**6**]$^{2-}$, [**7**]$^{2-}$ or [**8**]$^{2-}$ does not depend on the fact that aliphatic 1,2-dithiolates bridge metal centres. This was found in control reactions with $S_2C_6R_4^{2-}$ ligands (R = H, Cl, Me) according to eq 9. Again,

$$Li_2[Cr(CO)_3(S_2C_6R_4)] \xrightarrow{+[Cr(CO)_4(nor)]} Li_2[Cr_2(CO)_7(S_2C_6R_4)]$$

$$[\mathbf{9}]^{2-}, R = H; [\mathbf{10}]^{2-}, R = Cl; [\mathbf{11}]^{2-}, R = Me \quad (9)$$

dinuclear anions formed in which now aromatic 1,2-dithiolates act as bridging ligands. $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_4)]$, $(NEt_4)_2$[**9**], $(PPh_4)_2[Cr2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$, $(PPh_4)_2$[**10**]·MeCN, and $(NEt_4)_2[Cr_2(CO)_7(S_2C_6Me_4)]$, $(NEt_4)_2$[**11**], were isolated and largely exhibit properties analogous those for $(NEt_4)_2$[**5**] and $(NEt_4)_2$[**6**], and only their formation requires slightly longer reaction times.

In order to investigate the formation of coordinatively unsaturated complexes with dithiolates of chromium in a higher oxidation state, the reaction according to eq 10 was carried out.

$$CrCl_2 + 2\,Li_2S_2C_6H_4 \xrightarrow[+2NEt_4Cl]{MeOH} (NEt_4)_2[Cr(S_2C_6H_4)_2] + 2LiCl \quad (10)$$

$$(NEt_4)_2[\mathbf{12}]$$

$(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**], formed whose anion is mononuclear and possesses a $Cr^{II}$ center exclusively surrounded by thiolate donors. $(NEt_4)_2$[**12**] separates as violet-brown rod-shaped crystals from the reaction solution and is sparingly soluble in DMSO only.

**X-ray Structure Determinations.** A majority of the salts described above were structurally characterized by X-ray crystallography. All compounds that were investigated consist of discrete cations and anions. For the sake of clarity the salts with mononuclear anions will be discussed first.

Figure 2 displays the molecular structures of the anions of $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[**1**], $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**], and $(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**]; Tables XI–XIII summarize selected distances and angles.

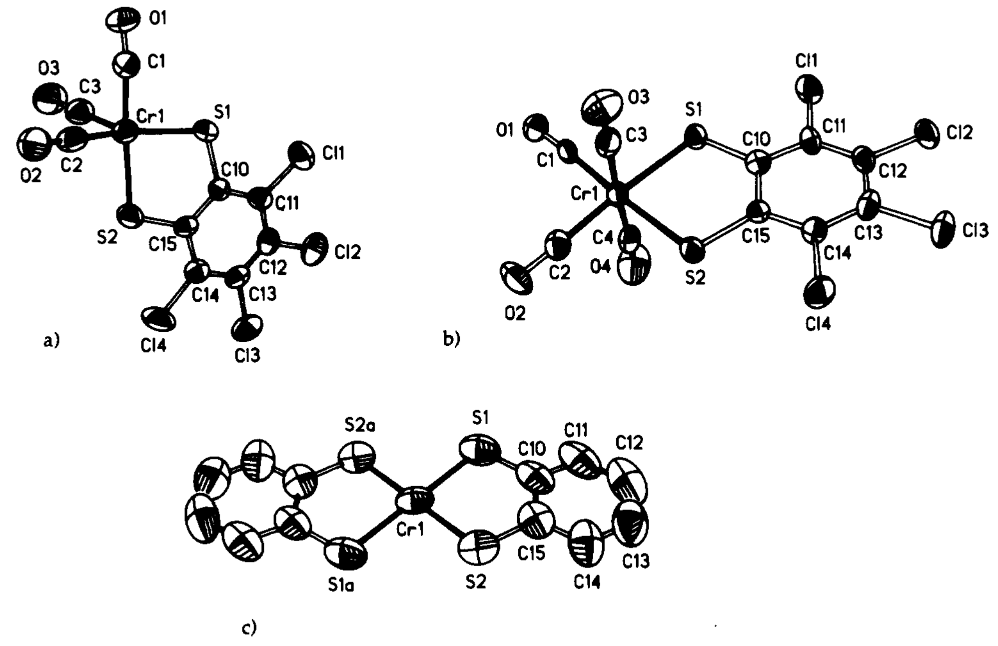


**Figure 2.** Molecular structures of the anions of (a) $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[**1**], (b) $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**]*, and (c) $(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**]* (H atoms omitted). In part b only one of the two independent anions is shown.

