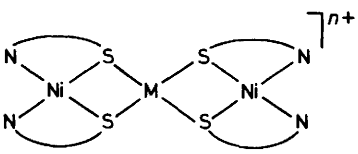
In memory of S. M. Nelson

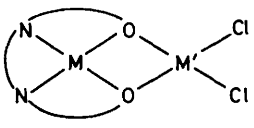
Metallo-ligands containing Terminal Oxygen Donors bonded to a Manganese–Carbonyl Moiety†

Mark Mason, Ding-Xue Kang, Irene Cihon, Andy Kintz, and Elliott L. Blinn *
Chemistry Department, Bowling Green State University, Bowling Green, Ohio 43403, U.S.A.
Marvin Tegen and Paul M. Treichel
Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

The reactions of [Mn(CO)$_5$Br] with [M(salen)] [M = Co, Cu, Zn, Pd, Ni, or Sn; salen = *N,N'*-ethylenebis(salicylideneiminate)], [Co(salphen)] [salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate)], or [Co(salchd)] [salchd = *N,N'*-cyclohexane-1,2-diylbis(salicylideneiminate)] in a variety of solvents resulted in the substitution products having the general formula [(ML)Mn(CO)$_3$Br] (L = salen, salphen, or salchd). The reaction of 4-ethyl-5-methyl-3,6-diazaocta-3,5-diene-1,8-dithiolatonickel(II), [NiL'], with [Mn(CO)$_5$Br] resulted in the substitution product [(NiL')Mn(CO)$_3$Br]. These complexes were characterized by i.r. and electronic spectra and magnetic and cyclic voltammetry measurements. Chemical and physical data indicate that the metallo-ligand moieties of these bimetallic complexes bond weakly to the Mn(CO)$_3$Br moiety.

Metal complexes can function as chelating agents if the co-ordinated atoms on the ligand have non-bonding electron pairs which are available for bonding to another metal ion. Both co-ordinated thio and phenyloxy groups have non-bonding electron pairs which are sufficiently nucleophilic to form bridges with various metal ions.[1–4] As a result molecules such as bis(2-aminoethylthio)nickel(II) and *N,N'*-ethylenebis(salicylideneiminate)–metal {[M(salen)] M = Cu or Ni} complexes can function as bidentate chelating agents (metallo-ligands) and form bi- and tri-nuclear complexes of the types (**I**) (M = Ni, Pd, Cd, Cu, or Hg) and (**II**) (M = Ni or Cu; M' = Cu, Fe, or Mn) shown below.[1–4]


(I)

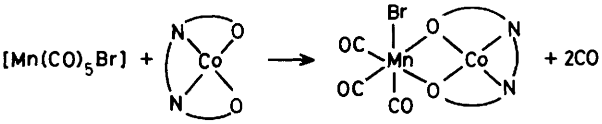

(II)

Most of the polymetallic complexes of this type contain metal ions in the +2 or +3 oxidation states. However, Lukehart and Zeile[5] have prepared related complexes by reacting metallo-acetylacetonate complexes which contain a soft low-oxidation state metal ion with hard metal ions such as aluminium(III). Hobday and Smith[6] approached this problem in a different fashion, reacting a traditional metal complex, [Ni(salen)], with a variety of low-oxidation state organometallic complexes. This bidentate metallo-ligand replaced two carbonyl groups on the organometallic complex.

We have carried out reactions of other bidentate metallo-ligands, ML, having terminal oxygen or sulphur atoms with [Mn(CO)$_5$Br], to form complexes of the type [(ML)Mn(CO)$_3$Br]. The work reported in this paper focuses primarily on manganese(I) complexes having metallo-ligands containing cobalt(II) and terminal oxygen groups. We note in passing that manganese–carbonyl compounds containing two or more ligands which are oxygen donors are rare.

