Crystal and Molecular Structure of Tetracarbonyl(3,6-dithiaoctane)-chromium(0): Evidence for π Bonding by a Thioether Ligand

By **Edward N. Baker** * and **Nigel G. Larsen**, Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North, New Zealand

The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction techniques, from diffractometer data. Crystals are monoclinic, $a = 13.657(6)$, $b = 14.168(5)$, $c = 8.560(3)$ Å, $\beta = 123.48°$, space group $P2_1/a$. The structure has been refined by full-matrix least-squares methods to R 0.040 for 2 453 independent reflections. Co-ordination about the central chromium atom is distorted octahedral. Mean metal–ligand bond lengths are: Cr–S 2.418(1), Cr–C(*cis*) 1.887(3), and Cr–C(*trans*) 1.831(3) Å, consistent with a significant π component in the Cr–S bonds. The different bond orders of the *cis*- and *trans*-Cr–C bonds is also reflected in the lengths of the C–O bonds.

THERE have been numerous suggestions that the π acidity of alkyl sulphides is similar to that of the related phosphines,[1,2] and that metal–sulphur bonds may therefore have an appreciable π component. Some evidence to support this comes from i.r. spectra [2] but there has been little unequivocal structural data. Substituted metal-carbonyl complexes of the type $[ML_n(CO)_{6-n}]$ offer a convenient means of investigating the nature of the M–L bond, since its bond-order influences that of the M–CO bonds. Thus the crystal structure of pentacarbonyl(trimethylphosphine sulphide)chromium(0), $[Cr(CO)_5(SPMe_3)]$, is consistent with an essentially single Cr–S bond, with no appreciable π component,[3] while the structures of pentacarbonyl(triphenylphosphine)chromium(0), $[Cr(CO)_5(PPh_3)]$, and pentacarbonyl(triphenylphosphine oxide)chromium(0), $[Cr(CO)_5(OPPh_3)_3]$, suggest some π character in the Cr–P bonds.[4]

Although the structure of $[Cr(CO)_5(SPMe_3)]$ indicated that the sulphur ligand was co-ordinated to the chromium atom by simple σ donation, the effect on the Cr–S bond length of steric interactions between the bulky $SPMe_3$ ligand and the equatorial carbonyl groups was uncertain. It was expected that other sulphur ligands might show different bonding characteristics, and it was therefore decided to determine the crystal structure of the complex tetracarbonyl(3,6-dithiaoctane)chromium(0), $[Cr(CO)_4(dto)]$, first prepared and characterised by Ainscough *et al.*[5] A particular point of interest in the thioether ligand, 3,6-dithiaoctane(dto), was its resemblance to the side chain of the amino-acid methionine, an important ligand in biological systems. Information on its bonding characteristics is clearly relevant to metalloproteins. It was also expected that steric interactions between the dto ligand and neighbouring carbonyl groups would be minimal.

EXPERIMENTAL

The complex $[Cr(CO)_4(dto)]$ was crystallised from benzene as clear yellow prismatic crystals. The space group and approximate cell dimensions were obtained from oscillation and Weissenberg photographs. More accurate cell dimensions were determined from least-squares analysis of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

Crystal Data.—$C_{10}H_{14}CrO_4S_2$, $M = 314$, Monoclinic, $a = 13.657(6)$, $b = 14.168(5)$, $c = 8.560(3)$ Å, $\beta = 123.48(2)°$, $U = 1\,387$ Å^3, $F(000) = 889$, $D_m = 1.503(3)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.504$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 11.4 cm^{-1}. Space group $P2_1/a$, from systematic absences.

