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Stabilisation of the $[Mn(CO)_2]^+$ fragment by thioether macrocyclic ligands; synthesis, spectroscopic and structural characterisation

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The *fac*-tricarbonyl manganese(I) species *fac*-$[Mn(CO)_3(L)]^+$ (L = [12]aneS_4, 1,4,7,10-tetrathiacyclododecane; [14]aneS_4, 1,4,8,11-tetrathiacyclotetradecane; or [15]aneS_5, 1,4,7,10,13-pentathiacyclopentadecane), formed by treatment of *fac*-$[Mn(CO)_3(Me_2CO)_3]^+$ with L in MeCN solution, were readily decarbonylated with Me_3NO to yield the first dicarbonyl manganese(I) thioether complexes, *cis*-$[Mn(CO)_2(L)]^+$. The crystal structures of $[Mn(CO)_3([12]aneS_4)]CF_3SO_3$ and $[Mn(CO)_3([15]aneS_5)]CF_3SO_3$ confirm the *fac* tricarbonyl arrangement, with the macrocycle bonded in a tridentate manner, leaving one or two non-bonding S atoms respectively. The crystal structure of *cis*-$[Mn(CO)_2([12]aneS_4)]CF_3SO_3{\cdot}0.5CHCl_3$ reveals a distorted octahedral geometry at Mn^I with the two CO ligands mutually *cis* and with the tetradentate macrocycle occupying the other four co-ordination sites. IR spectroscopic studies reveal that the CO stretching vibrations occur at very low frequency, indicating very significant π-back bonding to the CO ligands, with the thioether ligands behaving essentially as pure σ donors to the low-valent manganese(I) ion in these systems.

Introduction

A wide variety of transition metal elements form complexes with macrocyclic thioether ligands, and these ligands have been shown to impart unexpected structural, electronic and/or redox properties.[1] As part of our study of the relative donating abilities of thio-, seleno- and telluro-ether ligands we have investigated the binding of these ligands to manganese(I) carbonyls and carbonyl halides. For the neutral species *fac*-$[MnX(CO)_3(L\text{–}L)]$ (X = Cl, Br or I; L–L = dithio-, diseleno- or ditelluro-ether) or the cationic species *fac*-$[Mn(CO)_3(L_3)]^+$ (L_3 = trithio-, triseleno- or tritelluro-ether), there is an increase in σ donation along the series $S < Se \ll Te$.[2,3] While the macrocyclic trithioether species *fac*-$[Mn(CO)_3([9]aneS_3)]^+$ ([9]aneS_3 = 1,4,7-trithiacyclononane) and *fac*-$[Mn(CO)_3([10]aneS_3)]^+$ ([10]aneS_3 = 1,4,7-trithiacyclodecane) are known,[3,4] manganese(I) complexes with thioether ligands of higher denticity have not been studied. We have therefore conducted a study of the co-ordination of tetra- and penta-thioether macrocycles to Mn^I with particular interest in establishing whether these ligands would facilitate the stabilisation of the $[Mn(CO)_2]^+$ fragment. There are very few well characterised dicarbonyl manganese(I) complexes known, and they typically incorporate strong σ-donor/π-acceptor ligands such as phosphines, phosphonites or phosphites.[5,6] Transition metal dicarbonyl complexes of the Group 6 and 7 elements are considerably less well known than the corresponding tri- and tetra-carbonyl species. In the course of their studies of macrocyclic thioether complexes of Mo^{II} and Mo^0 and subsequent preparation of dinitrogen adducts, Yoshida and co-workers have reported the preparation and structure of the molybdenum(0) species *trans*-$[Mo(CO)_2(L')]$ (L′ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane), the first example of a molybdenum(0) dicarbonyl complex of a thioether ligand.[7] This species is obtained by either chemical or electrochemical reduction of *trans*-$[MoBr_2(L')]$. However, there are no examples of manganese(I) dicarbonyl complexes with thioether ligands. We report here the preparation and spectroscopic characterisation of *cis*-dicarbonyl manganese(I) complexes incorporating tetrathia and pentathia macrocyclic ligands, including *cis*-$[Mn(CO)_2(L)]CF_3SO_3$ (L = [12]- or [14]-aneS_4 or [15]aneS_5) ([12]aneS_4 = 1,4,7,10-tetrathiacyclododecane, [14]aneS_4 = 1,4,8,11-tetrathiacyclotetradecane, [15]aneS_5 = 1,4,7,10,13-pentathiacyclopentadecane), together with crystallographic characterisation of *cis*-$[Mn(CO)_2([12]aneS_4)]CF_3SO_3{\cdot}0.5CHCl_3$. The spectroscopic characterisation and crystal structures of the tricarbonyl precursors *fac*-$[Mn(CO)_3([12]aneS_4)]CF_3SO_3$ and *fac*-$[Mn(CO)_3([15]aneS_5)]CF_3SO_3$ are also reported and comparisons of the spectroscopic and structural properties of these species are made.

