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# Reactions of Cryptand-Solubilized NaSH in Aprotic Solvents with the Group 6B Metal Hexacarbonyls. X-ray Structural Analysis and Ligand Lability Studies of the Isolated $M(CO)_5SH^-$ Anions

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The reaction of cryptand-solubilized NaSH with the group 6B metal hexacarbonyls provides the metallo thiol derivatives [Na-kryptofix-221][$M(CO)_5SH$] in good yield. Although the intermediacy of a metallo carboxylic acid species is implied, no direct evidence for such a transient was obtained. This reaction is contrasted with the analogous process of cryptand-solubilized KOH with $M(CO)_6$ (M = Cr, Mo, W) in aprotic solvent. The thiol complexes were characterized spectroscopically, and the chromium derivative was subjected to single-crystal X-ray diffraction analysis. Crystals of [Na-kryptofix-221][$Cr(CO)_5SH$] crystallize in the orthorhombic space group *Pbca* with cell dimensions $a = 13.45$ (3) Å, $b = 20.067$ (3) Å, and $c = 20.725$ (4) Å. The structure was refined to values of $R_1 = 0.046$ and $R_2 = 0.052$ for 37 atoms (36 anisotropic) and 2635 reflections with $I > 3\sigma(I)$. The thiol ligand was found to be a strongly CO-labilizing ligand, on a par with good oxygen donor bases and better than halide ions. The origin of the labile carbon monoxide ligand was established to be cis to the $SH^-$ ligand via $^{13}C$ NMR spectroscopy. The proton on the thiol ligand was observed to readily undergo exchange with $H_2O$ in acetonitrile solvent.

## Introduction

We have recently characterized the reaction between cryptand-solubilized KOH and the group 6B metal hexacarbonyls in aprotic solvents.[1-3] This process is thought to occur via the metallo carboxylic acid intermediate (eq 1) with a subsequent reaction affording the metal pentacarbonyl hydride anion and bicarbonate.

$$M(CO)_6 + OH^- \rightleftharpoons [M(CO)_5COOH^-] \xrightarrow{OH^-} M(CO)_5H^- + HCO_3^- \quad (1)$$

Earlier experience with the isoelectronic manganese hexacarbonyl cation revealed a reaction process similar to that described in eq 1 to be operative (eq 2), where a

$$Mn(CO)_6^+ + SH^- \rightarrow Mn(CO)_5H + COS \quad (2)$$

metallo thiocarboxylic intermediate is suspect.[4] In this report the reaction between cryptand-solubilized (kryptofix-221)[5] NaSH with $M(CO)_6$ (M = Cr, Mo, W) carried out under identical reaction conditions to those employed in eq 1 is described. The initiative for this investigation was the desire to observe, and possibly isolate and fully characterize, the $M(CO)_5COSH^-$ species. However, the only observed products from reaction 3 were those derived from CO substitution by the anionic $HS^-$ ligand.

$$Na(krypt\text{-}221)SH + M(CO)_6 \rightarrow [Na(krypt\text{-}221)][M(CO)_5SH] \quad (3)$$

The tetraethylammonium salt of one of these anions, $W(CO)_5SH^-$, has previously been reported by Herberhold and Süss,[6] whereas Gingerich and Angelici[7] have published the preparation and spectral characterization of all three anions of the group 6B metals as the PPN (bis(triphenylphosphin)iminium) salts. Recently, during the course of our studies, Cooper and co-workers[8] have isolated the anions $M(CO)_5SH^-$ as salts of sodium 18-crown-6 and have reported the X-ray structural analysis of the tungsten species. The structure of [Na(krypt-221)][$Cr(CO)_5SH$] we report upon herein is to be contrasted with that of the Na(18-crown-6)$^+$ salt where contact ion pairing between the sodium cation and the oxygen atom of a carbonyl ligand is observed in the solid-state structure.

The ability of oxygen-donor ligands to labilize metal–CO bonds is now well-documented.[1,2,9-13] Sulfur donor ligands would be anticipated to possess similar properties.[2,14] Hence, we have performed comparative studies of the CO-labilizing ability of the $SH^-$ ligand with other good labilizing ligands,[15] as well as an investigation of the site specificity of the labile CO group in these $M(CO)_5SH^-$ species.

## Experimental Section

**Materials.** Anhydrous sodium hydrogen sulfide and $M(CO)_6$ (M = Cr, Mo, W) were purchased from Alfa Products and Strem Chemicals, respectively. Bis(triphenylphosphiniminium chloride was obtained from Research Organic/Inorganic Chemical Corp. Carbon monoxide enriched to 91.6% in $^{13}C$ was supplied by Prochem, B.O.C. Ltd., London. 4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (crypt-221, kryptofix-221) and 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane

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(crypt-222, kryptofix-222) were purchased from Parish Chemicals, Provo, UT. Acetonitrile was dried by refluxing with phosphorus pentoxide followed by distillation, and tetrahydrofuran was dried by refluxing over Na benzophenone followed by distillation. All reactions were carried out under an atmosphere of dry nitrogen in standard Schlenk ware.

**Preparation of [Na-kryptofix-221]$^+$SH$^-$ Solution.** One milliliter of kryptofix-221 was diluted with acetonitrile to obtain 3 mL of solution. In a typical experiment a mixture of 2.90 g (51.7 mmol) of NaSH and 1.5 mL of the kryptofix-221 solution prepared above was vigorously stirred in 45 mL of freshly distilled acetonitrile at room temperature for ~24 h. The colorless solution was centrifuged of white solid and the solid disposed. The concentration of SH$^-$ anion in the solution was 0.037 M as equal to the concentration of cryptand. A [Na-kryptofix-222]$^+$[SH]$^-$ solution was prepared in an analogous manner from the solid cryptand and NaSH in acetonitrile.

