

## Preliminary communication

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### STABILISATION OF TRANSITION METAL CARBONYLATE COMPLEXES BY ALKALI METAL CROWN-ETHER CATIONS: THE X-RAY STRUCTURE ANALYSIS OF TWO SODIUM-CARBONYL LINKED POLYMERIC STRUCTURES

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#### Summary

Ultraviolet irradiation has provided a convenient synthetic route to the anions  $[M(CO)_5SH]^-$  and  $[M_2(CO)_{10}(\mu-SH)]^-$  ( $M = Cr, Mo, \text{ and } W$ ) which were isolated as the sodium 18-crown-6-ether salts. X-ray analysis has shown that the complexes  $[Na(18\text{-crown-}6)][W(CO)_5SH]$  (I) and  $[Na(18\text{-crown-}6)][W_2(CO)_{10}(\mu-SH)]$  (II) are chain polymeric in nature with sodium-carbonyl linkages between alternating cations and anions.

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As an extension of our work [1—4] on anionic organosulphur ligands and their transition metal compounds we have prepared the anionic complexes of chromium, molybdenum and tungsten pentacarbonyl with the ligand  $HS^-$ . Both the monomeric and dimeric anions,  $[M(CO)_5SH]^-$  and  $[M_2(CO)_{10}(\mu-SH)]^-$  have been prepared by irradiating the appropriate mixtures of  $M(CO)_6$  and  $Na_2S \cdot 9H_2O$  in the presence of (18-crown-6). In the course of this work the monomeric anions  $[M(CO)_5SH]^-$  were reported as the  $(PPN)^+$  salts and one of the dimeric anions,  $[W_2(CO)_{10}(\mu-SH)]^-$  was isolated as the  $(NEt_4)^+$  salt [5]. With these counterions, the salts were relatively unstable in the solid state. We have found that use of  $(Na-18\text{-crown-}6)^+$  as the counterion gives salts of much greater stability. Crystals of the  $(Na-18\text{-crown-}6)^+$  salts of  $[W(CO)_5SH]^-$  and  $[W_2(CO)_{10}(\mu-SH)]^-$  are stable indefinitely whereas the  $PPN^+$  salt of

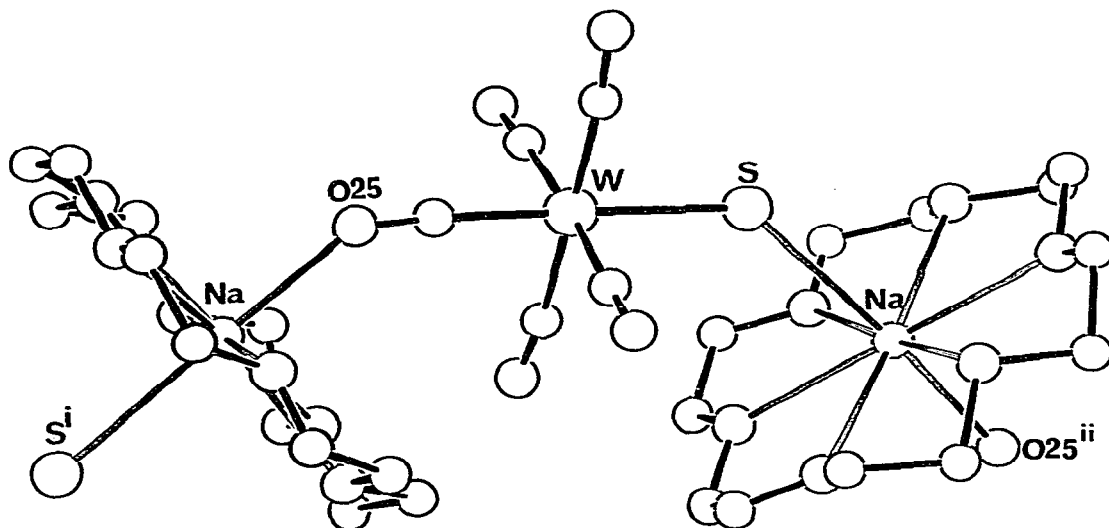


Fig. 1. The structure of  $[\text{Na}(18\text{-crown-6})][\text{W}(\text{CO})_5\text{SH}]$  (I), bond lengths ( $\text{\AA}$ ) to the Na atom are:

Na—O(1)	2.91(2)	Na—O(4)	2.62(2)	Na—O(7)	2.74(2)
Na—O(10)	2.69(2)	Na—O(13)	2.71(2)	Na—O(16)	2.84(2)
Na—O(25)	2.41(2)	Na—S <sup>i</sup>	3.014(9)	W—S	2.567(5)
W—C <sub>eq</sub>	2.021–2.051(11)		W—C <sub>ax</sub>	1.947(21)	

Crystal data for (I):  $Pna2_1$ ,  $a$  16.484(3),  $b$  7.622(2),  $c$  19.220(3)  $\text{\AA}$ ,  $R = 0.044$  for 2561 unique observed data. The symmetry related atom S<sup>i</sup> is at  $1-x, 1-y, 0.5+z$ .

