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Sulfur Dioxide Insertion. VIII.[1] Substituted Sulfinatocarbonylmanganese(I) Complexes*

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Substituted sulfinatotricarbonyl and -tetracarbonyl complexes of manganese(I) containing monodentate (L) and bidentate (L–L) amines, triphenylphosphine (L′), and iodide ion (X^-) have been prepared utilizing one or more of the following methods: (a) reaction of $Mn(CO)_5(SO_2R)$ with the ligand (L, L–L, and X^-), (b) methathesis involving $Mn(CO)_3(L{-}L)Cl$ and RSO_2Na, and (c) sulfur dioxide insertion into Mn–R bond of $Mn(CO)_4L'R$. With the exception of $[Mn(CO)_3(C_5H_5N)(SO_2CH_2C_6H_5)]_x$, which is probably polymeric and contains $MnOS(CH_2C_6H_5)OMn$ bridges, all derivatives have been assigned S-sulfinato structures. The syntheses, physical properties, and infrared spectra of the new complexes are discussed.

Introduction

In an earlier paper of this series we reported the synthesis and characterization of S-sulfinatopentacarbonylmanganese(I) complexes.[2] From the infrared spectra of these compounds it was inferred that the sulfur-bonded alkyl- and arylsulfinato ligands exhibit appreciable π-acceptor capacity.

In order to expand the scope of the foregoing investigation we have now directed our attention to substituted sulfinatocarbonylmanganese(I) complexes. Several aspects of the undertaken study appeared of special interest. First, the compounds $Mn(CO)_5(SO_2R)$, in contrast to most of the manganese(I) pentacarbonyls, contain π-bonding ligands only. An investigation of substitution reactions of these sulfinates was expected to provide a basis for qualitative comparison of the rates of replacement of CO from $Mn(CO)_5(SO_2R)$ and from the corresponding halogenopentacarbonyls, reported earlier,[3,4] where the halide effectively lacks π-acceptor behavior. Second, elucidation of the degree of substitution and the stereochemistry of the resulting derivatives should complement similar studies on other manganese pentacarbonyls, reported in the literature.[4-15] Third, the nature of the bonding in $MnSO_2R$ moieties of the substituted sulfinatocarbonyls deserved particular attention because of the possibility of prevalence of two type of linkage—$MnS(O)_2R$ and $MnOS(O)R$—and interconversion between them. Some precedent for linkage rearrangement existed in the behavior of manganese(I) carbonyls containing another ambidentate ligand, thiocyanate.[15] Finally, the stereochemistry of the complexes derived from the insertion of SO_2 into a manganese-alkyl carbon bond in $Mn(CO)_4LR$ appeared of special interest in connection with related studies on the carbon monoxide insertion.[14,16-20]

Reported in this paper are the resuls of our investigation on substituted sulfinatocarbonylmanganese(I) complexes.

Experimental Section

Materials. The carbonyls $Mn(CO)_5(SO_2R)$[2] (R= CH_3, C_6H_5, and $CH_2C_6H_5$), *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$,[20] and $Mn(CO)_3(bipy)Cl$[15] were prepared according to the literature methods. The following were purchased and used without further purification: $C_6H_5SO_2Na$ (Aldrich Chemical Co.), 2,2′-bipyridine (bipy), *p*-fluoroaniline (*p*-fan), 1,10-phenanthroline (*o*-phen), triphenylphosphine (Matheson Coleman and Bell), tetrabutylammonium iodide, *p-toluidine* (p-tol) (Eastman Organic Chemicals), and pyridine (py) (Baker Chemical Co.).

Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}—$CaCl_2$ column before condensation. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere

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[1] For Part VII of this series, see F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta, 2,* 289 (1968).

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immediately before use. Acetonitrile was distilled from P_4O_{10}, and ether was dried over sodium and distilled. Technical grade pentane and hexane and petroleum ether (b.p., 30-60°) were used without further purification. All other chemicals and solvents were of reagent grade or equivalent.

Preparation of Sulfinatotricarbonylmanganese(I) Amine Complexes. In general these were prepared by the interaction of $Mn(CO)_5(SO_2R)$ with a slight excess of the amine in acetonitrile at 55° or in chloroform at 60°. No apparent reaction occurred between $Mn(CO)_5(SO_2R)$ ($R=CH_3$ and $CH_2C_6H_5$) and pyridine in $CHCl_3$ at 30° within 48 hr. The synthesis of $Mn(CO)_3(bipy)(SO_2CH_3)$ is described in detail to illustrate the procedure.