Data Collection and Reduction.—Intensity measurements were made with a computer-controlled Hilger and Watts four-circle *X*-ray diffractometer, by use of zirconium-filtered Mo-K_α radiation. The crystal chosen for data collection had dimensions *ca.* 0.05 × 0.02 × 0.02 cm, and was mounted along the longest dimension. The orientation of the crystal was defined by a least-squares treatment of the positions of 12 general reflections. Intensities were measured by means of a θ—2θ scan, consisting of 40 steps of 0.01°, through each reflection, with a count of 1 s at each step, and a background count of 5 s at the beginning and end of each scan. Three standard reflections, chosen from different regions of reciprocal space, were monitored every 100 general reflections as a check against possible crystal deterioration or misalignment. No significant change in the standard reflections was noted during data collection. Reflections hkl, $h\bar{k}l$, $\bar{h}kl$, and $\bar{h}\bar{k}l$ were measured, up to θ 27°, and equivalent reflections (hkl and $h\bar{k}l$) and ($\bar{h}kl$ and $\bar{h}\bar{k}l$) merged. Those reflections for which the intensity $I_{hkl} < 2\sigma(I_{hkl})$ were considered unobserved and omitted from later calculations, leaving a total of 2 453 independent reflections. The usual Lorentz and polarisation corrections were applied, but no correction was made for absorption.

Structure Determination.—The position of the chromium atom was determined from a three-dimensional Patterson synthesis, and two successive Fourier syntheses were then used to obtain unequivocal positions for the remaining non-hydrogen atoms. The structure was refined using a full-matrix least-squares program CUCLS (a local version of the program ORFLS,[6] adapted for the Burroughs B6700 computer by the University of Canterbury). The quantity minimised was $\Sigma w(\Delta F)^2$, where $\Delta F = K|F_o| - |F_c|$, and the weight $w = 4F_o^2/[\sigma(F_o)^2]^2$. Four cycles of least-squares refinement, with isotropic temperature factors for all the atoms, lowered the conventional R factor to 0.087. A difference-Fourier synthesis at this stage revealed the positions of 11 out of 14 hydrogen atoms, and the remaining three were placed in positions consistent with normal bond

---

[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 720.

[2] F. A. Cotton and F. Zingales, *Inorg. Chem.*, 1962, **1**, 145.

[3] E. N. Baker and B. R. Reay, *J.C.S. Dalton*, 1973, 2205.

[4] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.

[5] E. W. Ainscough, E. J. Birch, and A. M. Brodie, *Inorg. Chim. Acta*, to be published

[6] Program ORFLS written by W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

lengths and angles. A structure-factor calculation, in which the hydrogen atoms were given isotropic temperature factors equal to those of the carbon atoms to which they were attached, then gave R 0.080. Five further cycles of least-squares refinement, in which all non-hydrogen atoms were given anisotropic temperature factors, reduced R to 0.041. Hydrogen atoms were included in the structure-factor calculations but were not refined. A further difference Fourier, following a structure-factor calculation from which the hydrogen atoms were omitted, gave improved positions for all the 14 hydrogen atoms, and was otherwise relatively featureless. A final least-squares cycle saw refinement converge with R 0.040.

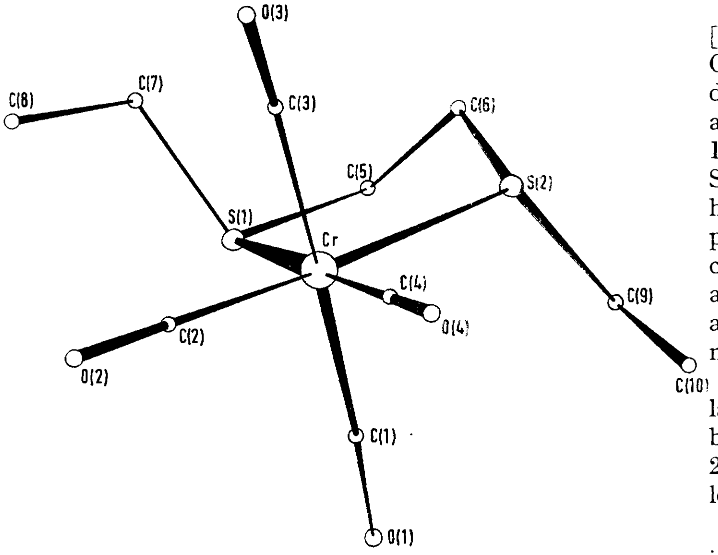
TABLE 1

Final atomic co-ordinates and anisotropic thermal parameters * ($\times 10^4$), with standard deviations in parentheses

