Isolation of the Anions $[M(CO)_5(SH)]^-$ and $[M_2(CO)_{10}(\mu\text{-}SH)]^-$ (M = Cr, Mo, and W) as Salts of the Sodium (18-Crown-6-Ether) † Cation. *X*-Ray Analysis of the Sodium Carbonyl Linked 'Polymeric' Structures of the Tungsten Species

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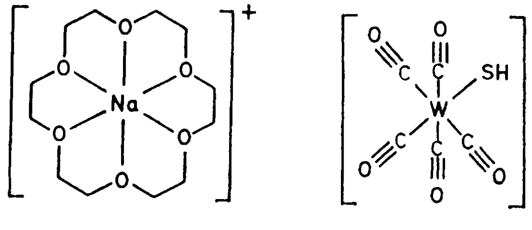
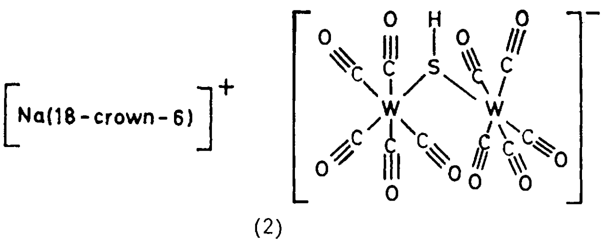
Ultraviolet irradiation has provided a convenient synthetic route to the anions $[M(CO)_5(SH)]^-$ and $[M_2(CO)_{10}(\mu\text{-}SH)]^-$ (M = Cr, Mo, and W) which have been isolated as their sodium (18-crown-6-ether) salts. *X*-Ray analysis of [Na(18-crown-6)]$[W(CO)_5(SH)]$ (1) and of [Na(18-crown-6)]$[W_2(CO)_{10}(\mu\text{-}SH)]$ (2) have shown them to be chain-polymeric in nature with sodium–carbonyl linkages between alternating cations and anions. The Na–O(carbonyl) distances are in the range 2.41—2.47 Å. In addition to the Na–O distances, compound (1) also shows a weaker Na–S interaction of 3.01 Å. Crystals of (1) are orthorhombic, space group $Pna2_1$ with a = 16.484(3), b = 7.622(2), c = 19.220(3) Å, and Z = 4. Crystals of (2) are triclinic, space group $P\bar{1}$, with a = 15.014(3), b = 11.874(2), c = 9.636(2) Å, α = 102.28(2), β = 96.29(2), γ = 100.63(2)°, and Z = 2. Data were collected on a four-circle diffractometer using Mo-K_α radiation from a graphite monochromator. Blocked full-matrix refinement converged to R 0.044 for (1) and 0.031 for (2).

SEVERAL earlier papers report our studies of the interaction between anionic organosulphur ligands (monothio-β-diketonates[1,2] and monothiophenolates[3,4]) and the transition metals Pt, Cr, Mo, and W. We now report an extension of this work to the anionic complexes of chromium, molybdenum, and tungsten pentacarbonyls with the ligand HS^-. Although one of these anions, $[W(CO)_5(SH)]^-$, had been isolated previously by Herberhold and Süss[5] as the NEt_4^+ salt, we chose the sodium complex of 1,4,7,10,13,16-hexaoxacyclo-octadecane, [Na(18-crown-6)]$^+$, as the cation for the present synthesis of the complex anions $[M(CO)_5(SH)]^-$ (M = Cr, Mo, and W) and $[M_2(CO)_{10}(\mu\text{-}SH)]^-$ (M = Cr, Mo, and W) as the 18-crown-6 alkali-metal cations had been shown to be effective counter ions in the synthesis[6] of the related anions $[M(CO)_5(OH)]^-$ (M = Cr, Mo, and W).



(1)



(2)

In the course of this work the synthesis of the mononuclear anions as the $N(PPh_3)_2^+$ salts and one of the dinuclear anions, $[W_2(CO)_{10}(\mu\text{-}SH)]^-$, as the NEt_4^+ salt were reported by Gingerich and Angelici.[7] With these cations, the salts were relatively unstable in the solid state. We have found that the use of the [Na(18-crown-6)]$^+$ complex as the counter ion gives a greatly enhanced stability. Crystals of the [Na(18-crown-6)]$^+$ salt of the anions $[W(CO)_5(SH)]^-$ and $[W_2(CO)_{10}(\mu\text{-}SH)]^-$ are stable indefinitely and their *X*-ray structure analyses are reported here. The use of the [Na(18-crown-6)]$^+$ cation also enabled us to obtain the hitherto unreported dinuclear anions $[Cr_2(CO)_{10}(\mu\text{-}SH)]^-$ and $[Mo_2(CO)_{10}(\mu\text{-}SH)]^-$ and the corresponding mixed-metal dinuclear anions of all three metals.

EXPERIMENTAL

Apparatus and Techniques.—All photolyses utilised a 125 W mercury discharge lamp obtained from the interior of a commercial GEC MBW/U 125-W u.v. lamp. This was enclosed in a water-cooled Pyrex jacket which was inserted into the reaction mixture. Nitrogen was bubbled through the mixture during the irradiation.

Infrared spectra were recorded on Perkin-Elmer 297 and 457 grating spectrophotometers. Solution spectra were run in tetrahydrofuran (thf). Solid-state spectra were run as Nujol mulls at room temperature and at −196 °C; CO_2 and polystyrene film were used to calibrate the spectra. Reported bands are believed accurate to ±2 cm^{-1}. Microanalyses were performed by the Australian Microanalytical Service (C.S.I.R.O., Melbourne). Absolute ethanol was stored over 4 Å molecular sieves. All other solvents were of reagent grade quality. Diethyl ether and thf were dried over sodium wire. Metal hexacarbonyls, 18-crown-6, and $NaSH\cdot H_2O$ were obtained from commercial sources and used without further purification. The salt $Na_2S\cdot 9H_2O$ was purified by selecting crystals of a suitable size which were then washed with distilled water, then acetone and dried in air.