2,2′-Bipyridine (0.20 g., 1.3 mmoles) was added to a solution of 0.30 g. (1.1 mmoles) of $Mn(CO)_5(SO_2CH_3)$ in 3 ml. of CH_3CN and the mixture was maintained at 55° under nitrogen. During the first hour the solution changed from light yellow to orange-red. After 24 hr. the mixture was cooled to room temperature yielding bright orange crystals. These were collected on a filter and washed with two 5-ml. portions of ether. The acetonitrile filtrate was evaporated to dryness in a stream of nitrogen and the residue was dissolved in 15 ml. of $CHCl_3$. The solution was filtered and the filtrate treated slowly with 25 ml. of pentane. The resulting orange precipitate was collected on a filter, washed with 5 ml. of ether, and air-dried. The combined yield was 0.31 g. (81%). The analytical data for this and other substituted carbonyl sulfinates are given in Table I.

$Mn(CO)_3(bipy)(SO_2C_6H_5)$ was prepared by the reaction of $Mn(CO)_3(bipy)Cl$ (0.33 g., 1.0 mmole) with $C_6H_5SO_2Na$ (1.64 g., 10 mmoles) in 60 ml. of anhydrous methanol. The solution was maintained under nitrogen at 60° for 15 hr. before removing the solvent under reduced pressure. The solid residue was extracted with three 60-ml. portions of CH_2Cl_2. The combined extracts were filtered and treated with 100 ml. of pentane. The orange precipitate which formed on storage was collected and air-dried. The product (0.36 g., 82%) had an infrared spectrum and decomposition point identical with those of the compound obtained from $Mn(CO)_5(SO_2C_6H_5)$ and 2,2′-bipyridine in CH_3CN.

$[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$ resulted from the reaction of $Mn(CO)_5(SO_2CH_2C_6H_5)$ (0.30 g., 8.63 mmoles) and pyridine (3.00 g., 37.5 mmoles) in 20 ml. of tetrahydrofuran at 55° under nitrogen. After 12 hr. the solvent was removed leaving an orange oil. This was washed with three 10-ml. portions of petroleum ether and then dissolved in 10 ml. of absolute ethanol. Addition of ether (15 ml.), followed by cooling to –20°, afforder a pale yellow powder (0.16 g., 50%) which was insoluble in chloroform, acetone, acetonitrile, and hydrocarbons.

Preparation of $[(n\text{-}C_4H_9)_4N][Mn(CO)_4(SO_2CH_3)I]$. Tetrabutylammonium iodide (0.37 g., 1.0 mmole) and $Mn(CO)_5(SO_2CH_3)$ (0.27 g., 1.0 mmole in) 10 ml. of CH_3CN were allowed to react at 60° until the evolution of CO ceased (*ca.* 3 hr.). The solution was then cooled and treated with 30 ml. of a 5:2 by volume petroleum ether-ether mixture. After storage in the dark for 24 hr., pale yellow crystals separated. They were collected on a suction filter and vacuum-dried. The yield was 0.55 g. (90%).

Preparation of $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$. A 100-ml. glass pressure bottle equipped with a threaded Teflon stopper and a sidearm take-off was charged with 0.50 g. (1.13 mmoles) of *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$. The vessel was cooled to –70° and evacuated. After *ca.* 3 ml. of liquid SO_2 had been condensed onto the carbonyl, the reaction mixture was maintained at –10° for 20 hr. Removal of excess SO_2 gave a virtually quantitative yield of the orange-yellow product.

This reaction was also carried out at *ca.* –65° for 30 hr. and at –10° for 4 hr. In all cases, the chemical analyses, infrared spectra, and decomposition temperatures of the isolated products were identical.

Table I. Synthetic Procedures, Reaction Times, Yields, Melting Points, and Analytical Data for Sulfinato Manganese(I) Carbonyl Complexes