**Table XI.** Selected Distances (pm) and Angles (deg) for $(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[**1**]

| | | | |
|---|---|---|---|
| | Distances | | |
| Cr(1)-S(1) | 231.7(4) | Cr(1)-S(2) | 231.8(4) |
| Cr(1)-C(1) | 181.3(8) | Cr(1)-C(2) | 179.1(8) |
| Cr(1)-C(3) | 175.2(7) | S(1)-C(10) | 175.1(6) |
| S(2)-C(15) | 173.2(7) | C(10)-C(15) | 140.9(9) |
| | Angles | | |
| S(1)-Cr(1)-S(2) | 85.4(1) | S(1)-Cr(1)-C(1) | 92.6(2) |
| S(2)-Cr(1)-C(1) | 170.1(2) | S(1)-Cr(1)-C(2) | 155.6(2) |
| S(1)-Cr(1)-C(3) | 118.4(3) | S(2)-Cr(1)-C(3) | 105.1(2) |
| Cr(1)-S(1)-C(10) | 107.1(2) | Cr(1)-S(2)-C(15) | 107.4(2) |
| S(2)-C(15)-C(10) | 120.2(4) | S(1)-C(10)-C(15) | 119.5(5) |
| | Dihedral Angles | | |
| C(10)-S(1)-Cr(1)-C(1) | 175.4 | C(10)-S(1)-Cr(1)-S(2) | 5.0 |

**Table XII.** Selected Distances (pm) and Angles (deg) for $(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**]

| | | | |
|---|---|---|---|
| | Distances | | |
| Cr(1)-S(1) | 241.6(3) | Cr(2)-S(3) | 242.3(4) |
| Cr(1)-S(2) | 243.0(3) | Cr(2)-S(4) | 241.0(3) |
| Cr(1)-C(1) | 185.0(11) | Cr(2)-C(8) | 183.3(11) |
| Cr(1)-C(2) | 182.6(11) | Cr(2)-C(5) | 183.2(11) |
| Cr(1)-C(3) | 190.7(11) | Cr(2)-C(7) | 191.5(12) |
| Cr(1)-C(4) | 189.3(12) | Cr(2)-C(6) | 190.4(11) |
| S(1)-C(10) | 172.4(11) | S(3)-C(20) | 175.4(10) |
| S(2)-C(15) | 174.3(10) | S(4)-C(25) | 172.3(10) |
| C(15)-C(10) | 143.6(14) | C(25)-C(20) | 143.0(14) |
| | Angles | | |
| S(1)-Cr(1)-S(2) | 84.3(1) | S(3)-Cr(2)-S(4) | 85.0(1) |
| S(1)-Cr(1)-C(3) | 88.0(3) | S(3)-Cr(2)-C(7) | 92.5(4) |
| S(2)-Cr(1)-C(3) | 86.2(3) | S(4)-Cr(2)-C(7) | 86.8(3) |
| S(1)-Cr(1)-C(1) | 93.1(3) | S(3)-Cr(2)-C(8) | 91.3(3) |
| S(1)-Cr(1)-C(2) | 176.2(3) | S(3)-Cr(2)-C(5) | 176.5(3) |
| S(2)-Cr(1)-C(1) | 176.7(3) | S(4)-Cr(2)-C(8) | 175.6(3) |
| S(2)-Cr(1)-C(2) | 93.5(4) | S(4)-Cr(2)-C(5) | 93.6(3) |
| C(3)-Cr(1)-C(4) | 177.1(5) | C(6)-Cr(2)-C(7) | 173.3(5) |
| | Dihedral Angles | | |
| C(10)-S(1)-Cr(1)-C(3) | 86.2 | C(20)-S(3)-Cr(2)-C(7) | 87.4 |
| C(10)-S(1)-Cr(1)-S(2) | 0.2 | C(20)-S(3)-Cr(2)-S(4) | 0.8 |

**Table XIII.** Selected Distances (pm) and Angles (deg) for of $(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**]

| | | | |
|---|---|---|---|
| | Distances | | |
| Cr(1)-S(1) | 235.5(2) | Cr(2)-S(3) | 236.5(3) |
| Cr(1)-S(2) | 236.5(3) | Cr(2)-S(4) | 236.3(2) |
| S(1)-C(10) | 174.9(12) | S(3)-C(20) | 173.0(11) |
| S(2)-C(15) | 173.7(10) | S(4)-C(25) | 174.3(12) |
| C(15)-C(10) | 141.7(15) | C(25)-C(20) | 140.4(16) |
| | Angles | | |
| S(1)-Cr(1)-S(2) | 87.3(1) | S(3)-Cr(3)-S(4) | 87.1(1) |
| S(1)-Cr(1)-S(1a) | 180.0(1) | S(3)-Cr(2)-S(3a) | 180.0(1) |
| S(2)-Cr(1)-S(1a) | 92.6(1) | S(4)-Cr(2)-S(3a) | 92.9(1) |
| Cr(1)-S(1)-C(10) | 104.1(4) | Cr(2)-S(3)-C(20) | 104.4(5) |
| Cr(1)-S(2)-C(15) | 104.2(4) | Cr(2)-S(4)-C(25) | 103.8(4) |

