the noble gas type of cations in which there can be no electron donation. The position of chloro substitution does have a specificity which, however, must apply mainly to the acid and anion, not to the metal complex.

The most stable complexes reported here are those with the anion of 6-chlorosalicylaldehyde. The behavior of this ligand is unique by reason of proximity and/or steric interactions of the chloro and carbonyl groups.[6] A normal pK_0 for this acid would be that of the other isomer with the chloro substituent in the position *meta* to the hydroxyl group, 4-chlorosalicylaldehyde. The difference in pK_0 values, 1.08, is caused by the stronger hydrogen bond and a reduction in the energy of the flip effect, the rotation of the carbonyl oxygen away from the negative oxygen in the anion.[2] The reduced flip energy is a specific property of the anion and will be a constant contribution to the bonding of hydrogen ion or any metal ion. In support, we note that the difference in the log K_1 values for 6- and 4-chlorosalicylaldehyde with any of the cations falls in the range 0.67–0.78.

A reversal in the stability of the complexes with the 3- and 5-nitro derivatives is observed between Cu(II) and the noble gas type of ions. Insofar as the dashed lines in Figure 1 can be considered to define a normal relation between substituent effects, the reversal in stability appears to be caused by a specific effect in the 3-nitro derivative. The results for the complexing of La(III) with the phenols (Table I) show that La(III) forms a chelate complex with the anion of *o*-nitrophenol, but it is unlikely that the difference between the log K_1 values for La(III) with 3- and 5-nitrosalicylaldehyde can be accounted for entirely by the formation of species in which the La(III) is chelated by nitro oxygen and phenoxy oxygen. If one assumes the log K_1 value for 5-nitrosalicylaldehyde to be the normal value for chelation between the carbonyl and phenoxy oxygens and adds the concentration of species with nitro–phenoxy chelation given by the log K_1 value for *o*-nitrophenol, one obtains 2.84 for the log K value for the formation of both species. This value is smaller than that for 3-nitrosalicylaldehyde and, furthermore, is probably an upper limit because the nitro–phenoxy chelation would be weakened by the substitution of a formyl group *ortho* to the phenoxy oxygen.

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Transition Metal Dithiolate Complexes. I. π-Cyclopentadienyl Maleonitrile Dithiolate Compounds[1]

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New complexes of Co, Mo, W, and Ti containing the π-cyclopentadienyl and the maleonitrile dithiolate ($[S_2C_2(CN)_2]^{2-}$) ligands have been prepared. These complexes are compared with the π-cyclopentadienyl bis(perfluoromethyl)dithiete ($S_2C_2(CF_3)_2$) derivatives of Cr, Mo, and Co, and their further reactions with excess $Na_2S_2C_2(CN)_2$ to give simple unsubstituted maleonitrile dithiolate complexes are described.

Introduction

The reactions of sulfur ligands related to ethylene *cis*-dithiol with metal carbonyl and π-cyclopentadienyl carbonyl derivatives are well documented.[3,4] For example, bis(perfluoromethyl)dithiete, $S_2C_2(CF_3)_2$, reacts with the carbonyls and π-cyclopentadienyl carbonyls of V, Cr, Mo, Co, and Ni, generally causing displacement of CO and forming simple dithiolate derivatives, *e.g.*, $MoS_6C_6(CF_3)_6$, or π-cyclopentadienyl compounds, *e.g.*, $[\pi\text{-}C_5H_5MoS_2C_2(CF_3)_2]_2$. Few reactions of carbonyl derivatives with $Na_2S_2C_2(CN)_2$ have been described, but it has been reported[5] that this ligand displaces only one CO group from $Mn(CO)_5Br$ forming $[Mn(CO)_4S_2C_2(CN)_2]^-$ and, in the hope of obtaining anionic carbonyl derivatives of the type $[\pi\text{-}C_5H_5M(CO)_nS_2C_2(CN)_2]^-$ (where M = Fe and $n = 1$ or M = Mo or W and $n = 2$, etc.), the reaction of the appropriate π-cyclopentadienyl metal carbonyl halide with $Na_2S_2C_2(CN)_2$ was investigated.

Experimental Section

All melting points are uncorrected and all solvents were degassed before use. All analyses were carried out by the Microanalytical Laboratory of this department or by Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr), Germany.

Physical Measurements.—Infrared spectra were recorded using a Unicam SP 100 spectrophotometer, and proton magnetic resonance spectra were obtained using a Varian A-60 spectrometer.

Disodium Maleonitrile Dithiolate.—Initially this salt was prepared from $NaS_2C\cdot CN\cdot 3DMF$ by the standard methods[6]

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[2] Supported by the Scientific Research Council.