Preparation of the Mononuclear Compounds [Na(18-crown-6)]$[M(CO)_5(SH)]$ (M = Cr, Mo, *and* W).—The metal

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† 18-Crown-6-ether = 1,4,7,10,13,16-hexaoxacyclo-octadecane.

hexacarbonyl (1.9 mmol), $Na_2S\cdot 9H_2O$ (1.9 mmol), and 18-crown-6 (1.9 mmol) were irradiated with stirring in absolute ethanol (250 cm^3) at room temperature until the hexacarbonyl was consumed (about 50 min). The resultant yellow solution was evaporated (25 mmHg, 40 °C)* to *ca.* 5 cm^3 and an equal volume of diethyl ether was added. The precipitate thus formed was collected by filtration, washed with diethyl ether, and crystallised from either thf–ether or acetone–ether solutions as $[Na(18\text{-crown-}6)][Cr(CO)_5(SH)]$, yellow crystals (Found: C, 39.1; H, 4.95; S, 5.8; Ash, 30.6. Calc. for $C_{17}H_{25}CrNaO_{11}S$: C, 39.85; H, 4.9; S, 6.3; Ash, 28.7%). $[Na(18\text{-crown-}6)][Mo(CO)_5(SH)]$, brown powder (Found: C, 35.7; H, 4.65; O, 31.8; S, 5.7; Ash, 33.4. Calc. for $C_{17}H_{25}MoNaO_{11}S$: C, 35.65; H, 4.5; O, 31.7; S, 5.8; Ash, 36.5%). $[Na(18\text{-crown-}6)][W(CO)_5(SH)]$, orange crystals (Found: C, 30.15; H, 3.7; O, 26.5; S, 4.1; Ash, 43.7. Calc. for $C_{17}H_{25}NaO_{11}SW$: C, 31.70; H, 3.90; O, 27.3; S, 5.0; Ash, 45.2%).

Preparation of the Dinuclear Compounds $[Na(18\text{-crown-}6)][M_2(CO)_{10}(\mu\text{-SH})]$ (M = Cr *and* W).—The metal hexacarbonyl (3.8 mmol), $Na_2S\cdot 9H_2O$ (1.9 mmol), and 18-crown-6 (1.9 mmol) were irradiated with stirring in absolute ethanol (250 cm^3) until the hexacarbonyl was consumed (about 90 min). The resultant yellow solutions were evaporated under reduced pressure (25 mmHg, 40 °C) to about 5 cm^3 and an equal volume of diethyl ether was added to precipitate the small amount of mononuclear material formed. This was removed by filtration. Addition of hexane to the filtrate gave an orange-yellow oil which crystallised on addition of more hexane. A purer product was subsequently obtained by substituting $NaSH\cdot H_2O$ (1.9 mmol) for $Na_2S\cdot 9H_2O$ with a reduction in irradiation time to about 60 min. Yields were about 65%. Crystals suitable for elemental analysis and *X*-ray crystallography were grown from di-isopropyl ether–diethyl ether–chloroform (2 : 4 : 5) (11 cm^3/0.2 g of complex). $[Na(18\text{-crown-}6)][Cr_2(CO)_{10}(\mu\text{-SH})]$, orange crystals (Found: C, 37.5; H, 3.6; O, 36.3; S, 4.6; Ash, 31.7. Calc. for $C_{22}H_{25}Cr_2NaO_{16}S$: C, 37.5; H, 3.6; O, 35.9; S, 4.7; Ash, 29.0%). $[Na(18\text{-crown-}6)][W_2(CO)_{10}(\mu\text{-SH})]$, orange crystals (Found: C, 27.55; H, 2.6; S, 3.3; Ash, 49.0. Calc. for $C_{22}H_{25}NaO_{16}SW_2$: C, 27.3; H, 2.6; S, 3.3; Ash, 54.0%).

Conductivity Measurements.—Measurements were made in acetonitrile (dried over 4 Å molecular sieves): for (1) $\Lambda = 109$ cm^2 Ω^{-1} mol^{-1} and (2) $\Lambda = 105$ cm^2 Ω^{-1} mol^{-1}. Conductivity values of 114 and 142 cm^2 Ω^{-1} mol^{-1} were reported for the corresponding NEt_4^+ salts in acetonitrile.[7] Both (1) and (2) are 1 : 1 electrolytes in acetonitrile.

Preparation of the Dimolybdenum and the Mixed Dinuclear Compounds $[Na(18\text{-crown-}6)][MM'(CO)_{10}(\mu\text{-SH})]$ (M,M' = Cr, Mo, *or* W).—The compound $[M(CO)_5(thf)]$ was prepared by irradiating a solution of the hexacarbonyl in thf (7.6 mmol dm^{-3}). The appropriate solid $[Na(18\text{-crown-}6)][M'(CO)_5(SH)]$ was then added to this solution and the reaction mixture was monitored by i.r. spectroscopy. The compounds prepared in this manner were not isolated.

Crystal Data.—(1): $C_{17}H_{25}NaO_{11}SW$, $M = 644.3$, Orthorhombic, space group $Pna2_1$, $a = 16.484(3)$, $b = 7.622(2)$, $c = 19.220(3)$ Å, $U = 2\,414.8$ $Å^3$, $Z = 4$, $D_c = 1.722$ g cm^{-3}, $F(000) = 1\,240$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 47.08 cm^{-1}.

(2) $C_{22}H_{25}NaO_{16}SW_2$, $M = 968.4$, Triclinic, space group $P\bar{1}$, $a = 15.014(3)$, $b = 11.874(2)$, $c = 9.636(2)$ Å, $\alpha = 102.28(2)$, $\beta = 92.29(2)$, $\gamma = 100.63(2)°$, U 1 629.8 $Å^3$, $Z = 2$, $D_c = 1.973$ g cm^{-3}, $F(000) = 920$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 68.77 cm^{-1}.

Intensity Measurements.—Data were collected with crystals of dimensions *ca.* 0.15 × 0.15 × 0.12 mm (1) and 0.42 × 0.35 × 0.28 mm (2) on a Philips PW1100 four-circle diffractometer with Mo-K_α radiation from a graphite monochromator. A θ—2θ scan mode was used with a constant scan speed of 0.5° s^{-1} and scan width of 0.8° for (1) and (2) and reflections with $3.0 \leqslant \theta \leqslant 32.0°$ for (1) and $3.0 \leqslant \theta \leqslant 30.0°$ for (2) were examined, using the technique previously described.[8] The variance of the intensity (I) was calculated as $\{[\sigma_c(I)]^2 + (0.04I)^2\}^{\frac{1}{2}}$, where $[\sigma_c(I)]$ is the variance due to counting statistics, and the term in I^2 was introduced to allow for other sources of error.[9] A semi-empirical absorption correction based on a pseudo-ellipsoid model[10] was applied to the data for (2). 437 Azimuthal-scan data from 14 independent reflections were used, relative transmission factors ranged from 1.0 to 0.531 for the full data set. Equivalent reflections were averaged to give totals of 2 561 and 5 492 unique observed reflections with $I/\sigma(I) \geqslant 3$, for (1) and (2) respectively.