Compound	Synthetic procedure[a]	Reaction time, hrs	Yield, %	M.p., °C [b]	Analyses, %							
					Calcd.				Found			
					C	H	N/P	S	C	H	N/P	S
$Mn(CO)_3(bipy)(SO_2CH_3)$ [c,d,e]	A	20	81	196-199 [f]	44.93	2.96	7.48 (N)	8.57	44.78	2.90	7.36 (N)	8.40
$Mn(CO)_3(bipy)(SO_2CH_2C_6H_5)$ [g,h]	A	24	89	165-168 [f]	53.34	3.36	6.22 (N)		52.68	3.33	5.97 (N)	
$Mn(CO)_3(bipy)(SO_2C_6H_5)$	B (A)	15 (24)	82 (80)	180 [f]	52.30	3.00		7.35	52.43	3.24		7.55
$Mn(CO)_3(o\text{-phen})(SO_2CH_3)$	A′	24	96	190 [f]	48.25	2.78	7.03 (N)		48.18	3.00	6.82 (N)	
$Mn(CO)_3(o\text{-phen})(SO_2CH_2C_6H_5)$	A′	24	82	173 [f]	55.70	3.19	5.90 (N)		55.75	3.11	6.12 (N)	
$Mn(CO)_3(p\text{-tol})_2(SO_2CH_3)$	A′	28	77	127	50.00	4.90	6.48 (N)		49.95	4.94	6.15 (N)	
$Mn(CO)_3(p\text{-fan})_2(SO_2CH_3)$	A′	24	91	130	43.64	3.43	6.36 (N)		43.65	3.52	6.45 (N)	
$Mn(CO)_3(py)_2(SO_2CH_3)$	A	18	73	114 [f]	44.69	3.48	7.44 (N)		44.90	3.36	6.90 (N)	
$[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$	A″	12	50		48.26	3.24	3.75 (N)		48.01	3.41	3.85 (N)	
$[(n\text{-}C_4H_9)_4N][Mn(CO)_4(SO_2CH_3)I]$ [i,j]	A	3	90	95-100 [f]	40.98	6.39			40.63	6.59		
$Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$	C	20	99	58 [f]	54.35	3.55	6.09 (P)		54.10	3.58	5.85 (P)	

[a] Procedure $A=Mn(CO)_5(SO_2R)+$ligand at 55° in CH_3CN; $A'=Mn(CO)_5(SO_2R)+$ligand at 60° in $CHCl_3$; $A''=Mn(CO)_5(SO_2R)+$ligand at 55° in tetrahydrofuran; $B=Mn(CO_3)(L\text{—}L)Cl+RSO_2Na$ at 60° in CH_3OH; $C=Mn(CO)_4LR+$liquid SO_2. [b] Determinated with a Fisher-Johns melting-point block and uncorrected, [c] Calcd.: Mn, 14.68; O, 21.38. Found: Mn, 14.95; O, 21.65. [d] Calcd. mol. wt.: 374. Found (osmometry, $5.3\times10^{-3}\,m$ $CHCl_3$ soln.): 396, 358. [e] $\Lambda_M=0.378$ cm² ohm^{-1} M^{-1} (*ca.* 10^{-3} *M* CH_3CN soln.). [f] Decomposition point. [g] Calcd.: Mn, 12.20. Found: Mn, 12.42. [h] $\Lambda_M=0.287$ cm² ohm^{-1} M^{-1} (*ca.* 10^{-3} *M* CH_3CN soln.). [i] Calcd.: I, 20.62. Found: I, 21.90. [j] $\Lambda_M=110$ cm² ohm^{-1} M^{-1} (*ca.* 10^{-3} *M* acetone soln.).

When SO_2 was passed through solutions (benzene or ether) of *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$ for 3 hr. at 0° or 27°, yellow powders separated. These substances gave reproducible infrared spectra, showing absorption bands at 2056 (s), 1974 (sh), 1968 (vs), and 1917 (s) cm^{-1} (metal carbonyl stretching region, CH_2Cl_2 solution) and at 1136 and 1005 cm^{-1} (sulfur-oxygen stretching region, KBr pellet). They decomposed at 125°. However, consistent analytical data could not be obtained, typical results being: C, 49.16, 47.40; H, 3.89, 3.66; S, 6.72; P, 5.91, 5.47.

Reaction of $Mn(CO)_5(SO_2R)$ with $P(C_6H_5)_3$. (a) *$Mn(CO)_5(SO_2CH_2C_6H_5)$ and $Mn(CO)_5(SO_2CH_3)$ with $P(C_6H_5)_3$ in CH_3CN.* A solution of 0.50 g. (1.91 mmoles) of $P(C_6H_5)_3$ and 0.50 g. (1.42 mmoles) of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in 8 ml. of CH_3CN was heated at 55° for 24 hr. under nitrogen. Upon cooling yellow crystals separated. These were collected and washed successively with 5-ml. portions of benzene and hexane. Recrystallization was effected from a CH_2Cl_2 (40 ml.)–benzene (100 ml.) mixture. Yield, 0.40 g. The compound turns orange on heating to 90-95° and decomposes at *ca.* 120°. Its infrared spectrum showed absorption bands at 2046 (m-s), 1980 (s), 1953 (vs), and 1925 (m) cm^{-1} (CH_2Cl_2 solution) and at 1170 (s), 1133 (s), and 1022 (s) cm^{-1} (KBr pellet). Again, consistent analytical data could not be obtained.

Anal. Calcd. for $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_2C_6H_5)$: C, 59.62; H, 3.77; S, 5.47; P, 5.30. Found: C, 58.41, 57.14; H, 4.55, 4.51; S, 6.17; P, 4.62.