**Preparation of [Na(cryptand)][M(CO)$_5$SH] (M = Cr, Mo, W).** In a representative synthesis 0.364 g (1.65 mmol) of Cr(CO)$_6$ and 45 mL (1.67 mmol) of the Na(kryptofix-221)$^+$SH$^-$ solution prepared above were stirred at ~60 °C for 48 h. The reaction solution was cooled to ambient temperature, and the solvent was removed under reduced pressure. The solid residue was redissolved in 5 mL of tetrahydrofuran to provide a red-brown solution which upon addition of hexane yielded a brown solid. Yellow-brown crystals suitable for X-ray analysis were grown from a concentrated CH$_3$CN solution maintained at <0 °C for several days. Anal. Calcd for $C_{21}H_{33}N_2O_{10}SCrNa$: C, 43.45; H, 5.72; S, 5.52. Found: C, 43.17; H, 6.06; S, 5.80.

The analogous metal carbonyl derivatives containing the [PPN]$^+$ counterion were synthesized according to the published procedure of Gingerich and Angelici.[7]

**$^{13}$CO Enrichment Studies.** [PPN][Cr(CO)$_5$SH] was enriched to a level of 10.5% in total $^{13}$CO content by stirring a CDCl$_3$ solution of the hydrogen sulfide species with carbon monoxide (91.6% enriched in $^{13}$CO) at 0 °C for 5 min. The extent of enrichment was determined from the relative intensities of the equatorial carbonyl resonance with those of the [PPN]$^+$ counterion by using a natural abundance sample as a basis for comparison.

Qualitative $^{13}$CO enrichment studies were performed by employing the [Na-kryptofix-221][M(CO)$_5$SH] (M = Cr, Mo, W) salts in CD$_3$CN.

**Infrared Measurements.** The infrared spectra were recorded in 0.1- or 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an infrared data station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm$^{-1}$ and against a CO spectrum above 2000 cm$^{-1}$.

**$^{13}$C NMR Spectra.** The $^{13}$C NMR spectra were recorded on a JEOL FX 60 spectrometer operated at 15.03 MHz with an internal deuterium lock. Samples were run in either CD$_3$CN or CDCl$_3$ solvent in 10-mm tubes. Spectra were determined by employing a sweep width of 4000 Hz (16K data block) with an acquisition time of 2 s, a pulse repetition rate of 5 s, and a flip angle of 30°.

**$^1$H NMR Spectra.** The $^1$H NMR spectra were measured on a Varian EM-390 spectrometer in CD$_3$CN solutions with Me$_4$Si as reference.

**Crystallographic Studies.** Crystallographic analyses were carried out by Dr. Cynthia S. Day at Crystalytics Co. (Lincoln, Nebraska). Crystals of [Na-kryptofix-221][Cr(CO)$_5$SH] are, at 20 ± 1 °C, orthorhombic with $a$ = 13.451 (3) Å, $b$ = 20.067 (3) Å, $c$ = 20.725 (4) Å, $V$ = 5594 (2) Å$^3$, $Z$ = 8 ($\mu_a$(Mo K$\bar{\alpha}$)$^{16a}$ = 0.57 mm$^{-1}$, and $d_{calcd}$ = 1.38 g cm$^{-3}$). Systematic absences indicated the space group to be $Pbca$—$D_{2h}^{15}$ (No. 61).[17]

Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer by using 1.0° wide $\omega$ scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation for a specimen having the shape of a cube with dimensions of 0.80 mm. This crystal was mounted on the goniometer head with its long dimension nearly parallel to the phi axis of the diffractometer. A total of 6422 independent reflections having $2\theta \leq 55°$ were measured in two shells. A scanning rate of 6.0°/min was used to measure intensities for reflections having $3° \leq 2\theta \leq 43°$, and a rate of 4.0°/min was used for all others. Each of these 1.00° scans was divided into 17 equal time intervals, and those 13 contiguous intervals that had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan, were measured at $\omega$ settings 1.0° above and below the calculated value for each reflection. The intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

The positions of the Cr and S atoms were derived by using the SHELXTL direct methods software from Nicolet; the 34 remaining nonhydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the chromium and sulfur atoms [$R_1$ = 0.526 for 2635 independent reflections having $2\theta_{MoK\bar{\alpha}} \leq 55°$ and $I > 3\sigma(I)$]. Isotopic unit-weighted full-matrix least-squares refinement for the 36 nonhydrogen atoms gave $R_1$(unweighted, based on $F$) = 0.105 and $R_2$(weighted) = 0.105, where anisotropic refinement converged to $R_1$ = 0.070 and $R_2$ = 0.075. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ for 2635 reflections having $2\theta_{MoK\bar{\alpha}} \leq 55°$ and $I > 3\sigma(I)$.[18] These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[19] and an anomalous dispersion correction to the scattering factors of the chromium, sulfur, and sodium atoms.[16b]

The position for the hydrogen atom of the anion was derived from a difference Fourier. The hydrogen positions for the cation were not varied and were calculated before the final cycle of least-squares refinement by using idealized sp$^3$-hybridized geometry and a C–H bond length of 0.95 Å. These hydrogen atoms were assigned a fixed isotropic thermal parameter of 6.00 Å. Further unit-weighted least-squares refinement with those reflections having $2\theta_{MoK\bar{\alpha}} < 55.0°$, which employed an isotropic thermal parameter for the hydrogen atom of the SH ligand (final value of 15 (2) Å$^2$) but was otherwise anisotropic, gave $R_1$ = 0.046 and $R_2$ = 0.045 for 2635 reflections having $I > 3\sigma(I)$.