Structure Solution and Refinement.—For (1) and (2), the tungsten and sulphur atoms were located from Patterson syntheses; the remaining non-hydrogen atoms were found from subsequent difference syntheses. In (1), the overall symmetry of the unit cell is close to that of the centrosymmetric space group *Pnam* (non-standard setting of *Pnma*). In this space group the cation would have exact C_i symmetry but the $[W(CO)_5(SH)]^-$ anion would be required to have C_s symmetry perpendicular to the direction of the W–S bond. Consequently, the non-centric space group $Pna2_1$ was indicated. Satisfactory refinement was obtained in this space group but, to prevent correlations between the parameters which would have been related by the centre of symmetry in the space group *Pnam*, it was necessary to refine the atoms at positions (x,y,z) in different cycles to the pseudo-related atoms at $(1 - x, 1 - y, 0.5 - z)$. A difference-Fourier using data with $\sin\theta \leqslant 0.35$ failed to reveal the position of the thiol hydrogen in (1); however, the corresponding atom was located in the structure of (2) and was included in the refinement without constraint.

For (1) and (2), all non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of refinement in which the reflections were weighted as $1/\sigma^2(F_o)$. Hydrogen atoms, except that of the thiol, were included at calculated positions with their thermal parameters set to be equal to an extra variable in the refinement [0.067(11) $Å^2$ for (1) and 0.083(9) $Å^2$ for (2)]. The final R and R' were 0.044 and 0.044 for (1), and 0.031 and 0.031 for (2), where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$. The SHELX-76 programs[11] were used and the scattering factors were those of Cromer and Mann[12] and correction for the real and imaginary parts of the anomalous dispersion were applied For (1), the overall symmetry was so close to the centrosymmetric space group that reversing the hand of the structure made no measurable difference to the R value.

In the structure of (2), the atoms of three of the ethyl bridges in the crown ether [C(2)–C(3), C(5)–C(6), and C(8)–C(9)] had large thermal parameters. A difference synthesis calculated without these atoms showed a rather extended region of electron density corresponding to the location of each atom. Although this may indicate some conformational disorder of these bridges it proved impossible to resolve the electron density into separate components.

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* Throughout this paper: 1 mmHg = (101 325/760) N m^{-2}.

The final atomic co-ordinates are given in Tables 1 and 2 for compounds (1) and (2) respectively, bond lengths and angles in Tables 3 and 4. Thermal parameters, atomic co-ordinates for the hydrogen atoms, bond angles for the cations, intermolecular contact distances, and important non-bonded intramolecular contacts, torsional angles within the crown-ether fragments of the molecules, least-squares planes in direct space, and the observed and calculated structure factors for (1) and (2) are in Supplementary Publication No. SUP 23158 (57 pp.).*

RESULTS AND DISCUSSION

The complex anions $[M(CO)_5(SH)]^-$ and $[M'_2(CO)_{10}(\mu\text{-}SH)]^-$ (M = Cr, Mo, and W; M' = Cr and W) were prepared at ambient temperatures by irradiating mixtures of $[M(CO)_6]$ and the appropriate stoicheiometric amounts of $Na_2S{\cdot}9H_2O$ and 18-crown-6 in absolute alcohol. This contrasts with Gingerich and Angelici's observation that, under reflux in diglyme–thf solution, the reaction between $[W(CO)_6]$ and NaSH produced the anion $[W_2(CO)_{10}(\mu\text{-}SH)]^-$ exclusively with no evidence for any $[W(CO)_5(SH)]^-$.

The mononuclear anions $[M(CO)_5(SH)]^-$ were found to be extremely reactive towards excess $[M(CO)_5(thf)]$ (M = Cr, Mo, and W), and when solutions of these two species were mixed the thiol group readily displaced the co-ordinating thf and only the thiol-bridged dinuclear anion was found to be present. This reaction enabled the synthesis of the $[Na(18\text{-crown-}6)]^+$ salts of the mixed dinuclear anions $[MM'(CO)_{10}(\mu\text{-}SH)]^-$ (M and M' = Cr, Mo, and W) and of the $[Mo_2(CO)_{10}(\mu\text{-}SH)]^-$ anion; these salts were not isolated from solution.

Solutions of all the compounds were moderately air-sensitive but could be handled in air for short periods without significant decomposition. It was found that the order of stability was W > Cr >> Mo with the binuclear anions being slightly more air-sensitive than their mononuclear counterparts. The stability of the complex anions in the solid state appears to be sensitive to the nature of the counter ion present, since the $[Na(18\text{-crown-}6)]^+$ salts are considerably more stable than the reported [7] $N(PPh_3)_2^+$ and NEt_4^+ salts. For example, the $[Na(18\text{-crown-}6)]^+$ salt of (1) is stable in air indefinitely whereas the analogous $N(PPh_3)_2^+$ salt decomposes after one month. Although the $[Na(18\text{-crown-}6)][Mo(CO)_5(SH)]$ salt decomposes after 48 h it is nevertheless readily isolated, whereas $[N(PPh_3)_2][Mo(CO)_5(SH)]$ is reported [7] to be too unstable to be obtained in the solid state. The only one of the dinuclear anions to be previously reported was $[W_2(CO)_{10}(\mu\text{-}SH)]^-$ as the NEt_4^+ salt which, in the solid state, turns green when exposed to air for 12 h; [7] in contrast, the orange crystals of the $[Na(18\text{-crown-}6)]^+$ salt (2) are stable indefinitely. The synthesis for the first time of the less stable dinuclear anions $[Cr_2(CO)_{10}(\mu\text{-}SH)]^-$ (orange crystals) and $[Mo_2(CO)_{10}(\mu\text{-}SH)]^-$ (yellow solution) appears to be further evidence of a stabilising effect of the $[Na(18\text{-crown-}6)]^+$ counter ion.

Examples of transition-metal carbonyl anions stabilised by alkali-metal cations solvated with polyethers have been reported [13] but few workers have used the related crown ethers for this purpose. The use of crown-ether alkali-metal cations in the synthesis of transition-metal carbonyl complexes was first reported by Cihonski and Levenson.[6] These authors were interested in the ease of solubilising the cations required for these reactions and suggested that ion pairing may have the disadvantage of reducing the reaction rates. Our results emphasise that in the synthesis of anionic metal carbonyls the stability of the product is enhanced by ion interactions and that the alkali-metal crown-ether complexes may be more effective than other large cations for this purpose.

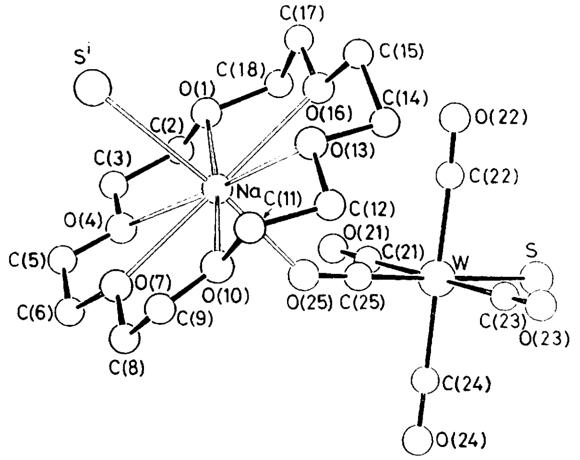

FIGURE 1 Perspective view of complex (1) showing only the S atom of the anion at the symmetry position $(1 - x, 1 - y, \frac{1}{2} + z)$

The *X*-ray analysis has shown that the anion in (1) (Figure 1) has the expected octahedral co-ordination of the tungsten atom, with angles at W in the ranges S–W–C(eq.) 89.2—92.7°, C(eq.)–W–C(ax.) 87.2—92.1°, and C(eq.)–W–C(eq.) 87.1—92.2°, so that the symmetry is approximately C_{4v}. The mononuclear complexes $[M(CO)_5(SH)]^-$ (M = Cr, Mo, and W) in solution show the carbonyl stretching pattern expected for this symmetry (Table 5).

