Contribution from the Chemistry Department,
The University, Sheffield S3 7HF, United Kingdom

Transition Metal Dithiolene Complexes. VI.[1]
Tetracarbonyl Dithiolato Compounds of Manganese

N. G. Connelly,[2] J. Locke,[2] and J. A. McCleverty

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Introduction

Manganese pentacarbonyl bromide reacts readily with disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate ($Na_2S_2C_2(CN)_2$) and its isomer disodium 1,1-dicyanoethylene-2,2-dithiolate ($Na_2S_2C=C(CN)_2$) in mixtures of methanol and acetone forming the tetracarbonyl dithiolate anions $[Mn(CO)_4S_2C_2(CN)_2]^-$ [3] and $[Mn(CO)_4S_2C=C(CN)_2]^-$. The analogous complexes $[Mn(CO)_4S_2C_6Cl_4]^-$ and $[Mn(CO)_4S_2C_6H_3CH_3]^-$ are obtained when the carbonyl halide is treated with disodium tetrachlorobenzene-1,2-dithiolate ($Na_2S_2C_6Cl_4$) and disodium toluene-3,4-dithiolate ($Na_2S_2C_6H_3CH_3$). The complexes were isolated as the salts of heavy organic cations, and were obtained as beautifully crystalline solids whose formulations are consistent with elemental analyses and conductivity measurements. The colours of the 1,2-dithiolato species in solution are red to magenta in contrast to $[Mn(CO)_4S_2C=C(CN)_2]^-$ and the isoelectronic diethyldithiocarbamate $Mn(CO)_4S_2CN(C_2H_5)_2$ [4] which are yellow-brown or yellow.

Results and Discussion

The new complexes are moderately stable to air in the solid state but rapidly decompose in solution. Treatment of $[Mn(CO)_4S_2C_2(CN)_2]^-$ with $P(C_6H_5)_3$ and with an excess of water results in the decomposition of the carbonyl complex and formation of small amounts of $[MnS_6C_6(CN)_6]^{2-}$ [5] which has been isolated and characterised as the $[(C_6H_5)_3(CH_3)P]^+$ salt. A reaction occurred between $[Mn(CO_4)S_2C_2(CN)_2]^-$ and NO and transient green colours, which may have been due to $[Mn(NO)S_4C_4(CN)_4]^{2-}$,[6] were observed, but we were unable to isolate and characterise the product. It is interesting that the reaction of $Mn(CO)_5Br$ with $\{S_2C_6H_3CH_3\}^{2-}$ gives the anionic tetracarbonyl dithiolate as the exclusive product whereas that with neat toluene-3,4-dithiol gives two different products, $[Mn(CO)_3S(HS)C_6H_3CH_3]$ and $[Mn(CO)_3S_2C_6H_3CH_3]_2$.[7]

The infrared spectra of the new complexes are entirely consistent with their expected C_{2v} symmetry, exhibiting four infrared active carbonyl stretching frequencies which are recorded in the Table. It is clear from a comparison of the average positions of the CO stretching frequencies in the 1,2-dithiolato species and in $[Mn(CO)_4S_2C=C(CN)_2]^-$ with those in $Mn(CO)_4S_2CN(C_2H_5)_2$ that the 1,2-dithiolato ligands and $\{S_2C=C(CN)_2\}^{2-}$ can function as better π-acceptors than $\{S_2CN(C_2H_5)_2\}^-$ in these systems. Within the 1,2-dithiolato series itself, the average values of the CO stretching frequencies decrease in the order $S_2C_2(CN)_2 > S_2C_6Cl_4 > S_2C_6H_3CH_3$, which reflects, as expected, the relative electron-withdrawing properties of the sulphur ligand substituents. It may also be noted that the average positions of ν_{CO} in $[Mn(CO)_4S_2C_2(CN)_2]^-$ and $[Mn(CO)_4S_2C=C(CN)_2]^-$ are very close suggesting that the 1,1-dithiolate is as good a π-acceptor as the 1,2-dithiolate ligand.

The tetracarbonyl dithiolates were investigated by voltammetry and were found to have no significant redox properties. This observation indicates that in the 1,2-dithiolato species, the sulphur ligand can be correctly visualised as being derived from *cis*-1,2-disubstituted ethylene-1,2-dithiolates.

Experimental Section

The infrared spectra were recorded in dichloromethane solution using Infracord 457 and Unicam SP100 spectrophotometers. Conductivities were measured at room temperature (22°) with a Phillips conductivity meter. Elemental analyses were carried out by the Microanalytical Laboratory of this Department and all melting points are uncorrected.

*Triphenylmethylphosphonium Tetracarbonyl-*cis*-1,2-dicyanoethylene-1,2-dithiolato Manganese,* $[(C_6H_5)_3(CH_3)P][Mn(CO)_4S_2C_2(CN)_2]$. $Mn(CO)_5Br$ (1.6 g) was treated with $Na_2S_2C_2(CN)_2$ (1.4 g) in a flask containing 150 ml of a methanol/acetone (1:1 v/v) mixture. The solution, which rapidly became red, was shaken for 4 hrs, filtered and to the filtrate was added $[(C_6H_5)_3(CH_3)P]I$ (2.4 g) dissolved in 30 ml ethanol. Excess cold water was added to this mixture and it was allowed to stand at −5° for 3 hrs. A tarry red solid had formed which was recrystallised

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Table I. Carbonyl Stretching Frequencies of Manganese Tetra carbonyl Dithiolates and Related Complexes

