

S–S Bond-activation of diorganyl disulfide by anionic $[\text{Mn}(\text{CO})_5]^-$: crystal structures of $[\text{Mn}^{\text{II}}(-\text{SC}_5\text{H}_4\text{NO}-)_3]^-$ and $[(\text{CO})_3\text{Mn}(\mu-\text{SR})_3\text{Co}(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{NHCOPh}$)

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Abstract

The S–S bond-activation of diorganyl disulfide by the anionic metal carbonyl fragment $[\text{Mn}(\text{CO})_5]^-$ gives rise to an extensive chemistry. Oxidative decarbonylation addition of 2,2'-dithiobis(pyridine-N-oxide) to $[\text{Mn}(\text{CO})_5]^-$, followed by chelation and metal-center oxidation, led to the formation of $[\text{Mn}^{\text{II}}(-\text{SC}_5\text{H}_4\text{NO}-)_3]^-$ (**1**). The effective magnetic moment in solid state by SQUID magnetometer was 5.88 μ_B for complex **1**, which is consistent with the Mn^{II} having a high-spin d⁵ electronic configuration in an octahedral ligand field. The average Mn(II)–S, S–C and N–O bond lengths of 2.581(1), 1.692(4) and 1.326(4) Å, respectively, indicate that the negative charge of the bidentate 1-oxo-2-thiopyridinato $[\text{SC}_5\text{H}_4\text{NO}]^-$ ligand in complex **1** is mainly localized on the oxygen atom. The results are consistent with thiolate-donor $[-\text{SC}_5\text{H}_4\text{NO}]^-$ stabilization of the lower oxidation state of manganese (Mn(I)), while the O,S-chelating $[-\text{SC}_5\text{H}_4\text{NO}-]^-$ ligand enhances the stability of manganese in the higher oxidation state (Mn(II)). Activation of S–S bond as well as O–H bond of 2,2'-dithiosalicylic acid by $[\text{Mn}(\text{CO})_5]^-$ yielded $[(\text{CO})_3\text{Mn}(\mu-\text{SC}_6\text{H}_4-\text{C}(\text{O})-\text{O}-)_2\text{Mn}(\text{CO})_3]^{2-}$ (**4**). Oxidative addition of bis(*o*-benzamidophenyl) disulfide to $[\text{Mn}(\text{CO})_5]^-$ resulted in the formation of *cis*- $[\text{Mn}(\text{CO})_4(\text{SR})_2]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{NHCOPh}$) which was employed as a chelating metalloc ligand to synthesize heterotrinuclear $[(\text{CO})_3\text{Mn}(\mu-\text{SR})_3\text{Co}(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]^-$ (**8**) possessing a homoleptic hexathiolatocobalt(III) core. © 2002 Published by Elsevier Science B.V.

Keywords: Manganese(II)-thiolate; S–S Bond-activation; Heterotrinuclear Mn–Co–Mn–thiolate

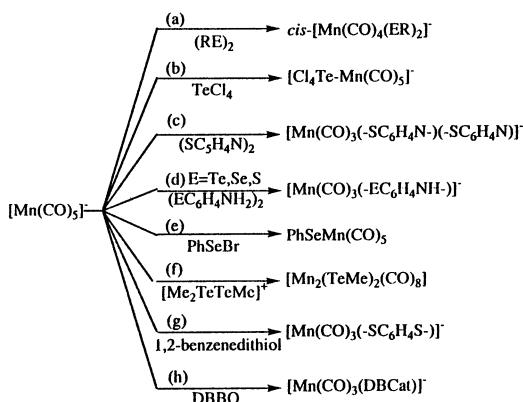
1. Introduction

Anionic metal carbonyls are known to function as nucleophiles and show a range of reactivity that depends on its substituents, the ligand environment, the metal, and its oxidation state [1]. Recently, the reaction of the anionic metal carbonyl fragment $[\text{Mn}(\text{CO})_5]^-$ has been shown to give rise to an extensive chemistry [2–8]. Some known reactions are outlined in Scheme 1: oxidative addition of diorganyl dichalcogenides to $[\text{Mn}(\text{CO})_5]^-$ affording *cis*- $[\text{Mn}(\text{CO})_4(\text{ER})_2]^-$ ($\text{E} = \text{Se}, \text{Te}; \text{R} = \text{phenyl, alkyl}$) (Scheme 1(a)) [2], coordinative addition of $[\text{Mn}(\text{CO})_5]^-$ to TeCl_4 to form a discrete chlorotellurate $[\text{Cl}_4\text{Te}-\text{Mn}(\text{CO})_5]^-$ (Scheme 1(b)) [3], the six-

