

is different, however. In one case the π -bonding is by the donation of a pair of electrons from the metal to antibonding π -orbitals on the carbon and in the other by the donation to empty 3d orbitals on the phosphorus.

One of the most intriguing aspects of this research has been the complex infrared spectra and their interpretation in terms of structures of these substituted iron carbonyls. The trigonal bipyramid structure of $\text{Fe}(\text{CO})_5$ was to have been expected for each of these substitution products. However, a comparison of the spectra of the tetra- and tricarbonyl complexes with those calculated on the basis of group theory by Cotton and Parish¹² shows no similarity. For example, the monosubstituted phosphine $\text{Fe}(\text{CO})_4(\text{PF}_3)$ should show two to four peaks in the various trigonal bipyramid and square pyramid configurations. Five major peaks are observed. For the disubstituted compound, one or three should be observed. Four are seen.

Careful chromatographic purification of these compounds would seem to exclude impurities as an explanation. However, several possible explanations can be proposed, although none has yet been proven. It is possible that two or more stereoisomers exist with properties so similar that attempts to separate them have failed. The vapor phase chromatography peaks of all compounds were highly symmetrical, showing no indi-

cation of two compounds being present. Infrared spectra of two fractions of the most clearly resolved compound $\text{Fe}(\text{CO})_4(\text{PF}_3)$ after it had been separated into head and tail cuts were identical—still showing no evidence for separation into isomers. About 15 different types of columns have not allowed the separation of the various potential isomers.

The possibility of moderately rapid internal inversion between isomer forms is a potentially attractive explanation. This is similar to postulations made by several workers for compounds like $\text{Fe}(\text{CO})_5$, PF_5 , and VF_5 .¹³⁻¹⁵ In their work they postulated this form of inversion at a rapid rate to account for the lack of an n.m.r. chemical shift expected for two types of non-equivalent atoms attached to the central atom. If this is the case, then two isomers exist, but there would be no chance to isolate them through chromatography, although they would be clearly indicated by infrared spectroscopy. A phosphorus and fluorine n.m.r. study of the various compounds is in progress in an effort to clear up the matter.

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(14) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

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Dimethyl- and Diethyldithiocarbamate Complexes of Some Metal Carbonyl Compounds¹

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The reactions of *N,N*-dialkyldithiocarbamate ions (alkyl = CH_3 , C_2H_5) and tetramethyldithiuramyl disulfide $[(\text{CH}_3)_2\text{NC}(\text{S})\text{S}]_2$ with various metal carbonyl derivatives have been studied. The characteristic reaction of the former with metal carbonyl halides is displacement of the halide and one carbonyl group, while the dithiuramyl disulfide characteristically cleaves binuclear carbonyls displacing one CO from each metal atom at the same time. All compounds prepared evidently contain bidentate dithiocarbamate ligands. The infrared spectra show that there is partial double bond character in the CN bonds and that the dithiocarbamate groups have no marked effect on metal-CO multiple bonding.

Introduction

A number of transition metal dithiocarbamate complexes have been previously studied and characterized.² The dithiocarbamate group has been found to act as a uninegative bidentate ligand, coordinating through both sulfur atoms,³ and both four- and six-coordinated complexes of a number of transition metal ions have been isolated.

(1) Supported by the National Science Foundation.

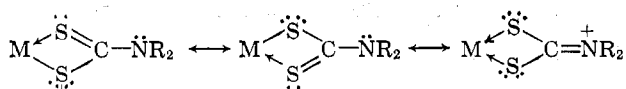
(2) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemi*, **75** (1956).

(3) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

A characteristic feature of the dialkyldithiocarbamate group is its infrared spectrum. The C-N single bond stretching frequencies in amines⁴ fall in the region 1250–1350 cm^{-1} , close to the C-H deformation bands, and the $>\text{C}=\text{N}$ - stretching frequency in the region 1640–1690 cm^{-1} . Chatt, Duncanson, and Venanzi² have found that dithiocarbamate complexes exhibit a band of medium intensity in the region 1480–1550 cm^{-1} , that is between the ranges for C-N and C=N. This band has been assigned to a CN stretching mode,

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

where the CN bond order is between 1 and 2 due to the sort of resonance shown below.