Results and Discussion

Reactions of [Mn(CO)$_5$Br] with a variety of tetradentate Schiff-base cobalt(II) complexes were carried out in refluxing CH$_2$Cl$_2$ for varying lengths of time with displacement of two carbonyl groups by the metallo-ligand occurring; equation (1). The


(1)

products, insoluble orange-red solids, precipitated as the reaction proceeded. After the reaction mixture was allowed to cool, the products could be collected by filtration. The products, [{Co(salen)}Mn(CO)$_3$Br], [{Co(salphen)}Mn(CO)$_3$Br], and [{Co(salchd)}Mn(CO)$_3$Br] (salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate), salchd = *N,N'*-cyclohexane-1,2-diylbis(salicylideneiminate)] obtained in this way were analytically pure, which was fortunate because the lack of solubility of these species in most solvents prevented further purification *via* crystallization. These bimetallic complexes do not dissolve in organic solvents at room temperature, while forcing conditions caused decomposition to give non-carbonyl containing products.

Attempted syntheses of these complexes in solvents other than dichloromethane were unsatisfactory. Using benzene, the reaction of [Co(salen)] and [Mn(CO)$_5$Br] gave an impure sample of [{Co(salen)}Mn(CO)$_3$Br], identified by ν(CO) absorptions. Use of xylene (isomeric mixture) as a solvent (at reflux) results in insoluble species which do not contain carbonyl groups.

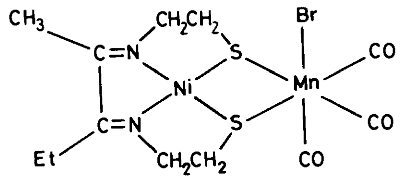
High temperatures cause the decomposition of products and/or starting materials, presumably by causing cleavage of either metal–carbonyl or metallo-ligand–metal bonds. The carbonyl groups in the complexes appear to be easily lost as illustrated by the attempted synthesis in refluxing xylene. The oxygen donor atoms on the metallo-ligands are expected to have fairly low basicity and thus would form weak bonds to the manganese(I). Therefore, prolonged heating should also be expected to cause dissociation of the metallo-ligand from the heterobimetallic complex. These heterobimetallic complexes

---

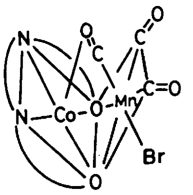
† *Non-S.I. unit employed:* B.M. = 9.27×10^{-24} J T^{-1}.

Table. Physical properties of bimetallic complexes

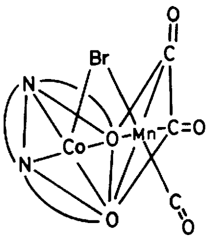
Complex	Colour	ν(CO)/cm^{-1}				$\mu_{\text{eff.}}$/B.M.
[{Zn(salen)}Mn(CO)$_3$Br]	Yellow	2 021		1 926	1 909	
[{Cu(salen)}Mn(CO)$_3$Br]	Brown	2 026		1 924	1 898	
[{Ni(salen)}Mn(CO)$_3$Br]	Orange	2 029	1 940		1 900	
[{Co(salen)}Mn(CO)$_3$Br]	Orange-brown	2 030	1 948	1 934	1 927	3.19
[{Pd(salen)}Mn(CO)$_3$Br]	Greenish yellow	2 020	1 945	1 930		
[{Sn(salen)}Mn(CO)$_3$Br]	Golden yellow	2 020		1 930	1 910	
[{Co(salphen)}Mn(CO)$_3$Br]	Purple	2 033	1 950	1 931	1 905	3.27
[{Co(salchd)}Mn(CO)$_3$Br]	Orange	2 033	1 948		1 903	3.34
[Mn(CO)$_5$Br]	Yellow	2 064	2 017			
[(NiL')Mn(CO)$_3$Br]	Black	2 007		1 921	1 899	1.88
[(NiL')Mn(CO)$_3$Br] in CH$_2$Cl$_2$		2 019		1 930	1 913	



(III)



(IV)



(V)

decompose on exposure to light with loss of carbonyl groups to give uncharacterized (decomposition) products. This was observed by irradiating a KBr pellet containing the heterobimetallic complex with visible and/or u.v. light and observing the decrease in ν(CO) bands in the i.r. spectra as a function of time.

We have also prepared heterobimetallic complexes of the type [{M(salen)}Mn(CO)$_3$Br], where M = Fe, Ni, Cu, Zn, Pd, or Sn, using similar procedures. Although we have either marginal or no analytical data on most of these complexes, we are reasonably certain of their formulation based on the similarity of the i.r. spectra [ν(CO) values] with spectra of the known complexes described above. It is presumed that the samples of these compounds are obtained in varying degrees of purity. The impurities would not be expected to cause perturbations in the i.r. spectra. For example, in [(CoL)Mn(CO)$_3$Br] (L = salen, salphen, or salchd) only a trivial difference between the i.r. spectra of the impure samples compared to the analytically pure sample were observed.