[3] (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963); **4**, 55 (1965); G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); (b) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964); *Inorg. Chem.*, **3**, 814 (1964); R. B. King, *ibid.*, **2**, 641 (1963).

[4] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[5] J. Locke and J. A. McCleverty, *Chem. Commun.*, 102 (1965).

[6] G. Bahr and G. Schleitzer, *Chem. Ber.*, **90**, 438 (1954); A. Davison and R. H. Holm, *Inorg. Syn.*, submitted for publication.

and later by the following more facile method. $NaS_2C\cdot CN\cdot 3DMF$ (150 g) was dissolved in 600 ml of chloroform and refluxed for 8 hr on a steam bath. During this time the solution turned from red-brown to deep red, and a fine yellow powder precipitated. The mixture was filtered hot (the hot solvent retains most of the eliminated sulfur), and the solid yellow residue was washed with 300 ml of boiling chloroform and dissolved in 300 ml of boiling methanol. The orange-yellow solution was filtered and 400 ml of chloroform was added to precipitate the $Na_2S_2C_2(CN)_2$. After storing the mixture at 0° for 3 hr, the yellow powder was filtered off, washed with 100 ml of chloroform, and dried *in vacuo*. The yield of the pale yellow solid was 30.2 g (74% based on $NaS_2C\cdot CN\cdot 3DMF$), and it was sufficiently pure for the preparations described in this paper.

$[\pi\text{-}C_5H_5Fe(CO)_2]_2S_2C_2(CN)_2$.—$\pi\text{-}C_5H_5Fe(CO)_2Cl$ (0.53 g) and $Na_2S_2C_2(CN)_2$ (0.47 g) were shaken together for 12 hr in 100 ml of distilled water; a red solution and a brown tarry solid formed during this time. The brown solid was filtered off, washed with water, and redissolved in the minimum volume of acetone, and water was added until precipitation began. The red-brown solid was filtered off and washed with ethanol (which removed much brown impurity), and the resulting red crystals were washed with ether and air dried. Recrystallization was effected from acetone–ethanol, affording 0.17 g of the complex, mp 136–138° dec. The yield was 28% (based on $\pi\text{-}C_5H_5Fe(CO)_2Cl$) but was subsequently found to be variable.

Anal. Calcd for $C_{18}H_{10}O_4N_2S_2Fe_2$: C, 43.8; H, 2.0; N, 5.7; S, 13.0. Found: C, 43.8; H, 2.4; N, 5.8; S, 12.8.

Conductivity.—The compound is nonconducting in 10^{-4} *M* nitromethane solution.

Infrared Spectrum.—The spectra (cm^{-1}) were recorded in KBr disks, hexachlorobutadiene mulls, and chloroform. In chloroform solution: 3120 w, 2200 m (ν_{CN}), 2050 vs (ν_{CO}), 2010 vs (ν_{CO}), 1960 m (ν_{CO}), 1824 w, 1715 vw, 1484 m, 1448 s, 1432 m, 1242 m, 1157 s, 1127 w, 1108 w, 1052 w, 1018 vw, 1006 w, 848 m. In hexachlorobutadiene mulls in the region 2300–1000 cm^{-1}: 2220 sh (ν_{CN}), 2200 m (ν_{CN}), 2030 vs (ν_{CO}), 1995 vs (ν_{CO}), 1810 vw, 1614 w, 1570 m, 1453 m, 1435 m, 1428 m, 1170 m, 1135 m, 1124 m, 1074 vw, 1024 w, 1008 w. In KBr disks: 3150 vw, 3095 vw, 3080 w, 2210 sh (ν_{CN}), 2194 s (ν_{CN}), 2032 vs (ν_{CO}), 1995 vs (ν_{CO}), 1805 vw, 1452 m, 1431 m, 1422 sh, 1155 m, 1133 s, 1122 s, 1071 vw, 1025 w, 1015 sh, 1008 w, 950 w, 882 w, 853 sh, 845 s, 835 sh.

Proton Magnetic Resonance Spectra.—These were recorded in acetone solution; a single sharp resonance was observed at τ 4.64 attributable to the $\pi\text{-}C_5H_5$ protons.