Evidence for the intermediate order of the C-N bond has been provided by a crystallographic study³ of $\text{NOCo}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$, where it was shown that the bond in question was *ca.* 1.3 Å., while those bonds between the methyl groups and the tertiary nitrogen atom were *ca.* 1.5 Å.; the position of the C-N stretching frequency in this particular compound was 1544 cm^{-1} . It was also found² that generally the frequency is influenced by the stereochemistry of the complex (and probably the oxidation state of the metal) and that it apparently follows the order planar > tetrahedral > octahedral.

No carbonyl compounds containing dithiocarbamate ligands have been reported, although various nitrosyls are known.⁵ It is known that trifluoroacetate metal carbonyl derivatives contain a unidentate acetate group,⁶ and it seemed of interest to determine whether the dithiocarbamate group would function as a uni- or bidentate ligand in metal carbonyl systems.

Both tetramethyldithiuramyl disulfide and the sodium salts of dialkyl dithiocarbamates have now been found to react readily with metal carbonyls and carbonyl halides, forming stable derivatives which contain a bidentate dithiocarbamate group.

Experimental

Materials.—All melting points are uncorrected. All solvents were degassed before use. Sodium diethyldithiocarbamate trihydrate (Eastman Organic Chemicals), sodium dimethyldithiocarbamate dihydrate (Aldrich Chemical Co., Inc.), and bis(dimethyldithiocarbamyl) disulfide (tetramethylthiuramyl disulfide $[(\text{CH}_3)_2\text{NC}(\text{S})\text{S}]_2$, practical grade, Eastman Organic Chemicals) were used without further purification. Manganese pentacarbonyl bromide was prepared by standard methods⁷ from a sample of manganese carbonyl very kindly donated by the Ethyl Corporation. Rhodium dicarbonyl chloride was prepared⁸ from rhodium trichloride hydrate (Engelhard Industries). Di- π -cyclopentadienyliron tetracarbonyl⁹ and di- π -cyclopentadienylmolybdenum hexacarbonyl¹⁰ were prepared as described in the literature.

Tetracarbonyl(diethyldithiocarbamate)manganese(I).—A solution of manganese pentacarbonyl bromide (2.7 g.) and $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ (2.4 g.) in 100 ml. of acetone was warmed gently for 15 min. under nitrogen on a steam bath. The dark yellow solution was filtered to remove precipitated NaBr and the mixture evaporated under vacuum (40°, 0.1 mm.). The gummy residue was extracted with 200 ml. of *n*-pentane and the yellow extract evaporated (20°, 0.1 mm.), leaving a pale yellow solid. This solid was sublimed at 50° (0.1 mm.) onto a water-cooled probe giving 0.6 g. of $\text{Mn}(\text{CO})_4\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$ (m.p. 70° dec.; yield 18% based on $\text{Mn}(\text{CO})_5\text{Br}$).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{NO}_4\text{S}_2\text{Mn}$: C, 34.3; H, 3.2; N, 4.4;

(5) L. Cambi and A. Cagnasso, *Atti. Accad. Nazl. Lincei*, **13**, 404 (1931); L. Cambi and L. Szegö, *Chem. Ber.*, **64**, 2591 (1931); L. Malatesta, *Gazz. chim. ital.*, **70**, 729 (1940); R. L. Carlin, F. Canziani, and W. K. Bratton, *J. Inorg. Nucl. Chem.*, **26**, 898 (1964).

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(7) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).

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(9) R. B. King and F. G. A. Stone, *ibid.*, **7**, 110 (1963).

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S, 20.3; mol. wt., 315. Found: C, 34.5; H, 3.3; N, 4.3; S, 20.2; mol. wt., 310 (isopiestic in benzene).