Under similar conditions $Mn(CO)_5(SO_2CH_3)$ reacted with excess $P(C_6H_5)_3$ to yield a yellow powder the infrared spectrum and physical characteristics of which were identical with those of the product obtained from *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$ and SO_2 in ether or benzene (*vide supra*).

(b) *$Mn(CO)_5(SO_2CH_2C_6H_5)$ with Molten $P(C_6H_5)_3$.* A finely ground mixture of $P(C_6H_5)_3$ (0.37 g., 1.42 mmoles) and $Mn(CO)_5(SO_2CH_2C_6H_5)$ (0.50 g., 1.42 mmoles) was heated under nitrogen at 90° for 3 hr., during which time it melted and turned orange. The melt was cooled to room temperature; the resulting solid was pulverized and extracted with two 10-ml. portions of benzene. The extracts were combined, filtered to remove a white, noncarbonyl solid, concentrated, and chromatographed on a Florisil column (25 × 2.5 cm.). A bright orange band was eluted with benzene and collected under nitrogen. Removal of the solvent yielded an orange powder (0.21 g.), which was recrystallized from benzene-pentane.

Anal. Calcd. for $Mn(CO)_4[P(C_6H_5)_3]$: C, 61.55; H, 3.52; mol. wt., 429. Found: C, 61.05; H, 3.71; mol. wt. (osmometry in benzene), 471.

The solid product is diamagnetic. Further, the infrared spectrum of this compound is identical with that of «$Mn(CO)_4[P(C_6H_5)_3]$», prepared according to the literature[21] and purified by chromatography (carbonyl stretching absorptions at 1989 (vw) and 1958 (s) cm^{-1}, tetrachloroethylene solution). Both samples react with $CHCl_3$ and CH_2Cl_2 to give $Mn(CO)_4[P(C_6H_5)_3]Cl$.

Infrared Spectra. Spectra were recorded on a Beckman Model IR-9 spectrophotometer. Solutions were placed in a 0.05-mm. KBr cell, a matched reference cell being used at all times. Solids were examined as Nujol and hexachlorobutadiene mulls or as KBr pellets.

Conductivity. Measurements were made using an Industrial Instruments Co. Model RC16B2 conductivity bridge and a cell with platinum electrodes.

Magnetism. A Faraday magnetic balance, constructed in Professor D. W. Meek's laboratories, was employed in making measurements.

Molecular Weights. Measurements were made using a Mechrolab Model 301-A osmometer.

Analyses. Microanalyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany.

Results and Discussion

Substituted manganese(I) sulfinatotricarbonyl and -tetracarbonyl complexes have been obtained via three general procedures, illustrated by equations (1)-(3).

$$Mn(CO)_5(SO_2R) + 2L \text{ (or L–L) } \xrightarrow[\text{or } CHCl_3]{CH_3CN} Mn(CO)_3L_2(SO_2R) \text{ (or } Mn(CO)_3(L{-}L)(SO_2R)) + 2CO \qquad (1a)$$

$$Mn(CO)_5(SO_2R) + R'_4NX \xrightarrow{CH_3CN} (R'_4N)[Mn(CO)_4(SO_2R)X] + CO \qquad (1b)$$

$$xMn(CO)_5(SO_2R) + xL \xrightarrow{\text{tetrahydrofuran}} [Mn(CO)_3L(SO_2R)]_x + 2xCO \qquad (1c)$$

$$Mn(CO)_3(L{-}L)Cl + RSO_2Na \longrightarrow Mn(CO)_3(L{-}L)(SO_2R) + NaCl \qquad (2)$$

$$Mn(CO)_4LR + SO_2 \longrightarrow Mn(CO)_4L(SO_2R) \qquad (3)$$

The first method ((1a), (1b), and (1c)) is applicable to monodentate (L) and bidentate (L–L) amines and to iodide (X^-), providing good yields of the substituted sulfinato-carbonyls. Using triphenylphosphine as the entering ligand, one isolates yellow solids which analyze approximately for $Mn(CO)_4[P(C_6H_5)_3](SO_2R)$. Nevertheless, the infrared spectrum and physical characteristics of the complex obtained from $Mn(CO)_5(SO_2CH_3)$ and $P(C_6H_5)_3$ differ from those of an authentic sample of $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$. Since the latter was shown to be unstable toward air and light and to decompose on crystallization, it is quite conceivable that the products isolated from $Mn(CO)_5(SO_2R)$ and $P(C_6H_5)_3$ result from decomposition of the initially formed tetracarbonyls, $Mn(CO)_4[P(C_6H_5)_3](SO_2R)$. No further work is planned to elucidate the nature of these species.