coordinate Mn^{I} complex *fac*- $[\text{Mn}(\text{CO})_3(-\text{SC}_5\text{H}_4\text{N}-)(-\text{SC}_5\text{H}_4\text{N})]^-$ prepared from the reaction of $[\text{Mn}(\text{CO})_5]^-$ and bis(2-pyridyl) disulfide by oxidative addition and the subsequent chelation (Scheme 1(c)) [4], the formation of the five-coordinate Mn^{I} complex $[\text{Mn}(\text{CO})_3(-\text{EC}_6\text{H}_4\text{NH}-)]^-$ ($\text{E} = \text{S, Se, Te}$) in the reaction of $[\text{Mn}(\text{CO})_5]^-$ with 2-aminophenyl dichalcogenides by combining the dichalcogen synthetic methodology with the terminal chalcogenolate ligand oxidation followed by deprotonation (Scheme 1(d)) [5], a nucleophilic displacement/a metathesis reaction to give $[\text{PhSeMn}(\text{CO})_5]$ and $[\text{Mn}_2(\mu-\text{TeMe})_2(\text{CO})_8]$, respectively (Scheme 1(e) and (f)) [2a,6], oxidative addition of 1,2-benzenedithiol to $[\text{Mn}(\text{CO})_5]^-$ followed by a Lewis acid–base reaction to yield the five-coordinate $[\text{Mn}(\text{CO})_3(-\text{SC}_6\text{H}_4\text{S}-)]^-$ (Scheme 1(g)) [4,7], oxidative substitution of two CO ligands of $[\text{Mn}(\text{CO})_5]^-$ by 3,5-di-*tert*-butyl-1, 2-benzoquinone (DBBQ) to give

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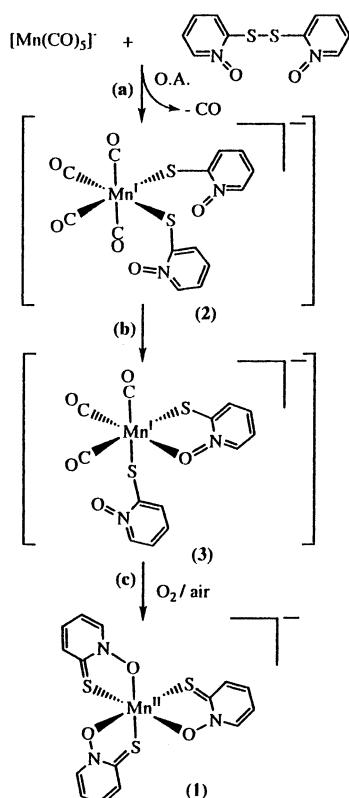
Scheme 1.

$[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ (DBCat = 3,5-di-*t*-butyl-1,2-catecholate) (Scheme 1(h)) [8].

Reaction of the anionic $[\text{Mn}(\text{CO})_5]^-$ with the varieties of diorganyl disulfides has been further investigated. Specifically, the synthesis and characterization of the hexacoordinate Mn^{II} complex $[\text{Mn}(-\text{SC}_5\text{H}_4\text{NO}-)_3]^-$ (**1**), and $[(\text{CO})_3\text{Mn}(\mu-\text{SC}_6\text{H}_4-\text{C}(\text{O})-\text{O}-)_2\text{Mn}(\text{CO})_3]^{2-}$ (**4**) are described. In addition, the synthesis and structure of a linear trinuclear $\text{Mn}^{\text{I}}-\text{Co}^{\text{III}}-\text{Mn}^{\text{I}}$ complex possessing a hexathiolatocobalt(III) core, $[(\text{CO})_3\text{Mn}(\mu-\text{SR})_3\text{Co}(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{NHCOPh}$) (**8**) is also reported [9]. The variable valence tris(1-hydroxy-2-pyridinethionato) manganese(II,III,IV), characterized by UV–Vis, EPR, and cyclic voltammogram, were investigated by Chakravorty and coworkers [10].

2. Results and discussion

The reaction of 2,2'-dithiobis(pyridine-*N*-oxide) with $[\text{Mn}(\text{CO})_5]^-$ in a 2:1 stoichiometry proceeds cleanly in dry THF to form anionic tris(1-oxo-2-pyridinethionato) manganese(II) complex $[\text{Mn}(-\text{SC}_5\text{H}_4\text{NO}-)_3]^-$ (**1**) identified by X-ray diffraction analysis. Compound **1** was isolated as the PPN^+ salt and a yellow solid from CH_3CN –diethyl ether in 60% yield. This result may be accounted for by the following sequences of reaction (Scheme 2); the oxidative addition of 2,2'-dithiobis(pyridine-*N*-oxide) to $[\text{Mn}(\text{CO})_5]^-$ yields monodentate (*S*-bonded) *cis*- $[\text{Mn}(\text{CO})_4(-\text{SC}_5\text{H}_4\text{NO})_2]^-$ (**2**) (Scheme 2(a)) [2]. Chelation of one terminal thiolate ligand of intermediate **2** yields the *fac*- $[\text{Mn}(\text{CO})_3(-\text{SC}_5\text{H}_4\text{NO})(-\text{SC}_5\text{H}_4\text{NO})]^-$ (**3**) where one of the anionic $[-\text{SC}_5\text{H}_4\text{NO}-]^-$ ligands bound to the Mn^{I} metal in a bidentate manner (*S,O*-bonded) while the second one in a monodentate (*S*-bonded) manner (Scheme 2(b)) [5,2]. Oxidation of intermediate **3** (by O_2) leads to the formation of complex **1** (Scheme 2(c)) [8]. Apparently, the metal-center oxidation ($\text{Mn}^{\text{I}} \rightarrow$



Scheme 2.