Infrared spectrum in CH_2Cl_2 solution: 2091 w, 2019 s, 1996 s, 1953 m, 1516 m, 1440 w, 1360 w, 1302 vw, 1278 s, 1209 s, 1145 m, 1084 m (broad), 996 w, 910 w, and 845 cm^{-1} .

(Dimethyldithiocarbamate)dicarbonylrhodium(I).—To a solution of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (1.2 g.) in 50 ml. of acetone was added $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1.3 g.) in 20 ml. of acetone. A yellow precipitate formed immediately and the color of the solution changed from red to orange. After stirring in air for 15 min., the solution was filtered to remove NaCl and the clear filtrate evaporated under vacuum (60°, 0.1 mm.). The residue from the evaporation was extracted repeatedly with boiling *n*-pentane and the yellow extract evaporated at room temperature using a water pump, giving 0.59 g. of $\text{Rh}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$ (yield 63%, based on $\text{Rh}_2(\text{CO})_4\text{Cl}_2$). The complex forms orange-red crystals, m.p. 130° dec., and is very soluble in common organic solvents.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{O}_2\text{S}_2\text{NRh}$: C, 21.5; H, 2.2; N, 5.0; S, 22.9; mol. wt., 279. Found: C, 21.5; H, 2.2; N, 4.8; S, 22.9; mol. wt., 295 (ebullioscopically in methylene chloride).

Infrared spectrum in CH_2Cl_2 : 2071 vs, 2005 vs, 1545 m, 1398 m, 1248 m, 1214 m, 1153 m, 1044 w, 1006 vw, 966 m, 921 w, 902 vw, and 843 cm^{-1} .

(Diethyldithiocarbamate)dicarbonylrhodium(I) was prepared in the same way as its dimethyl analog. However, when $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ was added, effervescence took place and, after filtration, crystals of $\text{Rh}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ were obtained in 35% yield. $\text{Rh}(\text{CO})_2[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ (0.4 g., yield 40% based on $\text{Rh}_2(\text{CO})_4\text{Cl}_2$), was obtained as orange-red crystals, m.p. 195° dec., extremely soluble in organic solvents and decomposing slowly in chlorinated hydrocarbons.

Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{O}_2\text{NS}_2\text{Rh}$: C, 27.4; H, 3.3; N, 5.5; S, 20.9; mol. wt., 307. Found: C, 27.7; H, 3.5; N, 5.2; S, 20.8; mol. wt., 296 (isopiestic in benzene).

Infrared spectrum in CH_2Cl_2 solution: 2062 vs, 2000 vs, 1520 s, 1461 m, 1438 m, 1375 m, 1365 m, 1295 w, 1253 s, 1205 m, 1149 m, 1095 w, 1075 m, 1065 msh, 1008 w, (broad), 906 w, 844 w, and 805 cm^{-1} .

Bis(dimethyldithiocarbamate)dicarbonyliron(II).—To an ice-cooled solution of $\text{Fe}(\text{CO})_4\text{Br}_2$ (3.3 g.) in 100 ml. of acetone was added a cold solution of $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ (3.7 g.). The mixture was stirred at ice temperature and after the effervescence had stopped (*ca.* 1 hr.) it was filtered. The brown-red filtrate was evaporated to dryness under vacuum (35°, 0.1 mm.), and the solid residue was extracted with 150 ml. of methylene chloride. After reducing the volume of the solution to about 40 ml., enough *n*-pentane was added to initiate crystallization and, after 30 min., golden yellow crystals (1.9 g., 54% yield based on $\text{Fe}(\text{CO})_4\text{Br}_2$) were collected, m.p. 125° dec. The product is soluble in most organic solvents, but only slightly soluble in hydrocarbons. It is moderately stable in air, decomposition becoming evident only after about 2 days, but it decomposes more rapidly in solution. If the preparation is carried out at room temperature or above, small amounts of $\text{Fe}(\text{CO})_2[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ are obtained, but the main product of the reaction is $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{O}_2\text{N}_2\text{S}_4\text{Fe}$: C, 27.3; H, 3.4; N, 8.0; S, 36.4; mol. wt., 351. Found: C, 27.6; H, 3.4; N, 7.9; S, 36.2; mol. wt., 380 (isopiestic in benzene).