Results and discussion

The complex *fac*-$[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$[6] reacts with one molar equivalent of L (L = [12]- or [14]-aneS_4 or [15]aneS_5) at room temperature to yield the yellow species $[Mn(CO)_3(L)]CF_3SO_3$ as powdered solids. Electrospray mass spectrometry (MeCN) shows the most intense peak in each case corresponding to $[Mn(CO)_3(L)]^+$, with further fragment ions corresponding to CO loss at much lower intensity (<5%). IR spectroscopy (CsI disk) shows three CO stretching vibrations in each case, consistent with the *fac*-tricarbonyl species (Table 1), in which the thioether adopts an η^3-co-ordination mode, giving C_s local symmetry at Mn^I. The CO stretching frequencies are comparable with those observed for other *fac*-tricarbonyl manganese(I) trithioether species.[3,4,8] Together with ^1H NMR spectroscopic and microanalytical data, these results indicate the formulation *fac*-$[Mn(CO)_3(L)]CF_3SO_3$ for the products. The $^{13}C\text{-}\{^1H\}$ NMR spectra of these compounds show rather broad resonances associated with the methylene groups of the macrocyclic ligand, and the δ(CO) resonances are also substantially broadened mainly due to their interaction with the directly bonded ^{55}Mn quadrupole ($I = 5/2$, 100%, $Q = 0.55 \times 10^{-28}$ m^2). There is also evidence for partial decarbonylation of the tetrathia macrocyclic complexes during the acquisition of the $^{13}C\text{-}\{^1H\}$ NMR data (*ca.* 12 h), with additional resonances associated with $[Mn(CO)_2(L)]CF_3SO_3$ evident in the spectra.

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Table 1 IR (ν_{CO}) and ^{55}Mn NMR spectroscopic data

Complex	ν_{CO}/cm^{-1}	δ(^{55}Mn)^a	$w_{1/2}$/Hz
fac-[Mn(CO)$_3$([12]aneS$_4$)]CF$_3$SO$_3$	2061, 1973, 1951^b	−334	3000
fac-[Mn(CO)$_3$([14]aneS$_4$)]CF$_3$SO$_3$	2042, 1966, 1953^b	−471	1700
fac-[Mn(CO)$_3$([15]aneS$_5$)]CF$_3$SO$_3$	2047, 1974, 1951^b	−658	2200
cis-[Mn(CO)$_2$([12]aneS$_4$)]CF$_3$SO$_3$	1964, 1893^c	−1540^d	18000
cis-[Mn(CO)$_2$([14]aneS$_4$)]CF$_3$SO$_3$	1961, 1890^c	−1350^d	30000
cis-[Mn(CO)$_2$([15]aneS$_5$)]CF$_3$SO$_3$	1958, 1897^c	−980^d	12000

^{a} Recorded in CH$_2$Cl$_2$–CDCl$_3$, 89.27 MHz. ^{b} CsI disk. ^{c} Solution in MeCN. ^{d} Very broad resonance, estimated chemical shifts ±100 ppm.

Table 2 Selected bond lengths (Å) and angles (°) for *fac*-[Mn(CO)$_3$([12]aneS$_4$)]$^+$

Mn(1)–S(1)	2.3881(7)	Mn(1)–C(9)	1.809(3)
Mn(1)–S(2)	2.3461(7)	Mn(1)–C(10)	1.815(3)
Mn(1)–S(3)	2.3728(7)	Mn(1)–C(11)	1.837(3)
S(1)–Mn(1)–S(2)	87.10(3)	S(2)–Mn(1)–C(11)	176.44(8)
S(1)–Mn(1)–S(3)	104.87(3)	S(3)–Mn(1)–C(9)	172.34(8)
S(1)–Mn(1)–C(9)	82.76(8)	S(3)–Mn(1)–C(10)	84.45(8)
S(1)–Mn(1)–C(10)	170.65(8)	S(3)–Mn(1)–C(11)	90.53(8)
S(1)–Mn(1)–C(11)	91.84(8)	C(9)–Mn(1)–C(10)	87.9(1)
S(2)–Mn(1)–S(3)	86.47(2)	C(9)–Mn(1)–C(11)	89.9(1)
S(2)–Mn(1)–C(9)	93.35(8)	C(10)–Mn(1)–C(11)	88.8(1)
S(2)–Mn(1)–C(10)	92.76(8)		