**Table XIV.** Average Cr–S Distances for the Chromium Complexes Determined by X-ray Analyses

| complex anion | $d_{Cr-S}$ (pm) |
|---|---|
| $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ | 229.5[3] |
| $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$, [**1**]$^{2-}$ | 231.8 |
| $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$, [**3**]$^{2-}$ | 242.0 |
| $[Cr_2(CO)_7(S_2C_6Cl_4)]^{2-}$, [**10**]$^{2-}$ | 243.5 |
| $[Cr_2(CO)_7(S_2C_2H_4)]^{2-}$, [**5**]$^{2-}$ | 241.9 |
| $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$, [**6**]$^{2-}$ | 242.9 |
| $[Cr(S_2C_6H_4)_2]^{2-}$, [**12**]$^{2-}$ | 236.2 |

The Cr center of [**1**]$^{2-}$ is five-coordinate and surrounded by three carbon and two sulfur donors in a distorted trigonal bipyramid. The sulfur donors occupy one equatorial and one apical position, and [**1**]$^{2-}$ possesses the same coordination geometry as the parent compound $[Cr(CO)_3(S_2C_6H_4)]^{2-}$. The six-coordinate Cr center of [**3**]$^{2-}$ is surrounded by four carbon and two cis sulfur donors in a pseudooctahedron. The Cr center of [**12**]$^{2-}$ is only four-coordinate. The four sulfur donors and chromium atom form a planar $CrS_4$ framework which exhibits crystallographically imposed centrosymmetry. The $C_6H_4$ rings deviate slightly from the Cr–S–S planes.

The average Cr–S distances (Table XIV) increase from the $Cr^0$ complexes, $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ (229.5 pm) and $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$ (231.8 pm), via the $Cr^{II}$ complex, $[Cr(S_2C_6H_4)_2]^{2-}$ (236.2 pm), up to the $Cr^0$ complex $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ (242.0 pm). This indicates that oxidation states and the different radii of the Cr centers hardly influence the Cr–S distances.

The Cr–S distances can be plausibly explained, however, by assuming that the sulfur donors do not form only σ-donor but additionally also π-donor bonds to the Cr centers when these centers are electronically unsaturated. The strength of these π-donor bonds can be expected to be influenced both by the π-donor ability of the sulfur donors and by the degree of electron deficiency at the metal centers.

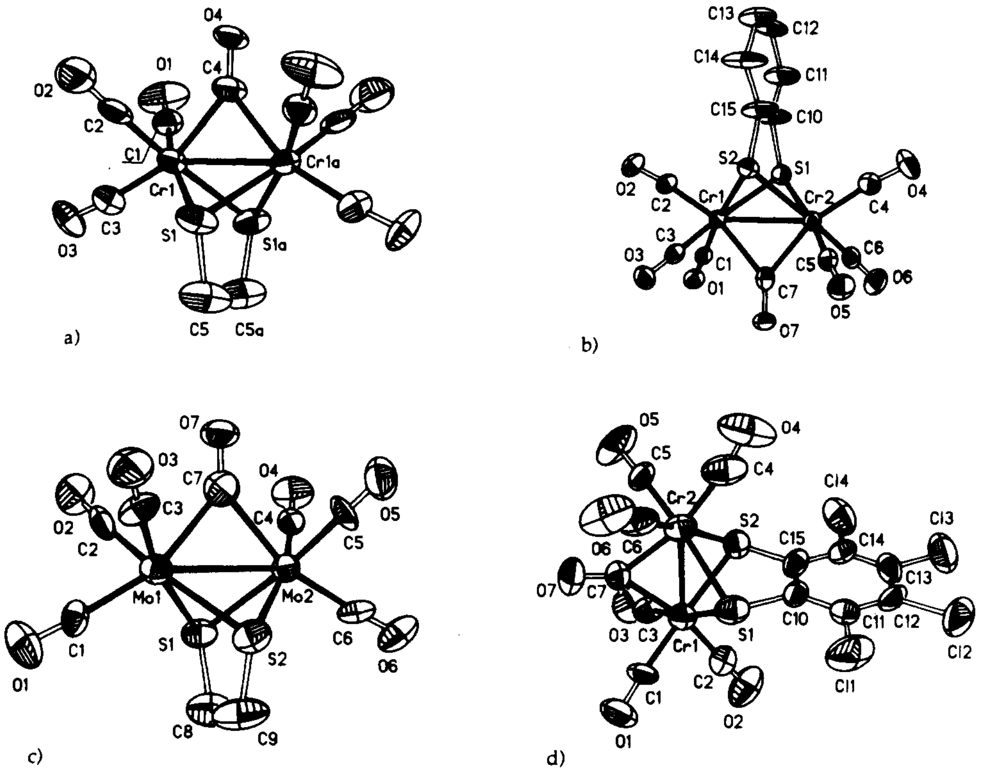


**Figure 3.** Molecular structures of the anions of (a) $(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$, $(PPh_4)_2$[**5**], (b) $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$, $(NEt_4)_2$[**6**]·0.55MeOH, (c) $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$, $(PPh_4)_2$[**7**]·THF, and (d) $(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$, $(PPh_4)_2$[**10**]·MeCN (H atoms omitted).

Accordingly, the slight increase of the Cr–S distance from 229.5 pm in $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ to 231.8 pm in $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$ can be attributed to the fact that the electron-withdrawing chloro substituents reduce the $\pi$-donation ability of the thiolate donors of the $S_2C_6Cl_4{}^{2-}$ ligands.