Infrared spectrum in CH_2Cl_2 solution: 2090 vs, 2040 vs, 1534 m, 1402 m, 1359 w, 1238 w, 1216 s, 1148 m, 1046 w, 1021 sh, 986 m, 924 w, 894 m, and 842 cm^{-1} .

π -Cyclopentadienylcarbonyl(dimethyldithiocarbamate)iron(II).—A mixture of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (3.5 g.) and tetramethylthiuramyl disulfide (2.5 g.) was refluxed in 100 ml. of cyclohexane under nitrogen for 18 hr. The solution was filtered while hot and from the filtrate, on cooling, purple needles (0.5 g.) were deposited. These were collected by filtration and washed with *n*-pentane. The residue from the first filtration was sublimed (140°, 0.1 mm.), deep red crystals forming on the water-cooled probe. The over-all yield of the complex, m.p. 142° dec., was 3.1 g. (57% based on $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$). The complex is gen-

erally soluble in organic solvents, but only sparingly so in pentane, hexane, and ether.

Anal. Calcd. for $C_9H_{11}ONS_2Fe$: C, 40.1; H, 4.0; N, 5.5; S, 23.8; mol. wt., 269. Found: C, 40.1; H, 4.0; N, 5.5; S, 23.8; mol. wt., 280 (isopiestic in benzene).

Infrared spectrum in CH_2Cl_2 solution: 1940 vs, 1530 m, 1395 m, 1258 w, 1216 s, 1148 m, 1108 vw, 1046 vw, 1021 vw, 986 w, 925 w, 894 m, and 811 sh cm^{-1} .

π -Cyclopentadienyldicarbonyl(dimethyldithiocarbamato)molybdenum(II) was prepared in the same way as its iron analog using $[\pi-C_5H_5Mo(CO)_2]_2$ (4.9 g.) and $[(CH_3)_2NCS_2]_2$ (2.4 g.) in 100 ml. of methylcyclohexane. The reaction mixture was filtered while still hot and the residue, after washing with *n*-pentane, was sublimed (160°, 0.1 mm.) to give 3.2 g. (48% based on $[\pi-C_5H_5Mo(CO)_2]_2$) of deep purple crystals, m.p. 191° dec. A small yield of red-purple crystals was obtained from the cooled filtrate and these were shown, by their infrared spectrum in CH_2Cl_2 solution, to be $\pi-C_5H_5Mo(CO)_2S_2CN(CH_3)_2$. The compound is soluble in common organic solvents, but only slightly soluble in hydrocarbons.

Anal. Calcd. for $C_{10}H_{11}O_2NS_2Mo$: C, 35.6; H, 3.3; N, 4.2; S, 19.0; mol. wt., 337. Found: C, 36.0; H, 3.4; N, 4.2; S, 19.2; mol. wt., 338 (isopiestic in benzene).

Infrared spectrum in CH_2Cl_2 solution: 1955 vs, 1865 vs, 1527 s, 1293 s, 1250 m, 1146 m, 1111 w, 1026 w, 1006 w, 926 m, 871 w, and 844 m cm^{-1} .

Bis(dimethyldithiocarbamato)nickel(II) was prepared by treating an aqueous solution of $NiCl_2 \cdot 6H_2O$ with excess $Na_2S_2CN(CH_3)_2 \cdot 2H_2O$. The pale green precipitate was filtered off and washed repeatedly with acetone and ether. It was dried under vacuum, affording fine, light olive-green crystals, sparingly soluble in chlorinated hydrocarbons and acetone, but insoluble in ether and hydrocarbons. The compound is diamagnetic.

Anal. Calcd. for $C_8H_{12}N_2S_4Ni$: C, 24.0; H, 4.0; N, 9.3; S, 42.7. Found: C, 23.9; H, 4.1; N, 9.2; S, 41.0.

Infrared spectrum: 1550 m cm^{-1} (in CH_2Cl_2); 1243 s, 1148 s, 1050 w, 976 s, 895 w, and 741 w cm^{-1} (in Nujol mull).