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cr	0.326 6(1)	0.319 8(1)	0.207 4(1)	52(1)	28(1)	150(2)	0(1)	54(1)	2(1)
S(1)	0.153 4(1)	0.418 2(1)	0.080 6(1)	50(1)	32(1)	166(2)	1(1)	40(1)	0(1)
S(2)	0.400 6(1)	0.408 9(1)	0.491 5(1)	50(1)	40(1)	138(1)	−1(1)	48(1)	−2(1)
C(1)	0.253 0(3)	0.225 5(2)	0.263 0(5)	86(3)	43(2)	244(9)	1(2)	93(5)	11(3)
C(2)	0.270 0(3)	0.260 1(2)	−0.016 5(4)	69(3)	33(2)	195(7)	−2(2)	69(4)	−2(3)
C(3)	0.404 6(3)	0.405 7(2)	0.142 2(4)	74(3)	43(2)	153(7)	−10(2)	63(4)	−12(3)
C(4)	0.457 8(3)	0.245 2(2)	0.314 4(4)	73(3)	41(2)	201(8)	2(2)	71(4)	−7(3)
C(5)	0.179 1(3)	0.487 4(2)	0.279 1(4)	73(3)	45(2)	193(7)	14(2)	66(4)	2(3)
C(6)	0.307 3(3)	0.511 9(2)	0.413 3(4)	79(3)	36(2)	191(7)	3(2)	65(4)	−18(3)
C(7)	0.152 9(3)	0.511 5(2)	−0.065 6(5)	87(3)	39(2)	195(8)	10(2)	62(4)	22(3)
C(8)	0.124 0(4)	0.471 6(3)	−0.242 8(5)	126(4)	65(3)	191(8)	8(3)	75(5)	16(4)
C(9)	0.365 6(3)	0.355 6(2)	0.647 8(4)	78(3)	64(2)	177(7)	6(2)	82(4)	14(3)
C(10)	0.449 0(4)	0.275 2(3)	0.754 8(6)	109(5)	108(3)	300(10)	40(3)	118(6)	99(5)
O(1)	0.210 8(3)	0.163 7(2)	0.289 7(5)	181(4)	60(2)	530(12)	−24(2)	221(6)	33(4)
O(2)	0.238 1(2)	0.221 6(2)	−0.155 5(3)	119(3)	53(1)	232(6)	−12(2)	92(3)	−35(3)
O(3)	0.453 6(2)	0.451 2(2)	0.098 0(4)	128(3)	78(2)	278(7)	−41(2)	134(4)	−12(3)
O(4)	0.538 8(2)	0.196 2(2)	0.375 1(4)	89(3)	65(2)	341(8)	31(2)	80(4)	5(3)

Atom	x/a	y/b	z/c	B/Å^2	Atom	x/a	y/b	z/c	B/Å^2
H(51)	0.140	0.550	0.215	3.6	H(82)	0.045	0.4444	−0.294	5.0
H(52)	0.158	0.444	0.332	3.6	H(83)	0.095	0.510	−0.350	5.0
H(61)	0.340	0.550	0.345	3.6	H(91)	0.290	0.333	0.580	3.9
H(62)	0.320	0.545	0.515	3.6	H(92)	0.368	0.400	0.730	3.9
H(71)	0.238	0.535	−0.015	4.1	H(101)	0.430	0.235	0.840	6.2
H(72)	0.092	0.558	−0.073	4.1	H(102)	0.440	0.246	0.630	6.2
H(81)	0.170	0.432	−0.265	5.0	H(103)	0.530	0.293	0.815	6.2

* In the form: $f = f_0 \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.