The reaction of [Mn(CO)$_5$Br] with 4-ethyl-5-methyl-3,6-diazaocta-3,5-diene-1,8-dithiolatonickel(II), [NiL'],[7] gave a bimetallic complex with the bridging sulphur group. Availability of [(NiL')Mn(CO)$_3$Br] (**III**), has allowed a comparison to be made between manganese(I) complexes which contain metallo-ligands with oxygen donors and with sulphur donors.*

These bimetallic complexes, except [(NiL')Mn(CO)$_3$Br], are insoluble in most organic solvents tested. Several of them appear to dissolve in donor solvents like dimethylformamide (dmf) and dimethyl sulphoxide (dmso) but the bimetallic complexes cannot then be recovered from solution. The solids recovered from solution have no ν(CO) stretching frequencies. The solid bimetallic complexes, [(ML)Mn(CO)$_3$Br] (L = salen, salphen, or salchd) are moderately air stable but will decompose even under an inert atmosphere with time. In contrast, [(NiL')Mn(CO)$_3$Br] is soluble in CH$_2$Cl$_2$ and appears to be more stable in solution and the solid state than the cobalt–manganese complexes.

Three ν(CO) absorptions for the complex [{Co(salchd)}-Mn(CO)$_3$Br] are consistent with three carbonyl groups (Table). Facial stereochemistry for these complexes is suggested by the approximately equal intensity of these three bands.[8] This is also true for [(NiL')Mn(CO)$_3$Br] which has three ν(CO) peaks of approximately equal intensity in the solid state and in CH$_2$Cl$_2$. In contrast, [{Co(salen)}Mn(CO)$_3$Br] and [{Co(salphen)}-Mn(CO)$_3$Br] have four ν(CO) bands. This may be due to the presence of both *mer* and *fac* isomers. An alternative is geometric isomers which have either an axial carbonyl group or a bromide bridging the two metal ions [(**IV**) and (**V**)].

The heterobimetallic complexes synthesized by Hobday and Smith[6] exhibit unusually low ν(CO) values: [{Ni(salen)}-Mo(CO)$_4$], 1 910, 1 798, 1 696, and 1 665 cm^{-1}; [{Ni(salen)}-W(CO)$_4$], 1 899, 1 790, 1 667, and 1 630 cm^{-1}, which the authors suggest are due to [Ni(salen)] being a strong electron donor. However, the oxygen atoms of ethers do not typically have such an extreme effect on ν(CO), nor in fact do any other ligands; the lowest frequency absorptions in [MoY(CO)$_4$] (Y represents any two donor atoms) species occur with ligands such as ethylenediamine (en) {[Mo(en)(CO)$_4$] which has ν(CO) bands at 2 015, 1 890, 1 864, and 1 818 cm^{-1}}.[9] Another possible explanation for these low values is that one carbonyl group is functioning as a four-electron donor, bridging the two metal ions, (**IV**). A carbonyl group with a similar mode of co-ordination is found in [Mn$_2$(CO)$_5$(dppm)$_2$] [dppm = bis(diphenylphosphino)methane] and it has a ν(CO) of 1 645 cm^{-1},[10] which is near the values reported for these heterobimetallic complexes. The co-ordination of CO to nickel(II) would also accord with the tendency of this metal to form five- and six-co-ordinate complexes.

One of the objectives of this research was to determine whether the low ν(CO) values result from the strong electron-donor ability of the metallo-ligand, or if a carbonyl group bridges the metals as a four-electron donor. To determine whether the oxygen atoms on a metallo-ligand can function as strong electron donors, we have compared the average ν(CO) of

---

* Unfortunately, a cobalt(II) metallo-ligand containing a tetradentate ligand with terminal sulphur atoms which is also soluble in organic solvents could not be found. This necessitates comparison here of metallo-ligand complexes of different metals.

a large series of [MnY(CO)$_3$Br] complexes, where Y represents any two donor atoms. Orgel* has suggested that the average ν(CO) stretching frequency for similar compounds is the most effective index when comparing bonding properties of ligands. The average ν(CO) value for a series of [MnY(CO)$_3$Br] compounds where the ligand contains phosphorus donor atoms is approximately 1 970 cm^{-1}, for a diamine it is 1 966 cm^{-1}, and for sulphide the average is 1 975 cm^{-1}.[11—14] The average ν(CO) value for complexes of the type [(ML)Mn(CO)$_3$Br] where ML is a metallo-ligand containing oxygen donor atoms is approximately 1 960 cm^{-1}. This is a relatively low average ν(CO) but not an unusually low value for hard donor atoms.