It was proposed [7] from the similarity of the i.r. spectra that in $[NEt_4][W_2(CO)_{10}(\mu\text{-}SH)]$ the dinuclear anion has a structure similar to the iodide-bridged structure established [14] for $[Cr_2(CO)_{10}(\mu\text{-}I)]^-$. The *X*-ray analysis of the $[Na(18\text{-crown-}6)]^+$ salt (2) confirms this prediction and the H atom of the bridging thiol group has been directly located (Figure 2). In spite of the large W(1)–S–W(2) angle of 124.2° the bonds round the S atom are not coplanar and the S atom is 0.69 Å above the plane through W(1), W(2), and H. An even larger W–S–W angle of 132.1° was found in the pentachlorothiophenolato-bridged anion $[W_2(CO)_{10}(\mu\text{-}SC_6Cl_5)]^-$ (3).[3] The bridging thiophenolate ligand in a dinuclear thallium(III) complex [15] has pyramidal co-ordination with approximately tetrahedral angles round the sulphur corresponding to sp^3 hybridisation and therefore the large deviation of the

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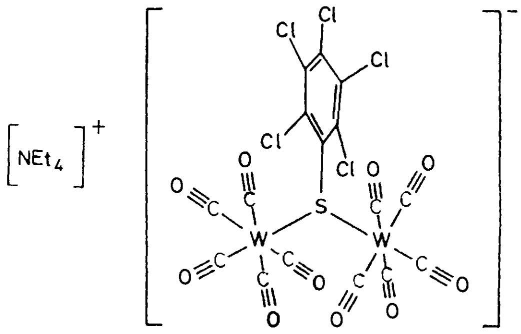
* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

W–S–W angle in (2) from the expected tetrahedral value may be, as in (3), the result of minimising carbonyl contacts between the two halves of the anion.



(3)

Each W atom in (2) has approximate octahedral geometry with the angles at W in the ranges S–W–C(eq.) 88.2—95.5, C(eq.)–W–C(ax.) 87.7—91.2, and C(eq.)–W–C(eq.) 87.2—91.5°. Overall, the anion in (2) has C_1 symmetry only, with the carbonyl ligands on the two $W(CO)_5$ units adopting a staggered conformation relative to each other. The equatorial carbonyl groups show torsional angles about the W • • •W distance in the range 38.3—57.8° (Table 6) with a mean value of 45.8°. A pure staggered conformation would require C–W • • • W–C angles of 45°. This staggered conformation minimises CO repulsions between the two halves of the anion in (2) and contrasts with the almost eclipsed arrangement of the CO ligands in (3) where the approach to C_{2v} symmetry appeared to be necessary to minimise contact between the Cl atoms of the bulky pentachlorothiophenolato-group and the carbonyl ligands.[3] The corresponding torsional angles in (3) form two sets in the ranges 8.1—11.8 and 74.5—101.3° with mean values of 10.3 and 80.0° respectively. An eclipsed conformation requires values of 0 or 90°. The differences in the W–S–W angles in the anions, 124.2 in (2) and 132.1° in (3), may also be related to the different conformations adopted by the CO ligands. An intermediate conformation was found[14] in the anion $[Cr_2(CO)_{10}I]^-$ with a much larger range in torsional angles (28.6—66.6°) than that in (2). In the dinuclear chromium species, the torsional angles can be divided into two sets of ranges 28.6—30.6 and 53.4—66.6° with mean values of 29.7 and 60.3° respectively, corresponding to a *gauche* conformation.

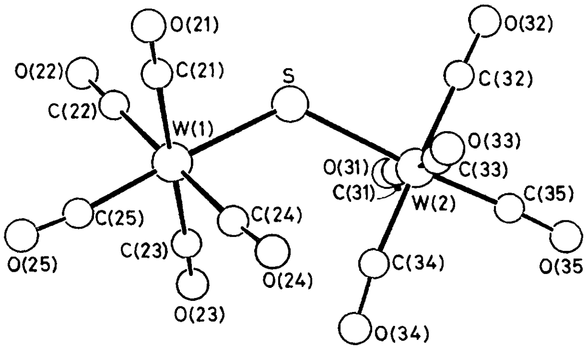


FIGURE 2 The complex anion in complex (2)

In the $[W(CO)_5(SH)]^-$ anion in (1) the W–S bond length of 2.567(5) Å is shorter than the bridging W–S bond lengths of 2.587(2) and 2.596(2) Å in (2). However, this bond in (1) is significantly longer than the W–S bond of 2.543(2) Å in the pentacarbonyl[1,1,1-trifluoro-4-(2-thienyl)-4-thio-oxobutan-2-onato-*S*]tungstate anion (4), in which there was evidence of considerable W–S back-bonding thought to be enhanced by conjugation extending from the W atom along the backbone of the ligand.[2] In the dinuclear anion of (2) the W–S bond lengths of 2.587(2) and 2.596(2) Å are more than 0.02 Å longer than the two values of 2.568(4) Å for the bridging W–S bonds in the anion $[(CO)_5W\text{-}(\mu\text{-}SC_6Cl_5)\text{-}W(CO)_5]^-$ of (3),[3] consistent with a greater π-acidity of the $C_6Cl_5S^-$ ligand compared to the HS^- ligand.