$[(C_6H_5)_4P][\pi\text{-}C_5H_5MoS_4C_4(CN)_4]$.—$\pi\text{-}C_5H_5Mo(CO)_3I$ (2.58 g) dissolved in 50 ml of acetone was treated with a solution of 2.58 g of $Na_2S_2C_2(CN)_2$ in 50 ml of methanol and allowed to stand for 3 days, during which time the solution became a deep blue-green. The solution was filtered, evaporated to dryness under reduced pressure (water pump), and extracted with 50 ml of water. The deep green aqueous extract was filtered and treated with 1 g of $[(C_6H_5)_4P]Br$, and the mixture of deep green and deep blue, nearly black, crystals which precipitated was collected. Recrystallization twice from acetone–ethanol effected separation of the black crystals of $[(C_6H_5)_4P][\pi\text{-}C_5H_5MoS_4C_4(CN)_4]$ (which is the less soluble) from the deep green $[(C_6H_5)_4P]_2[MoS_6C_6(CN)_6]$. Due to losses in recrystallization, only 0.07 g of the latter complex was obtained, and it was identified by comparison (mixture melting point 258–260°) with an authentic sample prepared from $MoCl_5$, $Na_2S_2C_2(CN)_2$, and $[(C_6H_5)_4P]Br$ in THF.[7] The residue retained after the first aqueous extract had been filtered was further extracted with 200 ml of water and gave a blue-green solution. On addition of 2 g of $[(C_6H_5)_4P]Br$ in 30 ml of methanol, a blue-green precipitate was formed. This was filtered off, washed with water, and twice recrystallized from acetone–water. The yield of the black crystals, mp 282–285°, was 0.79 g (15% based on $\pi\text{-}C_5H_5Mo(CO)_3I$). The complex is soluble in acetone, nitromethane, DMSO, DMF, and chloroform to give blue-green solutions.

Anal. Calcd for $C_{37}H_{25}N_4S_4PMo$: C, 56.9; H, 3.2; N, 7.2; S, 16.4. Found: C, 56.9; H, 3.3; N, 7.1; S, 16.3.

Conductivity.—The conductivity was recorded in 10^{-4} *M* acetone solution, $\Lambda = 126$ cm^2 ohm^{-1} $mole^{-1}$ (consistent for a 1:1 electrolyte).

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3110 w, 2200 s (ν_{CN}), 1710 w, 1640 vw, 1590 w, 1483 m, 1445 w, 1439 s, 1343 w, 1318 w, 1192 w, 1162 w, 1152 s, 1112 s, 1032 w, 1015 m, 997 m, 930 w, 853 m, 822 m, 758 s, 728 s, 692 s.

Proton Magnetic Resonance Spectrum.—This was recorded in DMSO solution; resonances occurred at τ 2.14 (multiple, phenyl protons, intensity 4) and τ 4.87 (singlet, $\pi\text{-}C_5H_5$ protons, intensity 1).

$[(C_6H_5)_4P][\pi\text{-}C_5H_5WS_4C_4(CN)_4]$.—$\pi\text{-}C_5H_5W(CO)_3Cl$ (0.55 g) was dissolved in 50 ml of acetone and treated with 0.55 g of $Na_2S_2C_2(CN)_2$ in 50 ml of methanol. The mixture was warmed on a steam bath at 60° for 4 hr and filtered, and the magenta filtrate was evaporated to dryness under reduced pressure. The residue was extracted with 80 ml of water and filtered, and 2.0 g of $[(C_6H_5)_4P]Br$ was added. The precipitated solid was filtered off, washed with water, and twice recrystallized from acetone–ethanol, the dark red-brown crystals being washed with ether and air dried. The yield of the complex, mp 269–272°, was 0.45 g (35% based on $\pi\text{-}C_5H_5W(CO)_3Cl$). It is soluble in acetone, chloroform, methylene chloride, THF, DMF, DMSO, and nitromethane forming magenta solutions.

Anal. Calcd for $C_{37}H_{25}N_4S_4PW$: C, 51.2; H, 2.9; N, 6.5; S, 14.7. Found: C, 51.4; H, 3.0; N, 6.4; S, 14.6.

Conductivity.—The conductivity was measured in 10^{-4} *M* nitromethane solution at 20°, $\Lambda = 65$ cm^2 ohm^{-1} $mole^{-1}$ (consistent for a 1:1 electrolyte).

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3123 w, 2200 s (ν_{CN}), 1710 w, 1640 w, 1583 w, 1488 m, 1436 s, 1388 w, 1342 w, 1317 w, 1190 w, 1161 w, 1152 m, 1111 s, 1030 w, 1010 w, 998 m, 928 w, 853 m, 820 m, 756 w, 726 s, 690 s.

Proton Magnetic Resonance Spectrum.—This was recorded in DMSO solution; resonances were observed at τ 2.3 (multiplet, phenyl protons, intensity 4) and at τ 4.87 (singlet, $\pi\text{-}C_5H_5$ protons, intensity 1). No W^{183} hyperfine splitting was observed.