Tris(dimethyldithiocarbamato)cobalt(III) was obtained by heating an acetone solution of $Co(NO_3)_2 \cdot 7H_2O$ with an excess of $Na_2S_2CN(CH_3)_2 \cdot 2H_2O$. The green reaction mixture was filtered and evaporated to dryness on a steam bath. The residue was extracted with methylene chloride and the green extract filtered and evaporated slowly, affording dark green crystals. The complex is moderately soluble in acetone, chloroform, and methylene chloride, but sparingly soluble in carbon disulfide and insoluble in ether and hydrocarbons.

Anal. Calcd. for $C_9H_{13}N_3S_6Co$: C, 25.8; H, 4.3; N, 10.0; S, 45.8. Found: C, 25.6; H, 4.4; N, 9.8; S, 45.9.

Infrared spectrum: 1496 m cm^{-1} (in CH_2Cl_2 solution); 1253 w, 1214 s, 1146 m, 1086 w, 1049 w, 1023 w, 985 m, 925 w, and 845 w cm^{-1} (in Nujol mull).

Tris(dimethyldithiocarbamato)chromium(III) was prepared by heating a tetrahydrofuran solution of $CrCl_3 \cdot 6H_2O$ with an excess of $Na_2S_2CN(CH_3)_2 \cdot 2H_2O$. The green-blue solution was filtered and evaporated to dryness on a steam bath. The residue was extracted with chloroform; after filtration and evaporation, this solution afforded a small amount of the complex as blue-violet crystals. It is soluble in chlorinated hydrocarbons and acetone, but only sparingly soluble in ether and carbon disulfide and insoluble in hydrocarbons.

Anal. Calcd. for $C_9H_{13}N_3S_6Cr$: C, 26.2; H, 4.4; N, 10.2; S, 46.6. Found: C, 26.1; H, 4.4; N, 10.4; S, 47.0.

Infrared spectrum: 1522 m cm^{-1} (in CH_2Cl_2 solution), 1260 m, 1240 m, 1133 s, 1040 w, 970 s, 880 w, and 723 s cm^{-1} (in Nujol mull).

Tris(dimethyldithiocarbamato)rhodium(III) was prepared by treating an acetone solution of rhodium trichloride hydrate with a slight excess of $Na_2S_2CN(CH_3)_2 \cdot 2H_2O$. The orange-red solution was filtered and evaporated to dryness. The residue was extracted with boiling *n*-pentane; this solution deposited, after filtration and cooling, orange-brown crystals. The complex is very soluble in most organic solvents.

Anal. Calcd. for $C_9H_{13}N_3S_6Rh$: C, 23.3; H, 3.9; N, 9.1; S, 41.5. Found: C, 23.3; H, 3.7; N, 8.9; S, 41.9.

Infrared spectrum: 1536 m cm^{-1} (in CH_2Cl_2 solution); 1258 s, 1245 s, 1133 s, 1036 w, 973 s, 885 w, and 725 s cm^{-1} (in Nujol mull).

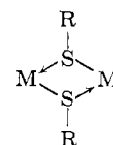
Tris(dimethyldithiocarbamato)rhodium(III) was prepared in the same way as its dimethyl analog and it is also very soluble in organic solvents.

Anal. Calcd. for $C_{15}H_{20}N_3S_6Rh$: C, 32.9; H, 5.5; N, 7.7; S, 35.1. Found: C, 32.4; H, 5.2; N, 7.4; S, 35.2.

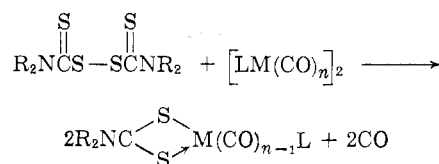
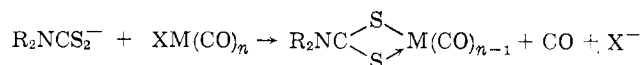
Infrared spectrum: 1495 m cm^{-1} (in CH_2Cl_2 solution); 1303 w, 1280 s, 1210 m, 1155 m, 1099 m, 1080 s, 1074 sh, 995 m, 916 m, 853 m, 793 w, 782 w, and 724 w cm^{-1} (in Nujol mull).