Table 3 Selected bond lengths (Å) and angles (°) for *fac*-[Mn(CO)$_3$([15]aneS$_5$)]$^+$

Mn(1)–S(1)	2.329(3)	Mn(1)–C(11)	1.82(1)
Mn(1)–S(2)	2.329(3)	Mn(1)–C(12)	1.81(1)
Mn(1)–S(3)	2.368(3)	Mn(1)–C(13)	1.81(1)
S(1)–Mn(1)–S(2)	85.7(1)	S(2)–Mn(1)–C(13)	176.9(3)
S(1)–Mn(1)–S(3)	92.00(10)	S(3)–Mn(1)–C(11)	175.2(4)
S(1)–Mn(1)–C(11)	92.1(4)	S(3)–Mn(1)–C(12)	88.1(3)
S(1)–Mn(1)–C(12)	178.3(3)	S(3)–Mn(1)–C(13)	91.0(3)
S(1)–Mn(1)–C(13)	91.8(3)	C(11)–Mn(1)–C(12)	87.7(5)
S(2)–Mn(1)–S(3)	87.3(1)	C(11)–Mn(1)–C(13)	91.3(4)
S(2)–Mn(1)–C(11)	90.6(3)	C(12)–Mn(1)–C(13)	90.0(5)
S(2)–Mn(1)–C(12)	92.6(3)		

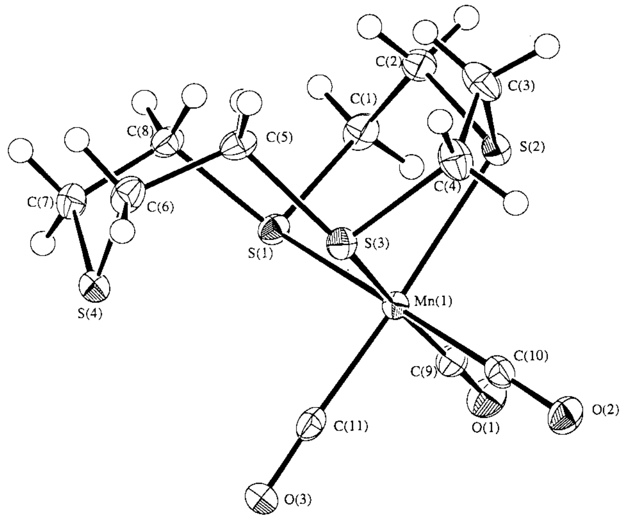

Fig. 1 View of the structure of *fac*-[Mn(CO)$_3$([12]aneS$_4$)]$^+$ with numbering scheme adopted. Ellipsoids (in all figures) are drawn at 40% probability.

^{55}Mn NMR spectra (Table 1) show one broad resonance in the range δ −334 to −658 associated with the *fac*-tricarbonyl species.

Crystals of [Mn(CO)$_3$([12]aneS$_4$)]CF$_3$SO$_3$ and [Mn(CO)$_3$([15]aneS$_5$)]CF$_3$SO$_3$ were obtained by vapour diffusion of light petroleum (bp 40–60 °C) into a solution of the complex in CHCl$_3$. The crystal structure of the former reveals (Fig. 1, Table 2) the central manganese(I) ion co-ordinated to three mutually *fac* CO ligands and to three thioether donor atoms from the macrocycle, giving a distorted octahedral environment, Mn–S(1) 2.3881(7), Mn–S(2) 2.3461(7), Mn–S(3) 2.3728(7) Å. The fourth thioether remains non-bonded, although the four S atoms are almost coplanar. The S–Mn–S angles involved in the 5-membered chelate rings are somewhat strained [87.10(3) and 86.47(2)°], while the third S–Mn–S angle within the 8-membered chelate ring is much more obtuse [104.87(3)°]. The [Mn(CO)$_3$([15]aneS$_5$)]CF$_3$SO$_3$ crystals were not as strongly diffracting, and the final residuals are correspondingly higher. However, the structure shows (Fig. 2, Table 3) a similar co-ordination environment at Mn^I, comprising of three *fac* CO ligands and three mutually *fac* thioether donor atoms from the potentially pentadentate macrocycle, Mn–S(1) 2.329(3), Mn–S(2) 2.329(3), Mn–S(3) 2.368(3) Å. The two other thioether functions remain non-co-ordinating and are directed away from the Mn. The S–Mn–S angles show a very similar pattern to those above, thus those involved in 5-membered chelate rings are restricted to less than 90°, while the one involving the much larger chelate ring is 92.00(10)°. In both structures a non-co-ordinating CF$_3$SO$_3^-$ anion maintains electroneutrality. The Mn–S bond lengths in these species compare well with those of other reported thioether complexes of Mn^I.[3,4,8]