All three cobalt—manganese complexes have approximately the same average ν(CO), 1 960 cm^{-1}, 1 955 cm^{-1}, and 1 961 cm^{-1}. Therefore, it can be concluded that the chelating agent, L, in the metallo-ligand has only a small influence on the bonding of these complexes. The nature of the metal inside the metallo-ligand also does not affect the average ν(CO) to any great degree. However, it appears that the salen complexes of transition-metal ions to the right side of the Periodic Table [copper(II) or zinc(II)] have average ν(CO) values at slightly lower frequencies (1 949 and 1 952 cm^{-1} respectively) than the salen complexes of the other metal ions such as cobalt(II) and nickel(II) (1 960 and 1 956 cm^{-1} respectively). The oxygen atoms on the metallo-ligands containing cobalt and nickel may be poorer donors to Mn^{I} than the metallo-ligands containing copper and zinc because the latter metal ions generally form weaker ligand to metal bonds. The weaker the metal to oxygen bond, the more nucleophilic will be the co-ordinated oxygen and as a result the ligand will be a better donor. As a consequence of the better donor ability, more π bonding should occur between Mn^{I} and the carbonyl groups.

Comparison of the average ν(CO) for [(NiL′)Mn(CO)$_3$Br] with [{Ni(salen)}Mn(CO)$_3$Br] should reflect the difference between an oxygen and a sulphur donor. The average ν(CO) for [(NiL′)Mn(CO)$_3$Br] is 1 942 cm^{-1} while for [{Ni(salen)}Mn(CO)$_3$Br] the value is 1 956 cm^{-1}. The lower value for the sulphur species suggests that the co-ordinated sulphur is a slightly better donor than the co-ordinated oxygen.

It seems unlikely that the low average ν(CO) for all the heterobimetallic complexes prepared in this study are the result of a bridging carbonyl group. There are three ν(CO) bands in the range 2 030—1 905 cm^{-1}. There are no strong bands between 1 905 and 1 625 cm^{-1}; between 1 625 and 1 595 cm^{-1}, there are several bands, but this is the range in which the co-ordinated ν(C=N) bands are expected to occur. Since the maximum of three ν(CO) bands expected for three carbonyl groups bonded to a metal ion have been identified it is likely that none of the bands in the range 1 625—1 595 cm^{-1} is due to a bridging carbonyl. However, this does not exclude the possibility of a bridging bromide, (**V**).

The [(CoL)Mn(CO)$_3$Br] complexes have slightly higher magnetic moments than the metallo-ligand, CoL. The magnetic moments of [Co(salen)], [Co(salphen)], and [Co(salchd)] are 3.27, 2.80, and 2.61 B.M. respectively while the magnetic moments of [{Co(salen)}Mn(CO)$_3$Br], [{Co(salphen)}Mn(CO)$_3$Br], and [{Co(salchd)}Mn(CO)$_3$Br] are 3.19, 3.27, and 3.34 B.M. respectively. A plausible explanation is bonding of the phenyloxy oxygens to a Mn(CO)$_3$Br moiety slightly weakens the ligand-field strength around cobalt(II), generating an intermediate field strength between high spin and low spin. The higher magnetic moment of [(NiL′)Mn(CO)$_3$Br] compared to [NiL′] can also be explained in the same manner. An alternative explanation for the higher magnetic moments of the bimetallic complexes is that the steric requirements of these metallo-ligands cause distortion of one of the two metal ions upon co-ordination of the metallo-ligand.[15] If the cobalt(II) or nickel(II) in the bimetallic complex is distorted from a planar geometry towards a tetrahedral geometry then the magnetic moments of these metal ions should increase. These theories could be resolved with crystal structures of these complexes. Unfortunately, crystals could not be grown because of the instability of the compounds in solution.