$\pi\text{-}C_5H_5CoS_2C_2(CN)_2$.—$Na_2S_2C_2(CN)_2$ (0.32 g) dissolved in 40 ml of ice-cold methanol was added over 0.75 hr to a stirred solution of 0.70 g of $\pi\text{-}C_5H_5Co(CO)I_2$ in 50 ml of ice-cold acetone. The color of the mixture changed from gray-violet to deep purple, and after the addition of $Na_2S_2C_2(CN)_2$ was complete, the solvent was gradually removed under reduced pressure. Fine purple-black crystals began to appear and after about two-thirds of the solvent had been removed, the crystals were filtered off, washed with ether, and air dried. Recrystallization was effected from acetone–water, affording a yield of 0.34 g of purple crystals, mp 282° dec (75% based on $\pi\text{-}C_5H_5Co(CO)I_2$). The complex is moderately soluble in chloroform, acetone, and nitromethane, giving purple solutions.

Anal. Calcd for $C_9H_5N_2S_2Co$: C, 40.9; H, 1.9; N, 10.6; S, 24.2; mol wt, 264. Found: C, 40.8; H, 2.1; N, 10.5; S, 24.3; mol wt, 260 (osmometrically in chloroform).

Conductivity.—This compound is a nonconductor in 10^{-4} *M* nitromethane solution.

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3108 m, 2608 w, 2334 w, 2223 sh (ν_{CN}), 2212 m (ν_{CN}), 1882 w, 1815 w, 1762 vw, 1731 vw, 1526 vw, 1422 s, 1413 s, 1347 m, 1264 w, 1167 s, 1111 m, 1051 m, 1014 m, 1003 m, 943 w, 877 m, 853 vs, 838 w, 798 w, 740 vw.

Proton Magnetic Resonance Spectrum.—This was recorded in chloroform solution; a single resonance was observed at τ 4.34 attributable to the $\pi\text{-}C_5H_5$ protons.

Reaction of $\pi\text{-}C_5H_5Co(CO)I_2$ and $\pi\text{-}C_5H_5CoS_2C_2(CN)_2$ with Excess $Na_2S_2C_2(CN)_2$. $[(C_6H_5)_4P]_3[CoS_6C_6(CN)_6]$.—$\pi\text{-}C_5H_5Co(CO)I_2$ (0.50 g) was dissolved in 50 ml of acetone and treated with 1.15 g of $Na_2S_2C_2(CN)_2$ in 100 ml of ethanol. The solution quickly changed from gray-violet to purple ($\pi\text{-}C_5H_5CoS_2C_2(CN)_2$?)

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[7] M. Gerloch, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.* (London), 29 (1966), and work to be published elsewhere.

and finally to green-brown. $[(C_6H_5)_4P]Br$ (1.72 g) in 40 ml of ethanol was then added and the mixture allowed to stand for 1 hr. During this time black crystals formed in the solution and these were filtered off, washed with ethanol and ether, and air dried. The complex, mp 224–227°, was found to be $[(C_6H_5)_4P]_3[CoS_6C_6(CN)_6]$ and was sufficiently pure for analytical purposes. It dissolved in chloroform, DMF, and DMSO to give yellow-brown solutions. As a finely divided solid it has a greenish hue. Similar chemical behavior was observed with $\pi\text{-}C_5H_5CoS_2C_2(CN)_2$.

Anal. Calcd for $C_{84}H_{60}N_6S_6P_3Co$: C, 67.3; H, 4.0; N, 5.6; S, 12.8. Found: C, 67.5; H, 4.0; N, 5.4; S, 12.7.

Conductivity.—The conductivity was measured in 10^{-4} *M* acetone solution, $\Lambda = 446$ cm^2 ohm^{-1} mole^{-1} (consistent for a 3:1 electrolyte).

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3035 vw, 2280 vw, 2245 vw, 2185 m ν_{CN}, 1670 w, 1588 m, 1545 m, 1535 m, 1487 m, 1474 sh, 1468 s, 1460 s, 1445 s, 1442 s, 1342 w, 1322 w, 1224 w, 1192 w, 1168 w, 1142 s, 1111 s, 1059 vw, 1045 vw, 1029 vw, 998 m, 858 m, 797 w, 763 sh, 757 m, 726 s, 692 s.

The complex was identical (mixture melting point) with that prepared from $[(C_6H_5)_4P][CoS_4C_4(CN)_4]$, $Na_2S_2C_2(CN)_2$, and $[(C_6H_5)_4P]Br$.[8]

$(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$.—A stirred solution of 0.3 g of $(\pi\text{-}C_5H_5)_2TiCl_2$ in 50 ml of acetone was treated with 0.25 g of $Na_2S_2C_2(CN)_2$ in 80 ml of methanol. The solution quickly turned from red to dark green, and after standing for 2 hr dark green crystals had formed. These were filtered off and recrystallized from acetone–methanol, affording 0.06 g of the complex, mp >260° (16% based on $(\pi\text{-}C_5H_5)_2TiCl_2$). Higher yields can be obtained if the reaction is carried out in benzene.[9] The compound is soluble in acetone, nitromethane, and benzene, giving green solutions.

