order of solution phase complex formation for the lanthanide ions.

In Fig. 7 it is seen that the difference in K_d between Am(III) and Eu(III) increases from $HClO_4$ to HBr to HCl, which would seem to indicate that Am(III) forms stronger complexes with chloride and bromide ions than does Eu(III). The data on the $HClO_4$, HI, and HBr systems are not in disagreement nor do they add any substantial weight to the theory offered from an earlier study[2] with HCl that 5f orbitals can be used by the actinide ions to form more stable halide complexes.

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Substituted Metal Carbonyls with Ligands Having Sulfur as the Donor Atom[1a]

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The preparation and properties of the first substituted metal carbonyls containing ligands which coördinate through bicovalent sulfur are reported. By direct reaction of the ligands, L, with cycloheptatrienemolybdenum tricarbonyl, the five compounds, $MoL_3(CO)_3$, with L representing $(CH_3)_2S$, $(C_2H_5)_2S$, $(CH_2)_4S$, $(NH_2)_2CS$, and CH_3CSNH_2, have been prepared. All are yellow crystalline solids ranging in stability in air from very unstable to moderately stable. The frequencies of the C–O stretching modes show that the dialkyl sulfides have a substantial tendency to function as pi acceptors though not so much as analogous phosphines and arsines, while the two C=S compounds have only a small (though definite) tendency to do so.

Introduction

It perhaps is surprising that although a great deal of effort has been devoted to the synthesis and spectroscopic study of metal carbonyl molecules in which one or several of the carbon monoxide groups are replaced by other ligands, especially amines, phosphines, and arsines, until very recently[1a] there was no report of the preparation of compounds in which the substituents have bicovalent sulfur as the donor atom.

This paper reports in detail the preparation and properties of five such compounds, all of the type $MoL_3(CO)_3$ in which the ligands, L, are $(CH_3)_2S$, $(C_2H_5)_2S$, $(CH_2)_4S$, $(H_2N)_2CS$, and CH_3CSNH_2. It was originally our intention, on finding that the compounds reported here were stable enough to encourage further study, to extend the work to similar substituted carbonyls, especially those containing chelate ligands where stability should be even greater. Upon the appearance of our preliminary note, however, we were informed by Professor G. Wilkinson that he and Miss Christina Mannerskantz already had succeeded in preparing several compounds with chelate ligands, and we therefore have concluded our own efforts in this area with the work reported here.

Experimental

For the preparation of the new compounds, the starting material was cycloheptatrienemolybdenum tricarbonyl which we prepared according to the procedure of Abel, *et al.*,[2] but using dry *n*-butyl ether as a solvent. In our experience the employment of this ether reduces the reaction time and increases the product yield.

Tricarbonyltris(tetramethylene sulfide)molybdenum.—One g. (0.012 mole) of tetramethylene sulfide was added, under nitrogen, to a solution of cycloheptatrienemolybdenumtricarbonyl (0.8 g. = 0.003 mole) in benzene (5 ml.). After a few minutes the red color of the cycloheptatriene complex had completely disappeared. The benzene then was distilled off in vacuum. The dry residue, dissolved in methylene chloride, was filtered under nitrogen, and precipitated by addition of petroleum ether. The product, pale yellow crystals, was filtered under nitrogen, washed with petroleum ether, and dried in high vacuum. It was stable in nitrogen atmosphere but in the presence of air it darkened rapidly owing to decomposition. *Anal.* Calcd. for $MoC_{15}H_{24}S_3O_3$: C, 40.53; H, 5.44; Mo, 21.59. Found: C, 39.94; H, 5.12; Mo, 21.0.

Tricarbonyltris(dimethyl sulfide)molybdenum.—This compound was prepared in much the same way as was the analogous tetramethylene sulfide derivative from dimethyl sulfide (0.75 g. = 0.012 mole) and cycloheptatrienemolybdenumtricarbonyl (0.8 g. = 0.003 mole) and

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[1] (a) Part of this work has been summarized earlier in a preliminary Communication, *Chem. & Ind.* (London), 1219 (1960). (b) Alfred P. Sloan Foundation Fellow. (c) On leave from Istituto di Chimica Generale dell' Universitá di Milano, 1959–60.

