

## NOTE

### DINUCLEAR PSEUDOHALOGENOCARBONYL ANIONS OF MANGANESE(I)

MICHAEL F. FARONA, LOWELL M. FRAZEE AND NOEL J. BREMER  
*Department of Chemistry, The University of Akron, Akron, Ohio 44304 (U.S.A.)*  
(Received March 17th, 1969)

Recent interest in the chemistry of dinuclear carbonyl anions of the group VIb hexacarbonyls containing bridged halide and pseudohalide groups<sup>1</sup> prompts us to report the results of our investigation on the manganese carbonyl system. Whereas the structures of the anionic chromium group carbonyl derivatives of halides and pseudohalides appear to be totally analogous, our synthetic approach reveals the above fact not to hold in the manganese carbonyl system. Not only are the structures derived from the pseudohalides different from those of the halides, but anionic complexes derived from thiocyanate, selenocyanate and cyanide are different from each other.

The reactions of potassium halides with  $\text{Mn}(\text{CO})_5\text{Cl}$  in methanol have been shown to yield the neutral dihalogenooctacarbonyldimanganese complexes,  $\text{Mn}_2(\text{CO})_8\text{X}_2$ .<sup>2</sup> In the reaction of KCN with  $\text{Mn}(\text{CO})_5\text{Cl}$ , only the mononuclear anion,  $\text{Mn}(\text{CO})_4(\text{CN})_2^-$  was obtained; cyanide ion shows no tendency to bridge in this system.

The reactions of  $\text{Mn}(\text{CO})_5\text{Cl}$  with selenocyanate or thiocyanate ion yield the dinuclear carbonyl anions  $[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$ ,  $[\text{Mn}_2(\text{CO})_6(\text{CNSe})_4]^{2-}$ , and  $[\text{Mn}_2(\text{CO})_6(\text{CNS})_4]^{2-}$ , respectively. The complexes  $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]$  and  $[(\text{CH}_3)_4\text{N}]_2[\text{Mn}_2(\text{CO})_6(\text{CNS})_4]$  are 2/1 electrolytes in nitromethane

TABLE I  
INFRARED STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE COMPLEXES<sup>a</sup>

Compound	CN <sup>b</sup>	CO <sup>b</sup>	CSe or CS <sup>c</sup>
$[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$	2119 m, 2091 m	2035 (sh), 2023 s, 1944 (sh), 1929 s, 1918 (sh)	634 m 616 w
$[\text{Mn}_2(\text{CO})_6(\text{CNSe})_4]^{2-}$	2105 m, 2083 m	2020 s(b), 1931 s(b)	634 m 616 w
$[\text{Mn}_2(\text{CO})_6(\text{CNS})_4]^{2-}$	2160 m, 2115 m-s	2045 (sh), 2037 s, 1944 (sh), 1936 s, 1929 (sh)	803 m 765 m

<sup>a</sup> Recorded on a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer. Abbreviations: s, strong; m, medium; w, weak; (sh), shoulder; (b), broad. <sup>b</sup> Acetone solution. <sup>c</sup> Nujol mull between KBr discs.

solution (mol. cond. 162 and 171  $\Omega^{-1}$ , respectively), which is consistent with their assigned ionic structures. The IR spectra of the selenocyanate and thiocyanate derivatives are shown in Table 1.

The similarity of the IR spectra in the carbonyl stretching region with respect to number and relative intensities of the bands suggests that the structures of the three pseudohalide derivatives are analogous. It should be noted that the shoulders appearing on the main carbonyl bands in the spectra of the mixed chloro-selenocyanato and thiocyanato derivatives are not resolved in the spectrum of  $[\text{Mn}_2(\text{CO})_6(\text{CNSe})_4]^{2-}$ , but the carbonyl bands for the latter compound are generally broad, and presumably are not single species.

With regard to structures of these anions, the mixed chloro-selenocyanato complex exhibits CN-stretching bands at 2119 and 2091  $\text{cm}^{-1}$ , as well as CSe absorptions at 634 and 616  $\text{cm}^{-1}$ ; these are in accord with terminal N-bonded selenocyanates. The CSe-stretching frequencies seem to be particularly diagnostic in determining the mode of bonding (N or Se) of coordinated selenocyanates. Those of N-bonded selenocyanates have been observed in the 600–700  $\text{cm}^{-1}$  region, whereas Se-bonded derivatives exhibit CSe stretches at distinctly lower frequencies, namely, in the 500–530  $\text{cm}^{-1}$  region<sup>3-5</sup>. It is concluded, therefore, that in the mixed halide-pseudohalide derivative,  $[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$  the chlorides are the bridging groups and the selenocyanates are terminal and N-bonded.