Cyclic voltammograms (c.v.s) of the metallo-ligands and heterobimetallic complexes of these metallo-ligands are almost identical in dmf at room temperature. These data are in accord with our assumption that the heterobimetallic complexes have decomposed in dmf and the c.v. is only detecting the metallo-ligand in solution.

The electronic spectra of these complexes taken in dmf change with time, suggesting that they are reacting with solvent. However, the peak maxima for the metallo-ligand (CoL) in dmf and the [(CoL)Mn(CO)$_3$Br] complexes in dmf are similar. For example, the [Co(salen)] has a band at 25.3 × 10^3 cm^{-1} while the mixture of [{Co(salen)}Mn(CO)$_3$Br] and decomposition products exhibits a band at 25.97 × 10^3 cm^{-1}. Since it is likely that only the chromophore around cobalt(II) is responsible for the bands at 25.97 × 10^3 cm^{-1}, this suggests a small perturbation by the manganese moiety on the field strength around cobalt(II). The electronic spectra of the metallo-ligand and heterobimetallic complex in dmso are also similar.

Attempts to obtain mass spectral data for [(CoL)Mn(CO)$_3$Br] were made but the highest mass peak to be observed was that for the metallo-ligand. Neither a parent ion peak nor peaks for [(CoL)Mn(CO)$_2$Br]$^+$ or [(CoL)Mn(CO)Br]$^+$ were seen. Presumably this reflects decomposition of the sample in the inlet system.

Experimental

Techniques.—All air-sensitive reactions were performed under nitrogen or argon using Schlenk-line techniques. The systems were evacuated and back-filled three times with nitrogen. Dichloromethane was obtained by distillation from phosphorus pentoxide. Dimethylformamide was dried by refluxing over calcium hydride. Light-sensitive reactions were carried out in glassware covered with aluminium foil. Some transfers were made in a nitrogen filled glove-box. Synthesis of [M(salen)],[16] [M(salphen)],[17,18] and [M(salchd)][19] were carried out by a known procedure.

Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Syntheses.—[{Co(salen)}Mn(CO)$_3$Br]. [Co(salen)] (0.55 g) and [Mn(CO)$_5$Br] (0.65 g) were placed in the reaction vessel equipped with a reflux condensor. The glassware system was covered with aluminum foil, evacuated, and back-filled with nitrogen three times. Dichloromethane (60 cm^3) was added to the solid mixture and the resulting solution was refluxed for 4 h. An orange-red solid precipitated and this was isolated by filtration under nitrogen. The solid was washed with CH$_2$Cl$_2$ and dried by nitrogen flow before being placed in a vacuum desiccator over P$_2$O$_5$ for 2 d. Unsuccessful attempts were made to recrystallize this compound from dmf and light petroleum. Evolution of gas along with the inability to isolate the compound suggested its decomposition (Found: C, 41.45; H, 2.85; Co, 10.90; Mn, 9.80. Calc. for C$_{19}$H$_{14}$BrCoMnN$_2$O$_5$: C, 41.95; H, 2.65; Co, 10.85; Mn, 10.10%).

[{Co(salphen)}Mn(CO)$_3$Br]. [Co(salphen)][16,17] (0.746 g) and [Mn(CO)$_5$Br] (0.55 g) were allowed to react under conditions analogous to those used above (Found: C, 46.65; H, 2.50; Co, 9.75; Mn, 9.25. Calc. for C$_{23}$H$_{14}$BrCoMnN$_2$O$_5$: C, 46.65; H, 2.40; Co, 9.95; Mn, 9.25%).

[{Co(salchd)}Mn(CO)$_3$Br]. [Co(salchd)][19] (0.76 g) and

---

* Personal communication as reported in M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

[$Mn(CO)_5Br$] (0.55 g) were allowed to react for 5 h under conditions analogous to those used above (Found: C, 46.30; H, 3.50; Co, 9.85; Mn, 8.50. Calc. for $C_{23}H_{18}BrCoMnN_2O_5$: C, 46.15; H, 3.40; Co, 9.85; Mn, 9.20%).

[{Ni(salen)}$Mn(CO)_3Br$]. [Ni(salen)] (0.776 g) and [$Mn(CO)_5Br$] (0.662 g) were allowed to react for 3 h under conditions analogous to those used in the synthesis of [{Co(salen)}$Mn(CO)_3Br$].