If the Cr centers in $Cr^0$ complexes are six-coordinate and already possess a 18 $e^-$ configuration, formation of S→Cr $\pi$-donor bonds is not necessary. This explains the considerably longer Cr–S distances of $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ (242.0 pm), $[Cr(CO)_5(SPMe_3)]$ (251.0 pm),[20] the thioether complex $[Cr(CO)_4(EtSC_2H_4SEt)]$ (241.8 pm),[21] or the thiolate complex $[Fe(CO)_2(\mu\text{-}'S_4')\{Cr(CO)_5\}]$ (246.5 pm)[22] in comparison to $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ (R = H, Cl). In all cases, the Cr–S bonds might exhibit single-bond character.

In $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$ as well as in $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$, the five-membered $[CrS_2C_2]$ rings are planar. This indicates $sp^2$ hybridization of the sulfur donors in both cases, and as follows from the preceding discussion of the Cr–S distances, the p lone pairs of the thiolate donors which are oriented perpendicular to the $[CrS_2C_2]$ planes form $\pi$-donor bonds to the metal center in $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$, but remain localized at the sulfur donors in $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$.

The Cr–S bonds in $[Cr(S_2C_6H_4)_2]^2$, [**12**]$^{2-}$, probably also possess partial double-bond character. This can be deduced not only from the average Cr–S distance (236.2 pm), which is still considerably shorter than in $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ (242.0 pm), but also from the Cr–S distances in the related $[Cr(S_2C_2H_4)_2]^{2-}$ ion (238.8 pm).[23]

The molecular structures of the dinuclear anions $[Cr_2(CO)_7(S_2C_2H_4)]^{2-}$, [**5**]$^{2-}$, $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$, [**6**]$^{2-}$, $[Mo_2(CO)_7(S_2C_2H_4)]^{2-}$, [**7**]$^{2-}$ and $[Cr_2(CO)_7(S_2C_6Cl_4)]^{2-}$, [**10**]$^{2-}$ are displayed in Figure 3, selected distances and angles are listed in Tables XV–XVIII.

The metal centers of all four anions are surrounded pseudooctahedrally by four carbon and two thiolate sulfur donors. Sulfur donors and one CO group triply bridge two $[M(CO)_3]$ fragments so that face connected octahedra result. In all cases, the distances between the $M^0$ centers are shorter than the sums

**Table XV.** Selected Distances (pm) and Angles (deg) for $(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$, $(PPh_4)_2$[**5**]

| | | | |
|---|---|---|---|
| Distances | | | |
| Cr(1)–Cr(1a) | 269.8(3) | Cr(1)–S(1) | 241.2(2) |
| Cr(1)–S(1a) | 242.5(3) | Cr(1)–C(1) | 180.7(7) |
| Cr(1)–C(2) | 180.2(10) | Cr(1)–C(3) | 184.8(8) |
| Cr(1)–C(4) | 209.2(9) | S(1)–C(5) | 178.6(8) |
| C(5)–C(5a) | 163.7(17) | | |
| Angles | | | |
| S(1)–Cr(1)–C(1) | 170.8(3) | S(1)–Cr(1)–C(2) | 94.9(3) |
| C(1)–Cr(1)–C(2) | 91.7(4) | S(1)–Cr(1)–C(3) | 103.1(2) |
| S(1)–Cr(1)–C(4) | 93.3(2) | C(1)–Cr(1)–C(4) | 81.3(3) |
| C(3)–Cr(1)–C(4) | 160.1(3) | S(1)–Cr(1)–S(1a) | 78.1(1) |
| Cr(1)–S(1)–C(5) | 103.0(2) | Cr(1)–S(1)–Cr(1a) | 67.8(1) |
| Cr(1)–C(4)–Cr(1a) | 80.3(4) | | |

**Table XVI.** Selected Distances (pm) and Angles (deg) for $(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$, $(NEt_4)_2$[**6**]·0.55MeOH

| | | | |
|---|---|---|---|
| Distances | | | |
| Cr(1)–Cr(2) | 270.4(2) | Cr(1)–S(1) | 244.1(2) |
| Cr(1)–S(2) | 240.9(2) | Cr(2)–S(1) | 244.0(2) |
| Cr(2)–S(2) | 242.4(2) | Cr(1)–C(7) | 213.1(8) |
| Cr(2)–C(7) | 205.5(9) | C(7)–O(7) | 116.6(11) |
| S(1)–C(10) | 181.4(11) | S(2)–C(15) | 182.7(10) |
| C(10)–C(15) | 139.6(12) | C(10)–C(11) | 144.3(16) |
| C(11)–C(12) | 147.5(16) | C(12)–C(13) | 144.2(17) |
| C(13)–C(14) | 147.3(17) | C(14)–C(15) | 144.6(16) |
| Angles | | | |
| S(1)–Cr(1)–S(2) | 77.7(1) | S(2)–Cr(1)–C(1) | 173.4(2) |
| S(1)–Cr(1)–C(2) | 100.9(2) | S(2)–Cr(1)–C(2) | 100.2(2) |
| C(1)–Cr(1)–C(2) | 85.7(3) | S(1)–Cr(1)–C(3) | 168.0(2) |
| S(1)–Cr(1)–C(7) | 91.1(2) | S(2)–Cr(1)–C(7) | 93.7(2) |
| C(2)–Cr(1)–C(7) | 163.2(3) | S(2)–Cr(2)–C(6) | 171.4(2) |
| S(1)–Cr(2)–C(7) | 93.0(2) | S(2)–Cr(2)–C(7) | 95.2(2) |
| Cr(1)–S(1)–Cr(2) | 67.3(1) | Cr(1)–S(2)–Cr(2) | 68.0(1) |
| Cr(1)–C(7)–O(7) | 137.1(6) | Cr(2)–C(7)–O(7) | 142.4(6) |