The lengths of the W–C bonds *trans* to the thiolato-sulphur atoms in (1) and (2) are in the range 1.947—1.975 Å and are all shorter than the *cis* W–C bond lengths which are in the range 2.001—2.057 Å (Table 3). This is consistent with the trend observed in other pentacarbonyltungsten(0) compounds that any π back-bonding from the metal to sulphur is less than that to the carbonyl ligands.[2,3]

The six dinuclear species exhibit a carbonyl stretching pattern similar to those reported for the related μ-SR^- [7] and halide-bridged[16] systems. The stretching frequencies are reported in Table 5. The corresponding

TABLE 1

Fractional atomic co-ordinates for (1)*

Atom	x	y	z
W	0.403 37(2)	0.641 22(5)	0
S	0.398 0(3)	0.643 2(6)	−0.133 5(2)
C(21)	0.514 4(7)	0.760 4(15)	0.002 0(16)
O(21)	0.576 4(6)	0.822 6(13)	0.000 5(17)
C(22)	0.454 2(7)	0.399 0(15)	−0.000 8(18)
O(22)	0.480 0(6)	0.261 1(11)	0.004 2(20)
C(23)	0.293 0(8)	0.517 7(15)	0.005 0(21)
O(23)	0.233 9(6)	0.448 3(17)	0.010 2(24)
C(24)	0.351 2(7)	0.881 2(16)	0.000 6(19)
O(24)	0.316 5(5)	1.016 9(12)	0.005 6(21)
C(25)	0.408 9(9)	0.634 7(18)	0.101 2(11)
O(25)	0.421 2(7)	0.644 9(14)	0.161 2(7)
Na	0.497 8(11)	0.499 5(32)	0.250 8(9)
O(1)	0.610 3(5)	0.792 9(14)	0.258 5(5)
C(2)	0.602 7(9)	0.874 3(19)	0.320 5(7)
C(3)	0.520 8(10)	0.899 3(17)	0.349 0(7)
O(4)	0.469 2(6)	0.736 9(12)	0.346 4(5)
C(5)	0.389 0(11)	0.760 3(29)	0.374 4(9)
C(6)	0.346 2(9)	0.600 9(23)	0.382 1(8)
O(7)	0.357 5(6)	0.502 1(14)	0.327 0(6)
C(8)	0.320 1(9)	0.330 8(16)	0.339 8(9)
C(9)	0.308 3(7)	0.251 8(23)	0.267 3(9)
O(10)	0.400 4(5)	0.216 8(13)	0.242 3(5)
C(11)	0.394 9(9)	0.148 3(17)	0.169 0(7)
C(12)	0.483 9(9)	0.080 0(18)	0.161 5(7)
O(13)	0.524 6(5)	0.240 2(11)	0.157 1(5)
C(14)	0.606 3(8)	0.211 5(19)	0.140 0(9)
C(15)	0.637 9(8)	0.392 8(18)	0.114 6(7)
O(16)	0.649 6(5)	0.500 7(13)	0.181 0(4)
C(17)	0.680 4(9)	0.662 7(23)	0.170 5(8)
C(18)	0.678 2(7)	0.766 0(17)	0.237 0(8)

* Estimated standard deviations are in parentheses in Tables throughout this paper.

ν(CO) frequencies are significantly lower in the mononuclear anions, which are closely related to the spectra reported[6] for the complexes $[M(CO)_5(OH)]^-$. This is again consistent with the view that a second $M(CO)_5$ moiety renders the thiol group much less basic. The pattern of six distinct carbonyl stretching frequencies in the spectra of the dinuclear species has been used as evidence for a bent structure in solution since an anion of C_{2v} symmetry should show 8 or 9 bands (there are two C_{2v} possibilities) while a C_s species should have 10 bands, whereas the linear D_{4d} or D_{4h} structures would exhibit only 3 bands. The structure of (2) shows that the anion is close to C_s symmetry in the solid state. Although the related anion (3) is intermediate between C_s and C_{2v} symmetry, both have solution spectra similar to each other and to other thiolato-bridged systems. This indicates that in solution there is some degree of rotation about the W–S bonds.

Table 2

Fractional atomic co-ordinates for (2)

Atom	*x*	*y*	*z*
W(1)	0.628 70(1)	0.140 02(2)	0.331 34(2)
W(2)	0.774 86(2)	−0.108 03(2)	0.053 26(2)
S	0.728 5(1)	0.093 3(1)	0.132 8(2)
C(21)	0.578 4(5)	0.246 4(6)	0.222 7(7)
O(21)	0.548 9(4)	0.310 0(5)	0.161 8(7)
C(22)	0.726 7(4)	0.281 1(5)	0.437 3(6)
O(22)	0.780 0(3)	0.363 8(4)	0.496 1(5)
C(23)	0.683 7(5)	0.036 6(6)	0.444 4(7)
O(23)	0.715 1(4)	−0.018 4(5)	0.511 9(7)
C(24)	0.527 8(4)	0.000 6(6)	0.219 0(7)
O(24)	0.470 9(4)	−0.076 3(5)	0.153 9(6)
C(25)	0.548 6(5)	0.177 7(6)	0.476 4(8)
O(25)	0.500 9(4)	0.200 9(5)	0.560 7(6)
C(31)	0.676 3(5)	−0.201 0(6)	0.142 2(8)
O(31)	0.622 1(4)	−0.257 6(5)	0.184 9(7)
C(32)	0.684 9(4)	−0.139 6(6)	−0.134 5(8)
O(32)	0.637 3(4)	−0.154 3(5)	−0.238 8(6)
C(33)	0.871 1(4)	−0.027 0(6)	−0.046 4(7)
O(33)	0.923 4(4)	0.016 6(5)	−0.106 4(6)
C(34)	0.866 1(5)	−0.068 7(6)	0.238 9(8)
O(34)	0.916 9(4)	−0.047 3(5)	0.341 4(6)
C(35)	0.813 5(4)	−0.254 5(5)	−0.014 1(6)
O(35)	0.835 1(3)	−0.344 1(4)	−0.053 4(5)
Na	0.835 8(2)	0.513 9(2)	0.724 7(2)
O(1)	0.883 3(4)	0.673 2(5)	0.565 0(7)
C(2)	0.971 3(8)	0.743 1(10)	0.609 1(15)
C(3)	1.011 8(10)	0.738 7(12)	0.727 9(19)
O(4)	1.003 6(4)	0.628 9(6)	0.773 7(7)
C(5)	1.067 8(7)	0.565 9(14)	0.729 6(13)
C(6)	1.056 6(8)	0.457 9(14)	0.790 7(13)
O(7)	0.965 7(5)	0.390 9(6)	0.740 8(8)
C(8)	0.948 4(11)	0.296 7(11)	0.812 5(18)
C(9)	0.856 9(8)	0.252 0(9)	0.805 0(17)
O(10)	0.807 3(4)	0.341 4(5)	0.850 5(6)
C(11)	0.713 6(7)	0.292 2(9)	0.855 3(12)
C(12)	0.661 0(6)	0.385 0(9)	0.872 1(10)
O(13)	0.668 4(3)	0.434 4(4)	0.752 8(5)
C(14)	0.606 1(5)	0.510 8(7)	0.738 7(10)
C(15)	0.617 1(5)	0.549 9(7)	0.606 4(9)
O(16)	0.708 3(3)	0.613 3(4)	0.622 1(5)
C(17)	0.725 6(7)	0.662 4(8)	0.503 0(9)
C(18)	0.816 6(7)	0.740 0(8)	0.539 5(11)