The final cycle of empirically weighted[20,21] least-squares refinement, which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others, converged to $R_1$ = 0.046, $R_2$ = 0.052, and GOF = 1.34[22] for 2635 reflections.

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic, and a Data General disk with 10 million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

## Results and Discussion

**Synthesis.** The reaction of cryptand-solubilized NaSH in acetonitrile solutions of M(CO)$_6$ (M = Cr, Mo, W) provides a route to [Na(cryptand)][M(CO)$_5$SH] derivatives in high yields. Although both [Na-kryptofix-221]$^+$[SH]$^-$ and [Na-kryptofix-222]$^+$[SH]$^-$ react to afford the same product, reactions involving the kryptofix-221 salt occurred at faster rates. Reaction 3 takes place slowly at ambient temperature; however, identical products are obtained at more reasonable rates for processes carried out at 60 °C.

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(16) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(17) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV: (a) pp 55–66; (b) pp 149–150; (c) pp 99–101.

(18) The anisotropic thermal parameter is of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

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(20) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma_F^2$.

(21) For empirical weights, $\sigma_F = \sum_0^3 a_n|F_o|^n = a_0 + a_1|F_o| + a_2|F_o|^2 + a_3|F_o|^3$ with the $a_n$ being coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$. In this case $a_0 = 1.86$, $a_1 = -1.36 \times 10^{-2}$, $a_2 = 1.66 \times 10^{-4}$, and $a_3 = -1.97 \times 10^{-7}$.

(22) GOF = $\{\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})\}^{1/2}$, where NO is the number of observations and NV is the number of variables.

Table I. Spectroscopic Data for [Na-kryptofix-221][$M(CO)_5SH$] Compounds[a]

| M | $\nu(CO)$,[b] cm$^{-1}$ $A_1^{(2)}$ | $A_1^{(1)}$ | E | $\delta(C)$[c] C(ax) | C(eq) | $^1H$ NMR,[c] $\delta$ |
|---|---|---|---|---|---|---|
| Cr | 2046 w | 1853 m | 1915 s | 225.7 | 220.6 | |
| | (2044) | (1849) | (1914) | (224.3) | (219.4) | (14.67) |
| Mo | 2058 w | 1850 m | 1920 s | | | |
| | (2037) | (1846) | (1913) | | | (13.38) |
| W | 2057 w | 1847 m | 1912 s | 203.5 | 200.6 | 13.45 |
| | (2056) | (1843) | (1912) | (203.4) | (199.8) | (12.93) |

[a] Values in parentheses were obtained on the [PPN]$^+$ salts as reported in ref 7. [b] In $CH_3CN$. [c] In $CD_3CN$.

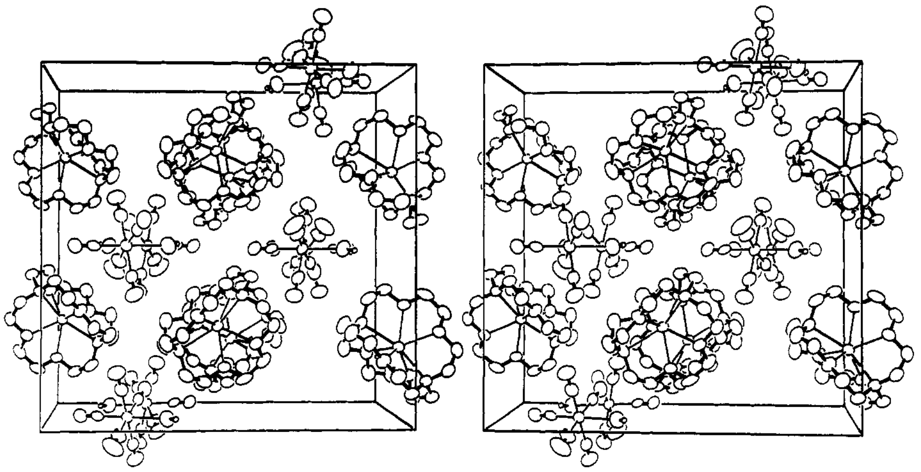

**Figure 1.** A stereoscopic view of the packing in [Na-kryptofix-221][$Cr(CO)_5SH$].

No intermediate, in particular, the metallo thiocarboxylic acid $M(CO)_5COSH^-$, was observed during the formation of the $M(CO)_5SH^-$ species. Nevertheless this species is the presumed transient since the rate of $M(CO)_5SH^-$ production was enhanced with increasing $SH^-$ concentration, i.e., an observation suggestive of nucleophilic addition of $SH^-$ to the metal carbonyl substrate at the carbonyl carbon atom center in the rate-determining step. Furthermore, the reaction rates as a function of metal, Mo ≫ W > Cr, are consistent with metal–CO bond dissociation. These observations taken in aggregate are indicative of a process as described in eq 4 and is reminiscent of hydroxide-as-

$$(CO)_5MC(=O)SH^- \rightarrow (CO)_4MC(=O)SH^- + CO \rightarrow (CO)_5MSH^- \quad (4)$$

sisted ligand substitution processes involving the group 6B metal hexacarbonyls.[23-25] On the other hand, unlike the analogous reaction of K(cryptand)$^+OH^-$ with $M(CO)_6$ in aprotic solvents, where 2 mol of $OH^-$ are required to effect the formation of $M(CO)_5H^-$ via the intermediacy of the $M(CO)_5COOH^-$ species,[2,3] the sole product from reaction 3 is $M(CO)_5SH^-$ regardless of the $M(CO)_6/SH^-$ mole ratio.

