

Synthesis and Characterization of the Five-Coordinate Sixteen-Electron Manganese(I) Complex $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$

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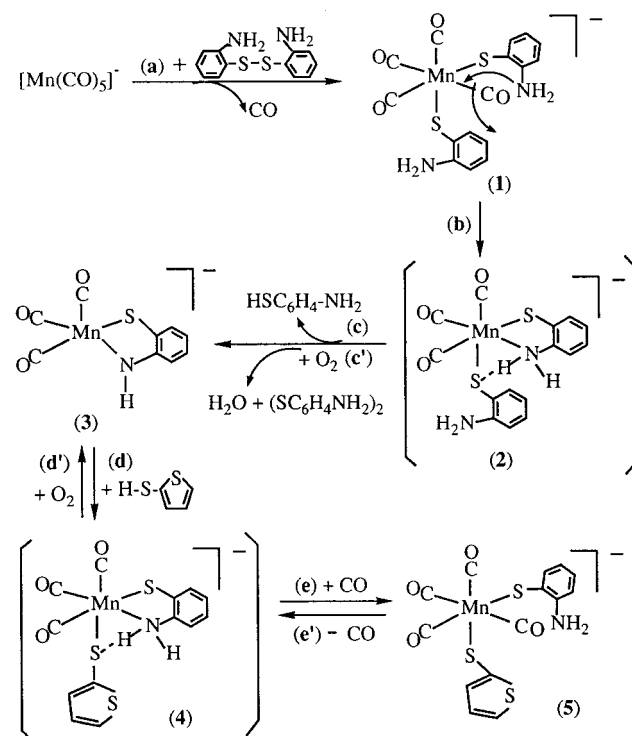
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Introduction

The $\text{NH}\cdots\text{S}$ hydrogen bond which arguably plays a major role in determining the redox potential and the electronic structure of biologically important metalloproteins and metalloenzymes (e.g., iron–sulfur proteins, ferredoxins, and rubredoxins)¹ has been observed in biomimetic structural model complexes.²

Recent work in this laboratory has shown that the anionic metal carbonyl fragments $[\text{Mn}(\text{CO})_5]^-$ and $[\text{PhFe}(\text{CO})_4]^-$ ($\text{E} = \text{Se}, \text{Te}$) activate the $\text{E}-\text{E}$ bond of diorganyl dichalcogenides to yield *cis*- $[\text{Mn}(\text{CO})_4(\text{ER})_2]^-$ and *fac*- $[\text{Fe}(\text{CO})_3(\text{EPh})_3]^-$ complexes which are useful in the syntheses of $(\text{CO})_4\text{Mn}(\mu\text{-ER})_2\text{Co}(\text{CO})(\mu\text{-ER})_3\text{Mn}(\text{CO})_3$ with a unique terminal $\text{Co}^{\text{III}}-\text{CO}$ bond,³ $[(\text{CO})_3\text{M}(\mu\text{-SePh})_3\text{M}'(\mu\text{-SePh})_3\text{M}(\text{CO})_3]^{-/0}$ ($\text{M} = \text{Mn}, \text{M}' = \text{Co}; \text{M} = \text{Fe}, \text{M}' = \text{Ni}, \text{Zn}, \text{Cd}, \text{Fe}$) with homoleptic hexaselenoatometal core,⁴ and distorted square planar $[\text{Ni}(\text{CO})(\text{SPh})_n(\text{SePh})_{3-n}]^-$ ($n = 0, 1, 2$),⁵ the biomimetic nickel-site structure of $[\text{NiFeSe}]$ hydrogenases and CO dehydrogenase. In this paper we combine the dichalcogen synthetic technology with the potential for intramolecular H-bonding to synthesize five-coordinate sixteen-electron Mn(I) complex $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$ stabilized by S,N π -donation of bidentate $[\text{S}-\text{C}_6\text{H}_4\text{-NH}]^{2-}$ ligand. To our knowledge, a few examples of transition-metal carbonyl complexes containing five-coordinate sixteen-electron metal core (d^6) have been reported,^{6,7} e.g. $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ prepared by oxidative substitution of two CO ligands of $[\text{Mn}(\text{CO})_5]^-$ by 3,5-di-*tert*-butyl-1,2-benzoquinone,^{6a} and $[\text{W}(\text{CO})_3(\text{NHC}_6\text{H}_4\text{NH})]^{2-}$ prepared from $\text{W}(\text{CO})_5(\text{THF})$ and 2 equiv of monodeprotonated ligands $[\text{NHC}_6\text{H}_4\text{NH}_2]^-$ by intermolecular deprotonation.^{7c}