By treating the normal modes of vibration of the D_{4d} or D_{4h} species as linear combinations (generally in and out of phase) of two constituent mononuclear modes and then perturbing these systems to approximate the best dinuclear anions we can expect each mononuclear mode to give rise to a pair of dinuclear modes. Furthermore, one of the modes in each pair will be of low intensity as it will have arisen from a forbidden mode in the linear (D_{4d} or D_{4h}) system. However, while the observed spectra consist of two a_1(eq.) type bands and two e_1 bands only one b_1 and a_1(ex.) are seen. The failure to observe a second b_1 type band may be due to its having a very low intensity (both b_1 types are derived from the i.r.-forbidden b_1 mononuclear mode) and the close proximity of the very strong e_1 type. The lack of a second a_1(ax.) mode is probably indicative of the distance between the two axial carbonyls and consequently the small amount of interaction taking place. The degeneracy of the e_1 type bands does not appear to have been lifted. This is also the case for Group 6 pentacarbonyls, $[M(CO)_5L]^-$, substituted with bulky asymmetric RS^- groups[17] indicating that this feature of the spectrum is relatively insensitive to the nature of L.

The weak π-acidity of the HS^- ligand would indicate that the *trans* oxygen atom is the most negatively charged. The presence of both *cis* and *trans* carbonyl oxygen–sodium bonds in the solid-state structure of (2) suggests that the energy difference between these two bonds is small compared to crystal packing forces. There was no evidence from the i.r. data as to which carbonyl oxygen atoms were interacting most readily with the Na cation in solution.

Table 3

Bond lengths (Å) for (1) and (2)

(*a*) The complex anions

	(1)	(2)	
	W, *n* = 2	W(1), *n* = 2	W(2), *n* = 3
W–S	2.567(5)	2.587(2)	2.596(2)
W–C(*n*1)	2.044(12)	2.001(8)	2.054(7)
W–C(*n*2)	2.027(11)	2.012(5)	2.057(7)
W–C(*n*3)	2.051(13)	2.031(7)	2.030(7)
W–C(*n*4)	2.021(12)	2.040(6)	2.040(7)
W–C(*n*5)	1.947(21)	1.975(8)	1.938(6)
O(*n*1)–C(*n*1)	1.13(2)	1.169(11)	1.129(10)
O(*n*2)–C(*n*2)	1.14(2)	1.141(6)	1.127(8)
O(*n*3)–C(*n*3)	1.11(2)	1.139(10)	1.139(9)
O(*n*4)–C(*n*4)	1.19(2)	1.144(7)	1.132(9)
O(*n*5)–C(*n*5)	1.17(3)	1.163(10)	1.168(8)
		S–H 1.19(7)	

(*b*) The complex cations *

(1)		(2)	
Na–O(1)	2.91(2)	Na–O(1)	2.727(7)
Na–O(4)	2.62(2)	Na–O(4)	2.575(6)
Na–O(7)	2.74(2)	Na–O(7)	2.654(9)
Na–O(10)	2.69(2)	Na–O(10)	2.588(7)
Na–O(13)	2.71(2)	Na–O(13)	2.581(5)
Na–O(16)	2.84(2)	Na–O(16)	2.637(6)
Na–O(25)	2.41(2)	Na–O(22)	2.471(5)
Na–S^{i}	3.014(9)	Na–O(35^{ii})	2.428(5)
O–C (crown ether)	mean 1.42(2)	O–C (crown ether)	mean 1.418(8)
C–C (crown ether)	mean 1.506(6)	C–C (crown ether)	mean 1.418(11)

* For explanation of Roman numeral superscripts see Table 4.

Dunitz *et al.*[18] have discussed the various conformations adopted by the 18-crown-6-ethers to accommodate Na^+ which is too small to fill it, with an ionic radius of 0.95 Å. The conformations known for the macrocycle in $[Na(18\text{-crown-}6)]^+$ complexes involve either the ring having near D_{3d} symmetry or the ring taking up a new irregular geometry. In the first case the sodium atom may be centrally placed at a non-optimum distance of 2.8 Å [19] or off-centre with some long and some short distances.[20] Examples of the second category are where the ring may be elongated about one diagonal [21] or an irregular pentagonal-pyramidal conformation may be possible.[22]

TABLE 4

Selected bond angles (°) for (1) and (2)

(*a*) The anionic complexes

	(1)	(2)	
	W, $n = 2$	W(1), $n = 2$	W(2), $n = 3$
S–W–C(n1)	92.7(9)	88.3(2)	95.5(2)
S–W–C(n2)	90.7(10)	90.5(2)	88.3(2)
S–W–C(n3)	91.1(11)	91.3(2)	88.2(2)
S–W–C(n4)	89.2(10)	89.1(2)	89.7(2)
S–W–C(n5)	178.7(4)	177.3(2)	176.6(2)
C(n1)–W–C(n2)	92.0(4)	87.4(3)	90.5(2)
C(n1)–W–C(n3)	176.1(14)	178.0(2)	175.8(2)
C(n1)–W–C(n4)	88.8(5)	90.5(3)	91.4(3)
C(n1)–W–C(n5)	87.2(10)	89.2(3)	87.8(3)
C(n2)–W–C(n3)	87.1(5)	90.6(2)	87.2(3)
C(n2)–W–C(n4)	179.2(5)	177.9(3)	177.3(3)
C(n2)–W–C(n5)	88.0(11)	90.4(2)	90.8(3)
C(n3)–W–C(n4)	92.2(5)	91.5(3)	90.9(3)
C(n3)–W–C(n5)	89.0(12)	91.2(2)	87.7(3)
C(n4)–W–C(n5)	92.1(11)	89.8(3)	91.2(3)
W–C(n1)–O(n1)	177(3)	178.6(6)	176.0(6)
W–C(n2)–O(n2)	174(3)	177.4(6)	177.8(6)
W–C(n3)–O(n3)	177(4)	177.6(5)	177.8(5)
W–C(n4)–O(n4)	174(3)	178.5(7)	179.6(4)
W–C(n5)–O(n5)	171(1)	179.1(7)	178.5(6)
W–S–H		101(4)	92(3)
W–S–W			124.2(1)

(*b*) The 18-crown-6-ether (mean values)

	(1)	(2)
C–O–C	112(1)	112(1)
O–C–C	108(1)	111(1)
Na–O–C	115.7(5)	115.1(4)

(*c*) Inter-ionic

(1)		(2)	
W–S–Na^{iii}	136(1)	Na–O–(22)–C(22)	145.9(5)
Na–O(25)–C(25)	140(1)	Na–O(35^{ii})–C(35^{ii})	139.8(5)

Roman numeral superscripts denote the following equivalent positions relative to the first atom at x, y, z:

i $1.0 - x$, $1.0 - y$, $0.5 + z$
ii x, $-1.0 + y$, $-1.0 + z$
iii $1.0 - x$, $1.0 - y$, $-0.5 + z$