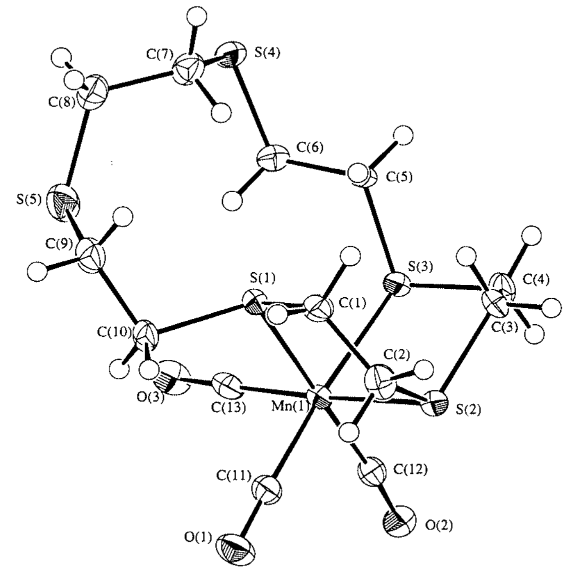

Fig. 2 View of the structure of *fac*-[Mn(CO)$_3$([15]aneS$_5$)]$^+$ with numbering scheme adopted.

The possibility that these macrocyclic thioethers may stabilise the rather unusual [Mn(CO)$_2$]$^+$ unit *via* tetradentate co-ordination was subsequently investigated. Thus, [Mn(CO)$_3$(L)]CF$_3$SO$_3$ (L = [12]aneS$_4$. [14]aneS$_4$ or [15]aneS$_5$) was treated with one molar equivalent of Me$_3$NO in Me$_3$CN solution at room temperature. This resulted in an immediate change from yellow to orange, which was associated with loss of the CO stretching bands due to the *fac* precursor, and the appearance of two new, strong CO stretches, indicative of formation of the *cis*-dicarbonyl species, *cis*-[Mn(CO)$_2$(L)]CF$_3$SO$_3$, in solution.

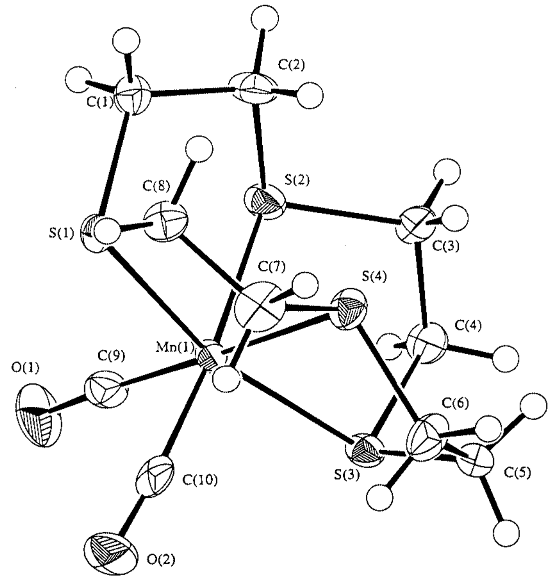

Fig. 3 View of the structure of one of the crystallographically independent *cis*-$[Mn(CO)_2([12]aneS_4)]^+$ cations in the asymmetric unit, with numbering scheme adopted (the other cation is disordered, see Experimental section).