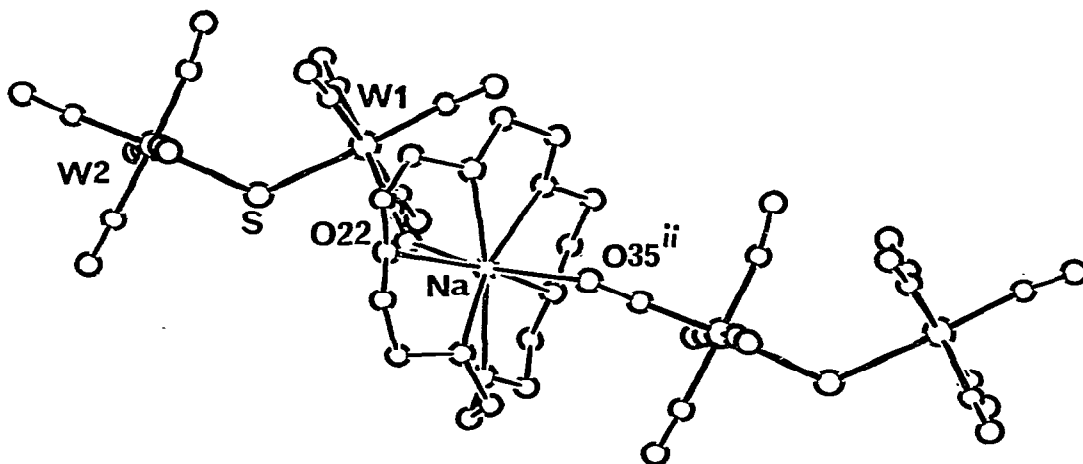


Fig. 2. The structure of  $[\text{Na}(18\text{-crown-6})][\text{W}_2(\text{CO})_{10}(\mu\text{-SH})]$  (II), bond lengths ( $\text{\AA}$ ) to the Na atom are:

Na—O(1)	2.727(7)	Na—O(4)	2.575(2)	Na—O(7)	2.654(9)
Na—O(10)	2.588(7)	Na—O(13)	2.581(5)	Na—O(16)	2.637(6)
Na—O(22)	2.471(5)	Na—O(35 <sup>ii</sup> )	2.458(5)	W—S	2.587(2), 2.596(2)
W—C <sub>eq</sub>	2.001–2.057(5)		W—C <sub>ax</sub>	1.975(8), 1.938(6)	

Crystal data for (II):  $P\bar{1}$ ,  $a$  15.014(2),  $b$  11.874(2),  $c$  9.636(2)  $\text{\AA}$ ,  $\alpha$  102.28(2),  $\beta$  96.29(2), and  $\gamma$  100.63(2)°,  $R = 0.031$  for 5492 unique observed data. The symmetry related atom O(35<sup>ii</sup>) is at  $x, -1+y, -1+z$ .

$[\text{W}(\text{CO})_5\text{SH}]^-$  decomposes after one month and  $[\text{NEt}_4][\text{W}_2(\text{CO})_{10}(\mu\text{-SH})]$  within 12 h [5].

X-Ray structural analyses show these (Na-18-crown-6)<sup>+</sup> salts, of  $[\text{W}(\text{CO})_5\text{SH}]^-$  (I) and  $[\text{W}_2(\text{CO})_{10}(\mu\text{-SH})]^-$  (II), have a chain polymeric structure with direct carbonyl oxygen to sodium linkages as shown in Fig. 1 and 2, respectively.

Tight ion-pairing in alkali metal salts of carbonyl anions in solution appear to be due to two main types of interaction [6]. The first is between the alkali metal cation and a carbonyl oxygen atom. The second type arises from a direct alkali metal interaction with the transition metal atom of the anion.

Evidence that these interactions persist in the solid state was first obtained from the X-ray structure determination of  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5\text{C}_4\text{H}_8\text{O}$  [7]. A short  $\text{Na}^+\text{-O}$  (carbonyl) distance of 2.32 Å was found together with a  $\text{Na}^+\cdots\text{Fe}$  interaction of ca. 3.0 Å whereby the close proximity of the  $\text{Na}^+$  cation caused a distortion of the  $\text{C-Fe-C}$  angle from tetrahedral to a value of 129.7°. Neither of these types of ion-pairing are possible with non-metallic cations such as  $(\text{PPN})^+$ .

Chihonski and Levenson [8] have reported the use of crown ether salts in the synthesis of transition metal carbonyl compounds; however these workers suggested that ion-pairing may have the disadvantage of reducing reaction rates. Our results emphasize that in the synthesis of anionic metal carbonyl complexes the use of alkali metal crown ether counterions such as (Na-18-crown-6)<sup>+</sup> allows  $\text{Na-O}$  (carbonyl) linkages to form and greatly improves the stability of the product.

A further advantage of encircling the sodium ion by an equatorial girdle of ether oxygen atoms is that the alkali-metal transition-metal type of interactions and the resulting geometrical distortions of the anions are prevented. The use of cryptand encapsulated cations, cations, however, would be expected to offer no advantage in stability compared to counterions such as  $(\text{PPN})^+$  and  $(\text{NEt}_4)^+$ .

We propose that this specificity of crown-ether alkali metal cations for one type of tight ion-pairing should lead to their widespread use in the synthesis and isolation of anionic transition metal carbonyl complexes and clusters.

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