Mn^{II}) of intermediate **3**, labilizing CO ligands and accompanied by intermetal $[-\text{SC}_5\text{H}_4\text{NO}-]^-$ ligand shift, yields complex **1** (Scheme 2(c)) [11].

Compound **1** displays intense charge-transfer transitions at 345, 304, 300 and 294 nm. The electrochemistry of complex **1**, in CH_3CN with 0.05 M $[\text{Nn-Bu}_4][\text{PF}_6]$ as supporting electrolyte, reveals two pseudoreversible redox reactions at -0.34 and 0.18 V (vs. $\text{Ag}-\text{AgNO}_3$), consistent with the observations by Chakravorty and coworkers [10]. The effective magnetic moment in solid state by SQUID magnetometer was $5.88 \mu_B$ for complex **1**, which is consistent with the Mn^{II} having a high-spin d^5 electronic configuration in an octahedral ligand field. Alternatively, complex **1** was also obtained by stirring overnight a mixture of 2 equiv. of 1-hydroxy-2-pyridinethione and $[\text{Mn}(\text{CO})_5]^-$ in THF at ambient temperature.

Fig. 1 depicts the structure of complex **1** as an ORTEP; significant bond distances and angles are given in Table 2. The constraints of the bidentate 1-oxo-2-pyridinethione ligand generate (ca. $76.12(8)^\circ$, $\text{O}(1)-\text{Mn}-\text{S}(1)$; $77.05(7)^\circ$, $\text{O}(2)-\text{Mn}-\text{S}(2)$; and $75.06(7)^\circ$, $\text{O}(3)-\text{Mn}-\text{S}(3)$ angles) a severe distortion from octahedron at the hexacoordinate manganese(II) sites. The three sulfur atoms are generally disposed trans to the oxygen atoms [$155.13(9)^\circ$, $\text{O}(1)-\text{Mn}-\text{S}(3)$; $162.92(8)^\circ$, $\text{O}(2)-\text{Mn}-\text{S}(1)$; and $159.36(8)^\circ$ $\text{O}(3)-\text{Mn}-\text{S}(2)$ angles]. Three *S* and three *O* atoms are in an almost ideal facial

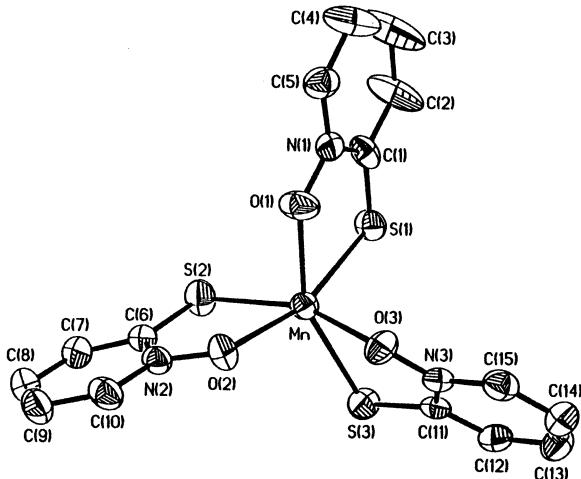


Fig. 1. ORTEP drawing and labeling scheme of $[\text{Mn}(-\text{SC}_5\text{H}_4\text{NO}-)_3]^-$ with thermal ellipsoids drawn at the 30% probability level.

Table 1
Crystal data and structure refinement parameters for complexes **1** and **8**

| | 1 | 8 · 2.25THF |
|-----------------------------------|---|---|
| Empirical formula | $\text{C}_{51}\text{H}_{42}\text{O}_3\text{N}_4\text{S}_3\text{P}_2\text{Mn}$ | $\text{C}_{129}\text{H}_{108}\text{O}_{14.25}\text{N}_7\text{S}_6\text{P}_2\text{CoMn}_2$ |
| Formula weight | 971.95 | 2407.33 |
| Crystal system | monoclinic | rhombohedral |
| Temperature (K) | 295 (2) | 150 (1) |
| λ (Å) (Mo K α) | 0.7107 | 0.7107 |
| Space group | $P2_1/n$ | $R\bar{3}c$ |
| Unit cell dimensions | | |
| a (Å) | 10.320(2) | 32.2239(2) |
| b (Å) | 23.333(4) | 32.2239(2) |
| c (Å) | 19.526(4) | 76.5564(7) |
| α (°) | 90 | 90 |
| β (°) | 94.593(15) | 90 |
| γ (°) | 90 | 120 |
| V (Å 3) | 4686.9(14) | 68 844.3(9) |
| Z | 4 | 24 |
| D_{calc} (g cm $^{-3}$) | 1.377 | 1.394 |
| μ (cm $^{-1}$) | 5.31 | 5.65 |
| R ^a | 0.0406 | 0.0667 |
| R_{WF}^2 ^b | 0.0801 | 0.1873 |
| Goodness-of-fit | 1.021 | 1.058 |