The electrospray mass spectra of the isolated compounds show intense peaks corresponding to $[Mn(CO)_2(L)]^+$, as well as peaks at lower *m*/*z* due to loss of CO. There are no peaks corresponding to the tricarbonyl precursor $[Mn(CO)_3(L)]^+$. Together with ^{1}H and ^{13}C-{^{1}H} NMR spectroscopic and microanalytical data, these results indicate the successful preparation of the dicarbonyl species *cis*-$[Mn(CO)_2(L)]CF_3SO_3$. These are the first thioether complexes incorporating the $[Mn(CO)_2]^+$ fragment, and their formation may be attributable to the strong binding capabilities of the macrocyclic thioethers. Comparison of ν(CO) for these species (Table 1) with those reported for *cis*-dicarbonylmanganese(I) complexes incorporating P-donor ligands reveals that the CO stretching frequencies for the latter are much higher compared to the thioether species, *e.g.* *cis*-$[Mn(CO)_2(PPh_2H)_4]^+$ ($\tilde{\nu}$(CO) = 1964, 1909 cm^{-1}) and *cis*-$[Mn(CO)_2\{PPh(OMe)_2\}_4]^+$ ($\tilde{\nu}$(CO) = 1992, 1938).[5,6] This is consistent with a build-up of electron density on Mn^{I} in the thioether species, and hence increased back bonding to the CO ligands. Thus, the anomalously low frequency CO stretching vibrations associated with the dicarbonyl species strongly suggest that the thioether donors act principally as σ-donor ligands, and that π-back bonding to the thioether functions is minimal in these compounds. These results are unexpected since thioether functions can, in principle, participate in π donation and/or π acceptance, and other workers have argued that π-back bonding is important in certain thioether macrocyclic species,[1,9] however this is not the case for these low spin d^6 manganese(I) compounds. These conclusions are also supported by the ^{13}C-{^{1}H} and ^{55}Mn NMR data. For a given macrocyclic ligand, δ(CO) for the dicarbonyl species lies to high frequency of the tricarbonyl species by some 5–7 ppm, while δ(^{55}Mn) for the dicarbonyl species lies to low frequency of the tricarbonyl species by several hundred ppm, indicative of significantly greater electron density on Mn^{I} in the former. The ^{55}Mn resonances for the dicarbonyl species are very much broader than those for the tricarbonyl complexes, consistent with the lower symmetry of the former.

In order to confirm unequivocally the presence of the *cis*-dicarbonylmanganese(I) unit, and to allow a comparison of the geometric parameters in the tricarbonyl and dicarbonyl species, a single crystal structure analysis was undertaken on $[Mn(CO)_2([12]aneS_4)]CF_3SO_3\cdot0.5CHCl_3$. The structure shows (Fig. 3, Table 4) two independent cations in the asymmetric unit with very similar gross stereochemistries, although, since one of these shows some disorder, this discussion will concentrate on the ordered one. The $[Mn(CO)_2([12]aneS_4)]^+$ cations adopt a distorted octahedral arrangement comprising two mutually *cis* CO ligands and four S-donor atoms derived from one tetradentate macrocycle which adopts a folded conformation. The macrocycle is rather strained, presumably due to the small hole size offered by the 12-membered ring, and this is reflected in the S–Mn–S angles within the five-membered chelate rings, all of which are considerably smaller than 90°. Within the dicarbonyl species the Mn–S bond distances *trans* to S are slightly shorter than those *trans* to CO, and the latter are very similar to those observed in *fac*-$[Mn(CO)_3([12]aneS_4)]^+$.

Table 4 Selected bond lengths (Å) and angles (°) for *cis*-$[Mn(CO)_2([12]aneS_4)]^+$ (see Experimental section for discussion of the other Mn cation)

Mn(1)–S(1)	2.311(2)	Mn(1)–S(4)	2.326(3)
Mn(1)–S(2)	2.338(3)	Mn(1)–C(9)	1.795(10)
Mn(1)–S(3)	2.316(3)	Mn(1)–C(10)	1.785(10)
S(1)–Mn(1)–S(2)	85.98(9)	S(1)–Mn(1)–C(9)	96.3(3)
S(1)–Mn(1)–S(3)	164.80(9)	S(1)–Mn(1)–C(10)	93.0(3)
S(1)–Mn(1)–S(4)	83.12(9)	S(2)–Mn(1)–C(9)	87.2(3)
S(2)–Mn(1)–S(3)	87.20(9)	S(2)–Mn(1)–C(10)	172.7(3)
S(2)–Mn(1)–S(4)	91.30(9)	S(3)–Mn(1)–C(9)	96.9(3)
S(3)–Mn(1)–S(4)	83.47(9)	S(3)–Mn(1)–C(10)	95.4(3)
C(9)–Mn(1)–C(10)	85.7(4)	S(4)–Mn(1)–C(9)	178.5(3)
S(4)–Mn(1)–C(10)	95.7(3)		

These results demonstrate that macrocyclic thioether coordination can facilitate the stabilisation of the rather unusual $[Mn(CO)_2]^+$ fragment which has only previously been observed in the presence of strong σ donor/π-acceptor ligands. Additionally, spectroscopic studies indicate that the thioethers function as σ-donors, with essentially no π-acceptor character in these compounds, resulting in very low frequency ν(CO) vibrations.