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**Table XVII.** Selected Distances (pm) and Angles (deg) for $(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$, $(PPh_4)_2[\mathbf{7}]\cdot THF$

| Distances | | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 292.5(1) | Mo(1)–S(1) | 256.4(5) |
| Mo(1)–S(2) | 257.1(4) | Mo(1)–C(7) | 224.2(20) |
| Mo(2)–S(1) | 256.7(6) | Mo(2)–S(2) | 255.9(4) |
| S(1)–C(8) | 183.5(16) | S(2)–C(9) | 180.1(25) |
| C(7)–O(7) | 115.8(26) | C(8)–C(9) | 149.7(24) |
| **Angles** | | | |
| S(1)–Mo(1)–S(2) | 75.3(1) | S(1)–Mo(2)–S(2) | 75.4(1) |
| S(1)–Mo(2)–C(7) | 92.2(6) | S(2)–Mo(2)–C(7) | 93.0(4) |
| Mo(1)–S(1)–Mo(2) | 69.5(1) | Mo(1)–S(2)–Mo(2) | 69.5(1) |
| Mo(1)–C(7)–Mo(2) | 81.6(7) | Mo(1)–C(7)–O(7) | 137.8(14) |
| Mo(2)–C(7)–O(7) | 140.4(15) | | |

**Table XVIII.** Selected Distances (pm) and Angles (deg) for $(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$, $(PPh_4)_2[\mathbf{10}]\cdot MeCN$

| Distances | | | |
|---|---|---|---|
| Cr(1)–Cr(2) | 266.5(4) | Cr(1)–C(7) | 209.2(16) |
| Cr(1)–S(1) | 245.1(5) | Cr(1)–S(2) | 242.1(5) |
| Cr(2)–C(7) | 208.5(16) | Cr(2)–S(1) | 244.9(5) |
| Cr(2)–S(2) | 241.7(5) | C(7)–O(7) | 117.1(18) |
| S(1)–C(10) | 174.8(18) | S(2)–C(15) | 174.9(19) |
| C(15)–C(10) | 141.7(29) | | |
| **Angles** | | | |
| C(7)–Cr(1)–S(2) | 97.3(4) | S(1)–Cr(1)–S(2) | 77.7(2) |
| S(1)–Cr(2)–S(2) | 77.8(2) | Cr(1)–C(7)–Cr(2) | 79.3(5) |
| Cr(1)–C(7)–O(7) | 140.1(13) | Cr(2)–C(7)–O(7) | 140.6(13) |
| Cr(1)–S(1)–Cr(2) | 65.9(1) | Cr(1)–S(2)–Cr(2) | 66.9(1) |

of the covalent radii ($r_{Cr}$ = 148 pm;[24] $r_{Mo}$ = 162 pm[25]) and accordingly indicate M–M single bonds in $[\mathbf{5}]^{2-}$ ($d_{Cr-Cr}$ = 269.8 pm), $[\mathbf{6}]^{2-}$ ($d_{Cr-Cr}$ = 270.4 pm), $[\mathbf{7}]^{2-}$ ($d_{Mo-Mo}$ = 292.5 pm), and $[\mathbf{10}]^{2-}$ ($d_{Cr-Cr}$ = 266.5 pm). As a result, the metal centers formally reach 18 $e^-$ configurations and the anions are diamagnetic.

The average Cr–S distances in $[\mathbf{5}]^{2-}$ (241.9 pm), $[\mathbf{6}]^{2-}$ (242.9 pm), and $[\mathbf{10}]^{2-}$ (243.5 pm) compare with the Cr–S distances in 18 $e^-$ $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ (242.0 pm), and indicate that the dinuclear complexes likewise exhibit Cr–S single bonds. Although the $S_2C_6Cl_4{}^{2-}$ ligand coordinates the metal center in $[\mathbf{3}]^{2-}$ as terminal and in $[\mathbf{10}]^{2-}$ as bridging, the Cr–S distances differ by only 1.5 pm. Apparently, the terminal or bridging mode of coordination does not influence the Cr–S single-bond distances which in all cases are ca. 243 pm.