Interestingly, the only carbonyl isolated from a melt of $Mn(CO)_5(SO_2CH_2C_6H_5)$ and $P(C_6H_5)_3$ analyzed for $Mn(CO)_4[P(C_6H_5)_3]$. The infrared spectrum in the CO stretching region of this complex is identical with that of a sample of the tetracarbonyl synthesized according to Hieber and Fryer[21] and purified by chromatography; however, our compound is diamagnetic in the solid. Since the corresponding dimer, $Mn_2(CO)_8[P(C_6H_5)_3]_2$, prepared by Osborne and Stiddard,[22] shows a similar infrared spectrum (CO stretches at 1980 (sh) and 1956 (vs) cm^{-1}, $CHCl_3$ solution), it is entirely possible that the complex obtained in this study may be also dimeric, despite the low value of the molecular weight, determined osmometrically. However, the hydride *trans*-$Mn(CO)_4[P(C_6H_5)_3]H$, still unreported, represents a plausible alternative. Our present data are insufficient to permit differentiation between these two formulations; additional experiments aimed at resolving this problem will be conducted.

The second procedure (equation (2)) has been employed in the synthesis of $Mn(CO)_3(bipy)(SO_2CH_3)$; it is probably equally applicable to the preparation of other amine-substituted sulfinatocarbonyls. However, the reaction of $Mn(CO)_3(diphos)Br$ (diphos = 1,2-bis(diphenylphosphino)ethane) with $C_6H_5SO_2Na$ yielded a product which displayed anomalies similar to those of the triphenylphosphine-containing substances, discussed above.

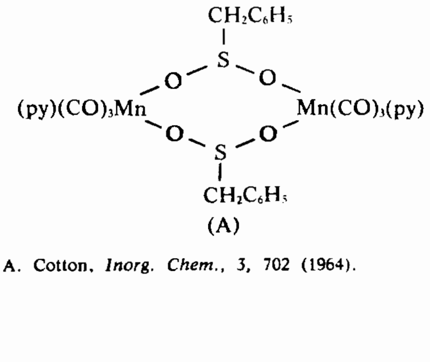
The phosphine complex $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$ was prepared in a virtually quantitative yield by SO_2 insertion into the $Mn-CH_3$ bond of *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$. Although this reaction proceeds even at –65°, it has limited applicability to the synthesis of substituted manganese(I) sulfinatocarbonyls because of a relatively small number of the corresponding alkylcarbonyls available. The insertion of SO_2 with *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$ also proceeds in benzene and ether solutions; however, the products of these reactions are again the ill-behaved solids mentioned earlier.

The substituted sulfinatocarbonyls of manganese(I) are yellow to orange solids; with the exception of $[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$, which is insoluble in organic solvents, they dissolve sparingly in chloroform, dichloromethane, and acetonitrile. This limited solubility precluded measurement of their proton magnetic resonance spectra. The tricarbonyl $Mn(CO)_3(bipy)(SO_2CH_3)$ has been found monomeric in $CHCl_3$; this is undoubtedly true also of the other soluble derivatives. Both $Mn(CO)_3(bipy)(SO_2CH_3)$ and $Mn(CO)_3(bipy)(SO_2CH_2C_6H_5)$ are nonelectrolytes in acetonitrile; $[(n-C_4H_9)_4N][Mn(CO)_4(SO_2CH_3)I]$ is, as expected, a 1:1 electrolyte in acetone.[23] With the exception of $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$, which undergoes a relatively facile decomposition (*vide supra*), the complexes are stable when kept in the dark.

The infrared spectra in the metal carbonyl stretching region of the amine complexes (Table II) show three strong-intensity absorption bands, thus indicating that the CO groups are all *cis* (C_s local symmetry).[25] The tetracarbonyls containing triphenylphosphine and iodide ion also possess C_s (*cis*) rather than C_{4v} (*trans*) symmetry around the metal, as inferred from the number and the relative intensities of the carbonyl stretching bands.[10]

