Inorganica Chimica Acta

LETTER

Synthesis and characterization of MnFe[μ-(SC₆H₅)]₃(CO)₆, a heterobimetallic complex formed by self-assembly

M. Anton Walters and John C. Dewan

Department of Chemistry, New York University, New York, NY 10003 (U.S.A.)

As part of an effort to understand the inhibition of iron–sulfur enzymes by carbon monoxide (CO) binding we have been investigating the chemistry of CO uptake by synthetic iron–sulfur compounds [1]. Herein we report the synthesis and structure determination of the heterobimetallic compound $MnFe(\mu\text{-}SPh)_3(CO)_6$ (1) (Ph = C₆H₅).

Recently we showed that the linear trimetallic complex $Fe_3(SPh)_6(CO)_6$ (2) was formed by the uptake of CO by an Fe^{2+} precursor [1]. This complex belongs to a class of low spin d^6 carbonyl compounds [2] with thiolate bridging ligands and a C_3 principle axis; the other members being $[Mn_2(SR)_3(CO)_6]^-$ (3) [3–5] and $[Fe_2(SMe)_3(CO)_6]^+$ (4) [6]. The mixed metal complex $MnFe(\mu\text{-}SPh)_3(CO)_6$ (1) constitutes an addition to this class. Like 2 it is formed from simple starting materials in a reaction that involves the uptake of CO by Fe^{2+}. The reaction is of particular interest because it illustrates a simple route to the formation of mixed metal thiolate complexes.

Experimental

NaSPh was generated by reaction of Na (0.11 g, 4.92 mmol) in ethanol (30 ml), followed by the addition of PhSH (0.51 g, 4.64 mmol) under an atmosphere of nitrogen. $Mn(CO)_5Br$ (0.45 g, 1.64 mmol) was added directly to the NaSPh solution and stirred for 1 h under an atmosphere of CO. $FeBr_2$ (0.35 g, 1.64 mmol) was then added forming a dark reddish brown solution. The solution was stirred under an atmosphere of CO for 20 min. During this period very little of the $Mn(CO)_5Br$

(orange crystals) dissolved. The CO atmosphere of the flask was then exchanged for N_2 and the solution was stirred overnight during which time the $Mn(CO)_5Br$ crystals dissolved and a deep red solution resulted. The solvent was evaporated under vacuum to give small dark red crystals. The product was redissolved in THF (30 ml) and filtered to remove NaBr. This solution was evaporated to form a red oil. Heptane was added and the solution was left overnight. The heptane was then removed by evaporation leaving a hardened, moderately air stable, product which was then dislodged from the walls of the flask (yield: 0.65 g, 65%). *Anal.* Calc. for $C_{24}H_{15}FeMnS_3O_6$: C, 47.54; H, 2.49; Fe, 9.21; Mn, 9.06; S, 15.86. Found: C, 47.23; H, 2.69; Fe, 9.00; Mn, 8.74; S, 16.06%. In an alternative synthetic route $FeCl_2 \cdot 4H_2O$ was substituted for $FeBr_2$ (yield 15%).

Crystals of sufficient quality for X-ray crystallography were isolated by the evaporation of the solvent ethanol under vacuum. Data were collected at 23 °C on an Enraf-Nonius CAD4F-11 diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å). IR data were collected at 4 cm⁻¹ resolution with the use of a Nicolet 5DXB FTIR spectrometer purged with dry air. For this purpose samples were prepared as KBr pellets.

Results and discussion

X-ray crystallographic characterization of 1 reveals a structure having approximate overall C_3 symmetry (Fig. 1). Despite the dimensional similarity between the iron and manganese ends of the molecule, no disorder was detected in the X-ray structure. The Mn and Fe atoms were assigned based on M–S distances observed in similar structures reported in the literature [1, 4, 7]. The average Mn(I)–S distance in 1 is 2.38 Å as compared with the average Fe(II)–S distance of 2.33 Å (Table 1). The lack of an approximate mirror plane through the three thiolate sulfur atoms of 1 presumably accounts for the apparent lack of disorder that might have been expected between the two ends of the molecule. The assigned average iron–sulfur distance of 1 compares favorably with that observed in 2 where the average Fe(II)–S distance is 2.34 Å [1].