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

^b $R_{\text{WF}}^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

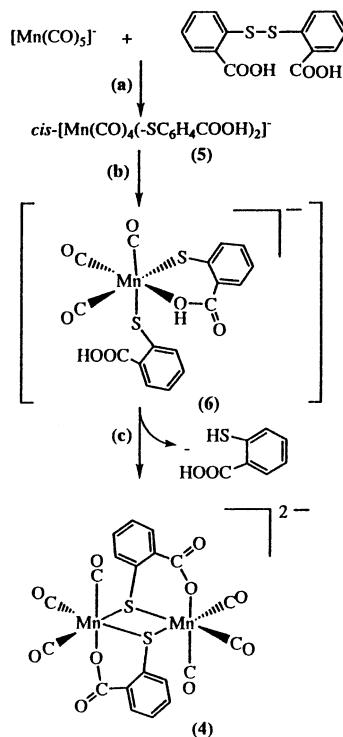
environment, individually, with torsion angle 35.67°. The average Mn(II)–S distance of 2.581(1) Å in complex **1** is significantly longer than the reported Mn(II)–SPh distance of 2.442(3) Å (average) in the $[\text{Mn}(\text{SPh})_4]^{2-}$ [12]. Also, the difference between the Mn(II)–S and Mn(II)–O lengths is approximately 0.43 Å in complex **1**, which is not consistent with the difference in the covalent radii of S (1.04 Å) and O (0.74 Å). In particular, the sum of the covalent radii of C (0.77 Å) and S (1.04 Å) is about 0.118 Å longer than the

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **1** and **8**

| Complex 1 | | | |
|-----------------------|------------|------------------|------------|
| <i>Bond distances</i> | | | |
| Mn–O(3) | 2.127(3) | Mn–O(2) | 2.172(2) |
| Mn–O(1) | 2.156(3) | Mn–S(1) | 2.5619(12) |
| Mn–S(2) | 2.5331(14) | Mn–S(3) | 2.6485(13) |
| S(1)–C(1) | 1.687(4) | S(2)–C(6) | 1.686(4) |
| S(3)–C(11) | 1.704(4) | O(1)–N(1) | 1.325(4) |
| O(2)–N(2) | 1.334(4) | O(3)–N(3) | 1.318(3) |
| <i>Bond angles</i> | | | |
| O(3)–Mn–O(1) | 90.44(11) | O(3)–Mn–O(2) | 85.63(10) |
| O(1)–Mn–O(2) | 89.88(10) | O(3)–Mn–S(2) | 159.36(8) |
| O(3)–Mn–S(1) | 103.94(8) | O(3)–Mn–S(3) | 75.06(7) |
| S(1)–Mn–S(3) | 87.72(4) | S(2)–Mn–S(1) | 95.69(4) |
| S(2)–Mn–S(3) | 99.74(4) | N(1)–O(1)–Mn | 123.8(2) |
| C(1)–S(1)–Mn | 98.28(14) | | |
| Complex 8 | | | |
| <i>Bond distances</i> | | | |
| Co(1)–S(1) | 2.277(1) | Co(1)–S(2A) | 2.292(1) |
| Co(1)–S(3) | 2.299(2) | Mn(1)–S(1) | 2.373(2) |
| Mn(1)–S(2A) | 2.367(2) | Mn(1)–S(3) | 2.386(2) |
| <i>Bond angles</i> | | | |
| S(1)–Co(1)–S(1A) | 180.00(5) | S(3)–Co(1)–S(2) | 98.21(5) |
| S(3)–Co(1)–S(1) | 82.94(5) | S(2)–Co(1)–S(1) | 98.26(4) |
| S(3)–Mn(1)–S(1) | 79.12(5) | S(2A)–Mn(1)–S(3) | 78.44(5) |
| S(2A)–Mn(1)–S(1) | 78.21(5) | Co(1)–S(1)–Mn(1) | 83.96(4) |

observed S–C distance (1.692(4) Å, average) in complex **1** which indicates the importance of a conjugated interaction along the ring π-system, the S and O lone-pair electrons, and the average S–C length of 1.692(4) Å (average) in complex **1** is in agreement with the thione form (Scheme 2(c)) [13]. The average N–O bond length of 1.326(4) Å is well within the range observed for pyridine 1-oxide [13c], indicating that the negative charge of the bidentate $[-\text{SC}_5\text{H}_4\text{NO}-]$ ligand in complex **1** is mainly localized on the oxygen atom [13d]. The results are consistent with the stabilization of the lower oxidation state of manganese (Mn(I)) by thiolate-donor $[-\text{SC}_5\text{H}_4\text{NO}-]$ ligand, while the *O,S*-chelating $[-\text{SC}_5\text{H}_4\text{NO}-]$ ligand enhances the stability of manganese in the higher oxidation state (Mn^{II}) (Scheme 2) [13].