Insight into the bonding in $MnSO_2R$ moieties is obtained upon examination of the infrared spectra of the complexes in the sulfur-oxygen stretching region (Table II). The assignment of the bands was made in each case by comparing the spectrum of the sulfinato compound with that of the corresponding halogeno derivative. With the exception of $[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$, all sulfinates show asymmetric S–O stretches in the range 1044-1009 cm^{-1}. These wavenumbers are appreciably lower than those for the pentacarbonyls $Mn(CO)_5(SO_2R)$.[2] However, as may be seen from Table III, sulfinato complexes containing metal-oxygen bonds, *e.g. IV, V, VI,* and *VII,* show sulfur-oxygen stretching absorptions at even lower energies, usually around 1000 cm^{-1} and below. Furthermore, compounds containing an MnS(O)O– linkage, such as the allene(oxy)-sulfinyl pentacarbonyl, *VIII,* are expected to exhibit one S–O stretchig vibration around 900 cm^{-1}. Thus, it is a virtual certainty that the S-sulfinato type of attachment, present in $Mn(CO)_5(SO_2R)$, also persists in these substituted derivatives. The lowering of the S–O stretching frequencies may be best attributed to an enhancement of $Mn=SO_2R$ π bonding (and, concomitantly, to a weakening of $Mn-SO_2R$ σ bonding) brought about by replacement of a weak base and a good π-acceptor CO with a stronger base and a poorer π-acceptor amine, phosphine, or iodide. A similar explanation was proposed earlier to account for the lowering of the S–O stretching frequencies in going from $Mn(CO)_5(SO_2C_6H_5)$ to the isoelectronic $Cr(CO)_5(SO_2C_6H_5)^-$ (*X*)[2].

The structure of $[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$ cannot be unequivocally elucidated from the spectral data. The insolubility of this compound reflects its probable polymeric nature, with the sulfinate functioning as a bridging group to provide manganese(I) with its usual coordination number of six. Several reasonable structures may be proposed; the dimeric one (A) and part of a polymeric network (B) containing MnOS(R)OMn linkages for the sulfinate are depicted below.



(A)

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Table II. Infrared Spectra of Sulfinato Manganese(I) Carbonyl Complexes (cm^{-1})