The infrared spectra in the $\nu$(CO) region (Table I) display the familiar three-band pattern consistent with $C_{4v}$ symmetry about the $M(CO)_5$ moiety and indicative of no perturbation of the anionic species by the encapsulated sodium counterion at the carbonyl oxygen atoms (vide infra).[26,27] Similarly, the $^{13}C$ NMR spectra, obtained on $^{13}C$-enriched samples of $M(CO)_5SH^-$, exhibit two resonances of the appropriate intensity pattern generally noted in $C_{4v}$ $M(CO)_5$ molecules. These $^{13}C$ resonances are tabulated in Table I along with comparable values reported for the PPN$^+$ salts by Gingerich and Angelici.[7] The anionic ions were further characterized by a $^1H$ resonance at ~13 ppm for the hydrogen sulfide ligand.

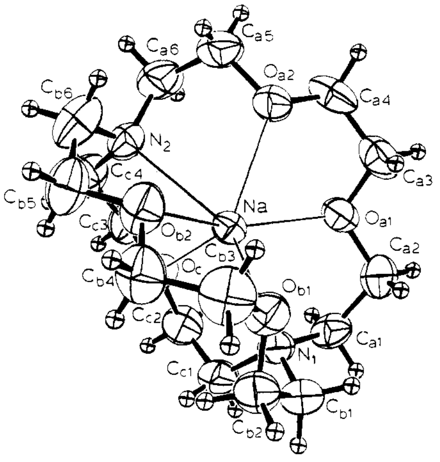

**Figure 2.** The [Na-kryptofix-221]$^+$ cation in [Na-kryptofix-221][$Cr(CO)_5SH$] with thermal ellipsoids at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

**Solid-State Structure.** The final atomic coordinates for all non-hydrogen atoms of both the cation and anion are provided in Table II. The anisotropic thermal parameters for all nonhydrogen atoms of both the cation and anion and the calculated atomic coordinates for the cation's hydrogen atoms in crystalline [$NaC_{16}H_{32}N_2O_5$][$Cr(CO)_5SH$] are available as supplementary material. Bond lengths and bond angles for the anion are presented in Table III, whereas the corresponding values for the cation are provided as supplementary material. The structure of [Na-kryptofix-221][$Cr(CO)_5SH$] consists of an array of the two discrete ionic units, at normal van der Waals distances

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Table II. Atomic Coordinates for Anionic and Cationic Non-Hydrogen Atoms in Crystalline $[Cr(CO)_5(SH)][NaC_{16}H_{32}N_2O_5]$[a]

| atom[b] | *x* | *y* | *z* |
|---|---|---|---|
| | Anion | | |
| Cr | 0.08749 (6) | 0.00444 (4) | 0.27664 (3) |
| S | 0.14612 (15) | 0.00379 (10) | 0.16354 (8) |
| $O_1$ | −0.0984 (3) | 0.0733 (2) | 0.2279 (2) |
| $O_2$ | −0.0103 (4) | −0.1283 (2) | 0.2534 (2) |
| $O_3$ | 0.2802 (3) | −0.0639 (2) | 0.3130 (3) |
| $O_4$ | 0.1770 (3) | 0.1394 (2) | 0.3060 (2) |
| $O_5$ | 0.0122 (3) | 0.0035 (2) | 0.4112 (2) |
| $C_1$ | −0.0288 (4) | 0.0471 (2) | 0.2457 (2) |
| $C_2$ | 0.0280 (4) | −0.0810 (2) | 0.2607 (2) |
| $C_3$ | 0.2089 (4) | −0.0386 (3) | 0.2989 (3) |
| $C_4$ | 0.1459 (4) | 0.0888 (3) | 0.2927 (2) |
| $C_5$ | 0.0394 (3) | 0.0040 (2) | 0.3628 (2) |
| H[c] | 0.224 (6) | 0.009 (4) | 0.139 (4) |
| | Cation | | |
| Na | 0.33680 (12) | 0.27937 (8) | 0.02730 (8) |
| $O_{a1}$ | 0.4112 (3) | 0.2340 (1) | −0.0747 (2) |
| $O_{a2}$ | 0.2979 (3) | 0.1623 (1) | 0.0083 (2) |
| $O_{b1}$ | 0.2255 (2) | 0.3671 (2) | −0.0142 (2) |
| $O_{b2}$ | 0.1971 (3) | 0.3009 (2) | 0.1020 (2) |
| $O_c$ | 0.4821 (2) | 0.3115 (2) | 0.0858 (2) |
| $N_1$ | 0.4377 (3) | 0.3690 (2) | −0.0361 (2) |
| $N_2$ | 0.3535 (3) | 0.2119 (2) | 0.1334 (2) |
| $C_{a1}$ | 0.4931 (4) | 0.3369 (3) | −0.0886 (2) |
| $C_{a2}$ | 0.4322 (4) | 0.2842 (3) | −0.1215 (2) |
| $C_{a3}$ | 0.3492 (4) | 0.1834 (3) | −0.0983 (3) |
| $C_{a4}$ | 0.3400 (4) | 0.1322 (2) | −0.0468 (3) |
| $C_{a5}$ | 0.2948 (5) | 0.1204 (3) | 0.0634 (3) |
| $C_{a6}$ | 0.3665 (5) | 0.1426 (3) | 0.1141 (3) |
| $C_{b1}$ | 0.3668 (4) | 0.4179 (2) | −0.0621 (3) |
| $C_{b2}$ | 0.2784 (4) | 0.4290 (2) | −0.0186 (3) |
| $C_{b3}$ | 0.1344 (4) | 0.3704 (3) | 0.0222 (3) |
| $C_{b4}$ | 0.1507 (4) | 0.3633 (3) | 0.0919 (3) |
| $C_{b5}$ | 0.2216 (4) | 0.2890 (3) | 0.1679 (3) |
| $C_{b6}$ | 0.2645 (5) | 0.2210 (3) | 0.1734 (3) |
| $C_{c1}$ | 0.5043 (4) | 0.4001 (2) | 0.0112 (3) |
| $C_{c2}$ | 0.5551 (4) | 0.3499 (3) | 0.0537 (3) |
| $C_{c3}$ | 0.5226 (4) | 0.2612 (3) | 0.1262 (2) |
| $C_{c4}$ | 0.4410 (4) | 0.2358 (3) | 0.1682 (3) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] The atomic coordinates for this hydrogen atom were derived from a difference Fourier map and were least-squares refined with a final value of 15 (2) Å$^2$ for the isotropic thermal parameter.