Experimental

Physical measurements were conducted as described elsewhere.[3] ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker AM300 spectrometer, ^{55}Mn and ^{13}C-{^{1}H} NMR spectra in CH_2Cl_2–$CDCl_3$ using a Bruker AM360 spectrometer operating at 89.27 or 90.55 MHz respectively and referenced to aqueous $K[MnO_4]$ and Me_4Si respectively (δ 0). The complex $[Cr(acac)_3]$ was added to the solutions prior to recording ^{13}C-{^{1}H} NMR spectra and a pulse delay of 2 s was introduced to alleviate the long relaxation times.

Preparations

One general method was used for the preparation of all of the *fac*-tricarbonyl species and one different general method was used for the *cis*-dicarbonyl species, hence only one of each is described in detail.

***fac*-$[Mn(CO)_3([12]aneS_4)]CF_3SO_3$.** The compound $[MnCl(CO)_5]$ (0.12 g, 0.50 mmol) was dissolved in degassed Me_2CO (50 cm^3) in a foil-wrapped flask, $AgCF_3SO_3$ (0.13 g, 0.50 mmol) was added and the solution refluxed for 1 h until the IR spectrum showed complete loss of the CO stretching vibrations associated with the starting material. The solution was then filtered through Celite *in vacuo* to remove the AgCl precipitate, leaving a yellow solution of *fac*-$[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$. The compound $[12]aneS_4$ (0.096 g, 0.40 mmol) was then added and the resulting solution stirred under N_2 at room temperature for *ca.* 2 h. The product was isolated as a yellow solid by removal of the Me_2CO *in vacuo*, dissolution of the resulting yellow oil in $CHCl_3$ and precipitation with light petroleum (bp 40–60 °C). Yield 0.16 g, 76%. Calc. for $[C_{12}H_{16}F_3MnO_6S_5]\cdot0.5CHCl_3$: C, 25.7; H, 2.8%. Found: C, 26.0; H, 2.8%. Electrospray mass spectrum (MeCN): found *m*/*z* = 379, 351; calculated

Table 5 Crystallographic data

	fac-$[Mn(CO)_3([12]aneS_4)]$-CF_3SO_3	*fac*-$[Mn(CO)_3([15]aneS_5)]$-CF_3SO_3	*cis*-$[Mn(CO)_2([12]aneS_4)]$-$CF_3SO_3\cdot 0.5CHCl_3$
Formula	$C_{12}H_{16}F_3MnO_6S_5$	$C_{14}H_{20}F_3MnO_6S_6$	$C_{10.5}H_{16.5}Cl_{1.5}F_3MnO_5S_5$
M	528.49	588.60	560.16
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	9.4610(9)	11.420(4)	14.095(2)
b/Å	11.593(2)	14.642(3)	15.267(3)
c/Å	9.372(1)	13.605(3)	9.641(2)
α/°	93.56(1)	90	90.983(17)
β/°	96.581(10)	96.55(2)	90.332(14)
γ/°	72.653(9)	90	86.531(13)
U/Å^3	974.3(2)	2260.0(9)	2070.6(6)
Z	2	4	4
μ(Mo-Kα)/cm^{-1}	12.68	11.91	13.83
Unique obs. reflections	3427	4168	73306
R_{int} (based on F^2)	0.023	0.030	0.068
Obs. reflections with $[I_o > 2\sigma(I_o)]$	3119	2847	3708
No. of params.	244	271	511
R	0.028	0.072	0.066[a]
R_w	0.039	0.101	0.1643[a]

[a] $R1$; w$R2$.[10]

for $[Mn(CO)_3([12]aneS_4)]^+$ $m/z = 379$, $[Mn(CO)_2([12]aneS_4)]^+$ $m/z = 351$. ^1H NMR: δ 2.5–4.0 (br m, CH_2). ^{13}C-$\{^1H\}$ NMR: δ 215.7 (br, CO), 38.2 (CH_2, 2C), 36.3 (CH_2, 4C) and 30.7 (CH_2, 2C).

