pyridine. A yellow precipitate of the desired product formed immediately and considerable heat was evolved. The crystalline product was removed by filtration, washed with dry ether, dried in a stream of dry nitrogen, and stored in a desiccator over calcium chloride.

Anal. Calcd. for $SeCl_4 \cdot 2py$: Se, 20.8; Cl, 37.4; N, 7.4. Found: Se, 20.8; Cl, 36.7; N, 7.4.

The material melts with decomposition at 78–84° in a sealed capillary. The sample decomposes immediately on exposure to moist air. The Bragg spacings (Å.) and relative intensities of the prominent reflections of the X-ray powder pattern are: 6.33, 100; 8.51, 36; 5.47, 36; 5.07, 32; 3.79, 32; 3.08, 32; 2.54, 28; 1.96, 14; 1.84, 14; 4.62, 12; 2.47, 12; 1.47, 10; 2.32, 8; 2.75, 8; 4.44, 6; 2.13, 6; 2.07, 6; 1.68, 6; 1.91, 4.

The infrared spectra showed the following absorptions (given in cm.$^{-1}$): 1650 w, 1620 m, 1610 m, 1540 m, 1350 w, 1250 m, 1200 s, 1170 w, 1160 m, 1080 w, 1061 s, 1030 w, 1010 s, 930 s, 855 vw, 750 vs, 690 s, 650 s, and 430 m. The compound is soluble in acetonitrile (about 4.5 g./100 ml. of acetonitrile at 27°), slightly soluble in chloroform, and insoluble in carbon tetrachloride, carbon disulfide, benzene, ether, tetrahydrofuran, alcohols, dioxane, and dimethylformamide. It is decomposed by acid solutions.

Dissociation of $SeCl_4 \cdot 2py$ in Acetonitrile.—Dissociation of $SeCl_4 \cdot 2py$ in acetonitrile was measured by a Mechrolab Model 301A vapor pressure osmometer. Benzil was used to calibrate the instrument for the solvent. The results of ten measurements on two solutions which were 0.018 and 0.01334 *F* indicated 2.05 ± 0.06 particles formed per formula unit of $SeCl_4 \cdot 2py$.

Conductivity measurements were taken using a Jones bridge. The results are given in Table I.

TABLE I

CONDUCTANCE OF ACETONITRILE SOLUTIONS OF $SeCl_4 \cdot 2py$

Concn., *M*	Spec. cond., mhos/cm.	Equiv. cond., mhos cm.^{2}/equiv.
Solvent	3.23×10^{-6}	...
1.81×10^{-2}	1.164×10^{-3}	64.55
1.64×10^{-2}	1.029×10^{-3}	52.80
1.29×10^{-2}	8.62×10^{-4}	66.90
9.02×10^{-3}	6.40×10^{-4}	71.00
8.20×10^{-3}	5.94×10^{-4}	72.40
6.02×10^{-3}	4.38×10^{-4}	72.80
4.1×10^{-3}	3.37×10^{-4}	82.10
2.1×10^{-3}	2.44×10^{-4}	116.10

Discussion

The possibility of a chlorine atom bonded to the pyridine ring in $SeCl_4 \cdot 2py$ can be eliminated on the basis of the infrared spectra. All of the recorded absorption peaks for the compound are observed in the spectra for free pyridine. Especially noteworthy is the absence of any new absorption in the range 600–800 cm.$^{-1}$ which would be expected for a C–Cl or N–Cl bond. The Se–Cl bond absorptions are all lower than 400 cm.$^{-1}$ and thus were not observed.

The dissociation of $SeCl_4 \cdot 2py$ into two ions in acetonitrile is indicated by the osmometer measurements and is qualitatively supported by the magnitude of the extrapolated value of the equivalent conductance at infinite dilution.[11] This suggests that the reaction is best represented by the equation

$$SeCl_4 + 2py \longrightarrow SeCl_3py_2^+ + Cl^-$$

The resulting cation with one lone pair and five bonded pairs of electrons is comparable in central atom bonding to $SeOCl_2 \cdot 2py$ and IF_5. By consideration of the known structure of the isoelectronic $SeOCl_2 \cdot 2py$, which has an octahedral structure with the two chlorines in *trans* positions, the two pyridines in *trans* positions, and the oxygen atom bonded *trans* to the lone pair of electrons,[12] one might expect the pyridine rings in $SeCl_3py_2^+$ to be *trans* also. A single-crystal X-ray study of the material will be started in the near future in order to determine the bonding in the solid state.