Discussion

The carbonyl complexes which have been prepared indicate clearly the bidentate nature of the dithiocarbamate ligand. The compounds are all monomeric, in contrast to a great many metal carbonyl sulfides, in which the sulfur atom acts as a bridging group¹¹ between two metals, *e.g.*



Two characteristic reactions of salts of the N,N-dialkylthiocarbamate ion and the tetraalkyldithiuramyl disulfides appear to be the following.



Thus, displacement of X^- by $R_2NCS_2^-$ or cleavage of the M-M or $M \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} M$ linkages by $(R_2NC(S)S)_2$ is accompanied by the expulsion of a CO by the other sulfur atom of the R_2NCS_2 group. In every case studied here, as well as in all previous ones, the dialkylthiocarbamate group functions as a bidentate ligand.

The structure of the rhodium derivatives is presumably square-planar with *cis* carbonyl groups similar to that found in $Rh(CO)_2(acac)$.¹² These derivatives are very easily oxidized as evidenced by their rapid decomposition when bromine or iodine is added, and by the formation of $Rh[S_2CN(C_2H_5)_2]_3$ in the preparation of the carbonyl derivative. The iron complex is also very unstable oxidatively. It evidently has a quasi-octahedral structure with *cis* carbonyls, since a *trans* dicarbonyl compound would be expected to exhibit only one infrared-active carbonyl stretching mode; it should then exist in optical isomers. The manganese carbonyl complex presumably also has a distorted octahedral

(11) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

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TABLE I
 INFRARED SPECTRA OF DITHIOCARBAMATE COMPLEXES: CARBONYL STRETCHING AND C=N STRETCHING FREQUENCIES

Compound	Metal and its oxidn. state	Expected stereochem.	ν_{CO} , cm.^{-1}	ν_{C-N} , cm.^{-1}	
				in CH_2Cl_2	in CHCl_3 (ref. 2)
$\text{Ni}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$	Ni(II)	Sq.-planar		1550	
$\text{Ni}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$	Ni(II)	Sq.-planar		1511	1512
$\text{Co}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$	Co(III)	Dist. octa.		1515	
$\text{Co}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$	Co(III)	Dist. octa.		1496	1489
$\text{Rh}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	Rh(I)	Sq.-planar	2071, 2005	1545	
$\text{Rh}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	Rh(I)	Sq.-planar	2062, 2000	1520	
$\text{Rh}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$	Rh(III)	Dist. octa.		1536	
$\text{Rh}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$	Rh(III)	Dist. octa.		1495	
$\text{Fe}(\text{CO})_2[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$	Fe(II)	Dist. octa.	2090, 2040	1534	
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$	Fe(III)	Dist. octa.		1518	
$\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$	Fe(III)	Dist. octa.		1495	1496
$\text{Mn}(\text{CO})_4\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	Mn(I)	Dist. octa.	2091, 2019, 1996, 1953	1516	
$\text{Mn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$	Mn(III)	Dist. octa.		1493	1494
$\text{Cr}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$	Cr(III)	Dist. octa.		1522	
$\text{Cr}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$	Cr(III)	Dist. octa.		1498	1496
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{S}_2\text{CN}(\text{CH}_3)_2$	Fe(II)	...	1940	1530	
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	Mo(II)	...	1955, 1865	1527	
$[(\text{CH}_3)_2\text{NCS}_2]_2$		1505	1504 ^a

^a Mull spectrum.