The 18-crown-6 macrocycles in (1) and (2) have different conformations. In (1) an approximately planar arrangement of the oxygen atoms is observed in which these atoms alternate above and below the plane of best fit with a maximum deviation of 0.17 Å. The Na atom lies 0.055 Å out of this plane towards the S atom. The co-ordination geometry of the Na$^+$ cation is slightly distorted hexagonal bipyramidal, with the oxygen-bonded carbonyl of one anion and the thiolato-sulphur atom of a second anion occupying the two axial sites (Figure 3). A similar co-ordination was found in the [Na(18-crown-6)]$^+$ cation in the dicyanophosphide salt.[23] In this structure there are two independent exactly centrosymmetric [Na(18-crown-6)]$^+$ cations with each Na$^+$ ion on an inversion centre. The Na–O distances are in the range 2.712—2.791(4) Å. In (1), the Na$^+$ ion is in an environment that is close to centrosymmetric with Na–O bond lengths of 2.62—2.91 Å. The inequality of the Na–O distances appears to be due to the Na$^+$ ion being displaced from the centre of the macrocycle so that some of the Na–O distances are optimised at the expense of others. Similar unequal Na–O distances of 2.54—2.89 Å were found in the two crystallographically independent, approximately hexagonal-planar, sodium (dibenzo-18-crown-6-ether) cations in a hydrated bromide salt.[20]

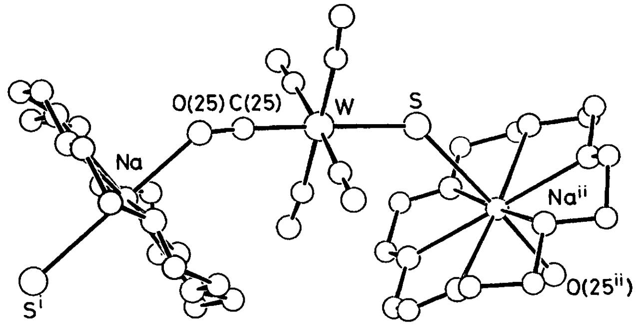


FIGURE 3 Part of the ' polymeric ' structure in the complex (1), showing the crown-ether conformation

In (2), the macrocycle has a markedly less planar arrangement of the oxygen atoms than to that found in (1). Four oxygen atoms [O(1), O(10), O(13), and O(16)] and the sodium atom are nearly coplanar (maximum deviation 0.111 Å, for Na) with the remaining two oxygen atoms above and below this plane [O(4) 1.035 and O(7) −0.581 Å] (Figure 4). This double ' kinking ' of the macrocycle allows a closer approach of the oxygen atoms to the sodium atom than in (1) with Na–O distances of 2.575—2.727 Å (mean 2.627 Å). Large distortions from a near planar conformation were found in the [Na(18-crown-6)]$^+$ cation in the thiocyanate salt where one oxygen is 1.95 Å out of the plane of the other five. This resulted in a more favourable set of Na–O distances of 2.45—2.62 Å [23] (the ideal distance should be 2.35 Å). A very distorted hexagonal-bipyramidal co-ordination for the Na$^+$ ion in (2) is completed by the oxygen atoms of carbonyl groups on adjacent dinuclear anions as discussed later.

TABLE 5

Carbonyl stretching frequencies ν(CO) (cm^{-1}) of the mono- and di-nuclear carbonyl anions

Anion	a_1(eq.)	b	e	a_1 (ax.)
[Cr(CO)$_5$(SH)]$^-$	2 046w	1 950sh	1 910vs	1 853s
[Mo(CO)$_5$(SH)]$^-$	2 056w	1 958sh	1 917vs	1 853s
[W(CO)$_5$(SH)]$^-$	2 055w	1 948sh	1 908vs	1 848s
[Cr$_2$(CO)$_{10}$(μ-SH)]$^-$	2 065vw, 2 049m	1 968w	1 939vs, 1 911m	1 875s
[Mo$_2$(CO)$_{10}$(μ-SH)]$^-$	2 070vw, 2 059m	*	1 942vs, 1 917m	1 873s
[W$_2$(CO)$_{10}$(μ-SH)]$^-$	2 071vw, 2 060m	1 974w	1 943vs, 1 918m	1 873s
[CrMo(CO)$_{10}$(μ-SH)]$^-$	2 070vw, 2 050m	1 970w	1 935vs, 1 919m	1 875s
[CrW(CO)$_{10}$(μ-SH)]$^-$	2 068vw, 2 052m	1 965w	1 932vs, 1 910m	1 873s
[MoW(CO)$_{10}$(μ-SH)]$^-$	2 069vw, 2 059m	1 965w	1 939vs, 1 920m	1 871s

* Obscured by a peak due to [Mo(CO)$_6$] impurity.

The large thermal parameters found for parts of the crown ether in (2) were consistent with the solid-state i.r. spectra. At ambient temperature the bands associated with internal modes of the crown ether were broad and ill defined. Upon cooling to liquid-nitrogen temperature these bands sharpened and much fine structure was apparent. A similar, though less marked, effect was observed in the spectra of (1). Negligible differences were observed in the carbonyl absorptions for both (1) and (2) at the two temperatures.

The most interesting result to emerge from this work is that the overall structures in both (1) and (2) are chain ' polymers '. In (1) the anion is linked to two sodium atoms of adjacent [Na(18-crown-6)]$^+$ cations *via* the oxygen atom O(25) of the *trans* carbonyl and the thiolato-sulphur atom as shown in Figure 3. In (2) the dinuclear anion is linked, *via* the oxygen atom O(22) of a *cis* carbonyl on W(1) and the oxygen of the *trans* carbonyl on W(2) [O(35)], to two adjacent sodium cations as shown in Figure 5. In the two structures the sodium carbonyl Na–O bonds are in the range 2.41—2.47 Å and are shorter than any of the Na–O bonds of the crown-ether complex cations (Table 3).