The product was also synthesized using the method of Hobday and Smith[6] (benzene as solvent, reaction time 1 h).

[{Cu(salen)}$Mn(CO)_3Br$]. [Cu(salen)][20] (0.66 g) and [$Mn(CO)_5Br$] (0.55 g) were allowed to react for 4 h under conditions analogous to those used in the synthesis of [{Co(salen)}$Mn(CO)_3Br$] (Found: C, 39.00; H, 3.05; Cu, 10.90. Calc. for $C_{19}H_{14}BrCuMnN_2O_5$: C, 41.95; H, 2.55; Cu, 10.85%).

[{M(salen)}$Mn(CO)_3Br$] (M = Pd, Sn, *or* Zn). [M(salen)], where M = Pd, Sn, or Zn, and [$Mn(CO)_5Br$] were allowed to react for 3 h in a 1:1 mole ratio under conditions analogous to those used in the synthesis of [{Co(salen)}$Mn(CO)_3Br$]. The solids obtained gave poor analyses although i.r. data indicated the presence of the product (Table).

[(NiL′)$Mn(CO)_3Br$]. This synthesis was carried out in a 150-cm^3 two-necked flask fitted with a reflux condenser, magnetic stirrer, and argon inlet. The flask was charged with [NiL′] (0.55 g, 0.02 mol), [$Mn(CO)_5Br$] (0.55 g, 0.002 mol), toluene (50 cm^3), and CH_2Cl_2 (50 cm^3). The solution was refluxed for 30 min. The colour of the reactants changed from purple to dark black. The reaction mixture was cooled to room temperature, and then filtered under argon. The filtrate was separated by column chromatography (20 × 250 mm) on silica gel. Dichloromethane was passed through the column until no more yellow eluted material was observed. Then a mixture of CH_2Cl_2–MeOH (3:1) was used as the second eluting solvent. The desired black compound was collected from this second solvent mixture and evaporated to dryness at 40 °C under vacuum, and dried in vacuum over P_2O_5 over 24 h (Found: C, 27.85; H, 3.25; Ni, 11.80. Calc. for $C_{12}H_{16}BrMnN_2NiO_3S_2$: C, 29.15; H, 3.25; Ni, 11.90%).

Reaction of [$Mn(CO)_5Br$] *and* [Co(salen)] *in Xylene*.—The procedure used was a modification of that employed by Hobday and Smith[6] for the reaction of [Ni(salen)] with [$Mo(CO)_6$]. [Co(salen)] (0.65 g, 2 mmol) was dissolved in xylene (700 cm^3) (isomeric mixture) under N_2 to produce a dark purple solution. [$Mn(CO)_5Br$] (0.632 g, 2.29 mmol) was added as a solid. The resulting solution was heated to reflux temperature, and the reaction followed by i.r. using samples of the solution removed in a N_2-purged syringe.

The original dark solution turned orange after 30 min, and a precipitate formed quickly after the colour change. Peaks at 2 115, 2 060, and 2 020 cm^{-1} at the initiation of the reaction decreased during the reflux procedure, and reflux was ended when the strongest of these peaks had totally disappeared. The solution was allowed to cool to room temperature, and then cooled further in an ice-bath. The bright orange solid was filtered off and dried under a N_2 flow.

The solubility of the product was tested in a variety of solvents. It was slightly soluble in tetrahydrofuran, acetone, xylene, dichloromethane, and carbon tetrachloride, and soluble in toluene, acetonitrile, and dmf. Maximum solubility was in dmf. To remove any unreacted [$Mn(CO)_5Br$] the product was placed in a vacuum sublimation apparatus, and heated at 170 °C using an oil-bath for 3 h. No visible sublimation occurred, however the i.r. spectrum of the orange solid after this process showed no ν(CO) peaks.

The filtrate from the [$Mn(CO)_5Br$] and [Co(salen)] reaction was placed in the freezer for 1 week and a second orange solid was isolated from the filtrate and dried under N_2. An i.r. spectrum of this substance was very similar to that of the first solid isolated with the addition of a peak at 1 980 cm^{-1}. I.r. spectrum: 1 980s, 1 595s, 1 530, 1 440, 1 325s, 1 280s, 885, 740s, and 700s cm^{-1} (KBr wafer).