Acknowledgment.—This work was supported by the Selenium and Tellurium Development Association.

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Dithiobenzoatotetracarbonylmanganese(I)

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Received May 4, 1964

Although a metal complex of dithiobenzoic acid has been used in the synthetic route to nickel tetracarbonyl,[1] no previous reference can be found to a metal carbonyl coordinated to the dithiobenzoate ion. We have isolated such a compound, $C_6H_5CSSMn(CO)_4$, from the reaction between C_6H_5CSSH and $Mn(CO)_5Br$. The product is a very stable red solid, monomeric in solution and with an infrared spectrum compatible with the C_{2v} symmetry required for a bidentate attachment of the dithiobenzoate group.[2]

Experimental

Dithiobenzoic Acid.[3]—K_2S (30 g.) was suspended in 200 ml. of boiling methanol and 50 g. of $C_6H_5CCl_3$ was slowly added. Upon starting, the reaction was exothermic and was cooled in an ice bath to retain control. The solution was then decanted and diluted with 500 ml. of ice water and made basic to litmus with NaOH. A clear oil separated from the dark red solution. This oil, assumed to be $C_6H_5CCl_3$, was returned to the excess sulfide with 200 ml. of fresh methanol and allowed to react again. The total water solution was acidified with HCl and extracted with ether. Removing the ether layer and distilling the ether left an oil which boiled at room temperature and 1 mm. pressure with $C_6H_5CCl_3$ condensing in a −78° trap. At 150° and 1 mm. pressure a red oil distilled to a room temperature trap with considerable H_2S collecting in a liquid nitrogen trap. The red oil was soluble in NaOH solutions and ether but decomposed rapidly. Within hours of its isolation it dissolved in ether but left a residue and in 2 or 3 weeks was insoluble in ether. The infrared absorption spectrum of the compound has strong bands at 1690 and 1270 cm.$^{-1}$.

Dithiobenzoatotetracarbonylmanganese(I).—Freshly prepared dithiobenzoic acid (2 g.) was dissolved in dry ether and filtered. The filtrate was added to 1.1 g. of $Mn(CO)_5Br$[4] in 175 ml. of dry ether. The flask was kept in the dark for 12 hr. at 25° during which a fine yellow powder was deposited. No attempt was

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made to identify the powder, which was present in only a very small amount. The solid was removed on a filter and the filtrate was concentrated under vacuum to 50 ml., yielding a red solid. The solid was collected on a filter and the filtrate cooled to −78°, yielding more of the red solid. This was again collected and the filtrate discarded. The two crops of solid were combined and recrystallized from ether; yield 1.2 g. (94%).

Anal. Calcd. for $C_6H_5CSSMn(CO)_4$: C, 41.4; H, 1.57; S, 20.1. Found: C, 41.4; H, 1.83; S, 19.0. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill. They suggest it is difficult to get good results for S in the presence of Mn.

Molecular Weight Determination.—The molecular weight of $C_6H_5CSSMn(CO)_4$ was determined by the isopiestic method.[5] Chloroform solutions of 0.0044 g. of $Mn(CO)_5Br$ and 0.0064 g. of $C_6H_5CSSMn(CO)_4$ equilibrated in a $CHCl_3$ atmosphere at 25° in the dark in 6 days with respective volumes of 0.760 and 0.602 ml. Mol. wt. calcd. for monomer, 320; found, 350.

Spectra.—The infrared spectrum was measured on a Beckman IR-9 in $CHCl_3$. In the carbonyl region bands were found at 2092 (s), 1918 (vs), 1906 (sh), and 1964 (s) cm.$^{-1}$. The visible and ultraviolet spectra were taken on a Beckman DK-2 in benzene (visible) and methanol (ultraviolet). Very intense bands were found at 4060 Å. (ϵ 6900) and 2970 Å. (ϵ 21,500).