The fact that five CO bands are observed is in accord with the *cis*- $C_{2v}$  rather than the *trans*- $C_{2h}$  structure. For the former structure, five CO-stretching modes are expected to be active ( $2A_1 + 2B_1 + B_2$ ) whereas for the latter structure, only three active CO stretches are predicted ( $A_u + 2B_u$ ). The structure is similar to that shown in Fig. 1 for  $[\text{Mn}_2(\text{CO})_6(\text{SCN})_4]^{2-}$ , except for bridging chloro groups.

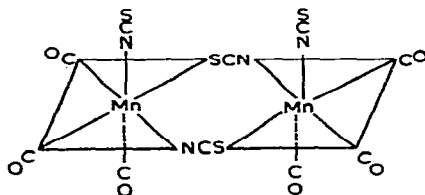


Fig. 1. Proposed structure for  $[\text{Mn}_2(\text{CO})_6(\text{SCN})_4]^{2-}$

The IR spectrum of  $[\text{Mn}_2(\text{CO})_6(\text{SCN})_4]^{2-}$  in the CN-, CO-, and CS-stretching regions lend support to the structure shown in Fig. 1. The CN-stretching frequencies at 2160 and 2115  $\text{cm}^{-1}$  are due to the bridging and terminal thiocyanates, respectively. Because of the asymmetrical nature of the bridging thiocyanate groups, this molecule cannot rigorously belong to the point group  $C_{2v}$ ; however, because of the very close similarity in the pattern of the CO-stretching bands with that of  $[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$ , which is rigorously  $C_{2v}$ , the *cis* rather than the *trans* structure seems more likely.

The CS-stretching band at 803  $\text{cm}^{-1}$  is indicative of an N-bonded thiocyanate, since N-bonded thiocyanates exhibit CS absorptions in the 780–860  $\text{cm}^{-1}$  region, and S-bonded derivatives absorb in the 680–720  $\text{cm}^{-1}$  region<sup>6</sup>. The band appearing at 765  $\text{cm}^{-1}$  in the spectrum of this complex is assigned to the CS stretch of the bridging thiocyanate. Although there is a general lack of information on CS absorption of

bridging thiocyanates, it appears at about the same frequency as that of  $[\text{M}_2(\text{CO})_{10}\text{-NCS}]^-$  ( $\text{M}=\text{Cr}, \text{W}$ ), in which the thiocyanato groups were shown to be bridging, rather than terminal<sup>1</sup>.

It is of interest to note that the fact that N-bonding is observed for the terminal thiocyanate groups is in accord with the change in the bonding mode from S to N observed previously for thiocyanatocarbonyl complexes, where less demand for  $\pi$ -electron density by the carbonyl groups favored N-bonding<sup>7,8</sup>.

The tetraselenocyanato complex is apparently analogous in structure to that of the thiocyanato derivative in that the complex contains both bridging and N-bonded terminal selenocyanato groups. Although its spectrum in the carbonyl stretching region is somewhat different from those of the other anions studied, the 400–800  $\text{cm}^{-1}$  region is virtually identical with that of  $[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$ . New bands due to  $\nu(\text{CSe})$  of the bridging group are not observed. This is rather surprising in view of the spectrum of the chloroselenocyanato derivative, where symmetric and asymmetric CN and CSe stretches are assigned. However, there is a definite element of uncertainty in assigning the bands in the carbonyl region because of the large number of CN- and CO-stretching modes which are active. Nonetheless, since the CS stretch arising from the bridging thiocyanate group is observed for  $[\text{Mn}_2(\text{CO})_6(\text{CNS})_4]^{2-}$ , it is possible that the corresponding CSe stretch for  $[\text{Mn}_2(\text{CO})_6(\text{CNSe})_4]^{2-}$  may be too weak to be apparent, or it may be covered by another band in that region.

It is interesting to compare the differences in structures of the thiocyanate complexes in this work with those presented in the accompanying paper by Treichel and Douglas<sup>9</sup>. The major difference in synthetic procedure is in the relative amounts of KSCN used in the reaction with manganese pentacarbonyl halides. Since less harsh conditions were employed in this study, it is possible that the trisubstituted intermediate,  $[\text{Mn}(\text{CO})_3(\text{NCS})_3]^{2-}$ , is formed which further reacts to give the bridged compounds. Apparently, this does not occur where an insufficient amount of  $\text{SCN}^-$  is present.

## EXPERIMENTAL

### Starting materials

All reactions were carried out in reagent grade methanol under a dry nitrogen atmosphere. Reagent grade KSCN was used as obtained. Tetraphenylarsonium selenocyanate was prepared by mixing equimolar aqueous solutions of  $(\text{C}_6\text{H}_5)_4\text{AsCl}$  and  $\text{KSeCN}$ . The white precipitate was collected and dried in a vacuum desiccator. Manganese pentacarbonyl chloride,  $\text{Mn}(\text{CO})_5\text{Cl}$ , was prepared as described elsewhere<sup>10</sup>.