Scheme 1



$[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$ stabilized by S,N π -donation of bidentate $[\text{S}-\text{C}_6\text{H}_4\text{-NH}]^{2-}$ ligand. To our knowledge, a few examples of transition-metal carbonyl complexes containing five-coordinate sixteen-electron metal core (d^6) have been reported,^{6,7} e.g. $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ prepared by oxidative substitution of two CO ligands of $[\text{Mn}(\text{CO})_5]^-$ by 3,5-di-*tert*-butyl-1,2-benzoquinone,^{6a} and $[\text{W}(\text{CO})_3(\text{NHC}_6\text{H}_4\text{NH})]^{2-}$ prepared from $\text{W}(\text{CO})_5(\text{THF})$ and 2 equiv of monodeprotonated ligands $[\text{NHC}_6\text{H}_4\text{NH}_2]^-$ by intermolecular deprotonation.^{7c}

Results and Discussion

When a THF solution of 2-aminophenyl disulfide (0.1 mmol, 0.025 g) and $[\text{PPN}][\text{Mn}(\text{CO})_5]$ (0.1 mmol, 0.073 g) is stirred under N_2 , a rapid reaction ensues over the course of 5 min at ambient temperature to give, by what may be described as an oxidative addition/decarbonylation reaction, a thermally unstable, monodentate (S-bonded) *cis*- $[\text{Mn}(\text{CO})_4(\text{S}-\text{C}_6\text{H}_4\text{NH}_2)_2]^-$ (1) (Scheme 1a), since the IR spectra match those of complex *cis*- $[\text{Mn}(\text{CO})_4(\text{SPh})_2]^-$ previously established (by IR and X-ray diffraction).^{3,8} As illustrated in Scheme 1b,c, the dark red, five-coordinate, S,N-chelate $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$ (3) with

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sixteen-electron Mn(I) core was finally isolated as a semisolid from THF–diethyl ether (0.056 g, 73%) after stirring the solution overnight in THF at room temperature. A reasonable reaction sequence accounting for the formation of complex **3** is shown in Scheme 1b,c. The dissociation of a carbonyl ligand resulting from chelate formation of one terminal thiolate ligand and $\text{Mn}^{\text{I}}\text{-S-C}_6\text{H}_4\text{-NH}_2$ of complex **1** yielded the intermediate *fac*- $[\text{Mn}(\text{CO})_3(\text{S-C}_6\text{H}_4\text{NH}_2)(\text{S-C}_6\text{H}_4\text{-NH}_2)]^-$ (**2**) with one anionic $[\text{S-C}_6\text{H}_4\text{NH}_2]$ ligand bound to the Mn^{I} metal in a monodentate (S-bonded) manner and the second anionic $[\text{S-C}_6\text{H}_4\text{-NH}_2]$ ligand bound to the Mn^{I} metal in a bidentate manner (S,N-bonded), forming a five-membered chelate ring.⁹ The intramolecular N–H···S interaction (cis arrangement of thiolate and NH_2 group in intermediate **2**)^{2c,f,7b} and the subsequent elimination of 2-aminothiophenol (the coordination of N atom presumably increases the acidity of amine protons to accelerate the deprotonation of NH_2)^{7b,c,10} yielded the five-coordinate complex **3**. The IR spectrum of complex **3** shows two strong CO stretching bands, which supports a facial orientation of three CO ligands. The ^1H and ^{13}C NMR spectra show the expected signals for the S,N chelate $[\text{S-C}_6\text{H}_4\text{-NH}]^{2-}$ ligand in a diamagnetic d^6 $\text{Mn}(\text{I})$ species. Oxidation chemistry was also successful in the synthesis of complex **3**. Upon contact with dry O_2 , the color of reaction mixture immediately turns from orange to dark red in THF/ CH_3CN . The IR and ^1H NMR spectra indicated the formation of complex **3** accompanied by byproducts, H_2O and 2-aminophenyl disulfide identified by ^1H NMR (Scheme 1c'). In this oxidative reaction, the $\text{Mn}(\text{I})$ was not observed to undergo oxidation, and consequently, the oxidation process is best assigned to the terminal thiolate ligand to yield 2-aminophenyl disulfide via radical $[\text{S-C}_6\text{H}_4\text{-NH}_2]^{\bullet}$ recombination, and the concomitant deprotonation of amine proton of intermediate **2** leads to formation of water.¹⁰