Reaction with Methanol.—It was observed that when 0.0269 g. of $C_6H_5CSSMn(CO)_4$ was suspended in 50 ml. of methanol and refluxed for 3 days the color changed from red to yellow. Removal of the methanol by vacuum left a solid. The solid was dissolved in ether and transferred to the base of a sublimation tube. The ether was evaporated in a nitrogen stream and the solid vacuum sublimed at room temperature and 0.5 mm. pressure. The yellow sublimate was washed with ether into a weighed flask and the ether removed in a nitrogen stream followed by drying under reduced pressure. The solid product weighed 0.0137 g. and the infrared spectrum confirmed that it was $Mn_2(CO)_{10}$. Thus 83.4% of the Mn was changed from $C_6H_5CSSMn(CO)_4$ to $Mn_2(CO)_{10}$.

Results and Discussion

The mild reaction conditions and good yield of the reaction

$$C_6H_5CSSH + Mn(CO)_5Br \longrightarrow C_6H_5CSSMn(CO)_4 + CO + HBr$$

must be contrasted with the fact that under identical conditions there was no reaction if C_6H_5COOH was used. Further, upon refluxing an ether solution of benzoic acid and $Mn(CO)_5Br$ for 24 hr. the only carbonyl product obtained was shown by its infrared spectrum to be $[Mn(CO)_4Br]_2$.[4] It was also found that dithiobenzoic acid will not cleave this dimer in boiling ether.

The attempted synthesis of an iron analog by the reaction between C_6H_5CSSH and $Fe(CO)_4Br_2$ in ether under the same conditions was rewarded only by vigorous bubbling and a color change from red to yellow, but immediately the yellow product decomposed to $Fe_3(CO)_{12}$. No method was found to be rapid enough to afford the separation of this yellow product from its decomposition products. However, the infrared spectrum in chloroform taken during the reaction, on a Baird-Associates 4-55, shows the production of three new bands: 2110 (s), 2060 (s), and 2045 (m) cm.$^{-1}$.

The conversion of $C_6H_5CSSMn(CO)_4$ to $Mn_2(CO)_{10}$ in methanol is interesting in regard to its 83% yield. Because the CO:Mn ratio changes from 4:1 in the reactant to 5:1 in the product the maximum expected yield should only be 80%. Thus an experimental yield on the order of 80% must mean that either the carbon monoxide is quantitatively transferred from one molecule of reactant to four other molecules of reactant in boiling methanol or that the methanol is a source of carbon monoxide. In view of the improbability of the first path the decomposition is postulated as the second; as a reaction with the methanol. Refluxing a hexane solution of the material led to the formation of a tar containing only small amounts of $Mn_2(CO)_{10}$. Transfers of a CO from an alcohol to a metal are already known[6] but it appears that this is the first example involving a member of the first row transition series as well as one resulting in a simple metal carbonyl.

The very intense absorption of $C_6H_5CSSMn(CO)_4$ at 4060 Å. (ϵ 6900) is in contrast to the weaker bands found for other disubstituted tetracarbonylmanganese(I) compounds. The λ_{max} for the series $Mn(CO)_4LBr$ where $L = CO$, $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(C_6H_5O_3)P$ are all in the range 3820–4090 Å. but the molar extinctions range from 340 to 730.[7] Dithiobenzoic acid itself has an intense ultraviolet spectrum, the edge of which extends into the visible region but at 4000 Å. ϵ is only 68. A simple explanation of this phenomenon can be based on the direct involvement of the metal in the aromatic system through π-bonding between the metal and the sulfurs. Coupling a cyclic conjugated system like this to the aromatic ring would be expected to enhance both the stability and the absorption of the compound.

Acknowledgment.—We wish to thank the Ethyl Corporation, Detroit, Mich., for a gift of $Mn_2(CO)_{10}$. The authors are thankful for a Dow Chemical Company Fellowship to I. A. C. This research was supported in part by National Science Foundation Grant NSF-GP-1471.

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Complexes of the Lanthanide Elements with Kojate and Acetylacetonate Ions

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Received May 13, 1964

Kojic acid (I) and acetylacetone have been shown to be good chelating agents for a large number of metal ions. There are several publications[1,2] describing the preparation of some kojate complexes and a few concern-

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