An analogous structure was found for the Mo complex $[Mo_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{7}]^{2-}$. This complex distinctly contrasts with the related $[Mo_2(CO)_8(SPh)_2]^{2-}$,[26] which consists of two $[Mo(CO)_4]$ fragments bridged by two $PhS^-$ groups. The formation of a Mo–Mo bond in $[\mathbf{7}]^{2-}$ can again be concluded from the Mo–Mo distance of 292.5 pm that is shorter than the sum of the covalent radii ($r_{Mo}$ = 162 pm) and considerably shorter than in $[Mo_2(CO)_8(SPh)_2]^{2-}$ (406.9 pm).

The following special features of $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$ are to be noted: (1) While in the dinuclear complex anions $[\mathbf{5}]^{2-}$, $[\mathbf{7}]^{2-}$, and $[\mathbf{10}]^{2-}$ the bridging CO group is symmetrically located between the metal centers, the Cr–C distances of the CO bridge in $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$ differ by 7.6 pm. (2) The cyclohexane ring of the $S_2C_6H_{10}{}^{2-}$ ligand is approximately planar. The C atoms exhibit a maximum deviation from the plane of ±6.2 pm, and the C–C distances within the ring (139.6–147.5 pm) are much shorter than expected for C–C single bonds. In this regard, the structure of $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$ contrasts with the structures of other cyclohexane dithiolate complexes such as $[Hg_2Me_2(S_2C_6H_{10})]$,[27] exhibiting angles and distances that were found also in $C_6H_{12}$ in which the C atoms deviate from an "ideal plane". We assume that the unusual structural features of the $C_6$ ring in $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$ are due to disorder of the crystal. This assumption is corroborated by the $^1H$ NMR spectrum that displays only signals which are characteristic of cyclohexane derivatives.

**Table XIX.** $^{13}C(CO)$ Signals (ppm) of the Mono- and Dinuclear Complex Anions

| compound | $CO_{terminal}$ | $CO_{bridge}$ |
|---|---|---|
| $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$, $[\mathbf{1}]^{2-}$ | 249.0 | *a* |
| $[Cr(CO)_3(S_2C_6Me_4)]^{2-}$, $[\mathbf{2}]^{2-}$ | 250.4 | *a* |
| $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$, $[\mathbf{3}]^{2-}$ | 233.7/220.7 | *b, c* |
| $[Cr(CO)_4(S_2C_6Me_4)]^{2-}$, $[\mathbf{4}]^{2-}$ | 237.0/222.6 | *b, c* |
| $[Cr_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{5}]^{2-}$ | 232.2/230.6 | 252.9[b] |
| $[Cr_2(CO)_7(S_2C_6H_{10})]^{2-}$, $[\mathbf{6}]^{2-}$ | 232.9/231.6/230.5 | 254.8[b] |
| $[Mo_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{7}]^{2-}$ | 223.3/218.4 | 232.2[b] |
| $[W_2(CO)_7(S_2C_2H_4)]^{2-}$, $[\mathbf{8}]^{2-}$ | 216.4/210.2 | 221.3[b] |
| $[Cr_2(CO)_7(S_2C_6H_4)]^{2-}$, $[\mathbf{9}]^{2-}$ | 230.4 | 255.8[b] |
| $[Cr_2(CO)_7(S_2C_6Cl_4)]^{2-}$, $[\mathbf{10}]^{2-}$ | 230.0/228.6 | 254.7[b] |
| $[Cr_2(CO)_7(S_2C_6Me_4)^{2-}$, $[\mathbf{11}]^{2-}$ | 230.6 | 256.9[b] |

[a] In $CD_3CN$. [b] In DMSO-$d_6$. [c] Solvent saturated with CO.

**NMR Spectra.** The NMR spectra show that the complexes adopt higher molecular symmetries in solution than in the solid state, that CO ligands of several complexes fluctuate, and that the $S_2C_2H_4$ bridges of the dinuclear ethane dithiolate complexes are flexible. The mononuclear complexes $(NEt_4)_2[Cr(CO)_3(S_2C_6R_4)]$, $(NEt_4)_2[\mathbf{1}]$ (R = Cl) and $(NEt_4)_2[\mathbf{2}]$ (R = Me), exhibit only one $^{13}C$ signal for the three CO groups (Table XIX). This can be explained by a fast exchange of equatorial and axial CO ligands as is often observed in five-coodinate complexes. In contrast, $(NEt_4)_2[\mathbf{3}]$ and $(NEt_4)_2[\mathbf{4}]$, which possess six-coordinate metal centers, show two $^{13}C(CO)$ signals indicating rigid structures with $C_{2v}$ symmetry.