To further add credibility to the proposed mechanism, a straightforward protonation of complex **3** was conducted. As illustrated in Scheme 1d, the dropwise addition of the excess thiophene-2-thiol to complex **3** in THF under N_2 at ambient temperature led to the formation of an orange yellow solution immediately. The bands at 1973 vs and 1870 s cm^{-1} disappeared, with concomitant formation of a spectrum (ν_{CO} (THF): 1991 vs, 1891 s, 1879 s cm^{-1}) similar to that observed for intermediate **2**, i.e., formation of six-coordinate *fac*- $[\text{Mn}(\text{CO})_3(\text{S-C}_4\text{H}_3\text{S})(\text{S-C}_6\text{H}_4\text{-NH}_2)]^-$ (**4**) (^1H NMR ($\text{C}_4\text{D}_8\text{O}$): δ 5.53 (br), 4.89 (br) ppm (NH_2)). Attempts to isolate this moderately stable anion **4** was unsuccessful. In common with intermediate **2**, complex **4** is very sensitive, converting to complex **3**, H_2O and di(2-thienyl) disulfide characterized by ^1H NMR, within seconds on exposure to O_2 (Scheme 1d'). Additionally, the ring-opened complex *cis*- $[\text{Mn}(\text{CO})_4(\text{S-C}_4\text{H}_3\text{S})(\text{S-C}_6\text{H}_4\text{NH}_2)]^-$ (**5**) (ν_{CO} (THF): 2055 m, 1981 vs, 1959 s, 1916 s cm^{-1}) was obtained upon exposing complex **4** to CO atmosphere in THF at room temperature (Scheme 1e). Apparently, protonation of the amide site of complex **3** labilizes the chelating ligand $[\text{S-C}_6\text{H}_4\text{-NH}_2]^-$ and results in the formation of complex **5**. The complete conversion of complex **5** to **4** was observed when removing CO atmosphere under vacuum in THF (Scheme 1e').

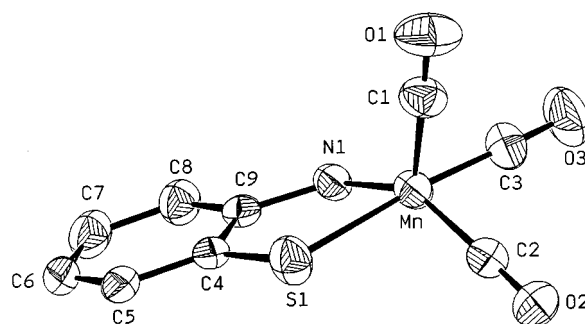


Figure 1. ORTEP drawing and labeling scheme of $[\text{Mn}(\text{CO})_3(\text{S-C}_6\text{H}_4\text{-NH})]^-$ with thermal ellipsoids drawn at the 50% probability level.

The reversibility of CO ligand-binding demonstrates the complexes **4** and **5** are chemically interconvertible.

The molecular structure of complex **3** is depicted in Figure 1. Manganese is best described as existing in a distorted tetragonal pyramidal coordination environment with the C(1)O-(1) ligand occupying the apex. The $\text{Mn}^{\text{I}}\text{-S}$ distance 2.268(1) Å in the title complex is significantly shorter than the reported $\text{Mn}^{\text{I}}\text{-Sph}$ bond 2.398(1) Å in the *cis*- $[\text{Mn}(\text{CO})_4(\text{Sph})_2]^-$,⁸ $\text{Mn}^{\text{II}}\text{-Sph}$ bond 2.442(3) Å in the $[\text{Mn}(\text{Sph})_4]^{2-}$,¹¹ The $\text{Mn}^{\text{I}}\text{-N}$ bond distance is 1.889(3) Å, which is also significantly shorter than that in $[\text{Mn}^0(\text{CO})_3(\text{TMPO})]$ (TMPO = 2,2,6,6-tetramethylpiperidiny-1-oxo) (1.981(3) Å),^{6b} and in $[\text{Mn}^{\text{III}}(\text{edt})_2(\text{ImH})]^-$ (edt = ethane-1,2-dithiolate) (2.224(7) Å).¹² This shortening of Mn–S and Mn–N bonds in complex **3** may be attributed to the significantly π -donating ability of the bidentate $[\text{S-C}_6\text{H}_4\text{-NH}]^{2-}$ ligand.^{7,13}