A view of the $[Cr(CO)_4(dto)]$ molecule, showing the atom-numbering system

Final atomic co-ordinates and thermal parameters are listed in Table 1, and calculated bond lengths and angles in Table 2. The atom-numbering system for non-hydrogen atoms is shown in the Figure; the numbering of the hydrogen atoms is based on that of the carbon atoms to which they are attached. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21788 (4 pp., 1 microfiche).*

DISCUSSION

Tetracarbonyl(3,6-dithiaoctane)chromium(0), $[Cr(CO)_4(dto)]$, exists in the crystal as discrete molecules. Co-ordination about the central chromium atom is distorted octahedral, with the deviation of the principal axes from linearity shown by the angles S(1)–Cr–C(4) 177.1, S(2)–Cr–C(2) 175.9, and C(1)–Cr–C(3) 174.7°. Similar angles have been observed for other substituted hexacarbonylchromium complexes.[3,4,7-9] Least-squares planes through groups of four ligand atoms were calculated, and their equations and distances of various atoms from them are listed in Table 3. There does not appear to be any obvious pattern to the distortion of the molecule from perfect octahedral symmetry.

As indicated earlier, the prime interest in the structure lay in the nature of the Cr–S bonding. The two Cr–S bonds have lengths 2.425(1) and 2.412(1) Å, mean 2.418 Å. This is *ca.* 0.1 Å shorter than the calculated length (2.52 Å) for a single bond [based on covalent radii

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[7] R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 653.

[8] O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1968, 642.

[9] M. J. Bennett, F. A. Cotton, and M. D. LaPrade, *Acta Cryst.*, 1971, **B27**, 1899.

TABLE 2

Molecular geometry, with standard deviations in parentheses

(*a*) Bond lengths (Å)

Cr–S(1)	2.425(1)	C(5)–H(51)	1.02
Cr–S(2)	2.412(1)	C(5)–H(52)	0.90
Cr–C(1)	1.883(3)	C(6)–H(61)	1.06
Cr–C(2)	1.831(3)	C(6)–H(62)	0.92
Cr–C(3)	1.892(3)	C(7)–H(71)	1.05
Cr–C(4)	1.832(3)	C(7)–H(72)	1.04
C(1)–O(1)	1.139(4)	C(8)–H(81)	0.91
C(2)–O(2)	1.153(3)	C(8)–H(82)	1.00
C(3)–O(3)	1.134(3)	C(8)–H(83)	0.91
C(4)–O(4)	1.158(4)	C(9)–H(91)	0.92
S(1)–C(7)	1.817(3)	C(9)–H(92)	0.93
S(1)–C(5)	1.820(3)	C(10)–H(10)	1.06
S(2)–C(6)	1.805(3)	C(10)–H(102)	1.09
S(2)–C(9)	1.815(3)	C(10)–H(103)	0.96
C(5)–C(6)	1.512(4)		
C(7)–C(8)	1.496(5)		
C(9)–C(10)	1.510(5)		

(*b*) Bond angles (°)