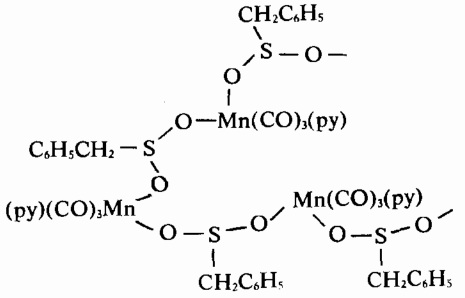
Compound	Metal carbonyl stretches[a]	Sulfur-oxygen stretches[b]	Other bands[c]
$Mn(CO)_3(bipy)(SO_2CH_3)$	2033 s, 1952 s, 1931 s	1148 s, 1044 s	3118 s, 3086 w-m, 3082 w-m, 3065 w, 3039 w, 3010 vw, 2999 vw, 2028 w, 1608 m-s, 1478 m-s, 1447 m-s, 1440 sh, 1417 w, 1406 w, 1320-w-m, 1297 w, 1291 vw, 1263 vw, 1248 w, 1219 vw, 1170 w, 1125 m, 1080 w, 1029 m-s, 1008 w, 986 vw, 941 m, 900 w, 774 s, 746 w, 733 m, 711 m-s, 687 m, 654 w, 638 m-s, 626 m-s, 550 m, 523 s, 452 w-m, 440 w-m
$Mn(CO)_3(bipy)(SO_2CH_2C_6H_5)$	2032 s, 1951 s, 1929 s	1161 sh, 1156 s, 1034 s, 1027 sh	3116 vw, 3087 w, 3075 w, 3042 w, 2936 w, 1607 m-s, 1497 w-m, 1477 m, 1446 m-s, 1325 w, 1319w-m, 1250vw, 1230 vw, 1181 vw, 1132 m-s, 1129 sh, 1079 w, 1073 vw, 1047 vw, 970 vw, 920 vw, 876 w-m, 786 m-s, 776 sh, 735 w, 694 m-s, 656 w, 637 m-s, 620 m-s, 548 w, 532 m, 512 m, 498 m, 475 vw, 450 vw, 434 w-m
$Mn(CO)_3(bipy)(SO_2C_6H_5)$	2035 s, 1953 s, 1941 s	1160 s, 1150 sh, 1040 s	3120 w, 3079 w-m, 3066 w, 3034 vw, 1609 w, 1604 w, 1480 s, 1450 m-s, 1445 m-s, 1324 m, 1248 m, 1126 w, 1095 m, 1080 w, 1068 w-m, 1029 m, 1020 m, 998 w-m, 972 w, 958 w, 900 w, 802 w, 772 s, 756 m, 749 m, 731 m-s, 702 m-s, 692 m-s, 685 m, 655 w, 635 m-s, 626 m-s, 582 s, 548 w, 536 m, 505 w, 448 w, 440 vw
$Mn(CO)_3(o\text{-phen})(SO_2CH_3)$	2034 s, 1952 s, 1932 s	1158 s, 1145 sh, 1136 s, 1032 s	3100 vw, 3052 vw, 3030 vw, 2931 w, 1610 w, 1588 w, 1525 m, 1428 m-s, 1416 m, 1409 sh, 1344 w, 1296 w-m, 1193 w-m, 1099 w, 1062 vw, 1054 w, 974 w, 947 m, 934 m, 842 s, 807 w, 780 w-m, 724 s, 678 m, 638 s, 625 s, 549 m, 541 m, 522 s, 440 w
$Mn(CO)_3(o\text{-phen})(SO_2CH_2CH_6)_5$	2033 s, 1952 s, 1930 s	1180 sh, 1175 s, 1037 s	3088 w, 3082 w-m, 3021 w, 2922 w, 1602 w, 1583 w, 1521 w-m, 1497 w-m, 1453 w-m, 1431 m-s, 1414 m, 1345 w, 1316 w, 1312 w, 1225 w, 1150 w, 1143 w, 1120 w-m, 1112 sh, 1097 w, 1070 vw, 1065 vw, 960 w, 942 vw, 913 vw, 850 m-s, 830 w, 823 w, 811 w, 775 w-m, 757 m, 725 m-s, 698 m, 680 w-m, 669 m, 636 m-s, 628 m-s, 540 m, 508 m-s, 490 w
$Mn(CO)_3(p\text{-tol})_2(SO_2CH_3)$	2040 s, 1948 s, 1932 s	1102 s, 1015 s	3280 m, 3210 m, 3130 m, 3030 w-m, 2915 w, 2860 vw, 1587 s, 1510 vs, 1450 w-m, 1400 m, 1379 w, 1375 sh, 1327 w, 1295 m-s, 1190 sh, 1170 s, 938 s, 840 w, 821 s, 747 w, 715 s, 667 s, 645 m, 628 m-s, 606 m-s, 552 m, 536 sh, 522 vs, 483 m, 478 sh, 435 m[d]
$Mn(CO)_3(p\text{-fan})_2(SO_2CH_3)$	2039 s, 1952 s, 1931 s	1113 s, 1025 s	3275 s, 3244 m, 3195 m, 3160 m, 3121 s, 3079 sh, 3067 w-m, 3035 w, 2998 w, 2965 w, 2924 w, 2861 w, 1612 m, 1592 s, 1517 vs, 1479 w-m, 1445 w, 1408 m-s, 1302 m, 1251 s, 1242 m-s, 1222 m, 1185 s, 1160 s, 1149 s, 1091 m-s, 960 vw, 950 m, 935 vw, 833 s, 752 m-s, 721 s, 668 m-s, 641 m, 629 m-s,. 610 m, 552 w-m, 541 m, 529 vs, 491 m, 482 w-m, 442 m
$Mn(CO)_3(py)_2(SO_2CH_3)$	2039 s, 1954 s, 1925 s	1125 s, 1039 s, 1009 sh	3080 vw, 3009 vw, 2962 w, 2928 w, 2880 vw, 2862 vw, 1604 m, 1489 w-m, 1457 w, 1446 m, 1409 w-m, 1301 m, 1233 w, 1220 w-m, 1212 w, 1070 w-m, 951 m, 762 m-s, 724 m-s, 703 m-s, 688 w-m, 660 m, 640 w, 630 sh, 624 m, 593 vw, 534 m, 525 m-s, 450 w-m
$[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$	2032 s, 1927 s, 1910 s[d]	1020 s, 1013 s, 958 s[d]	3130 vw, 3070 w, 3045 w, 2935 w, 1609 s, 1495 sh, 1490 m, 1451 s, 1221 m, 1155 m, 1120 m, 1073 m, 878 m, 760 s, 695 s, 655 w, 637 sh, 632 m-s, 536 m, 522 m, 481 m, 470 w, 442 m[d]
$[(n\text{-}C_4H_9)_4N][Mn(CO)_4(SO_2CH_3)I]$	2034 m-s, 1995 vw, 1960 s, 1941 s, 1919 sh	1168 sh, 1149 sh, 1138 s, 1030 s	2990 m, 2970 m-s, 2925 m, 2860 m, 1650 w, 1620 m, 1570 s, 1495 s, 1410 m, 1380 m, 1365 w, 1325 w, 1300 w, 1242 w, 1181 w, 1111 m, 1070 w, 1058 w, 1015 m, 995 sh, 950 m, 923 m, 897 m, 882 m, 795 w, 738 m-s, 722 m-s, 665 m, 621 m, 546 m-s, 533 m, 525 sh, 455 w
$Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$	2085 w-m, 2018 sh, 2010 vs, 1996 s	1145 s, 1035 s	3060 w, 3000 vw, 2925 w, 1580 w, 1480 m, 1430 m, 1300 w, 1112 s, 1082 m-s, 1065 sh, 991 m-s, 970 s, 931 m-s, 840 w, 740 m, 718 s, 689 s, 648 m, 620 s, 615 sh, 542 s, 526 sh, 515 s, 505 sh, 480 w-m, 460 w, 445 w