The dinuclear ethanedithiolate complexes $(NEt_4)_2[M_2(CO)_7(S_2C_2H_4)]$, $(NEt_4)_2$ [**5**] (M = Cr), $(NEt_4)_2$ [**7**] (M = Mo), and $(NEt_4)_2$ [**8**] (M = W), each show one $^{13}C(\mu\text{-}CO)$ signal and two $^{13}C(CO_{terminal})$ signals exhibiting an intensity ratio of 1:2. This indicates that the terminal CO ligands do not fluctuate at room temperature and that two of three terminal CO ligands have become equivalent in solution while in the solid state all three CO ligands are crystallographically different. Accordingly, in solution the ions might possess $C_{2v}$ symmetry instead of $C_1$ symmetry ($[\mathbf{7}]^{2-}$) or $C_2$ symmetry ($[\mathbf{5}]^{2-}$). $C_{2v}$ symmetry of the ions is also deduced from the $^1H$ NMR spectra, each showing only one sharp singlet for the $S_2C_2H_4$ group. This indicates a fast torsional motion of the $C_2$ fragment of the $S_2C_2H_4{}^{2-}$ ligand around the $C_2$ axis by which the $CH_2$ hydrogen atoms become magnetically equivalent. Without such a $C_2H_4$ torsion, the anions would exhibit only $C_2$ symmetry and should give rise to a AA′BB′ splitting pattern even if the terminal CO groups freely fluctuate.

The cyclohexane derivative $(NEt_4)_2[\mathbf{6}]$ exhibits three equally intensitive $^{13}C(CO_{terminal})$ signals. Accordingly, it can possess only $C_2$ symmetry in solution. In order to reach $C_{2v}$ symmetry by torsion of the $S_2C_2$ bridge the cyclohexane ring would have to invert, which does obviously not happen at room temperature.

The dinuclear $[Cr_2(CO)_7(S_2C_6Cl_4)]^{2-}$, $[\mathbf{10}]^{2-}$, shows two $^{13}C(CO_{terminal})$ signals indicating $C_{2v}$ symmetry in solution like the ethanedithiolate complexes. In this respect, it differs from the analogous $[Cr_2(CO)_7(S_2C_6H_4)]^{2-}$, $[\mathbf{9}]^{2-}$, and $[Cr_2(CO)_7(S_2C_6Me_4)]^{2-}$, $[\mathbf{11}]^{2-}$, which both exhibit only one $^{13}C(CO_{terminal})$ signal. Equilibration of the terminal CO ligands by fluctuation apparently is easier in $[\mathbf{9}]^{2-}$ and $[\mathbf{11}]^{2-}$ than in $[\mathbf{10}]^{2-}$. At 60 °C, however, also $[\mathbf{10}]^{2-}$ shows only one $^{13}C(CO_{terminal})$ signal, revealing that CO fluctuation is possible at higher temperatures.

**Reactions.** Simultaneous cleavage of both the $\mu$-CO bridge and the M–M bond in the dinuclear anions according to eq 11 potentially yields complexes in which one metal center possesses a vacant coordination site for coordination of an additional ligand. In order to investigate this possibility, $(NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$, $(NEt_4)_2[\mathbf{5}]$, was reacted with a couple of donor species. When $(NEt_4)_2[\mathbf{5}]$ was treated with CO or $PMe_3$, color changes

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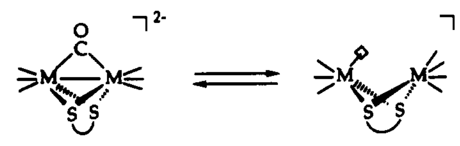

(11)

of the reaction solutions were observed indicating reactions, the compounds which were formed, however, proved to be so labile that reducing the CO pressure or $PMe_3$ concentration yielded $(NEt_4)_2$[**5**] again. Also with thiolates or thioethers as well as with MeLi and hydrides, no isolable addition products could be obtained. With NO gas, $NOBF_4$ or MeI cleavage into mononuclear complexes occurred, and these were not further characterized.

When $(NEt_4)_2$[**5**] was reacted with 2 equiv of proton acids such as HCl, $HBF_4$ and $CF_3SO_3H$, the sulfur ligands were split off according to eq 12. The resulting $[Cr(CO)_3(MeCN)_3]$ and

$$(NEt_4)_2[Cr_2(CO)_7(S_2C_2H_4)] + 2H^+ \xrightarrow{MeCN} S_2C_2H_4\text{-}H_2 + 2NEt_4^+ + [Cr(CO)_3(MeCN)_3] + [Cr(CO)_4(MeCN)_2] \quad (12)$$

$[Cr(CO)_4(MeCN)_2]$ complexes were identified by IR spectroscopy, and the liberated $S_2C_2H_4H_2$ ligand was identified by $^1H$ NMR spectroscopy.

## Discussion and Summary

When $[M(CO)_3(MeCN)_3]$ starting complexes are reacted with aromatic or aliphatic dithiolates, mononuclear $[M(CO)_3(\text{'}S_2\text{'})]^{2-}$ complexes (M = Cr, Mo, W; $\text{'}S_2\text{'} = S_2C_6R_4, S_2C_2H_4$) form which have five-coordinate and 16 $e^-$ $M^0$ centers and are thus coordinatively and electronically unsaturated. Analysis of the distances determined by X-ray crystallography suggests that the complexes are stabilized by π-donation from the thiolate donors to metal centers.

They can also be stabilized by coordination of a sixth ligand such as CO. Coordinatively and electronically saturated 18 $e^-$ $[M(CO)_4(\text{'}S_2\text{'})]^{2-}$ anions result whose stabilities depend on the metal and the dithiolate ligands and in the case of benzenedithiolate ligands also on the substituents of the benzene ring.