Under similar reaction condition, the known dianionic dinuclear Mn(I) compound $[(\text{CO})_3\text{Mn}(\mu-\text{SC}_6\text{H}_4-\text{C}(\text{O})-\text{O}-)_2\text{Mn}(\text{CO})_3]^{2-}$ (**4**) was obtained from reaction of 2,2'-dithiosalicylic acid and $[\text{Mn}(\text{CO})_5]^-$ in THF at room temperature (r.t.) [14]. A reasonable reaction sequence accounting for the formation of complex **4** is shown in Scheme 3(a)–(c). Activation of S–S bond instead of C(O)O–H bond of $(\text{SC}_6\text{H}_4\text{COOH})_2$ by $[\text{Mn}(\text{CO})_5]^-$ led to the formation of *cis*- $[\text{Mn}(\text{CO})_4(-\text{SC}_6\text{H}_4-\text{C}(\text{O})-\text{OH})_2]^-$ (**5**), as evident from the IR spectra (THF, cm $^{-1}$): $\nu(\text{CO})$ 2073 (w), 2000 (vs), 1979 (m), 1939 (m) which match those of complex *cis*- $[\text{Mn}(\text{CO})_4(\text{SPh})_2]^-$ previously established (by IR and X-ray diffraction) [15]. The elimination of a carbonyl



Scheme 3.

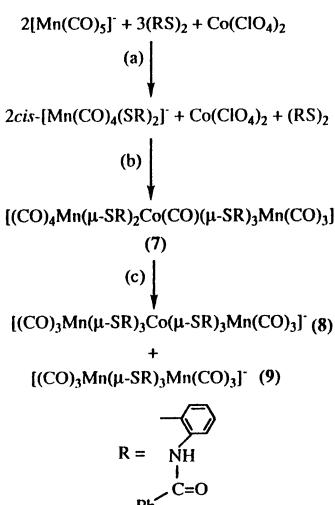
ligand resulting from chelate formation of one terminal thiolate ligand $\text{Mn}^{\text{I}}-\text{SC}_6\text{H}_4\text{COOH}$ of complex **5** yielded the intermediate *fac*- $[\text{Mn}(\text{CO})_3(-\text{SC}_6\text{H}_4\text{C}(\text{O})\text{OH})-(-\text{SC}_6\text{H}_4\text{COOH})]^-$ (**6**) IR (THF, cm^{-1}): $\nu(\text{CO})$ 2010 (vs), 1920 (s), 1912 (s) [4]. The subsequent elimination of $\text{HSC}_6\text{H}_4\text{COOH}$ and the concomitant dimerization of $[\text{Mn}(\text{CO})_3(-\text{SC}_6\text{H}_4\text{C}(\text{O})\text{O}-)]^-$ fragment yielded the dinuclear complex **4**. This result revealed that oxidative addition across the S–S bond of $(\text{SC}_6\text{H}_4\text{COOH})_2$ to $[\text{Mn}(\text{CO})_5]^-$ is the preferred pathway of the reaction of 2,2'-dithiosalicylic acid and $[\text{Mn}(\text{CO})_5]^-$.

Recent results suggested that $[\text{Mn}(\text{CO})_5]^-$ promoted the oxidative addition of diorganyl disulfide to yield six-coordinate *cis*- $[\text{Mn}(\text{CO})_4(\text{SR})_2]^-$ [15], although cleavage of S–S bond by nucleophiles is a well-known phenomenon which results in displacement of the group RS^- [16]. In addition, recent work also indicated that the complexes *cis*- $[\text{Mn}(\text{CO})_4(\text{ER})_2]^-$ ($\text{E} = \text{Te}, \text{Se}; \text{R} = \text{phenyl, alkyl}$) which contain the delocalized lone pairs of electrons around chalcogen atoms are useful in the syntheses of heterometallic $\text{Mn}(\text{I})-\text{Co}(\text{III})-\text{Mn}(\text{I})$ –chalcogenolate complexes such as $[(\text{CO})_4\text{Mn}(\mu-\text{TePh})_2\text{Co}(\text{CO})(\mu-\text{TePh})_3\text{Mn}(\text{CO})_3]$ possessing a unique $\text{Co}^{\text{III}}-\text{CO}$ bond [2a], and $[(\text{CO})_3\text{Mn}(\mu-\text{SePh})_3\text{Co}(\mu-\text{SePh})_3\text{Mn}(\text{CO})_3]^-$ possessing a homoleptic hexaselenolato cobalt(III) core [9]. To evaluate the influence of the weaker electron-donating thiolate ligand on the stability of the heterometallic $\text{Mn}(\text{I})-\text{Co}(\text{III})-\text{Mn}(\text{I})$ –chalcogenolate complexes, we surveyed the reactivity of bis(*o*-benzamidophenyl) disulfide towards $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