[a] Dichloromethane solution. [b] Nujol mull. [c] Nujol mull (2800-1500 and 1300-400 cm^{-1}) and hexachlorobutadiene mull (4000-2800 and 1500-1300 cm^{-1}). [d] KBr pellet. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

Table III. Sulfur-Oxygen Stretching Frequencies (cm^{-1}) of Some Metal Sulfinates[a]

	Compound	S–O stretches: Asymmetric	S–O stretches: Symmetric
(I)	$Na[C_6H_5SO_2]$	1024	976
(II)	$K[C_6H_5SO_2]$ [b]	1020	980
(III)	$Ba[C_6H_5SO_2]_2$	986	960
(IV)	$[(CH_3)_2AlOS(C_6H_5)O]_2$ [b]	1027-1005	980-970
(V)	$[(CH_3)_2GaOS(C_6H_5)O]_2$ [b]	1005	941
(VI)	$Cu(H_2O)_4[p\text{-}OS(O)C_6H_4CH_3]_2$ [c]	998	938
(VII)	$(C_6H_5)_3SnOS(O)C_6H_5$ [d]	979-954	933
(VIII)	$(CO)_5MnS(O)OCH{=}C{=}CH_2$ [e]	1110	906
(IX)	$(CO)_5MnS(O)_2C_6H_5$ [d]	1192	1033
(X)	$Na[Cr(CO)_5S(O)_2C_6H_5]$. $1.5CH_3OH$ [d]	1110-1102	1015-1001

[a] Determined in this study unless noted otherwise. [b] G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964). [c] G. B. Deacon and P. W. Felder, *J. Am. Chem. Soc.*, *90*, 493 (1968); structure determined by X-ray crystallography (D. A. Langs and C. R. Hare, *Chem. Comm.*, 853 (1967)). [d] From ref. 2. [e] J. E. Thomasson and A. Wojcicki, *J. Am. Chem. Soc.*, *90*, 2709 (1968).



(B)

The S–O stretching frequencies for $[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$ (Table II) are remarkably close to those reported for *IV* and *V* (Table III), which have been assigned structures with sulfinato bridges similar to the ones in (A). Nevertheless, structure (B) should give rise to comparable values of S–O stretching frequencies; moreover, it receives support from the insolubility of the compound. In the absence of additional data we cannot differentiate among these and other possible formulations.

It is noteworthy that substitution reactions of $Mn(CO)_5(SO_2R)$ require more vigorous conditions than those of manganese(I) pentacarbonyl chloride and bromide.[4] A contrary prediction arises from considerations of the relative frequencies of the carbonyl stretching modes of these compounds,[2,26] which are highest for $Mn(CO)_5(SO_2R)$. Thus, if substitution in $Mn(CO)_5(SO_2R)$ proceeds by a dissociative mechanism, factors other than the extent of Mn=CO π bonding in the parent pentacarbonyl determine the relative rate of carbon monoxide release from these complexes. Additional examples of such apparent discord between the rates of CO dissociation and the values of metal carbonyl stretching frequencies have been given and discussed earlier by Angelici.[27]

The influence of the solvent on the nature of the substitution product from reactions of $Mn(CO)_5(SO_2R)$ and the amines is also quite striking. In chloroform and acetonitrile, diamine sulfinatotricarbonyl complexes result, whereas in tetrahydrofuran, a polymeric $[Mn(CO)_3(py)(SO_2CH_2C_6H_5)]_x$ is formed instead. We have no ready explanation for this behavior.

The insertion reaction of *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$ with liquid SO_2 affords quantitative yields of $Mn(CO)_4[P(C_6H_5)_3](SO_2CH_3)$. The nature of this product is independent of the temperature and the reaction time employed; as far as we can tell from the infrared spectrum in the metal carbonyl stretching region, only the *cis* isomer of the sulfinate is present. Unfortunately, this inference cannot be corroborated (or refuted) by proton magnetic resonance spectroscopy because of a limited solubility of the tetracarbonyl in suitable organic solvents. In this connection it is noteworthy that a related complex, *cis*-$Mn(CO)_4[P(C_6H_5)_3](COCH_3)$, formed initially from $Mn(CO)_5CH_3$ and $P(C_6H_5)_3$, does equilibrate in solution to yield a mixture of the *cis* and *trans* isomers.[14]

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