Complex	Cation	Solvent	ν_{CO} (cm^{-1})	Reference
$[Mn(CO)_4S_2C_2(CN)_2]^-$	Bu_4N^+	CH_2Cl_2	2075 m; 2008 s; 1991 m; 1919 sh	This work
$[Mn(CO)_4S_2C_6Cl_4]^-$	Bu_4N^+	»	2065 m; 1998 s; 1968 m; 1907 s	» »
$[Mn(CO)_4S_2C_6H_3CH_3]^-$	Bu_4N^+	»	2056 m; 1987 s; 1956 m; 1892 s	» »
$Mn(CO)_4S_2CN(C_2H_5)_2$	—	»	2091 w; 2019 s; 1996 s; 1953 m	4
$[Mn(CO)_4S_2C{=}C(CN)_2]^-$	Bu_4N^+	»	2073 m; 1997 s; 1977 m; 1934 m	This work

from acetone/water affording 1.46 g of brick red crystals (43% based on $Mn(CO)_5Br$), m.p. 119-123°. The conductivity of the complex in 10^{-3} *M* nitromethane was 95 cm^2 ohm^{-1} mole^{-1}, consistent with a 1:1 electrolyte.

Anal. Calcd. for $C_{27}H_{18}O_4N_2S_2PMn$: C, 55.5; H, 3.1; N, 4.8; S, 11.0; Mn, 9.4. Found: C, 55.6; H, 3.3; N, 5.4; S, 10.9; Mn, 9.1.

The compound is soluble in acetone and dichloromethane giving deep red solutions.

*Tetra-*n*-butylammonium Tetracarbonyl-*cis*-1,2-dicyanoethylene-1,2-dithiolato Manganese,* $[(n{-}C_4H_9)_4N][Mn(CO)_4S_2C_2(CN)_2]$. The complex was prepared in the same way as the toluene-3,4-dithiolato species described below, using $Na_2S_2C_2(CN)_2$. It was obtained in 68% yields as brick red crystals, m.p. 79-81°, whose conductivity in 10^{-4} *M* acetone was 189 cm^2 ohm^{-1} mole^{-1}, consistent with a 1:1 electrolyte.

*Tetra-*n*-butylammonium Tetracarbonyltoluene-3,4-dithiolato Manganese,* $[(n{-}C_4H_9)_4N][Mn(CO)_4S_2C_6CH_3]$. To $Mn(CO)_5Br$ (0.69 g) dissolved in 40 ml acetone was added $Na_2S_2C_6H_3CH_3$ (0.5 g prepared from sodium metal (0.12 g) and toluene-3,4-dithiol (0.39 g) in 25 ml absolute ethanol). The cherry red solution was agitated for 30 min. and then filtered. To the filtrate was added $[(n{-}C_4H_9)_4N]I$ (0.83 g) dissolved in 50 ml absolute ethanol, and on gradual evaporation of the solution *in vacuo*, dark red crystals were formed. The complex was recrystallised from acetone/*iso*propanol/water mixtures which gave scarlet needles, m.p. 85-87°, in yields of 51%. The conductivity of the complex in 10^{-4} *M* acetone was 188 cm^2 ohm^{-1} mole^{-1}, consistent with a 1:1 electrolyte.

Anal. Calcd. for $C_{27}H_{42}O_4NS_2Mn$: C, 57.5; H, 7.5; N, 2.5; S, 11.4. Found: C, 57.5; H, 7.9; N, 2.5; S, 11.0.

The complex is soluble in polar organic solvents giving cherry red solutions.

*Tetra-*n*-butylammonium Tetracarbonyl-tetrachlorobenzene-1,2-dithiolato Manganese,* $[(n{-}C_4H_9)_4N][Mn(CO)_4S_2C_6Cl_4]$. This compound was prepared in the same way as the toluene-3,4-dithiolato species described above, using $Na_2S_2C_6Cl_4$. It was obtained in yields of 69% as golden-brown crystals, m.p. 118-120°. The conductivity of the complex in 10^{-4} *M* acetone was 161 cm^2 ohm^{-1} mole^{-1}, consistent with a 1:1 electrolyte.

Anal. Calcd. for $C_{26}H_{36}O_4NS_2Cl_4Mn$: C, 45.4; H, 3.5; N, 2.0; S, 9.3. Found: C, 45.7; H, 5.5; N, 2.2; S, 10.6.

The complex is soluble in polar organic solvents and dichloromethane giving magenta solutions.

*Tetra-*n*-butylammonium Tetracarbonyl-1,1-dicyanoethylene-2,2-dithiolato Manganese,* $[(n{-}C_4H_9)_4N][Mn(CO)_4S_2C_2{=}C(CN)_2]$. The complex was prepared in the same way as its toluene-3,4-dithiolato analogue described above, using $Na_2S_2C{=}C(CN)_2$. It was obtained in yields of 34% as pale green-yellow crystals, m.p. 125-126°. The conductivity of the complex in 10^{-4} *M* acetone was 169 cm^2 ohm^{-1} mole^{-1}, consistent with a 1:1 electrolyte.

Anal. Calcd. for $C_{24}H_{36}O_4N_3S_2Mn$: C, 52.5; H, 6.6; N, 7.6; S, 11.6. Found: C, 52.7; H, 6.8; N, 7.7; S, 11.6.

The complex dissolves in polar organic solvents and in dichloromethane giving yellow-brown solutions.