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (ethyl ether from CaH_2 ; acetonitrile from $\text{CaH}_2/\text{P}_2\text{O}_5$; hexane and tetrahydrofuran (THF) from Na/benzophenone; ethyl alcohol from CaH_2) and stored in dried, N_2 -filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were via stainless steel cannula under N_2 at a positive pressure. The reagents dimanganese decacarbonyl, 2-aminophenyl disulfide, thiophene-2-thiol, bis(triphenylphosphoranylidene)ammonium chloride (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-185) with sealed solution cells (0.1 mm) and KBr windows. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of ^1H and ^{13}C are relative to tetramethylsilane. UV–visible spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of $[\text{PPN}][\text{Mn}(\text{CO})_3(\text{S-C}_6\text{H}_4\text{-NH})]$ (3**).** $[\text{PPN}][\text{Mn}(\text{CO})_5]$ (0.1 mmol, 0.073 g) and 2-aminophenyl disulfide (0.1 mmol, 0.025 g) dissolved in 5 mL of THF were stirred under nitrogen at ambient temperature. A vigorous reaction occurred immediately with evolution of CO gas. IR spectrum, ν_{CO} (THF) 2050 w, 1965 vs, 1951 m, 1913 m cm^{-1} , indicated the formation of anionic *cis*- $[\text{Mn}(\text{CO})_4(\text{S-C}_6\text{H}_4\text{NH}_2)]^-$. The reaction mixture was stirred overnight at room temperature, and the yellow solution completely converted into a dark red solution. Alternatively, upon contact with dry O_2 , the color of

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Table 1. Crystallographic Data of Complex $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$

empirical formula	$\text{C}_{45}\text{H}_{35}\text{O}_3\text{N}_2\text{P}_2\text{SMn}$
fw	800.74
cryst syst	triclinic
space group	$P\bar{1}$
λ , Å (Mo K α)	0.7107
a , Å	9.925(3)
b , Å	14.251(2)
c , Å	14.202(3)
α , deg	89.84(1)
β , deg	88.89(2)
γ , deg	81.60(2)
V , Å ³	1986.8(7)
Z	2
d_{calcd} , g cm ⁻³	1.280
μ , cm ⁻¹	5.494
T , °C	25
R^a	0.041
R_w^b	0.039
GOF ^c	1.68

^a $R = \sum |(F_o - F_c)| / \sum F_o$. ^b $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$. ^c GOF = $[\sum (w(F_o - F_c)^2 / (M - N))]^{1/2}$ where M = number of reflections and N = number of parameters.

reaction mixture immediately turns from yellow to dark red. After the reaction was completed, diethyl ether was slowly added to precipitate a dark red semisolid. The mother liquor was removed via cannula, and the semisolid was dried under vacuum. The product [PPN]- $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]$, suitable for X-ray crystallography, was recrystallized from vapor diffusion of diethyl ether into concentrated THF solution at -15°C . The yield was 0.056 g (73%). IR (THF): 1973 vs, 1870 s (CO) cm⁻¹; 3339 br cm⁻¹ (N-H). ¹H NMR ($\text{C}_6\text{D}_6\text{O}$): δ 8.98 (br) ppm (N-H), 6.90 (d), 6.60 (t), 6.43 (t) ppm (SC_6H_4). ¹³C NMR ($\text{C}_6\text{D}_6\text{O}$): δ 115.04 (s), 115.43 (s), 119.79 (s), 128.65 (s), 133.12 (s), 133.23 (s) ppm ($\text{S}-\text{C}_6\text{H}_4\text{-NH}$). Absorption spectrum (THF) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 499 (6639), 403 (9745), 304 (10 400)]. Anal. Calcd for $\text{C}_{45}\text{H}_{35}\text{O}_3\text{N}_2\text{P}_2\text{SMn}$: C, 67.50; H, 4.41; N, 3.50. Found: C, 67.28; H, 4.64; N, 3.68.