S(1)–Cr–S(2)	85.05(3)	H(52)–C(5)–H(51)	130
S(1)–Cr–C(1)	89.8(1)	H(52)–C(5)–C(6)	109
S(1)–Cr–C(2)	93.0(1)	H(52)–C(5)–S(1)	99
S(1)–Cr–C(3)	93.9(1)	H(51)–C(5)–S(1)	101
S(1)–Cr–C(4)	177.1(1)	H(62)–C(6)–H(61)	110
S(2)–Cr–C(1)	95.8(1)	H(62)–C(6)–C(5)	112
S(2)–Cr–C(2)	175.9(1)	H(62)–C(6)–S(2)	110
S(2)–Cr–C(3)	88.3(1)	H(61)–C(6)–C(5)	111
S(2)–Cr–C(4)	92.7(1)	H(61)–C(6)–S(2)	101
C(1)–Cr–C(2)	87.8(1)	H(72)–C(7)–H(71)	120
C(1)–Cr–C(3)	174.7(1)	H(72)–C(7)–C(8)	116
C(1)–Cr–C(4)	88.5(1)	H(72)–C(7)–S(1)	102
C(2)–Cr–C(3)	88.2(1)	H(71)–C(7)–C(8)	98
C(2)–Cr–C(4)	89.3(1)	H(71)–C(7)–S(1)	111
C(3)–Cr–C(4)	88.0(1)	H(81)–C(8)–H(82)	113
C(5)–S(1)–C(7)	100.2(2)	H(81)–C(8)–H(83)	101
C(5)–S(1)–Cr	104.7(1)	H(18)–C(8)–C(7)	126
C(7)–S(1)–Cr	111.0(0)	H(82)–C(8)–H(83)	93
C(6)–S(2)–C(9)	101.0(2)	H(82)–C(8)–C(7)	99
C(6)–S(2)–Cr	103.4(1)	H(83)–C(8)–C(7)	120
C(9)–S(2)–Cr	113.0(1)	H(91)–C(9)–H(92)	106
O(1)–C(1)–Cr	174.7(3)	H(91)–C(9)–C(10)	109
O(2)–C(2)–Cr	177.8(3)	H(91)–C(9)–S(2)	110
O(3)–C(3)–Cr	174.5(3)	H(92)–C(9)–C(10)	111
O(4)–C(4)–Cr	177.2(3)	H(92)–C(9)–S(2)	111
C(6)–C(5)–S(1)	112.3(2)	H(103)–C(10)–H(101)	115
C(5)–C(6)–S(2)	112.3(2)	H(103)–C(10)–H(102)	96
C(8)–C(7)–S(1)	110.1(2)	H(103)–C(10)–C(9)	113
C(10)–C(9)–S(2)	110.1(2)	H(101)–C(10)–H(102)	122
		H(101)–C(10)–C(9)	115
		H(102)–C(10)–C(9)	93

of 1.48 Å for Cr^0 (ref. 10) and 1.04 Å for sulphur[11]], and therefore suggests a significant π contribution to the Cr–S bond. It also contrasts with the Cr–S bonding in $[Cr(CO)_5(SPMe_3)]$ where the Cr–S bond length[3] [2.510(2) Å] suggested an essentially single bond.

In both cases the influence of steric interactions on the Cr–S bond lengths must be considered before conclusions are drawn about bond types. In the structure of $[Cr(CO)_5(SPMe_3)]$ interatomic distances are such that steric repulsion between the $SPMe_3$ ligand and the equatorial carbonyl groups is probably insufficient to significantly affect the length of the Cr–S bond. In the structure of $[Cr(CO)_4(dto)]$ there are again no abnormally short intermolecular contacts (see Table 4) but there is some evidence of strain in the five-membered chelate ring. Thus the angle at the chromium atom (85.05°) is less than the ideal 90° and the angles at the bridging carbon atoms (112.3°) are greater than normal tetrahedral values. It could therefore be argued that a longer Cr–S bond is prohibited because it would produce further strain by decreasing the angles at the sulphur atoms and increasing those at the bridging carbon atoms. We have calculated that if the S–Cr–S angle is fixed at 85.1°, an increase of the Cr–S bond length by 0.1 Å could reduce the angles at the sulphur atoms by a maximum of *ca.* 3°, to *ca.* 101°, and increase those at the bridging atoms by a maximum of *ca.* 3°, to *ca.* 115°. We have, however, already found angles of this size in two similar structures,[12] *viz.* bis(2,5-dithiahexane)copper(II) tetrafluoroborate where the corresponding angles average