Light Sensitivity of [{Co(salen)}$Mn(CO)_3Br$].—Three solid pellets were made of [{Co(salen)}$Mn(CO)_3Br$] in KBr. The first was kept in darkness for 1 h, the second was kept in room light for 1 h, and the third was exposed to a mercury vapour light for 1 h. The i.r. spectrum of the pellet kept in the dark had the strongest carbonyl absorption while the pellet which was exposed to Hg vapour light had the weakest absorption.

Physical Measurements.—Spectra were obtained on a Cary 219 u.v. spectrometer. All solution spectra were performed under an atmosphere of argon in quartz cells. Infrared spectra were obtained on either a Nicolet 20 DX FTIR or Perkin-Elmer 337 spectrophotometer. Solid samples were taken as KBr pellets. Air-sensitive solution samples were handled as follows. A syringe was purged with argon three times and then used to sample the reaction mixture through a rubber septum. This sample was immediately transferred to an i.r. cell previously purged with argon. The reactions were monitored by observing decreases in intensities of the carbonyl stretching frequencies of starting materials and increases in intensity of the new carbonyl stretching frequencies due to product. Magnetic measurements were taken on a Cahn electrobalance under vacuum at a temperature of 297 K. The Faraday method was used, with $Hg[Co(SCN)_4]$ as a standard. Cyclic voltammetric measurements were made with a Princeton Applied Research model 173 three-electrode potentiostat and a model 175 Universal Programmer. The voltammograms were recorded on a Houston Instrument model 2000 Omnigraphic *X-Y* recorder. The working electrode was a platinum wire sealed into a glass tube. The reference electrode was a saturated calomel electrode. The experiments were carried out in a glass IBM voltammetric cell. The Pt electrodes were pretreated before each experiment by anodizing and cathodizing between +2.5 V and −2.0 V in 0.1 mol dm^{-3} H_2SO_4 acid solution for 1 h. Purity of acetonitrile, supporting electrolyte and electrodes used were checked by scanning the supporting electrolyte solution in the solvent before adding the sample solution through the potential range of interest until a reproducible flat cyclic voltammogram was obtained. Purified argon was flushed through the cell during use. Mass spectra were measured using a Kratos MS50 instrument with a fast-atom bombardment ionization source at Iowa State University.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bowling Green State University Faculty Research Committee for support of this research. We also thank Professor Angelici of Iowa State University for running the mass spectra of the complexes.

References

1 D. H. Busch and D. C. Jicha, *Inorg. Chem.*, 1962, **1**, 884.
2 R. E. DeSimone, T. Ontko, L. Wardman, and E. Blinn, *Inorg. Chem.*, 1975, **14**, 1313.
3 E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 391.
4 E. L. Blinn, P. Bulter, M. M. Chapman, and S. Harris, *Inorg. Chim. Acta*, 1977, **24**, 139.
5 C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1976, **98**, 2365.
6 M. D. Hobday and T. D. Smith, *J. Chem. Soc. A*, 1971, 3424.
7 M. C. Thompson and D. B. Busch, *J. Am. Chem. Soc.*, 1964, **86**, 213.
8 R. J. Angelici, F. Basolo, and A. J. Poë, *J. Am. Chem. Soc.*, 1963, **85**, 2215.
9 F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

10 R. Colton, C. J. Commons, and B. F. Hoskins, *J. Chem. Soc., Chem. Commun.*, 1975, 363.
11 R. H. Reiman and E. Singleton, *J. Organomet. Chem.*, 1972, **38**, 113.
12 N. J. Coville and I. S. Butler, *J. Organomet. Chem.*, 1973, **57**, 355.
13 R. J. Angelici, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2627.
14 A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4715.
15 S. L. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805.
16 S. L. Kessle, R. M. Emberson, D. S. Bebrunner, and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 1170.
17 L. S. Marzilli, R. A. Marzilli, and J. Halpern, *J. Am. Chem. Soc.*, 1971, **93**, 1374.
18 B. O. West, *J. Chem. Soc.*, 1954, 395.
19 R. M. McAllister and J. H. Weber, *J. Organomet. Chem.*, 1974, **77**, 91.
20 C. S. Marvel, S. A. Aspey, and E. A. Dudley, *J. Am. Chem. Soc.*, 1956, **78**, 4905.

Received 14*th January* 1987; *Paper* 7/072