For dithiolates, maximum overlap between thiolate lone pairs and empty metal acceptor orbitals leading to strong π-donor bonds can be expected when the five-membered $[MS_2C_2]$ rings are planar (Figure 4)[28] and no electron-withdrawing substituents reduce the Lewis basicity of the thiolates.

This explains the higher stability of $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ ions having planar $[CrS_2C_2]$ rings in comparison to the more labile $[Cr(CO)_3(S_2C_2H_4)]^{2-}$ ions, whose $[CrS_2C_2]$ rings are presumably puckered due to $sp^3$ hybridization of the carbon atoms.

The higher stability of $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ versus $[Cr(CO)_4(S_2C_6H_4)]^{2-}$ ions can be traced back to the different Lewis basicity of the thiolate donors. Salts of the former one can be readily isolated while the latter one is stable only under CO. The chloro substituents of the $C_6$ ring in $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ reduce the π-nucleophilicity of the thiolate lone pairs so much that formation of a S→Cr π-bond versus an additional Cr–CO bond is no longer favored, and consequently $[Cr(CO)_4(S_2C_6Cl_4)]^{2-}$ as well as $[Cr(CO)_3(S_2C_6Cl_4)]^{2-}$ both can be isolated without difficulties.

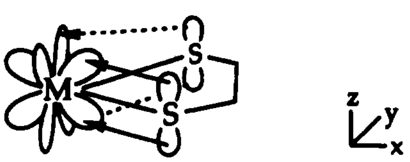
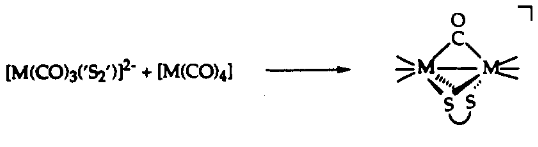


**Figure 4.** Schematic drawing of the S→Cr π donor bonds in $[M(CO)_3(\text{'}S_2\text{'})]^{2-}$ complex anions (M = Cr, Mo, W; $\text{'}S_2\text{'} = S_2C_6R_4, S_2C_2H_4$; R = H, Cl, Me).

The π-donor ability of thiolate ligands is expectedly also reduced by alkylation resulting in thioethers. Accordingly, only $[Cr(CO)_4(MeSC_6H_4S)]^-$ complexes possessing six-coordinate $Cr^0$ centers could be isolated when $[Cr(CO)_3(S_2C_6H_4)]^{2-}$ was methylated.[18]

A further possibility of stabilizing of $[M(CO)_3(\text{'}S_2\text{'})]^{2-}$ ions is the addition of $[M(CO)_4]$ fragments according to eq 13. It does



(13)

not depend on either the aromatic or aliphatic substituents of the thiolate donors, as revealed by the completely analogous structures of $[Cr_2(CO)_7(S_2C_2H_4)]^{2-}$ and $[Cr_2(CO)_7(S_2C_6Cl_4)]^{2-}$, but rather on the denticity of the thiolates as suggested by the different structure of $[Mo_2(CO)_8(SPh)_2]^{2-}$.

In conclusion the results indicate that the coordination chemistry of 1,2-dithiolates is determined by the π-donor properties of the thiolate donors and not by the fact that the thiolate donors are connected via saturated or unsaturated $C_2$ units such as in $S_2C_2H_4^{2-}$ or $S_2C_6H_4^{2-}$. No evidence was found that benzene-1,2-dithiolates behave as "noninnocent" ligands, and the results reported have corroborated our previous findings on completely different complexes containing $[Fe(S_2C_6H_4)_2]$ cores.[7]

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**Supplementary Material Available:** Listings of crystallographic data and data collection parameters, all bond lengths and bond angles, fractional coordinates and isotropic thermal parameters for non-hydrogen atoms, anisotropic thermal parameters, and fractional coordinates of hydrogen atoms (72 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, Germany, by citing the deposition numbers, the authors, and the reference: CSD 320501 {$(NEt_4)_2[Cr(CO)_3(S_2C_6Cl_4)]$, $(NEt_4)_2$[**1**]}, CSD 320503 {$(NEt_4)_2[Cr(CO)_4(S_2C_6Cl_4)]$, $(NEt_4)_2$[**3**]}, CSD 320500 {$(NEt_4)_2[Cr(S_2C_6H_4)_2]$, $(NEt_4)_2$[**12**]}, CSD 320498 {$(PPh_4)_2[Cr_2(CO)_7(S_2C_2H_4)]$, $(PPh_4)_2$[**5**]}, CSD 320497 {$(NEt_4)_2[Cr_2(CO)_7(S_2C_6H_{10})]\cdot 0.55MeOH$, $(NEt_4)_2$[**6**]·0.55MeOH}, CSD 320499 {$(PPh_4)_2[Mo_2(CO)_7(S_2C_2H_4)]\cdot THF$, $(PPh_4)_2$[**7**]·THF}, and CSD 320502 {$(PPh_4)_2[Cr_2(CO)_7(S_2C_6Cl_4)]\cdot MeCN$, $(PPh_4)_2$[**10**]·MeCN}.

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[28] Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297.