TABLE 3

Equations * of least-squares planes with, in square brackets, distances (Å) of relevant atoms from the planes

Plane (*i*): S(1), S(2), C(2), C(4)

$$0.6870X + 0.6718Y - 0.2770Z - 5.0411 = 0$$

[S(1) −0.042, S(2) 0.042, C(2) 0.054, C(4) −0.054, Cr −0.016, O(2) 0.114, O(4) −0.077, C(1) −1.899]

Plane (*ii*): S(1), C(1), C(3), C(4)

$$0.1306X - 0.4364Y - 0.8902Z + 2.8305 = 0$$

[S(1) −0.044, C(1) 0.054, C(3) 0.052, C(4) −0.061, Cr −0.011, O(1) 0.174, O(3) 0.167, O(4) −0.037, C(2) 1.819]

Plane (*iii*): S(2), C(1)–(3)

$$-0.6931X + 0.5636Y - 0.4494Z + 0.5329 = 0$$

[S(2) 0.038, C(1) −0.044, C(2) 0.053, C(3) −0.047, Cr 0.009, O(1) −0.136, O(2) 0.039, O(3) −0.151, C(4) −1.822]

Plane (*iv*): Cr, S(1), S(2)

$$0.6812X + 0.6662Y - 0.3034Z - 4.9406 = 0$$

[C(5) −0.176, C(6) 0.525, C(7) 1.663, C(8) 1.999, C(9) −1.670, C(10) −2.229]

* In the equations, *X*, *Y*, and *Z* are orthogonal co-ordinates obtained by the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

TABLE 4

Closest intermolecular approaches (Å)

(*a*) Not involving hydrogen atoms

$S(2) \cdots O(3^{I})$	3.54	$C(10) \cdots O(2^{V})$	3.59
$C(5) \cdots O(4^{II})$	3.59	$O(1) \cdots O(3^{II})$	3.36
$C(6) \cdots O(1^{III})$	3.44	$O(1) \cdots O(4^{II})$	3.44
$C(6) \cdots O(2^{IV})$	3.55	$O(3) \cdots O(3^{VI})$	2.95
$C(7) \cdots O(2^{IV})$	3.40	$O(4) \cdots O(2^{VII})$	3.58
$C(9) \cdots O(3^{I})$	3.52		

(*b*) Involving hydrogen atoms

$H(52) \cdots O(4^{II})$	2.7	$H(91) \cdots O(4^{II})$	2.9
$H(61) \cdots O(2^{IV})$	2.8	$H(92) \cdots O(3^{VIII})$	2.8
$H(62) \cdots O(1^{III})$	2.6	$H(92) \cdots O(3^{I})$	2.9
$H(71) \cdots O(2^{IV})$	2.9	$H(103) \cdots O(2^{VII})$	2.7
$H(72) \cdots O(4^{IV})$	2.9		

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecule at *x*, *y*, *z*:

I $1 - x, 1 - y, 1 - z$	V $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
II $-\frac{1}{2} + x, \frac{1}{2} - y, z$	VI $1 - x, 1 - y, -z$
III $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$	VII $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$
IV $\frac{1}{2} - x, \frac{1}{2} + y, -z$	VIII $x, y, 1 + z$

---

[10] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

[11] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 225.

[12] E. N. Baker and G. E. Norris, *J.C.S. Dalton*, to be submitted.

101.0 and 114.6° respectively, and bis(3,6-dithiaoctane)-copper(I) tetrafluoroborate, where the corresponding values are 95.9 and 115.2°. In view of this, and of the considerable conformational flexibility of ligands such as dithiaoctane, we believe that in the present case the dto ligand could readily accommodate a longer Cr–S bond, and that the shortening of this bond therefore probably represents a change in bond type.