(Figure 1). The three-dimensional structure of the cation is shown in Figure 2, which illustrates that the sodium ion is heptacoordinated, analogous to the original structural report of Weiss and co-workers[28] on the thiocyanate salt.

The bond lengths, polyhedral edge lengths, and bond angles subtended at the $Na^+$ ion in crystalline $[NaC_{16}H_{32}N_2O_5][Cr(CO)_5SH]$ are provided as supplementary material. These are quite similar to those reported for kryptofix-221 encircled sodium ion,[28] where the Na–N distances average 2.600 (4) Å. The four basal Na–O bond distances average 2.472 Å, with the apical Na–O distance being somewhat shorter at 2.389 (4) Å. The mean values of the bond lengths and angles in the cryptand ligand are similar to those found in related instances.[28,29]

In general, the dimensions of the metallo thiol anionic species are comparable to those found in other monosubstituted chromium carbonyls. Comparative Cr–C bond distances are tabulated for derivatives where structural

Table III. Anion Bond Lengths, Polyhedral Edge Lengths, and Bond Angles in Crystalline $[Cr(CO)_5(SH)][NaC_{16}H_{32}N_2O_5]$[a]

| | | | |
|---|---|---|---|
| | Bond Lengths, Å | | |
| Cr–S[b] | 2.473 (2) | $O_1$–$C_1$ | 1.134 (6) |
| Cr–$C_1$ | 1.895 (5) | $O_2$–$C_2$ | 1.090 (7) |
| Cr–$C_2$ | 1.921 (5) | $O_3$–$C_3$ | 1.123 (7) |
| Cr–$C_3$ | 1.905 (5) | $O_4$–$C_4$ | 1.132 (7) |
| Cr–$C_4$ | 1.895 (5) | $O_5$–$C_5$ | 1.069 (6) |
| Cr–$C_5$ | 1.898 (5) | S–H | 1.17 (8) |
| S···$C_1$ | 3.031 (5) | $C_1$···$C_5$ | 2.735 (7) |
| S···$C_2$ | 3.078 (5) | $C_2$···$C_5$ | 2.722 (7) |
| S···$C_3$ | 3.052 (6) | $C_3$···$C_5$ | 2.771 (7) |
| S···$C_4$ | 3.174 (5) | $C_4$···$C_5$ | 2.656 (7) |
| $C_1$···$C_2$ | 2.701 (7) | $C_2$···$C_3$ | 2.697 (7) |
| $C_1$···$C_4$ | 2.677 (7) | $C_3$···$C_4$ | 2.696 (8) |
| | Bond Angles, Deg | | |
| $SCrC_5$ | 178.6 (2) | CrSH | 134 (4) |
| $SCrC_1$ | 86.8 (2) | $CrC_1O_1$ | 179.0 (4) |
| $SCrC_2$ | 88.0 (2) | $CrC_2O_2$ | 176.0 (5) |
| $SCrC_3$ | 87.4 (2) | $CrC_3O_3$ | 179.0 (5) |
| $SCrC_4$ | 92.2 (2) | $CrC_4O_4$ | 175.4 (5) |
| | | $CrC_5O_5$ | 179.8 (4) |
| $C_1CrC_2$ | 90.1 (2) | $C_3CrC_5$ | 93.5 (2) |
| $C_1CrC_4$ | 89.9 (2) | $C_4CrC_5$ | 88.9 (2) |
| $C_1CrC_5$ | 92.3 (2) | $C_1CrC_3$ | 174.2 (2) |
| $C_2CrC_3$ | 89.7 (2) | $C_2CrC_4$ | 179.8 (2) |
| $C_2CrC_5$ | 90.9 (2) | | |
| $C_3CrC_4$ | 90.4 (2) | | |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3.