***fac*-$[Mn(CO)_3([14]aneS_4)]CF_3SO_3$.** Yield 81%. Calc. for $[C_{14}H_{20}F_3MnO_6S_3]$: C, 30.2; H, 3.6%. Found: C, 29.9; H, 3.3%. Electrospray mass spectrum (MeCN): found $m/z = 407$, 379; calculated for $[Mn(CO)_3([14]aneS_4)]^+$ $m/z = 407$, $[Mn(CO)_2([14]aneS_4)]^+$ $m/z = 379$. ^1H NMR: δ 2.1–4.0 (br m, CH_2).

***fac*-$[Mn(CO)_3([15]aneS_5)]CF_3SO_3$.** Yield = 85%. Calc. for $[C_{14}H_{20}F_3MnO_6S_6]$: C, 28.6; H, 3.4%. Found: C, 28.2; H, 3.1%. Electrospray mass spectrum (MeCN): found $m/z = 439$; calculated for $[Mn(CO)_3([15]aneS_5)]^+$ $m/z = 439$. ^1H NMR: δ 3.7–2.6 (br m, CH_2). ^{13}C-$\{^1H\}$ NMR: δ 215.6 (br, CO), 37.8 (CH_2, 2C), 35.0 (CH_2, 2C), 33.7 (CH_2, 2C) and 31.1 (CH_2, 4C).

***cis*-$[Mn(CO)_2([12]aneS_4)]CF_3SO_3$.** The compound *fac*-$[Mn(CO)_3([12]aneS_4)]CF_3SO_3$ (0.053 g, 0.10 mmol) was dissolved in dry, degassed MeCN (40 cm^3) in a foil covered flask, Me_3NO (0.082 g, 0.11 mmol) was added and the resulting solution stirred for *ca.* 1 h. The reaction was monitored by solution IR spectroscopy at regular intervals, showing loss of the CO stretching vibrations for the *fac*-tricarbonyl species and the appearance of two new bands. The solution was then evaporated to dryness *in vacuo* and washed with Et_2O (5 × 20 cm^3). The resulting product was dissolved in the minimum volume of CH_2Cl_2 and recrystallised by slow vapour diffusion of Et_2O into this solution. Yield 0.045 g, 90%. Calc. for $[C_{11}H_{16}F_3MnO_5S_5]\cdot 0.5CHCl_3$: C, 25.2; H, 3.2%. Found: C, 24.8; H, 3.0%. Electrospray mass spectrum (MeCN): found $m/z = 351$; calculated for $[Mn(CO)_2([12]aneS_4)]^+$ $m/z = 351$. ^1H NMR: δ 2.5–4.1 (br m, CH_2). ^{13}C-$\{^1H\}$ NMR: δ 220.8 (br, CO), 45.7, 42.1, 37.6 and 31.6 (CH_2, each 2C).

***cis*-$[Mn(CO)_2([14]aneS_4)]CF_3SO_3$.** Yield = 65%. Calc. for $[C_{13}H_{20}F_3MnO_5S_5]$: C, 29.5; H, 3.8%. Found: C, 29.3; H, 3.6%. Electrospray mass spectrum (MeCN): found $m/z = 379$; calculated for $[Mn(CO)_2([14]aneS_4)]^+$ $m/z = 379$. ^1H NMR: δ 2.3–2.9 (br m, CH_2). ^{13}C-$\{^1H\}$ NMR: δ 224.2 (br, CO),37.0, 34.0, 33.0, 31.0 and 23.5 (CH_2, each 2C).