A possible explanation for the different metal–sulphur bonding observed in the two cases can be seen in the nature of the ligands. In $SPMe_3$ it has been estimated[13] that the S–P bond has only partial double-bond character. Since phosphorus is less electronegative than sulphur, the bonding in $SPMe_3$ is probably intermediate between $\overset{-}{S}-\overset{+}{P}\equiv$ and $S=P\equiv$. In the dto ligand, however, each sulphur atom forms two bonds with atoms of roughly equal electronegativity (carbon). Thus the more negatively charged sulphur atom of $SPMe_3$ would be expected to be a weaker π acceptor than the sulphur atoms of dto, and this is what is observed in the crystal structures. Similar arguments have been used to rationalise differences in the Cr–P bonds in hexacarbonylchromium complexes substituted with phosphorus-containing ligands.[4]

Further evidence of the degree of double-bond character in the Cr–S bonds of $[Cr(CO)_4(dto)]$ is given by the *cis*- and *trans*-Cr–C bond lengths. As can be seen in Table 5, in complexes of the type $[CrL_n(CO)_{6-n}]$ the extent of multiple bonding in the M–L bonds is reflected in the lengths of the *cis*- and *trans*-Cr–C bonds. Thus, where no Cr–L π interaction appears to exist, as in $[Cr(CO)_5(SPMe_3)]$, the *trans* bonds are markedly shorter than the *cis*-Cr–C bonds. The accepted explanation for this is that a lack of π interaction in the Cr–L bond allows greater π interaction in the Cr–C bonds, particularly that in the *trans* position. The greater the degree of multiple bonding in the Cr–L bonds, the more equal the *cis*- and *trans*-Cr–C bond lengths become and the closer they approach the values observed in $[Cr(CO)_6]$.[14]

TABLE 5

Cr–C Bond lengths (Å)

Complex	*cis*-Cr–C	*trans*-Cr–C
$[Cr(CO)_6]$ [a]	1.909(3)	
$[Cr(CO)_5\{C(SPh)Me\}]$ [b]	1.910(2)	1.899(3)
$[Cr(CO)_5\{CPh(OMe)\}]$ [c]	1.89(1)	1.87(3)
$[Cr(CO)_5\{P(OPh)_3\}]$ [d]	1.896(5)	1.861(4)
$[Cr(CO)_5(PPh_3)]$ [d]	1.880(4)	1.844(4)
$[Cr(CO)_4(dppe)]$ [e]	1.884(7)	1.831(7) [e]
$[Cr(CO)_4(dto)]$ [f]	1.887(3)	1.832(3)
$[Cr(CO)_5(SPMe_3)]$ [g]	1.900(4)	1.815(8)
$[Cr(CO)_3(3NH\text{-}pd)]$ [h]		1.816(5) [e]

[a] Ref. 13. [b] Ref. 7. [c] Ref. 8. [d] Ref. 4. [e] Mean; ref. 9. [f] This work. [g] Ref. 3. [h] 3NH-pd = 3-Azapentane-1,5-diamine, ref. 10.

In the structure of $[Cr(CO)_4(dto)]$, the two *trans* bonds [1.831(3) and 1.832(3) Å] are significantly shorter than the two *cis*-Cr–C bonds [1.883(3) and 1.892(3) Å]. The difference between them is, however, less than that in $[Cr(CO)_5(SPMe_3)]$ (*ca.* 0.055 compared with 0.085 Å), consistent with significantly greater π interaction in the Cr–S bonds of $[Cr(CO)_4(dto)]$. Comparison with other complexes in Table 5 shows that the *cis*- and *trans*-Cr–C bonds of $[Cr(CO)_4(dto)]$ are closely comparable with those in [1,2-bis(diphenylphosphino)ethane]-tetracarbonylchromium(0),[9] $[Cr(CO)_4(dppe)]$. This would suggest that the sulphur atoms of dto and the phosphorus atoms of dppe are π acceptors of roughly equal strength, slightly less than the phosphorus atoms of triphenylphosphine. It should be noted, however, that the Cr–P bonds of $[Cr(CO)_4(dppe)]$ are 2.360(2) Å in length, significantly shorter than the Cr–S bonds of $[Cr(CO)_4(dto)]$, even though the covalent radius of phosphorus is normally taken to be greater than that of sulphur. We suggest, therefore, that, although the Cr–S bonds of $[Cr(CO)_4(dto)]$ do have a significant π component, the lengths of the Cr–S and Cr–P bonds indicate that thioethers such as dto have a slightly lower π acidity than corresponding phosphorus compounds such as dppe. The similarity of the *cis*- and *trans*-Cr–C bond lengths in the two cases may indicate that the sulphur ligands are weaker σ donors as well as weaker π acceptors, leaving the overall electron density on the chromium atom the same. Similar conclusions have been drawn from spectroscopic studies.[5]