Anal. Calcd for $C_{14}H_{10}N_2S_2Ti$: C, 52.9; H, 3.2; N, 8.8; S, 20.1. Found: C, 52.4; H, 3.7; N, 9.0; S, 20.4.

Conductivity.—This compound is a nonconductor in 10^{-4} *M* nitromethane solution.

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3115 m, 2285 w, 2210 sh (ν_{CN}), 2202 (ν_{CN}), 1802 w, 1437 s, 1432 sh, 1272 w, 1163 w, 1130 m, 1064 w, 1022 s, 950 vw, 872 m, 860 sh, 844 sh, 834 s.

Proton Magnetic Resonance Spectrum.—This was recorded in acetone solution; a single resonance was observed at τ 3.57, attributable to the $\pi\text{-}C_5H_5$ protons.

$[(C_2H_5)_4N][\pi\text{-}C_5H_5TiS_4C_4(CN)_4]$.—A solution of 1.0 g of $(\pi\text{-}C_5H_5)_2TiCl_2$ in 60 ml of acetone was treated with 1.5 g of $Na_2S_2C_2(CN)_2$ in 30 ml of methanol. The color of the solution quickly changed from red to green ($(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$?) and finally to magenta. After stirring for 0.5 hr the solution was filtered into 40 ml of ethanol containing 0.84 g of $[(C_2H_5)_4N]Br$. The volume of the solution was reduced *in vacuo* until crystallization began. The black crystals which formed were filtered off and recrystallized from acetone–ethanol. The yield of the complex, mp 204–205°, was 0.22 g (10% based on $(\pi\text{-}C_5H_5)_2TiCl_2$). The complex was also obtained in the same way, although in lower yields, from $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$. The compound dissolves in acetone, nitromethane, DMF, and DMSO to give magenta-colored solutions.

Anal. Calcd for $C_{21}H_{25}N_5S_4Ti$: C, 48.2; H, 4.8; N, 13.4; S, 24.4. Found: C, 48.1; H, 4.9; N, 13.2; S, 24.4.

Conductivity.—The conductivity was measured in 10^{-4} *M* acetone solution, $\Lambda = 159$ cm^2 ohm^{-1} mole^{-1} (consistent for a 1:1 electrolyte).

Infrared Spectrum.—This was recorded in KBr disks (cm^{-1}): 3093 w, 3085 w, 3065 w, 2987 w, 2069 w, 2011 m (ν_{CN}), 1999 s (ν_{CN}), 1487 s, 1455 m, 1446 m, 1439 m, 1402 s, 1373 m, 1340 vw, 1177 m, 1157 m, 1127 m, 1068 w, 1022 m, 1008 m, 856 w, 842 vw, 828 s, 788 m.

Proton Magnetic Resonance Spectrum.—This was recorded in acetone solution; resonances were observed at τ 3.69 (singlet, $\pi\text{-}C_5H_5$ protons, intensity 5) and τ 8.60 (triplet, CH_3 resonance of $(C_2H_5)_4N^+$, intensity 12). The solvent resonance obscured the $-CH_2-$ lines of the cation.

Reaction of $(\pi\text{-}C_5H_5)_2Ni$ with Excess $Na_2S_2C_2(CN)_2$.—$(\pi\text{-}C_5H_5)_2Ni$ (0.5 g) was heated on a steam bath with 2.0 g of $Na_2S_2C_2(CN)_2$ in 50 ml of acetone for 1 hr. The acetone was then removed *in vacuo*, the residue was extracted with *ca.* 100 ml of water, and 1.0 g of $[(C_6H_5)_4P]Br$ in 30 ml of methanol was added. The red precipitate was collected, washed thoroughly with water, and recrystallized from acetone–water, yielding red crystals, mp 260–266°. This compound was identical (mixture melting point) with a sample of $[(C_6H_5)_4P]_2[NiS_4C_4(CN)_4]$ prepared from $NiCl_2 \cdot 6H_2O$, $Na_2S_2C_2(CN)_2$, and $[(C_6H_5)_4P]Br$ by standard methods.