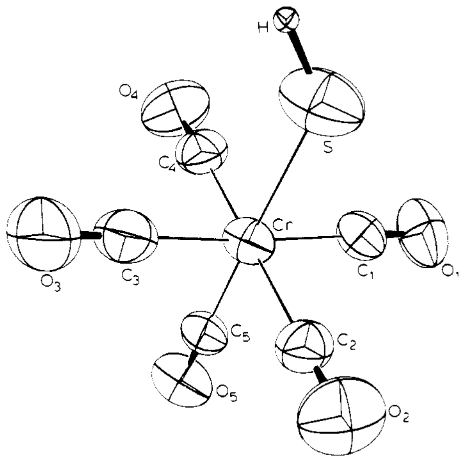

**Figure 3.** The $[Cr(CO)_5SH]^-$ anion in [Na-kryptofx-221][Cr(CO)$_5$SH]. All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density.

data are available in Table IV, with those parameters for the compound under consideration distinguished by an inclosure. The disposition of the ligands about the chromium atom is that of a regular octahedron, where the average C(ax)–Cr–C(eq) angle is 91.4° (Figure 3). The Cr–C(eq) distances average 1.904 (5) Å, while the axial Cr–$C_5$ bond length is essentially the same at 1.898 (5) Å. Hence, the thiol ligand, situated 2.473 (2) Å from the chromium metal center, does not exert a significant trans effect. This is to be contrasted with the trans influence, that is a shortening of the Cr–C(ax) bond by from 0.035 to 0.087 Å, observed for other sulfur and oxygen donor ligands as shown in Table IV. A best-fit least-square plane containing the thiol ligand and the chromium atom is perpendicular to the plane defined by the equatorial carbonyl groups and forms a dihedral angle of 36° with the

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(28) Mathieu, F.; Metz, B.; Moras, D.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4412.

(29) Metz, B.; Moras, D.; Weiss, R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 423.

**Table IV. Comparative Cr-C Bond Distances (Å) in $Cr(CO)_5L$ Derivatives**

| L | Cr-C(eq) | Cr-C(ax) | Δ | wt av (Cr-C) | ref |
|---|---|---|---|---|---|
| CO | 1.909 (3) | 1.909 (3) | 0.000 | 1.909 (3) | *a* |
| $S(O)C_4H_6$ | 1.917 | 1.858 | 0.059 | 1.905 | *b* |
| *$SH^-$* | *1.904 (5)* | *1.898 (5)* | *0.006* | *1.903 (5)* | *c* |
| $P(OPh)_3$ | 1.896 (4) | 1.861 (4) | 0.035 | 1.889 (4) | *d* |
| $P(CH_2CH_2CN)_3$ | 1.891 (4) | 1.876 (4) | 0.015 | 1.888 (4) | *e* |
| $I^-$ | 1.893 (16) | 1.859 (15) | 0.034 | 1.886 (16) | *f* |
| $SC(O)H^-$ | 1.894 (4) | 1.837 (4) | 0.047 | 1.883 (4) | *g* |
| $SPMe_3$ | 1.900 (4) | 1.815 (8) | 0.085 | 1.883 (5) | *h* |
| THF | 1.899 (5) | 1.812 (5) | 0.087 | 1.882 (5) | *i* |
| $O_2CCF_3^-$ | 1.896 (7) | 1.815 (7) | 0.081 | 1.880 (7) | *j* |
| $PPh_3$ | 1.880 (4) | 1.844 (4) | 0.036 | 1.873 (4) | *d* |
| $H^-$ | 1.865 (3) | 1.852 (4) | 0.013 | 1.862 (3) | *k* |
| $P(CH_3)_2SH$ | 1.87 (2) | 1.829 (2) | 0.041 | 1.862 (2) | *l* |

[a] Whitaker, A.; Jeffery, J. W. *Acta Crystallogr.* **1967**, *23*, 977. [b] Eekhof, H.; Hogeveen, H.; Kellogg, R. M. *J. Organomet. Chem.* **1978**, *161*, 361. [c] This work. [d] Plastas, H. J.; Stewart, J. M.; Grim, S. O. *J. Am. Chem. Soc.* **1969**, *91*, 4326. [e] Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 578. [f] Calhoun, H. P.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1974**, 377. [g] See ref 14. [h] Baker, E. N.; Reay, B. R. *Ibid.* **1973**, 2205. [i] Schubert, U.; Friedrich, P.; Orama, O. *J. Organomet. Chem.* **1978**, *144*, 175. [j] See ref 12. [k] Darensbourg, M. Y.; Bau, R.; Marks, M.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.*, in press. [l] Meier, Von W.-P.; Strahle, J.; Lindner, E. *Z. Anorg. Allg. Chem.* **1976**, *424*, 154.

plane defined by S, $C_1$, $C_3$, and $C_5$. The S–H distance is 1.17 (8) Å with a H–S–Cr bond angle of 134 (4)°.

The most striking difference seen in this structural report as compared with that of $[Na(18\text{-crown-}6)][W(CO)_5SH]$[8] is the lack of $Na–O(carbonyl)_{axial}$ interaction being observed. This further demonstrates that crown ether macrocycles do not completely encapsulate the sodium cation as does the cryptand ligand. Contact-ion formation of alkali-metal ions specifically at the axial carbonyl ligand of isoelectronic $V(CO)_5L^-$ species in solution has been reported and accounted for on the basis of charge distribution in the anion, by Darensbourg and Hanckel.[26,27]

**Solution Studies of the $M(CO)_5SH^-$ Anions.** We have previously demonstrated the ability of oxygen donor ligands to labilize metal–CO bonds in $M(CO)_5$(oxygen bases)$^-$ and related derivatives.[1,2,9–13] Similarly the thioformate ligand was shown to be a strong CO-labilizing ligand in the group 6B $M(CO)_5SC(O)H^-$ anionic species.[2,14] Hence it was of interest to characterize the metallo thiol derivatives with regard to the CO-labilizing ability of the $SH^-$ ligand.