Other bond lengths and angles in the $[Cr(CO)_4(dto)]$ molecule show a high degree of internal consistency, and agree well with those in comparable structures. The two *trans*-C–O bonds [1.153(3) and 1.158(4) Å] are significantly longer than the two *cis*-C–O bonds [1.134(3) and 1.139(4) Å]. This demonstrates clearly the inter-relation between the Cr–C and C–O bonds. As the bond order of the Cr–C bond increases (and hence the bond length decreases) the bond order of the associated C–O bond decreases (and hence its length increases). Hence, the two longer C–O bonds in this structure are associated with the two shorter Cr–C bonds. The carbonyl groups are co-ordinated in the usual angular fashion, the Cr–C–O angles being 174.7(3) and 174.5(3)° for the *cis*-carbonyl groups, and 177.8(3) and 177.2(3)° for the *trans*-carbonyl groups. In each case the carbonyl group is bent in the direction away from the dto ligand. The greater bending at the *cis*-carbonyl groups, C(1)–O(1) and C(3)–O(3), appears to arise from intra- rather than inter-molecular effects. Thus although O(3) is involved in a close contact with O(3) from a neighbouring molecule in the crystal (see Table 4), they are in fact bent towards each other, and the close similarity of the angles Cr–C(1)–O(1) and Cr–C(3)–O(3) suggests an intramolecular effect (perhaps repulsion from the lone pairs of the sulphur atoms).

The five-membered chelate ring has the expected puckered conformation, with the atoms C(5) and C(6) above and below the plane defined by the atoms S(1), Cr, S(2). The puckering is not symmetrical, however, C(5) being 0.176 Å below this plane and C(6) 0.525 Å above it (see Table 3). Bond lengths within the dto ligand agree well with comparable bonds in other

---

[13] J. Goubeau, *Angew. Chem.*, 1969, **8**, 328.

[14] A. Whittaker and J. W. Jeffery, *Acta Cryst.*, 1967, **23**, 977.

molecules (Table 2). Bond angles are all approximately tetrahedral, although those about the sulphur atoms vary considerably, from 100.2(2) to 113.0(1)°, with means of 105.3 and 105.9° for the two atoms. The wide range may arise mainly from a slight bending of the ethyl substituents away from the neighbouring carbonyl groups [thus increasing angles Cr–S(1)–C(7) and Cr–S(2)–C(9) and decreasing C(7)–S(1)–C(5) and C(9)–S(2)–C(6)].

Closest intermolecular approaches are listed in Table 4. Apart from the contact O(3) · · · O(3), previously mentioned, which does not appear to produce any molecular distortion, all apparently represent normal van der Waals interactions.

We thank E. J. Birch for the sample of [Cr(CO)$_4$(dto)], Drs. P. P. Williams and K. L. Brown of the Chemistry Division, D.S.I.R., Wellington, for use of their four-circle diffractometer and assistance with data collection, Drs. A. M. Brodie and E. W. Ainscough for many helpful discussions, and a referee for valuable comments.

[5/2403 *Received, 11th December,* 1975]