Discussion

Neutral Complexes.—The red solid, $[\pi\text{-}C_5H_5Fe(CO)_2]_2S_2C_2(CN)_2$, obtained from the reaction between $Na_2S_2C_2(CN)_2$ and $\pi\text{-}C_5H_5Fe(CO)_2Cl$ probably contains a bridging maleonitrile dithiolate group in which each sulfur atom is bonded to only one iron atom. The compound could thus be analogous to $\pi\text{-}C_5H_5Fe(CO)_2SCH_3$;[10] the infrared spectra of the two compounds in the carbonyl stretching region are comparable: $[\pi\text{-}C_5H_5Fe(CO)_2]_2S_2C_2(CN)_2$, 2031 and 1995 cm^{-1} (KBr disk and mull); $\pi\text{-}C_5H_5Fe(CO)_2SCH_3$, 2032 and 1985 cm^{-1} (mull).

Simmons and his co-workers[11] have identified both *cis*- and *trans*-$[S_2C_2(CN)_2]^{2-}$ by infrared spectroscopy, the former isomer having an absorption at *ca.* 1440 cm^{-1} ($\nu_{C=C}$) which is absent in the latter isomer. $[\pi\text{-}C_5H_5Fe(CO)_2]_2S_2C_2(CN)_2$ has two absorptions in the region 1300–1500 cm^{-1}, at 1454 (medium strong) and 1430 cm^{-1}. The latter band is a doublet (splitting 9 cm^{-1}), probably because of solid-state splitting effects; the spectra had to be recorded in KBr disks and hexachlorobutadiene mulls because the compound reacted rapidly with CCl_4, $CHCl_3$, and CH_2Cl_2, possibly forming $\pi\text{-}C_5H_5Fe(CO)_2Cl$ (extra bands were observed in the carbonyl stretching and $\pi\text{-}C_5H_5$ ring breathing regions). By comparison with the spectra of other monocyclopentadienyl compounds,[12] the absorption at 1430 cm^{-1} could be assigned to the $\pi\text{-}C_5H_5$ ring breathing mode and hence the absorption at 1454 cm^{-1} to $\nu_{C=C}$. Although these assignments are only tentative, that there are two absorptions in this region would suggest a *cis* configuration for the sulfur ligand.

$(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$ has been reported independently of this work,[9,13] and it has been shown that the compound and the analogous toluene-3,4-dithiolate derivative, $(\pi\text{-}C_5H_5)_2TiS_2C_6H_3CH_3$, are monomeric. It is probable that these molecules have an oyster-like structure similar to that of $(\pi\text{-}C_5H_5)_2TiCl_2Al(C_2H_5)_2$[14] and $(\pi\text{-}C_5H_5)_2MoH_2$.[15] Owing to its low solubility in

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[8] This method of preparation is similar to that reported for $[(C_4H_9)_4N]_3[CoS_6C_6(CN)_6]$: C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

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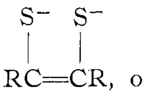
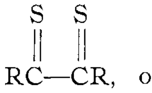
[15] M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1964).

suitable solvents, a study of the infrared spectra of $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$ was carried out in a KBr disk. A strong absorption was revealed at 1442 cm^{-1}, with a shoulder at 1432 cm^{-1}, which possibly was due to a solid-state splitting effect. Since the sulfur ligand must have the *cis* configuration, it seems that the $\pi\text{-}C_5H_5$ ring breathing mode and $\nu_{C=C}$ nearly coincide.

$\pi\text{-}C_5H_5CoS_2C_2(CN)_2$ and the analogous $\pi\text{-}C_5H_5\text{-}CoS_2C_2(CF_3)_2$ are monomeric in chloroform. If these compounds formally contain Co(III), it seems probable that the cobalt ion has an effective atomic numer of 36 and its preferred coordination number of six (the $\pi\text{-}C_5H_5$ ring is regarded as occupying three coordination sites). It is thus necessary to propose an interaction between the ethylenic function of the dithiolate ligand and the cobalt ion to account for the sixth coordination site. Evidence to support this has been presented by King,[4] who showed that $\nu_{C=C}$ in $\pi\text{-}C_5H_5CoS_2C_2(CF_3)_2$ was lowered relative to $\nu_{C=C}$ in $\pi\text{-}C_5H_5NiS_2C_2(CF_3)_2$ where an interaction of this type would be unlikely (the Ni(III) ion has an effective atomic number of 35 and the complex is paramagnetic). Although $\pi\text{-}C_5H_5NiS_2C_2(CN)_2$ could not be prepared, the infrared spectra of the cobalt analog revealed two absorptions between 1300 and 1500 cm^{-1}. The band at 1417 cm^{-1} is possibly the $\pi\text{-}C_5H_5$ ring breathing mode (by comparison with $\pi\text{-}C_5H_5Co\text{-}(CO)I_2$ and ref 12) and the band at 1347 cm^{-1} the perturbed $\nu_{C=C}$. If there is an interaction of the type envisaged, the $CoS_2C_2(CN)_2$ fragment cannot be planar, and a possible molecular configuration is shown in Figure 1.