Reaction of [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$] and Thiophene-2-thiol.

A portion (10 μL , 0.11 mmol) of thiophene-2-thiol was added dropwise by syringe into [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$] (0.08 g, 0.1 mmol) in THF under N_2 at ambient temperature. A vigorous reaction occurred immediately, with the color of reaction mixture turning from dark red to orange yellow, and was monitored with FTIR. The IR spectrum, ν_{CO} (THF) 1991 vs, 1891 s, 1879 s cm⁻¹, having the same pattern as, but differing slightly in position from that of, $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ (IR, ν_{CO} (THF): 1989 vs, 1887 s, 1883 s cm⁻¹) obtained from reaction of $\text{HSC}_6\text{H}_4\text{NH}_2$ and $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]$, indicated the formation of $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ (¹H NMR ($\text{C}_6\text{D}_6\text{O}$): δ 5.53 (br), 4.89 (br) ppm (NH_2)). Attempts to isolate this moderately stable $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ were unsuccessful. The orange yellow $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ solution was stirred under CO atmosphere for 5 min at room

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$

Mn-S(1)	2.268(1)	Mn-N(1)	1.889(3)
Mn-C(1)	1.753(4)	Mn-C(2)	1.761(4)
Mn-C(3)	1.776(4)	S(1)-C(4)	1.714(4)
N(1)-C(9)	1.375(5)	C(1)-O(1)	1.153(5)
C(2)-O(2)	1.167(5)	C(3)-O(3)	1.156(5)
S(1)-Mn-N(1)	83.42(9)	S(1)-Mn-C(1)	97.37(15)
S(1)-Mn-C(2)	88.55(13)	S(1)-Mn-C(3)	171.13(15)
N(1)-Mn-C(1)	120.34(16)	N(1)-Mn-C(2)	147.98(16)
N(1)-Mn-C(3)	90.84(17)	C(1)-Mn-C(2)	91.37(19)
C(1)-Mn-C(3)	91.36(20)	C(2)-Mn-C(3)	92.83(19)
Mn-S(1)-C(4)	100.16(13)	Mn-N(1)-C(9)	124.19(24)

temperature. The IR spectrum (ν_{CO} (THF) 2055 m, 1981 vs, 1959 s, 1916 s cm⁻¹) indicated the formation of the ring-opened complex $\text{cis}-[\text{Mn}(\text{CO})_4(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{NH}_2)]^-$. The complete conversion of $\text{cis}-[\text{Mn}(\text{CO})_4(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{NH}_2)]^-$ to $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ was observed when removing CO atmosphere under vacuum in THF. Oxidation of complex $\text{fac}-[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_4\text{H}_3\text{S})(\text{S}-\text{C}_6\text{H}_4\text{-NH}_2)]^-$ by adding dry O_2 leads to formation of $[\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})]^-$ accompanied by byproducts H_2O and di(2-thienyl) disulfide identified by ¹H NMR.

Crystallography. Crystallographic data for the structure of complex [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$] are collected in Table 1. Bond distances and angles are collected in Table 2. Crystals of [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$] used for the X-ray diffraction structural determination were obtained from vapor diffusion of diethyl ether into concentrated THF solution at -15°C under nitrogen atmosphere. The dark red crystal used for the study had approximate dimensions of $0.60 \times 0.50 \times 0.20$ mm. The crystal was mounted on a glass fiber and quickly coated in epoxy resin at 25°C . The unit-cell parameters were obtained from 25 reflections with 2θ between 16.40° and 23.22° for product [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$]. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo K α radiation, $\lambda = 0.7107$ Å, employing the $\theta/2\theta$ scan mode.¹⁴ A φ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.¹⁵

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of [PPN][$\text{Mn}(\text{CO})_3(\text{S}-\text{C}_6\text{H}_4\text{-NH})$] is available on the Internet only. Access information is given on any current masthead page.

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