***cis*-$[Mn(CO)_2([15]aneS_5)]CF_3SO_3$.** Yield = 68%. Calc. for $[C_{13}H_{20}F_3MnO_5S_3]$: C, 27.8; H, 3.6%. Found: C, 27.5; H, 3.4%. Electrospray mass spectrum (MeCN): found $m/z = 452$, 411, 383; calculated for $[Mn(CO)_2([15]aneS_5)\cdot MeCN]^+$ $m/z = 452$, $[Mn(CO)_2([15]aneS_5)]^+$ $m/z = 411$, $[Mn(CO)([15]aneS_5)]^+$ $m/z = 383$. ^1H NMR: δ 2.3–3.9 (br m, CH_2). ^{13}C-$\{^1H\}$ NMR: δ 222.2 (br, CO), 43.2, 40.9, 39.6, 38.5, 38.0, 37.9, 36.7, 33.7, 33.1 and 32.4 (CH_2).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5. Crystals of $[Mn(CO)_3([12]aneS_4)]CF_3SO_3$ and $[Mn(CO)_3([15]aneS_5)]CF_3SO_3$ were grown by vapour diffusion of diethyl ether onto solutions of the complexes in CH_2Cl_2, while crystals of *cis*-$[Mn(CO)_2([12]aneS_4)]CF_3SO_3\cdot 0.5CHCl_3$ were obtained by vapour diffusion of light petroleum (bp 40–60 °C) into a solution of the complex in $CHCl_3$. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems open-flow cryostat operating at 150 K, using graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). The solution[10] and refinement[11] of the structures of $[Mn(CO)_3([12]aneS_4)]CF_3SO_3$ and $[Mn(CO)_3([15]aneS_5)]CF_3SO_3$ were routine. The crystals of $[Mn(CO)_3([15]aneS_5)]CF_3SO_3$ were rather weakly diffracting, and this is reflected in the slightly higher than normal residuals. The highest peaks of unassigned electron density occur close to the unco-ordinated thioether S atoms. The structure of $[Mn(CO)_2([12]aneS_4)]CF_3SO_3\cdot 0.5CHCl_3$ was solved by heavy atom methods[10] and developed by iterative cycles of least-squares refinement.[12] This revealed two independent cations, two independent anions and one $CHCl_3$ solvent molecule in the asymmetric unit. One of the cations [containing Mn(2)] shows some disorder within the macrocyclic ring, giving two slightly different ligand conformations occurring in a 70% : 30% ratio. These arise due to S(6) and S(8) (and the C atoms adjacent to these) having alternative positions. In order to refine this model satisfactorily it was necessary to constrain the Mn–S bond lengths within the disordered component [S(6a), S(6b), S(8a), S(8b)] to be 2.32 Å, since otherwise the bond distances within the major component were unrealistically short and those within the minor component unrealistically long. All non-H atoms except for those in the minor component were refined anisotropically, and H atoms were included in fixed, calculated positions. While the structural information available from the Mn(2) cation is therefore of rather limited value, there is no doubt that it incorporates the *cis*-$[Mn(CO)_2]^+$ fragment. Since the other cation [involving Mn(1)] does not show any of these problems, discussion and comparisons of the geometric parameters focus on this.

CCDC reference number 186/1889.

See http://www.rsc.org/suppdata/dt/b0/b000446o/ for crystallographic files in .cif format.

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References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; S. R. Cooper and S. C. Rawle, *Struct. Bonding* (*Berlin*), 1990, **72**, 1.

2 W. Levason, S. D. Orchard and G. Reid, *Organometallics*, 1999, **18**, 1275.

3 J. Connolly, A. R. J. Genge, W. Levason, S. D. Orchard, S. J. A. Pope and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2343.

4 H. Elias, G. Schmidt, H.-J. Küppers, B. Nuber, M. Saher, K. Wieghardt and J. Weiss, *Inorg. Chem.*, 1989, **28**, 3021.

5 G. A. Carriedo, V. Riera, M. L. Rodriguez and J. J. Sainz-Velicia, *Polyhedron*, 1987, **6**, 1879.

6 R. Uson, V. Riera, J. Gimeno, M. Laguna and M. P. Gamasa, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 996.

7 T. Yoshida, T. Adachi, T. Ueda, M. Watanabe, M. Kaminaka and T. Higuchi, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 117; T. Yoshida, T. Adachi, M. Kaminaka and T. Ueda, *J. Am. Chem. Soc.*, 1988, **110**, 4872; T. Adachi, M. C. Durrant, D. L. Hughes, C. J. Pickett, R. L. Richards, J. Talarmin and T. Yoshida, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1464 and references therein.

8 J. Connolly, G. W. Goodban, G. Reid and A. M. Z. Slawin, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2125.

9 G. E. D. Mullen, M. J. Went, S. Wocadlo, A. K. Powell and P. J. Blower, *Angew. Chem.*, 1997, **36**, 1205.

10 PATTY, The DIRDIF Program System, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

11 TeXsan, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.

12 SHELXL 97, G. M. Sheldrick, University of Göttingen, 1997.