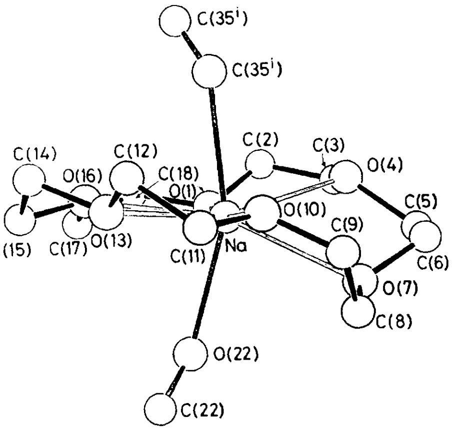


FIGURE 4 View of the [Na(18-crown-6)]$^+$ cation in complex (2)

The first structure reported in which bonding of carbonyl ligands *via* the oxygen atom occurs was [{Fe(η^5-C_5H_5)(CO)$_2$–C=O–Al(C_2H_5)$_3$}$_2$], in which the carbonyl groups which bridge the two iron atoms also form Al–O bonds of length 2.00 Å.[24] Several examples of Al–O=C–M linkages are now known but the first reported structure analyses of a compound with a bond of this type, from a carbonyl ligand to an alkali metal, was relatively recent.[25] Carbonyl-oxygen to sodium bonding in the solid state was first observed in $Na_2[Fe(CO)_4]\cdot 1.5C_4H_8O$, in which all four carbonyl oxygens of the dianion are bonded to sodium cations with a mean Na–O distance of 2.321 Å, slightly shorter than the mean Na–O(carbonyl) distances in the cations of (1) and (2) (Table 3).

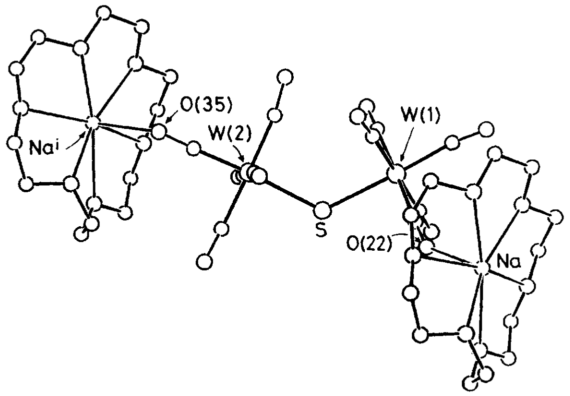


FIGURE 5 Part of the ' polymeric ' structure in the complex (2)

Tight ion pairing in alkali metal salts of carbonylate anions appears to be due to two main types of interactions. From work on $Na_2[Co(CO)_4]$ solutions, Edgell and co-workers[26] proposed that the ion-pair interaction was mainly between the Na$^+$ cation and a carbonyl-oxygen atom. More recently, Pannell and Jackson[27] have shown that in solutions of Na[Fe(η^5-C_5H_5)(CO)$_2$] there is evidence for direct Na$^+$–Fe bonded species in equilibrium with the Na$^+$–O=C–Fe linked species. The addition of dibenzo-18-crown-6 to these solutions shifts

TABLE 6

Torsional angles between the carbonyl carbons and the metal atoms in some of the dinuclear anions

$[W_2(CO)_{10}(\mu\text{-SH})]^-$		$[W_2(CO)_{10}(\mu\text{-SC}_6Cl_5)]^{-\,a}$		$[Cr_2(CO)_{10}(\mu\text{-I})]^{-\,b}$	
	Angle (°)		Angle (°)		Angle (°)
C(21)–W(1) · · · W(2)–C(32)	−38.3	C(11)–W(1) · · · W(2)–C(21)	10.8	C(21)–Cr(1) · · · Cr(2)–C(32)	−30.1
C(21)–W(1) · · · W(2)–C(33)	57.8	C(12)–W(1) · · · W(2)–C(22)	10.6	C(22)–Cr(1) · · · Cr(2)–C(33)	−28.6
C(22)–W(1) · · · W(2)–C(33)	−41.9	C(13)–W(1) · · · W(2)–C(23)	8.1	C(23)–Cr(1) · · · Cr(2)–C(31)	−29.4
C(22)–W(1) · · · W(2)–C(34)	45.5	C(14)–W(1) · · · W(2)–C(24)	11.8	C(24)–Cr(1) · · · Cr(2)–C(31)	−30.6
C(23)–W(1) · · · W(2)–C(31)	55.9				
C(23)–W(1) · · · W(2)–C(34)	−38.7		mean 10.3		mean 29.7
C(24)–W(1) · · · W(2)–C(31)	−42.1				
C(24)–W(1) · · · W(2)–C(32)	45.9	C(11)–W(1) · · · W(2)–C(22)	97.7	C(21)–Cr(1) · · · Cr(2)–C(33)	66.6
		C(11)–W(1) · · · W(2)–C(24)	−85.3	C(22)–Cr(1) · · · Cr(2)–C(34)	54.7
	mean 45.8	C(12)–W(1) · · · W(2)–C(21)	−76.3	C(23)–Cr(1) · · · Cr(2)–C(34)	66.6
		C(12)–W(1) · · · W(2)–C(23)	101.3	C(24)–Cr(1) · · · Cr(2)–C(32)	53.4
		C(13)–W(1) · · · W(2)–C(22)	−82.7		
		C(13)–W(1) · · · W(2)–C(24)	94.3		mean 60.3
		C(14)–W(1) · · · W(2)–C(21)	107.9		
		C(14)–W(1) · · · W(2)–C(23)	−74.5		
			mean 80.0		

[a] From ref. 3. [b] From ref. 14.

the equilibrium until the Na^+–Fe interaction disappears. Chin and Bau,[25] from an *X*-ray analysis of $Na_2[Fe(CO)_4]\cdot1.5C_4H_8O$, first showed the presence of the Na–O-(carbonyl) linkages in the solid state together with an unanticipated interaction between the Na^+ ion and the C–Fe–C portion of the $[Fe(CO)_4]^{2-}$ dianion. This secondary contact produced a large distortion of the angle from tetrahedral to 129.7°, and such an interaction may be identified with the Na^+–Fe ion pair found by Pannell and Jackson [27] in solution.

Further *X*-ray studies [28] of the effect of counter ions on the $[Fe(CO)_4]^{2-}$ ion geometry showed that encapsulation of the Na^+ ion by a cryptand ligand removed it from the sphere of influence of the dianion so that neither the Na^+–O nor the Na^+-Fe interactions could occur.

These types of ion pairing are not possible for the non-metallic cations, such as $N(PPh_3)_2{}^+$, which due to the stabilising influence of their large size are widely used in organometallic syntheses. In the present work the ' polymeric ' structures present in (1) and (2) demonstrate that crown-ether macrocycles, by encircling the sodium cation but not completely enveloping it as a cryptand would, allow strong Na–O(carbonyl) linkages to form, which we believe to be the key factor in the greater stability of these complexes relative to their $N(PPh_3)_2{}^+$ or $NEt_4{}^+$ counterparts. A further advantage of the encircling crown ether is that its size precludes tight ion pairing of the direct transition-metal–alkali-metal type. The carbonyl distortions produced by this type of interaction would clearly be an unfavourable influence in the synthesis of carbonylate species of high co-ordination number or of metal carbonyl cluster compounds where close packing of the carbonyl ligands is important.

This specificity of crown-ether encircled alkali-metal cations for one type of tight ion pairing may well lead to their more extensive use in the isolation of anionic transition-metal carbonyl complexes in the solid state.

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