### Preparation of $(\text{C}_6\text{H}_5)_4\text{As}[\text{Mn}(\text{CO})_4(\text{CN})_2]$

The reaction was carried out between  $\text{Mn}(\text{CO})_5\text{Cl}$  and  $\text{KCN}$  in a manner similar to that described elsewhere for the halides<sup>2</sup>. After removal of the solvent, the residue was taken up in water and the product precipitated upon addition of  $(\text{C}_6\text{H}_5)_4\text{AsCl}$  solution. The product was identified as the *cis*-dicyanotetracarbonylmanganate,  $(\text{C}_6\text{H}_5)_4\text{As}[\text{Mn}(\text{CO})_4(\text{CN})_2]$ , by comparing its IR spectrum with that reported by Angelici<sup>11</sup>.

*Preparation of*  $[(CH_3)_4N]_2[Mn_2(CO)_6(SCN)_4]$

Mn(CO)<sub>5</sub>Cl (0.10 g, 0.434 mmole), KSCN (0.25 g, 2.58 mmoles), and 10 ml of methanol were stirred and heated at 50° for one h. The solvent was removed (0.1 mm, 25°) and the solid residue was dissolved in 10 ml of water. A yellow solid precipitated upon addition of an aqueous solution of (CH<sub>3</sub>)<sub>4</sub>NCl. The product was collected on a filter, washed twice with 20 ml of H<sub>2</sub>O, and dried in a vacuum desiccator. The yield was 0.098 g, or 69% of theory. (Found: C, 33.20; H, 3.80; Mn, 16.7; N, 12.71; S, 19.65.  $[(CH_3)_4N][Mn_2(CO)_6(SCN)_4]$  calcd.: C, 32.80; H, 3.68; Mn, 16.69; N, 12.76; S, 19.48%.)

*Preparation of*  $[(C_6H_5)_4As]_2[Mn_2(CO)_6Cl_2(NCSe)_2]$

Mn(CO)<sub>5</sub>Cl (0.10 g, 0.434 mmole), (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsSeCN (0.205 g, 0.420 mmole) and 10 ml of methanol were stirred and heated at 50° for 30 min. The methanol was removed under vacuum and 3 ml of CHCl<sub>3</sub> was added, in which the carbonyl derivative is soluble. The chloroform solution was filtered, treated with 100 ml of petroleum ether, and cooled to 0°. The oil which separated was induced to crystallize to a fine yellow powder by scratching with a glass rod. The product was collected and dried in a stream of nitrogen. The yield was essentially quantitative. (Found: C, 49.86; H, 3.46; Cl, 5.76; N, 2.23.  $[(C_6H_5)_4As]_2[Mn_2(CO)_6Cl_2(NCSe)_2]$  calcd.: C, 50.72; H, 3.04; Cl, 5.35; N, 2.11%.)

*Preparation of*  $[(C_6H_5)_4As]_2[Mn_2(CO)_6(NCSe)_4]$

Synthesis of this complex was carried out in a manner analogous to that described above for the selenocyanato derivative, except that a 6:1 excess of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>-AsSeCN was employed. After removal of the methanol, the carbonyl complex was purified by recrystallization from ethanol/water. (Found: N, 3.82.  $[(C_6H_5)_4As]_2[Mn_2(CO)_6(NCSe)_4]$  calcd.: N, 3.82%.)

#### REFERENCES

- 1 J. K. RUFF, *Inorg. Chem.*, 8 (1969) 86; 7 (1968) 1821.
- 2 M. F. FARONA AND L. M. FRAZEE, *J. Inorg. Nucl. Chem.*, 29 (1967) 1814.
- 3 J. L. BURMEISTER AND L. E. WILLIAMS, *Inorg. Chem.*, 5 (1966) 1113.
- 4 D. FORSTER AND D. M. L. GOODGAME, *Inorg. Chem.*, 4 (1965) 1712.
- 5 A. SABATINI AND I. BERTINI, *Inorg. Chem.*, 4 (1965) 959.
- 6 A. TURCO AND C. PECILE, *Nature*, 191 (1961) 66.
- 7 M. F. FARONA AND A. WOJCICKI, *Inorg. Chem.*, 4 (1965) 1402.
- 8 A. WOJCICKI AND M. F. FARONA, *J. Inorg. Nucl. Chem.*, 26 (1964) 2289.
- 9 P. M. TREICHEL AND W. M. DOUGLAS, *J. Organometal. Chem.*, 19 (1969) 221.
- 10 E. W. ABEL AND G. WILKINSON, *J. Chem. Soc.*, (1959) 1501.
- 11 R. J. ANGELICI, *Inorg. Chem.*, 3 (1964) 1099.

*J. Organometal. Chem.*, 19 (1969) 225-228