Reaction 5 was carried out on the $[PPN]^+$ salt in order to be consistent with previous rate investigations.[30]

$$M(CO)_5SH^- + n^{13}CO \rightleftharpoons M(CO)_{5-n}(^{13}CO)_nSH + n^{12}CO \quad (5)$$

However, qualitative CO-exchange rate studies illustrated no significant differences in the $[PPN]^+$ or [Na-kryptofix-221]$^+$ counterions. Both the chromium and tungsten pentacarbonyl derivatives were found to undergo complete CO exchange with free $^{13}CO$ in $CH_3CN$ within 1 h at 20 kPa of carbon monoxide, with $Cr(CO)_5SH^-$ reacting faster than $W(CO)_5SH^-$ (70% vs. 50% in 10 min at ambient temperature). Quantitatively, in the chromium species the thiol ligand is slightly less CO-labilizing than the acetate ligand (10.5% vs. 15% CO exchange at 0 °C for 5 min), either of which is much more CO-labilizing than the bromide ion (14% at 23 °C for 30 min).[30]

The natural abundance $^{13}C$ NMR spectrum of $[PPN][Cr(CO)_5SH]$ in $CDCl_3$ exhibits two carbonyl resonances at 226.4 and 220.6 ppm assignable to the axial and equatorial carbon monoxide ligands, respectively. Upon incorporation of $^{13}CO$ into the $Cr(CO)_5SH^-$ anion at 0 °C in $CDCl_3$ for 5 min, the sample was enriched to a total $^{13}CO$ content of 10.5% with the peak for the cis CO ligands at 220.6 ppm, accounting for all the $^{13}CO$ uptake. This is illustrated in Figure 4 where the $^{13}C$ NMR spectrum of the

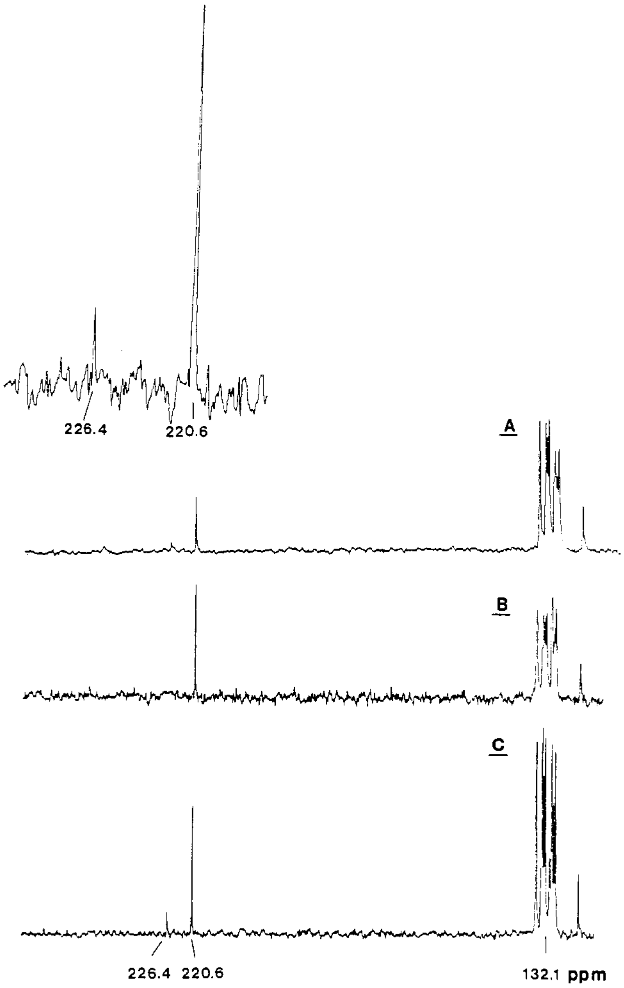

**Figure 4.** $^{13}C$ NMR spectra of $[PPN][Cr(CO)_5SH]$ in $CDCl_3$: A, natural abundance spectrum with δ(C(ax)) at 226.4 ppm and δ(C(eq)) at 220.6 ppm. The most upfield multiplet corresponds to the carbon resonances of the $[PPN]^+$ cation; B, after exchange with $^{13}CO$ at 0 °C for 5 min (spectrum determined at −50 °C); C, sample in B allowed to equilibrate CO groups at ambient temperature for several hours ($^1J^{13}C(ax)–Cr–^{13}C(eq)$ = 5.46 Hz).

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[30] Darensbourg, D. J.; Kudaroski, R. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, Aug 1981; American Chemical Society, Washington, DC, 1981, INOR #50.

$^{13}C$-enriched sample was determined at −50 °C to avoid subsequent processes leading to CO rearrangement in the sample during the acquisition of the NMR data.

Thus the thiol ligand represents another example of a cis-labilizing ligand.[31] That is, the $SH^-$ ligand stabilizes the intermediate afforded upon CO dissociation, $[M(CO)_4SH]^-$, by exhibiting a strong preference for the equatorial site in the square-pyramidal structure.[31] A characteristic feature seen in other $M(CO)_5L$ complexes where L is a CO-labilizing ligand, which is absent in this instance, is a trans shortening of the axial M–CO bond relative to that of the equatorial M–CO bonds (e.g., see Table IV).