[2] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

crystallized from methylene chloride and petroleum ether. It was obtained as yellow crystals. The compound was very unstable even in nitrogen atmosphere and immediately decomposed in air. *Anal.* Calcd. for $MoC_9H_{18}S_3O_3$: C, 29.5; H, 4.95; Mo, 26.19. Found: C, 28.9; H, 4.2; Mo, 25.6.

Tricarbonyltris(diethyl sulfide)molybdenum.—This compound was prepared from 5 ml. of diethyl sulfide and 0.8 g. (0.003 mole) of cycloheptatrienemolybdenumtricarbonyl using an excess of ethyl sulfide as the solvent. When the red color of the cycloheptatriene complex had completely disappeared, the excess of ethyl sulfide was taken off under vacuum. The dry residue, dissolved in methylene chloride, was filtered under nitrogen and precipitated by slow addition of petroleum ether. The product, filtered under nitrogen, was washed with petroleum ether and dried in vacuum. It was obtained as gray-yellow crystals, which started to decompose at 90°. This compound was moderately stable in air, darkening after about 6 hr. *Anal.* Calcd. for $MoC_{15}H_{30}O_3S_3$: C, 39.98; H, 6.71; Mo, 21.3. Found: C, 39.2; H, 6.3; Mo, 20.9.

Tricarbonyltris(thiourea)molybdenum.—A solution of thiourea (0.95 g. = 0.012 mole) in ethanol (80 ml.) was added under nitrogen to a solution of $Mo(CO)_3C_7H_8$ (0.8 g. = 0.003 mole), also in ethanol (60 ml.). After a few minutes yellow crystals separated and then were filtered, washed with ethanol, and dried in vacuum. The compound was insoluble in organic solvents. It decomposed at about 150° without melting. The compound, when dry, did not decompose in the presence of air for several days. *Anal.* Calcd. for $MoC_6H_{12}N_6S_3O_3$: C, 17.65; H, 2.96; N, 20.58; Mo, 23.50. Found: C, 17.90; H, 3.05; N, 20.31; Mo, 23.1.

Tricarbonyltris(thioacetamide)molybdenum.—A solution of thioacetamide (0.9 g. = 0.012 mole) in dry ether (70 ml.) was added, under nitrogen, to a solution of cycloheptatrienemolybdenumtricarbonyl (0.8 g. = 0.003 mole) in dry ether (60 ml.). After a few minutes green-yellow crystals separated. These were filtered, washed with dry ether, and dried in vacuum. The compound was insoluble in most organic solvents, but could be crystallized from tetrahydrofuran and petroleum ether. The compound, when dry, did not decompose in the presence of air for several days. It melted at 122°. *Anal.* Calcd. for $MoC_9H_{15}S_3O_3N_3$: C, 26.66; H, 3.73; N, 10.36; Mo, 23.67. Found: C, 26.77; H, 3.76; N, 10.02; Mo, 23.1.

All solvents used were purified and dried and liquid reagents were freshly distilled. Microanalyses for C, H, and N were by S. M. Nagy, M.I.T., and Schwarzkopf Microanalytical Laboratories, Long Island. Molybdenum was determined either by direct ignition of the compound to MoO_3 or as the 8-hydroxyquinolinate after digestion in boiling H_2SO_4.

Infrared spectra were recorded on a Perkin–Elmer Model 21 spectrometer equipped with a rock-salt prism.

Discussion

All of the compounds reported here are yellow crystalline solids. They vary quite considerably in their stabilities. The thiourea and thioacetamide compounds are stable for periods of at least a year in vacuum and for a week or more in the air under normal laboratory conditions. The diethyl and tetramethylene sulfide complexes are stable for at least a few weeks in vacuum but they decompose within a few hours in the presence of air. The dimethyl sulfide compound is immediately decomposed by air and is stable for only a few hours in vacuum. The marked instability of the dimethyl sulfide complex in vacuum doubtless is due to the volatility of the ligand. Solutions of all of the compounds are very unstable toward air. No sensitivity toward ordinary (fluorescent) laboratory light was noted.