TABLE II

CO STRETCHING FREQUENCIES IN SOME COMPOUNDS TO BE COMPARED WITH THE N,N-DIALKYLDITHIOCARBAMATO COMPLEXES

Compounds	Solvent	ν_{CO} , cm.^{-1}	Remarks
$\text{Rh}_2(\text{CO})_4\text{Cl}_2$	CH_2Cl_2	2105 m, 2095 s, 2034s, 2003 w	Bridging Cl
$\text{Rh}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	CH_2Cl_2	2071 s, 2005 s	
$\text{Rh}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	CH_2Cl_2	2062 s, 2000 s	
$[\text{Mn}(\text{CO})_4\text{Cl}]_2^a$	CCl_4	2104 w, 2045 s, 2012 m, 1977 m	Bridging Cl
$\text{Mn}(\text{CO})_4\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	CH_2Cl_2	2091 w, 2019 s, 1996 s, 1953 m	
$[\text{Mn}(\text{CO})_4\text{SCH}_3]_2^b$	CS_2	2095 w, 2074 s, 2016 vs 2002 vs, 1985 m, 1969 s, 1937 w	Mixture of isomers
$[\text{Fe}(\text{CO})_2\text{I}_2]_n^c$	THF	2100 s, 2050 s	Polymeric, bridging I
$\text{Fe}(\text{CO})_2[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$	CH_2Cl_2	2090 s, 2040 s	
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{S}_2\text{CN}(\text{CH}_3)_2$	CH_2Cl_2	1940 s	
$(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3)_2^d$	CS_2	1958 s	Bridging S
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	CH_2Cl_2	1955 s, 1865 s	
$(\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{SCH}_3)_2^b$	CS_2	1965 s, 1947 s, 1877 s, 1869 s, 1852 msh	Mixture of isomers
$(\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{SCH}_3)_2^b$	CS_2	2034 s, 1948 s	Bridging S

^a M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963). ^b P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963). ^c F. A. Cotton and B. F. G. Johnson, unpublished results. ^d R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

structure and appears to be the first monomeric tetra-carbonyl manganese sulfide reported.

The infrared spectra of the compounds (Table I) indicate that again the canonical form containing the C=N bond contributes significantly to the structure of these new derivatives. The importance of this form presumably arises from the strong mesomeric electron-releasing effect of the $-\text{NR}_2$ group and the ability of S atoms and CO groups to accept electrons. It has been shown¹³ that S atoms can function as good synergistic donors with back accepting capacity comparable to that of P or As ligands. However, in the dithiocarbamate ligand, the $-\text{NR}_2$ group acts as a very strong elec-

tron-releasing group, forcing the S atoms to accept electrons from it and thus to a lesser extent from the metal. This effect can be observed by a comparison of the CO stretching frequencies of the new compounds and some analogous halo and sulfur compounds (Table II). In all cases, the dithiocarbamate carbonyls have CO stretching frequencies at least 10 cm.^{-1} lower than their analogs.

It can be seen from a comparison of the dimethyl- and diethyldithiocarbamates, both the carbonyl and simple species, that the former have higher C-N stretching frequencies than the latter. This is particularly noticeable in the square-planar Ni(II) complexes, where the difference between the two is 39 cm.^{-1} ; this difference is less in octahedral trivalent derivatives. The

(13) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962); F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962); M. H. B. Stiddard, *J. Chem. Soc.*, 4715 (1962).

difference can be attributed to the stronger inductive effect of a methyl group, compared with an ethyl group.

As was mentioned, the C-N frequencies of the square-planar compounds are higher than those of the octahedral ones. While the reason for these higher frequencies in the carbonyl species can be explained by the ease of charge acceptance by the CO groups (and

also by NO groups² as in $\text{NOCo}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$, $\nu_{\text{C-N}} = 1544 \text{ cm.}^{-1}$, mull, and $\text{NOFe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$, $\nu_{\text{C-N}} = 1542 \text{ cm.}^{-1}$, mull), it is tempting to suggest that in the nickel derivatives electrons are being donated from the dithiocarbamate group into a nonbonding molecular orbital, consisting mainly of Ni p_z , thus permitting the C-N frequency to be exceptionally high.