Some argument as to the nature of the dithiolato ligands in metal complexes, *i.e.*, whether they are truly represented as ethylene dithiolates,  $R\overset{\overset{S^-}{|}}{C}{=}\overset{\overset{S^-}{|}}{C}R$, or dithioketones,  $R\overset{\overset{S}{\|}}{C}{-}\overset{\overset{S}{\|}}{C}R$, or some intermediate, still remains,[16] and a structure involving a dicyano dithioketone cannot be dismissed. Here, the cobalt ion would be in the +1 oxidation state (effective atomic number 36), and the $CoS_2C_2(CN)_2$ fragment could be planar. In view of the infrared evidence, it is thought that this is unlikely, and a single-crystal X-ray analysis[17] of the compound will settle this particular problem.

Anionic Complexes.—$\pi\text{-}C_5H_5Mo(CO)_3I$ and $\pi\text{-}C_5H_5W(CO)_3Cl$ react with $Na_2S_2C_2(CN)_2$ to give black crystalline complexes, $[(C_6H_5)_4P][\pi\text{-}C_5H_5MS_4C_4(CN)_4]$. In solution these compounds are green-blue (Mo) and magenta (W): no evidence for a bridged species, $[\pi\text{-}C_5H_5M(CO)_3]_2S_2C_2(CN)_2$, was discovered. $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$ and $(\pi\text{-}C_5H_5)_2TiCl_2$ react with 1 and 2 moles, respectively, of $Na_2S_2C_2(CN)_2$ to form the magenta complex ion, $[\pi\text{-}C_5H_5TiS_4C_4(CN)_4]^-$. These molecules are diamagnetic, and their proton magnetic spectra exhibit the expected phenyl and $\pi\text{-}C_5H_5$ proton resonances; the metal ions can be regarded as formally in the +4 oxidation state.

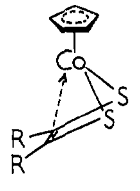


Figure 1.

These reactions of the carbonyl halides can be compared with those between bis(perfluoromethyl)dithiete, $S_2C_2(CF_3)_2$, and $[\pi\text{-}C_5H_5M(CO)_3]_2$, M = Cr or Mo.[4] In common with the maleonitrile dithiolate anion, $S_2C_2(CF_3)_2$ displaced CO completely from the carbonyls but apparently did not attack the $\pi\text{-}C_5H_5$ ring. However, only neutal dimeric species, $[\pi\text{-}C_5H_5MS_2C_2\text{-}(CF_3)_2]_2$, were formed.

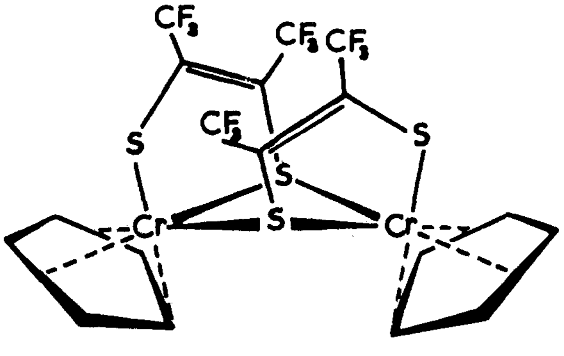


Figure 2.

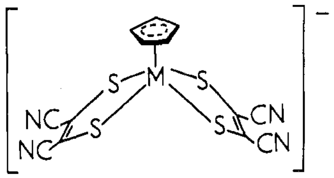


Figure 3.

A single-crystal X-ray analysis of $[\pi\text{-}C_5H_5CrS_2C_2\text{-}(CF_3)_2]_2$ has recently been completed,[18] and the molecular geometry is shown in Figure 2. There is a direct Cr–Cr interaction (internuclear distance 2.98 A), thereby rendering each Cr atom effectively seven-coordinate (effective atomic number 35). The molecule is diamagnetic, and it is likely that $[\pi\text{-}C_5H_5MoS_2C_2\text{-}(CF_3)_3]_2$ (which is also diamagnetic) has a similar structure.

The maleonitrile dithiolato cyclopentadienyls of molybdenum, tungsten, and titanium have a more regular seven-coordinate (3:4 coordination) structure (Figure 3), probably based on the 3:4 coordination found in $\pi\text{-}C_5H_5Nb(CO)_4$.[19]

Reactions with Excess $Na_2S_2C_2(CN)_2$.—During the preparation of $[\pi\text{-}C_5H_5MoS_4C_4(CN)_4]^-$, small amounts of the green $[MoS_6C_6(CN)_6]^{2-}$ ion were isolated, and

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[16] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483, 3585, (1965).