The $M(CO)_5SH^-$ species were shown to undergo proton exchange in protic medium; i.e., the reversible reaction (6)

$$M(CO)_5SH^- + D_2O \xrightleftharpoons{CH_3CN} M(CO)_5SD^- + H_2O \quad (6)$$

was observed at ambient temperature. On the other hand, Gingerich and Angelici[7] have reported that they were unable to deprotonate $W(CO)_5SH^-$ with large excesses of very strong bases, e.g., NaOEt, NaH, or LiMe. It is hoped to resolve this apparent inconsistency by performing more detailed studies aimed at determining the acidity of the thiol ligand's proton in these derivatives, for the resulting $M(CO)_5S^{2-}$ complexes might serve as quite useful models for metal carbonyls adsorbed at sulfide sites on surfaces.[32]

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**Registry No.** $[Na(cryptand)][Cr(CO)_5SH]$, 82374-30-9; $[Na(cryptand)][Mo(CO)_5SH]$, 82374-31-0; $[Na(cryptand)][W(CO)_5SH]$, 82374-32-1; $[Na(kryptofix\text{-}221)]^+SH^-$, 82374-33-2; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

**Supplementary Material Available:** Tables of the structure factor amplitudes, anisotropic thermal parameters, cation bond lengths and angles, bond lengths and angles subtended at the sodium ion, and the idealized atomic coordinates for cation hydrogen atoms (19 pages). Ordering information is given on any current masthead page.

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(32) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456 and references therein.

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# Enthalpy of Formation of Acyl-, Alkyl-, and Hydridopentacarbonylmanganese Complexes. The Enthalpy Contributions of Manganese–Hydrogen and Manganese–Carbon Bonds in these Molecules. Thermochemical Aspects of Models in Fischer–Tropsch Reactions

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Microcalorimetric measurements at elevated temperatures of the enthalpies of sublimation, thermal decomposition, bromination, and iodination of pentacarbonylmanganese complexes, $[Mn(CO)_5R]$, have been made to obtain the standard enthalpies of formation, $\Delta H_f°(c)$ and $\Delta H_f°(g)$ (in that order) as follows (values in kJ $mol^{-1}$): $[Mn_2(CO)_{10}]$ −(1675 ± 8), −(1585 ± 5); $[Mn(CO)_5Br]$ −(964 ± 4), −(876 ± 5); $[Mn(CO)_5I]$ −(911 ± 5), −(834 ± 5); $[Mn(CO)_5H](l)$ −(778 ± 10), −(740 ± 10); $[Mn(CO)_5CH_3]$ −(813 ± 4), −(753 ± 4); $[Mn(CO)_5CF_3]$ −(1464 ± 4), −(1386 ± 4); $[Mn(CO)_5C_6H_5]$ −(675 ± 5), −(590 ± 7); $[Mn(CO)_5CH_2C_6H_5]$ −(726 ± 8), −(642 ± 8); $[Mn(CO)_5COCH_3]$ −(977 ± 7), −(897 ± 10); $[Mn(CO)_5COCF_3]$ −(1587 ± 5), −(1508 ± 8); $[Mn(CO)_5COC_6H_5]$ −(848 ± 5), −(725 ± 6). The enthalpy of formation of $[Mn(CO)_5H]$ was obtained from solution calorimetric measurements at 298 K of the heat of reaction of the liquid hydride with excess iodine in benzene solvent. The $\Delta H_f°(g)$ values are used to derive the bond enthalpy contributions $D(R\text{–}Mn(CO)_5)$, relative to an accepted value of 94 kJ $mol^{-1}$ for $D(Mn\text{–}Mn)$ in $[Mn_2(CO)_{10}]$ at 298 K. For the organic radicals R = $CH_3$, $CH_2C_6H_5$, $C_6H_5$, and $COC_6H_5$, values of $D(R\text{–}Mn(CO)_5)$ vary with changes in R in the same way as the values of $D(R\text{–}H)$ and $D(R\text{–}CH_3)$. For R = $CF_3$ and $COCH_3$, the values of $D(R\text{–}Mn(CO)_5)$ are slightly higher than expected from direct comparison with $D(R\text{–}H)$. The energetics of carbonylation of $[Mn(CO)_5R]$ to give $[Mn(CO)_5COR]$ (R = $CH_3$, $C_6H_5$, $CF_3$) are considered. The formation of the unknown $[Mn(CO)_5CHO]$ from $[Mn(CO)_5H]$ is shown to be unfavorable. Reductive elimination reactions between $[Mn(CO)_5H]$ and $[Mn(CO)_5R]$ or $[Mn(CO)_5COR]$ to form $Mn_2(CO)_{10}$ and RH or RCHO or $RCH_2OH$, respectively, are shown to be favorable on the basis of the calculated enthalpy change.

## Introduction

A previous study reported[1] microcalorimetric measurements of the enthalpy of iodination of methylpentacarbonylmanganese from which the enthalpy of formation was derived. The present work reexamines this complex and extends the study to other derivatives, $[Mn(CO)_5R]$ (R = H, Br, I, $CF_3$, $C_6H_5$, $CH_2C_6H_5$, $COCH_3$, $COCF_3$, and $COC_6H_5$). The microcalorimetric measurements include enthalpies of sublimation, of thermal decomposition, of

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