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The Existence of the Re_3Cl_9 Cluster in Anhydrous Rhenium(III) Chloride and Its Persistence in Solutions of Rhenium(III) Chloride

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The crystal structure of anhydrous rhenium(III) chloride, prepared by vacuum sublimation, has been determined by single crystal X-ray work. The space group is $R\bar{3}m$, with 18 ReCl_3 per hexagonal unit cell. The structure is built up of well-defined Re_3Cl_9 units, each having rigorous C_{3v} symmetry, and approximately the same structure as the Re_3Cl_9 moieties previously found in $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$ and $\text{Re}_3\text{Cl}_9[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$. The Re_3Cl_9 groups are arranged in double layers perpendicular to the crystallographic c axis and joined together by chlorine atom bridges. This structure appears to account for all reported aspects of the behavior of rhenium(III) chloride, except the claim by Wrigge and Biltz that it is dimeric in glacial acetic acid. The spectra of rhenium(III) chloride in a variety of solvents are practically identical and essentially the same as spectra of systems in which the presence of Re_3Cl_9 units seems certain. It is therefore concluded that, in general, fresh solutions of rhenium(III) chloride (including the acetic acid solution) contain Re_3Cl_9 units. A molecular weight measurement in sulfolane confirms this.

Introduction

The homophilicity¹ of Re(III) has been well-established.² One manifestation of this property is the important role which the Re_3X_9 ($\text{X} = \text{Cl}, \text{Br}$) clusters play in its chemistry. It has been observed in this laboratory² that whenever compounds of Re(III) are prepared directly (*i.e.*, without change in oxidation state or the use of strenuous reaction conditions) from rhenium(III) chloride, the products contain the rhenium solely in the form of Re_3Cl_9 clusters and derivatives thereof. We wish to emphasize that we are only reporting that degradation of the Re_3Cl_9 cluster has not yet been observed under mild conditions. While we think it likely that this is the general rule, exceptions may possibly be found in the future. Single crystal X-ray structure determinations have established the presence of such species in several cases.²⁻⁶ On the basis of this observation, as well as the observations reported later in this paper concerning the spectra of rhenium(III) chloride in a variety of solvents, it appeared likely

that the Re_3Cl_9 cluster would be present in anhydrous rhenium(III) chloride itself. A single-crystal X-ray structure determination was therefore undertaken. The results, which will be described below, have shown that rhenium(III) chloride does, in fact, consist of Re_3Cl_9 clusters.

Experimental

A sample of resublimed rhenium(III) chloride was very kindly supplied by Dr. R. H. Busey of the Oak Ridge National Laboratory. This material was obtained by Dr. Busey and his associates in the following way.⁷ A small portion of a batch of very pure rhenium(III) chloride (*Anal.* Calcd. for ReCl_3 : Cl, 36.35. Found: Cl, 36.33 ± 0.03) used previously in heat capacity measurements was transferred in an argon-filled vacuum-type drybox to a two-bulb quartz sublimation tube and the latter sealed under vacuum. The sample was slowly sublimed at *ca.* 400° into the second bulb, some residue remaining in the first bulb. The tube was then opened in the argon-filled drybox and selected crystals were placed in a second quartz sublimation tube. This tube was then connected to a high vacuum system equipped with a diffusion pump and liquid N_2 trap. Approximately half of the contents was sublimed (at *ca.* 500°) into the second bulb, at which point it was noted that the remaining un-sublimed material appeared nicely crystalline, whereas the sublimate was depositing as a layer. The remaining un-sublimed material was sealed off and sent to us for the crystallographic work.

A series of about twenty fragments, which were picked from the sample and mounted in sealed capillaries in a drybox, were examined on a precession camera before one was found which was not cracked or twinned. From precession pictures of the $hk0$ -

(1) The words *homophilicity* and *homophilic* have previously² been proposed to designate the tendency of an atom (or ion) to form bonds to other identical atoms (or ions) in comparison to its tendency to form bonds to different atoms (*heterophilicity*).

(2) F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, in press.

(3) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1106 (1963).

(4) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

(5) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

(6) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

(7) This procedure, explained to us in detail by Dr. Busey, is recorded here in case it might later turn out that ReCl_3 is polymorphic.