in the presence of *cis*- $[\text{Mn}(\text{CO})_4(\text{SR})_2]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{NHCOPh}$). Reaction of $(\text{RS})_2$, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and *cis*- $[\text{Mn}(\text{CO})_4(\text{SR})_2]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{NHCOPh}$) in a 0.5:1:2 molar ratio in THF at ambient temperature led to the formation of $[(\text{CO})_3\text{Mn}(\mu-\text{SR})_3\text{Co}(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]^-$ (**8**) (Scheme 4). The formation of the stable complex **8** can be accounted for as: (i) oxidative addition of bis(*o*-benzamidophenyl) disulfide to the coordination compound $[(\text{CO})_4\text{Mn}(\mu-\text{SR})_2\text{Co}^{\text{II}}(\mu-\text{SR})_2\text{Mn}(\text{CO})_4]$ led to the presumed intermediate $[(\text{CO})_4\text{Mn}(\mu-\text{SR})_2\text{Co}^{\text{III}}(\text{SR})(\mu-\text{SR})_2\text{Mn}(\text{CO})_4]$, (ii) subsequent rearrangement of the terminal *o*-benzamidophenylthiolate ligand to bridge two metals (Mn and Co) and shift of a labile carbonyl group from Mn(I) to Co(III) yielded neutral $[(\text{CO})_4\text{Mn}(\mu-\text{SR})_2\text{Co}(\text{CO})(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]$ (**7**) (Scheme 4(b)) [2], (iii) extended periods of stirring in THF at r.t., the extremely thermally unstable complex **7** converted into **8** and the known $[(\text{CO})_3\text{Mn}(\mu-\text{SR})_3\text{Mn}(\text{CO})_3]^-$ (**9**) (Scheme 4(c)) [17]. We attribute the formation of the heterotrimetallic complex **8** to the lability of ‘ $\text{Co}^{\text{III}}-\text{CO}$ ’ carbonyl group in neutral complex **7** and rapid intermetal transfer of the *o*-benzamidophenylthiolate group. The compound **8** can be crystallized from THF–hexane after being separated from the CH_3CN –diethyl ether-soluble complex **9**.

The trinuclear dark green anion **8** and the known brown anion **9**, individually, exhibit a two-band pattern in the $\nu(\text{CO})$ region of the infrared, but at different positions, IR (THF, cm^{-1}): $\nu(\text{CO})$ 2008 (vs), 1929 (s,br) for **8** and 2001 (vs), 1922 (s,br) for **9**, which are consistent with a tricarbonyl derivative of approximately C_{3v} symmetry. The ^1H NMR spectra of complex **8** shows the expected signals for the phenyl groups involved and display characteristics of diamagnetic d^6 $\text{Co}(\text{III})$ and d^6 $\text{Mn}(\text{I})$ species.

The X-ray structural analysis (Fig. 2) of complex **8** reveals a centrosymmetric trinuclear manganese–



Scheme 4.

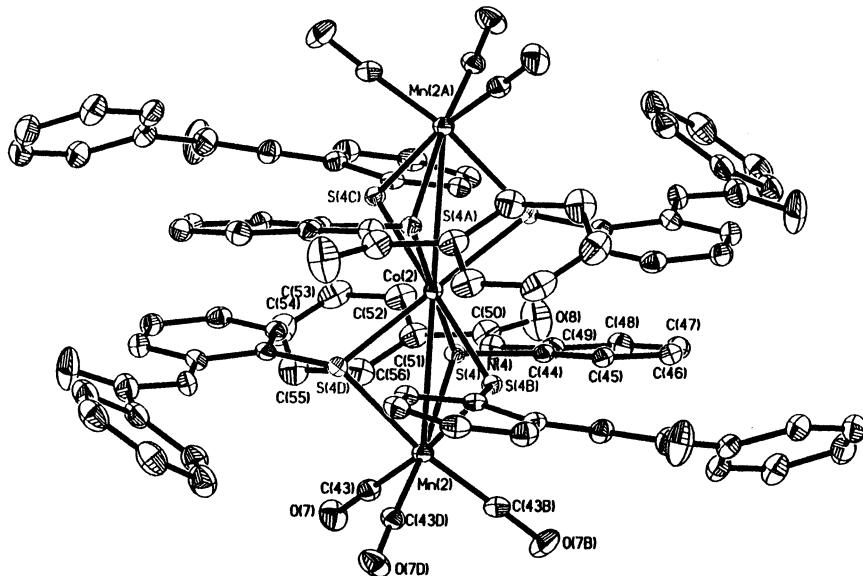


Fig. 2. ORTEP drawing and labeling scheme of $[(\text{CO})_3\text{Mn}(\mu-\text{SC}_6\text{H}_4\text{NHCOPh})_3\text{Co}(\mu-\text{SC}_6\text{H}_4\text{NHCOPh})_3\text{Mn}(\text{CO})_3]^-$ with thermal ellipsoids drawn at the 30% probability level.