Solid 1 in a KBr matrix reveals carbonyl bands at 2089(s), 2043(s), 2031(m), 2016(vs), 1992(sh), 1941(s), 1923(sh) and 1905(m) cm⁻¹. The two sets of three higher and three lower frequency distinct bands are assigned to the iron and manganese carbonyl groups, respectively. The Fe(II) and Mn(I) ions in 1 both have d^6 electron configurations. The lower nuclear charge on manganese allows stronger π bonding with carbon monoxide which results in
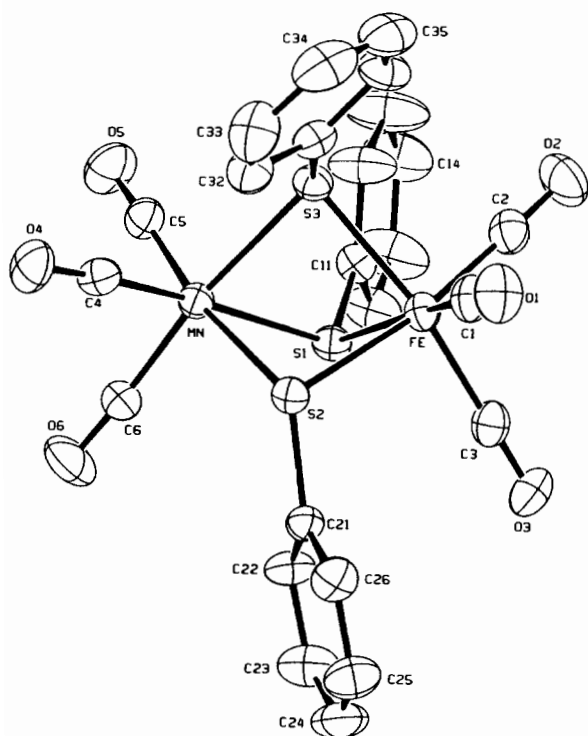
Fig. 1. ORTEP diagram of MnFe(μ-SPh)$_3$(CO)$_6$ (**1**) showing the atom labelling scheme and 30% probability thermal ellipsoids. Crystallographic data: orthorhombic, space group Pna2$_1$ (No. 33) with $a = 22.668(3)$, $b = 12.462(2)$, $c = 9.077(1)$ Å, $V = 2564(1)$ Å^3, $Z = 4$ and $R = 0.043$ for 2294 unique observed reflections with $I > 2\sigma(I)$.

TABLE 1. Selected bond distances (Å) and angles (°) for MnFe(SC$_6$H$_5$)$_3$(CO)$_6$ (**1**)

Atoms	Distance	Atoms	Angles
Mn–Fe	3.129(1)	C4–Mn–C6	87.4(3)
Mn–S1	2.375(2)	C4–Mn–C5	92.3(3)
Mn–S2	2.370(2)	C6–Mn–C5	91.4(3)
Mn–S3	2.393(2)	C2–Fe–C1	95.5(3)
Fe–S1	2.323(2)	C2–Fe–C3	95.3(3)
Fe–S2	2.341(2)	C1–Fe–C3	94.7(3)
Fe–S3	2.333(2)	S2–Mn–S1	79.97(7)
Mn–C4	1.778(8)	S2–Mn–S3	79.45(7)
Mn–C5	1.812(8)	S1–Mn–S3	79.82(7)
Mn–C6	1.804(8)	S1–Fe–S3	82.14(6)
Fe–C1	1.815(8)	S1–Fe–S2	81.64(6)
Fe–C2	1.795(9)	S3–Fe–S2	81.26(7)
Fe–C3	1.825(8)		

lower carbonyl frequencies. As might be expected, these bands are observed in the same frequency range as the carbonyl bands of **3** which occur at 2000(m), 1950(sh), 1935(s) and 1915(s) cm^{-1} [3].

Some differences in frequency, intensity and numbers of bands are anticipated because of a larger carbonyl vibrational coupling along the molecular axis in **1** as compared with **4**. The higher frequency bands however are nearly identical both in frequency and intensity to those observed in **4** [16]. In heptane solution, the carbonyl bands of **1** are observed at 2089(s), 2080(w), 2037(s), 2026(vs), 2001(w), 1970(w) and 1944(s). The four strong bands of **1** in heptane constitute two doublets. The higher frequency doublet at 2089 and 2037 cm^{-1} is assigned to the Fe(II)(CO)$_3$ fragment and the one at lower frequency, 2026 and 1944 cm^{-1}, to the Mn(I)(CO)$_3$ fragment. The weak bands are assigned to the minor species Mn$_2$(SPh)$_2$(CO)$_8$ [8] which we have directly synthesized and characterized by IR spectroscopy in heptane solution. This product is possibly derived from the disproportionation of **1**. Other expected products containing Fe are not observed, perhaps because of their insolubility in heptane.

The formation of compound **1** further underscores the facile uptake of CO by Fe(II) coordinated by good electron donor ligands. The route presented here for the synthesis of a heterobimetallic complex may find synthetic applications as well.

Supplementary material

A general structure report for **1**, including details of the structure determination, listings of experimental details, positional and thermal parameters, inter- and intramolecular distances and bond angles involving non-hydrogen atoms, ORTEP and PLUTO diagrams of the structure and a listing of final observed and calculated structure factors are available from the authors.

References

1 M. A. Walters and J. C. Dewan, *Inorg. Chem.*, 25 (1986) 4889.
2 M. Elian and R. Hoffmann, *Inorg. Chem.*, 14 (1975) 1058.
3 J. W. McDonald, *Inorg. Chem.*, 24 (1985) 1734.
4 P. M. Treichel and M. H. Tegen, *J. Organomet. Chem.*, 292 (1985) 385.
5 P. M. Treichel and P. C. Nakagaki, *Organometallics*, 4 (1986) 711.
6 A. J. Schultz and R. Eisenberg, *Inorg. Chem.*, 12 (1973) 518.
7 S. Jeannin, Y. Jeannin and G. Lavigne, *J. Cryst. Mol. Struct.*, 7 (1977) 241.
8 Von W. Hieber and W. Schropp, Jr., *Z. Naturforsch., Teil B*, 14 (1959) 460.