[17] M. R. Churchill, Chemistry Department, Harvard University.

[18] S. F. Watkins and L. F. Dahl, Abstracts of Papers presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p. 23-O.

[19] L. F. Dahl, private communication.

it was discovered that the yields of this salt could be slightly increased by using excess $Na_2S_2C_2(CN)_2$ in the initial reaction between the carbonyl halide and the sulfur ligand. These observations prompted an investigation of the reactions between excess $Na_2S_2C_2(CN)_2$ and the carbonyl halides and cyclopentadienyl maleonitrile dithiolato complexes described earlier in this paper.

Treatment of $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$, $[\pi\text{-}C_5H_5TiS_4C_4(CN)_4]^-$, and $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with excess $Na_2S_2C_2(CN)_2$ almost certainly resulted in the cleavage of the $\pi\text{-}C_5H_5$ ring. It is thought that unsubstituted maleonitrile dithiolato complexes were formed since red-brown solids which were precipitated on addition of heavy organic cations exhibited infrared spectral features similar to known simple maleonitrile dithiolato compounds.[20] However, these solids defied purification, and hence characterization, although on one occasion a low yield of $[(C_6H_5)_4As]_2[FeS_6C_6(CN)_6]$[7] was isolated. $[(C_6H_5)_4P]_3[CoS_6C_6(CN)_6]$ was obtained from $\pi\text{-}C_5H_5CoS_2C_2(CN)_2$, and nickelocene afforded a moderate yield of $[(C_6H_5)_4P]_2[NiS_4C_4(CN)_4]$. Only $\pi\text{-}C_5H_5W(CO)_3Cl$ and $[\pi\text{-}C_5H_5WS_4C_4(CN)_4]^-$ were inert to further attack by $Na_2S_2C_2(CN)_2$ even after refluxing together for several hours in methanol. Behavior of this kind was not observed with bis(perfluoromethyl)dithiete, although derivatives of the type $MS_6C_6(CF_3)_6$, M = Fe, Cr, Mo, or W, were obtained by allowing the appropriate carbonyls and $S_2C_2(CF_3)_2$ to react.[3b]

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[20] E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

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Spin–Spin Coupling in Binuclear Complexes. II.
The Magnetic Properties of Schiff's Base Complexes of Copper(II)[1]

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The magnetic behavior as a function of temperature has been determined for a number of binuclear copper(II) complexes with Schiff's bases derived from the condensation of substituted and unsubstituted salicylaldehydes with substituted and unsubstituted *o*-aminophenols. The magnetic properties are markedly affected by the nature and the position of the substituent on the chelate ring. Only one compound exhibited simple copper acetate like behavior. The data for the other compounds indicated that the systems were complicated by the presence of isomers and by inter- as well as intramolecular interactions. The spectra of selected compounds were studied as a function of temperature. There was no significant effect on either band position or intensity.

Introduction

Because of their low magnetic moments the copper complexes with tridentate Schiff's bases formed by the condensation of *o*-aminophenol with salicylaldehyde or acetylacetone have attracted much attention since they were initially reported by Kishita, Muto, and Kubo.[2] The Japanese workers attributed the low magnetic moments of these compounds to either tricoordination of the copper(II) ion or to dimerization in the solid state leading to a direct copper–copper interaction. In 1961, Barclay, Harris, Hoskins, and Kokot[3] showed by an X-ray examination of single crystals of the acetylacetonemono(*o*-hydroxyanil)copper(II) complex that the crystal structure was composed of dimeric molecules with the molecular structure shown in Figure 1. The temperature dependences of the magnetic susceptibilities of three related complexes were reported to be similar to that exhibited by copper acetate monohydrate.[3]

The mechanism by which the unpaired electrons on adjacent copper ions in the binuclear molecules pair their spins has not been elucidated. In their first paper Barclay, *et al.*,[3] suggested that the electron pairing occurred by superexchange through the bridging oxygens, but recently Barclay and Hoskins[4] have noted that a direct copper–copper interaction cannot be ignored. Since the copper–copper internuclear distance of 3.0 A in the compound shown in Figure 1 is intermediate between the 2.64 A found in copper acetate monohydrate[5] and the 3.3 A found in the binuclear pyridine

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[1] This work was supported by the North Carolina Board of Science and Technology, the National Science Foundation, and the Advanced Research Projects Agency, and was presented at the combined Southeast–Southwest Regional Meeting of the American Chemical Society at Memphis, Tenn., Dec 2–4, 1965.

[2] M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957).

[3] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

[4] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[5] J. N. van Niekerk and F. K. L. Schoening, *Nature*, **171**, 36 (1953); *Acta Cryst.*, **6**, 227 (1953).