cobalt–manganese–thiolate complex in which the Co^{III} is in a distorted octahedral arrangement with the sulfur atoms of thiolate in two parallel faces of the octahedron capped by tricarbonylmanganese(I) fragments. The structure of complex **8** contains two independent molecules of **8**. The Mn–Co–Mn angle of 180.0° and the staggered conformation of two parallel triangular thiolate faces promise the best minimization of interactions between the thiolates. The S–Co–S angles are divided into two groups (Table 2), 82.16(5) (same facial groups) and 97.84(5)° (different facial groups). The Co^{III}–S and Mn^I–S bond distances are 2.289(1) and 2.375(2) Å (average), respectively. The Mn^I…Co^{III} distance (3.1111(9) Å) is not short enough to suggest a bonding interaction between the two metals.

3. Experimental

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glove-box (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH₂; acetonitrile from CaH₂–P₂O₅; methylene chloride from P₂O₅; hexane and tetrahydrofuran (THF) from sodium-benzophenone) and stored in dried, N₂-filled flasks over 4 Å molecular sieves. Nitrogen was purged into these solvents before use and transferred to reaction vessels via stainless-steel cannula under a positive pressure of N₂. The reagents dimanganese decacarbonyl, 2,2'-dithiobis(pyridine N-oxide), 2,2'-dithiosalicylic acid, bis-(*o*-benzamidophenyl) disulfide, 1-hydroxy-2-pyridinethione, and bis(triphenylphosphoranylidene)ammo-

nium chloride (Lancaster/Aldrich) were used as received. Infrared spectra were recorded in a spectrometer (Bio-Rad FTS-185) with sealed solution cells (0.1 mm) and KBr windows. NMR spectra were recorded in a Bruker AC 200 spectrometer, ¹H chemical shifts being relative to tetramethylsilane. A GBC Cintra 10 spectrophotometer was used to record UV–Vis spectra. Cyclic voltammetric measurements were performed in a BAS-100B electrochemical analyzer, using glassy carbon as the working electrode. Cyclic voltammograms were obtained from 2 mM analyte concentration in CH₃CN using 0.1 M [n-Bu₄N][PF₆] as supporting electrolyte. Magnetic susceptibilities were carried out in the temperature range 300–5 K on a Quantum Design MPMS-5S SQUID magnetometer. Magnetic data were corrected for diamagnetic contribution. Analyses of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus).

3.1. Preparation of $[\text{PPN}][\text{Mn}(-\text{SC}_5\text{H}_4\text{NO}-)_3]$ (1)

2,2'-Dithiobis(pyridine N-oxide) (0.8 mmol, 0.202 g) and [PPN][Mn(CO)₅] (0.4 mmol, 0.298 g) were mixed together in THF solution [19], and stirred at ambient temperature for 5 min. The reaction was monitored immediately by IR. IR spectrum (CH₃CN, cm⁻¹): ν (CO) 2128 (w) 2043 (sh), 2036 (vs), 2005 (m), and 2020 (vs), 1937 (s), 1920 (s) was assigned to the formation of *cis*-[Mn(CO)₄(–SC₅H₄NO)₂][–] and *fac*-[PPN][Mn(CO)₃(–SC₅H₄NO)(–SC₅H₄NO)] individually. The mixture was then stirred under air–O₂ overnight at r.t. The orange solution was then removed via cannula, and the yellow precipitate was washed with THF. Acetonitrile was added to extract the yellow solid,

and then diethyl ether was slowly added to precipitate the product $[PPN][Mn(-SC_5H_4NO)_3]$ (**1**) (yield: 0.233 g, 60%) [10]. The crystals, suitable for X-ray crystallography, were obtained by vapor diffusion of diethyl ether into a concentrated CH_3CN solution of complex **1** at $-15\text{ }^\circ C$. Absorption spectrum: λ_{\max} (nm) (ε , $M^{-1} cm^{-1}$) (CH_2Cl_2): 345 (7787), 304 (2362), 300 (35 535), 294 (33 696). The effective magnetic moment in solid state by SQUID magnetometer was $5.88\text{ }\mu_B$ [10]. *Anal.* Found: C, 62.96; H, 4.41; N, 5.82. Calc. for $C_{51}H_{42}O_3P_2N_4S_3Mn$: C, 63.02; H, 4.36; N, 5.76%.