The infrared spectra of all of the compounds have been recorded in the rock salt region and the frequencies of the carbonyl stretching modes are listed in Table I along with those of some other compounds of the $MoL_3(CO)_3$ type.[3] These data enable us to make a direct estimate of the ability of bicovalent sulfur to function as a pi acceptor in competition with the CO groups. This is done by comparing our results with those obtained by Abel, Bennett, and Wilkinson[3] in their elegant study which embraced, *inter alia*, $MoL_3(CO)_3$ compounds with L representing amines, phosphines, arsines, etc. It can be seen that the CO frequencies for the three dialkyl sulfide compounds are just slightly below those for the analogous triphenyl phosphine compound, and at least a part of this difference must be due to the fact that phenyl groups are a little more electronegative than alkyl groups. Thus it is concluded that the intrinsic ability of the sulfur atom in a dialkyl

TABLE I

CO STRETCHING FREQUENCIES OF SOME SUBSTITUTED MOLYBDENUM CARBONYLS

Compound	Medium	Frequencies, cm.$^{-1}$
$Mo[(CH_3)_2S]_3(CO)_3$	CH_2Cl solution	1925, 1799
$Mo[(C_2H_5)_2S]_3(CO)_3$	CH_2Cl_2 solution	1930, 1826
	Nujol mull	1920, 1826 (sh), 1803
$Mo(C_4H_8S)_3(CO)_3$	CH_2Cl_2 solution	1925, 1821
$Mo[(NH_2)_2CS]_3(CO)_3$	Nujol mull	1900, 1758
$Mo(CH_3CSNH_2)_3$-$(CO)_3$	THF solution	1909, 1798, 1783 (sh)
	Nujol mull	1900, 1795, 1765
$Mo(dien)(CO)_3$	Data from reference 3	1883, 1723
$Mo(py)_3(CO)_3$		1888, 1746
$Mo(Ph_3P)_3(CO)_3$		1949, 1835
$Mo(Ph_3As)_3(CO)_3$		1957, 1847
$Mo(Cl_3P)_3(CO)_3$		2041, 1989

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[3] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

or diaryl sulfide to serve as a pi acceptor using its dπ orbitals is about equal to, or only slightly less than, that of phosphorus in a corresponding trialkyl or triaryl phosphine.

By a similar comparison it is found that bicovalent sulfur in thiourea and thioacetamide also has a definite capacity to function as a pi acceptor but to a significantly lesser extent. It appears somewhat superior to pyridine but definitely inferior to the phosphines and dialkyl sulfides. Several attempts to prepare compounds with thioketones and thioesters failed so that it cannot be stated with certainty whether the amino group, with its unshared electron pair, has a significant effect upon the pi acceptor power of the C=S group. There is some indication from the shift in the lower frequency band in the two compounds concerned that there may be such an effect and that a thioketone might be superior to a thioamide.

Our conclusions about the relative pi acceptor powers of the sulfur ligands, like those of Abel, *et al.*,[3] with respect to the ligands which they studied, do not require any assumption about which geometrical isomer of the $MoL_3(CO)_3$ species we are dealing with, except, perhaps, that the same isomer is present in all compounds. Even this assumption probably is not essential, since each dπ orbital of the metal overlaps with pi orbitals of four of the six ligands so that distribution of the available pi electrons among all of the ligand and metal pi orbitals probably would be about the same for either isomer.

The infrared spectra can, in principle, give an indication of which isomer is present since the *cis* isomer has, neglecting asymmetry in the MoL_3 part of the molecule, C_{3v} symmetry while the *trans* isomer has C_{2v} symmetry. The former should have two infrared-active CO stretching modes, of A_1 and E symmetries, while the latter should have three, of symmetries $2A_1$ and B_1. In the compounds they studied, Wilkinson, *et al.*,[3] found only two bands and stated that while the lower one was in some compounds quite broad, in no case could any splitting be detected, even with a lithium fluoride prism. For the three dialkyl sulfide compounds and the thiourea compound we also find only two bands, the lower ones being broader than the upper ones but not exhibiting any splitting under the resolution available with the rock salt prism. Because of the instability of these compounds in solution and the necessity of using slow scanning speeds in order to obtain the high resolution of which the lithium fluoride prism is inherently capable, no studies were made with the lithium fluoride prism. We therefore cannot be quite as certain as were Wilkinson, *et al.*, of the *cis* configuration for our compounds.

As indicated in the Table, the lower energy band of the thioacetamide compound is split in both the mull spectrum and the solution spectrum using tetrahydrofuran as solvent. Whether this is attributable to deviation from C_{3v} symmetry in the $Mo(CH_3CSNH_2)_3$ part of the molecule, to a *trans* configuration (which seems unlikely), or to solvent effects in solution and distortions and intermolecular interactions in the crystal cannot be decided at present.

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