3.2. Preparation of $[Et_4N]_2[(CO)_3Mn(\mu-SC_6H_4-C(O)-O-)_2Mn(CO)_3]$ (**4**)

THF solution (6 ml) containing $[Et_4N][Mn(CO)_5]$ (0.4 mmol, 0.130 g) [19] and 2,2'-dithiosalicylic acid (0.4 mmol, 0.123 g) was stirred for 4 h at r.t. The reaction was monitored by IR. IR spectra (THF, cm^{-1}): $\nu(CO)$ 2073 (w), 2000 (vs), 1979 (m), 1939 (m) (major) and 2010 (vs), 1920 (s), 1912 (s) (minor) were assigned to the formation of *cis*- $[Mn(CO)_4(-SC_6H_4-C(O)OH)_2]^-$ and *fac*- $[Mn(CO)_3(-SC_6H_4-C(O)OH)-(-SC_6H_4-C(O)OH)]^-$, respectively. After 12 h of stirring the known orange product $[Et_4N]_2[(CO)_3Mn(\mu-SC_6H_4-C(O)-O-)_2Mn(CO)_3]$ (**4**) [14], as identified by X-ray diffraction and IR, precipitated upon addition of diethyl ether. Recrystallization from saturated CH_3CN solution with diethyl ether diffusion gave orange crystals of complex **4** at $-15\text{ }^\circ C$ (yield: 0.143 g, 62%). IR (CH_3CN, cm^{-1}): $\nu(CO)$ 1997(s), 1900 (vs); 1595 (C=O).

Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive; only small amounts of material should be prepared and handled with great caution.

3.3. Preparation of $[PPN][(CO)_3Mn(\mu-SR)_3Co(\mu-SR)_3Mn(CO)_3]$ (*R* = $C_6H_4NHCOPh$) (**8**)

A solution containing 0.596 g (0.8 mmol) of $[PPN][Mn(CO)_5]$ and 0.752 g (0.8 mmol) of bis-(*o*-benzamidophenyl)disulfide in THF (4 ml) was stirred at ambient temperature for 15 min. IR spectra, $\nu(CO)$ 2061 (w), 1985 (vs), 1966 (m), 1924 (m), 1670 (m) (C=O), 1574 (w) (N–H) (THF, cm^{-1}) were assigned to the formation of *cis*- $[Mn(CO)_4(-SC_6H_4NHCOPh)_2]^-$ [15]. To the same flask a THF solution of 0.2 mmol of bis-(*o*-benzamidophenyl) disulfide (0.188 g) and 0.4 mmol of $Co(ClO_4)_2 \cdot 6H_2O$ (0.107 g) were added slowly and stirred at r.t. overnight. The IR spectra, $\nu(CO)$ 2008 (vs), 1929 (s,br) (major) and 2001 (vs), 1922 (s,br) (minor) (THF, cm^{-1}) indicated the formation of $[(CO)_3Mn(\mu-SR)_3Co(\mu-SR)_3Mn(CO)_3]^-$ (*R* = $C_6H_4-NHCOPh$) (**8**) and the known $[(CO)_3Mn(\mu-SR)_3Mn(CO)_3]^-$ (**9**) individually [17,18]. The dark green solution was filtered to remove the insoluble solid, and

then dried under vacuum. The dark green pure complex **8** can be obtained after being separated from the CH_3CN –diethyl ether-soluble complex **9** (yield 0.467 g, 52%). Recrystallization by vapor diffusion of hexane–diethyl ether into THF solution at $-15\text{ }^\circ C$ afforded dark green crystals of complex **8** suitable for X-ray crystallography. IR (THF, cm^{-1}): $\nu(CO)$ 2008 (vs), 1929 (br,s); 1681 (C=O); 1515 (N–H). 1H NMR (C_4D_8O, δ ppm): 6.89 (t), 7.35 (t), 8.24 (d), 8.51 (d) (SC_6H_4NH); 3.85 (br) (NH). Absorption spectrum: λ_{\max} (nm) (ε , $M^{-1} cm^{-1}$) (THF): 595 (5049), 374 (14 560), 324 (26 964), 314 (36 388). *Anal.* Found: C, 63.96; H, 4.41; N, 4.92. Calc. for $C_{120}H_{90}O_{12}P_2N_7S_6Mn_2Co$: C, 64.06; H, 3.97; N, 4.39%.

4. Crystallography

Crystallographic data of complexes **1** and **8** are summarized in Table 1, and in the supporting information. The crystals of **1** and **8** are chunky. The crystals of **1** and **8** chosen for X-ray diffraction studies measured $0.50 \times 0.40 \times 0.06$ mm and $0.20 \times 0.20 \times 0.10$ mm, respectively. Each crystal was mounted on a glass fiber. Diffraction measurements for complex **1** was carried out on a Nonius CAD4 (complex **8** on a Nonius Kappa CCD) diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ 0.7107 Å) and θ between 1.75 and 25.00° for complex **1**, between 1.49 and 25.00° for complex **8**. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atoms contribution was based on F^2 . The SHELXTL package of programs was employed for structure solution and refinement [20].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 180392 and 180393 for compounds **1** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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