

Metal-Carbonyl and Metal-Nitrosyl Complexes. Part VI.¹ The Crystal and Molecular Structure of *trans*-Di- μ -phenylthio-dinitrosylbis-(π -cyclopentadienyl)dichromium(I)

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Crystals of *trans*-[C₅H₅Cr(NO)SPh]₂ are orthorhombic, space group *Pbcn*, with four molecules in a cell of dimensions $a = 11.75$, $b = 10.44$, $c = 17.51$ Å. The molecule is situated on a crystallographic centre of symmetry, and the (CrS)₂ ring is therefore planar. A three-dimensional single-crystal X-ray analysis has shown that the cyclopentadienyl, nitrosyl, and sulphur ligands are arranged around each chromium atom in an approximately tetrahedral manner. The CrNO grouping departs from linearity by 10°, and the Cr-N bond (1.66 Å) has appreciable multiple-bond character. The Cr-C(cyclopentadienyl) bond lengths range from 2.17 to 2.25 Å, and the mean value (2.21 Å) is in good agreement with chromium-hydrocarbon distances in other complexes. The Cr-Cr distance is 2.950 Å.

THERE has been increasing interest in transition-metal compounds containing metal-metal bonds,² and much detailed structural knowledge of these compounds has derived from crystallography. A number of binuclear metal complexes with bridging ligands contain the fragment (I), where X represents a bridging donor such as halogen, the sulphur atom of RS, the phosphorus atom of R₂P, or the carbon atom of CO, and both planar and markedly non-planar geometries have been reported for the four-membered ring. From the viewpoint of a localised orbital description of the bonding, the non-planar (MX)₂ bridging system can generally be accounted for by the concept of a 'bent' metal-metal bond involving the overlap of two σ -like orbitals which do not point directly towards each other. For example, in [Co(CO)₄]₂,³ [EtSFe(CO)₃]₂,⁴ [(MeC₆H₄)₂CNFe(CO)₃]₂,⁵ [SFe(CO)₃]₂,⁶ and [Ph₂PCoC₅H₅]₂,⁷ each metal atom has five locations of a distorted octahedral environment occupied by ligands (the cyclopentadienyl ring in the Co

complex may be regarded as occupying three co-ordination positions), and the sixth octahedral site can be associated, as in (II), with the orbital which forms the bent metal-metal bond, the dihedral angle XMX'/X'M'X being in the region of 90°. The pronounced puckering of the four-membered ring in these complexes clearly reflects the strength of the metal-metal bond, for valency angle strain in the (MX)₂ framework is generally minimized when the ring skeleton is planar; in [Ph₂PNiC₅H₅]₂⁷ there is no metal-metal bond, and the (MX)₂ ring is flat. Planar, or almost planar (MX)₂ fragments with metal-metal bonds have been observed in complexes where the ligands require four or six co-ordination sites around the metal atom, with the metal-metal bond assigned to an additional fifth or seventh co-ordination position; in [EtSFe(NO)₂]₂⁸ and [C₅H₅Fe(CO)₂]₂⁹ the (MX)₂ systems are planar, and in (C₅H₅)₂Fe₂(CO)₃(CNPh)¹⁰ the departure from planarity is slight, for the fold about the Fe-Fe vector is 166°.

¹ Part V, O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1967, 1619.

² J. Lewis and R. S. Nyholm, *Science Progress*, 1964, **52**, 557; J. Lewis, *Pure and Appl. Chem.*, 1965, **10**, 11; F. A. Cotton, *Quart. Rev.*, 1966, **20**, 389.

³ G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

⁴ L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

⁵ D. Bright and O. S. Mills, *Chem. Comm.*, 1967, 245.

⁶ C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1.

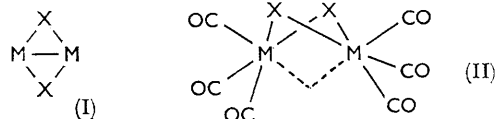
⁷ J. M. Coleman and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 542.

⁸ J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

⁹ O. S. Mills, *Acta Cryst.*, 1958, **11**, 620.

¹⁰ K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Comm.*, 1965, 181.

The recent preparation of $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SPh}]_2$ and $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$ by Knox and his associates¹¹ provides further examples of complexes containing the fragment (I), and we undertook *X*-ray diffraction studies



of these compounds to elucidate their molecular geometries, and to examine the effect on the metal-metal interaction of changes in the bridging ligand. An incentive was the comparative scarcity of accurate crystal-structure analyses of metal-nitrosyl complexes.¹²

The crystal structure of the *trans*-isomer of $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SPh}]_2$ was determined by the heavy-atom approach, and the atomic parameters adjusted by Fourier and least-squares methods. Two independent sets of least-squares calculations were conducted, one based on *X*-ray data collected with Mo- K_α radiation and the other with Cu- K_α radiation, and when these calculations were terminated the values of *R* were 6.8% (Mo data; 1225 reflexions; anisotropic atomic vibration parameters) and 14.4% (Cu data; 1535 reflexions; isotropic atomic vibration parameters). The differences between the resultant two sets of atomic co-ordinates are gratifyingly small, being less than 0.01 Å for 23 co-ordinates, between 0.01 and 0.03 Å for a further 17 co-ordinates, and in excess of 0.03 Å for only 5 co-ordinates [associated with C(10), C(9), and C(4)], the mean difference being 0.016 Å. In view of this agreement we conclude that our results are not affected significantly by absorption. The results derived from the Mo- K_α data are the more accurate, and only these are

TABLE 1

Atomic co-ordinates (as fractions of the cell edges) and their standard deviations (Å)

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	-0.2044	-0.0140	0.1183	0.008	0.008	0.008
C(2)	-0.1657	-0.1009	0.1711	0.011	0.009	0.009
C(3)	-0.2231	-0.1130	0.2420	0.012	0.011	0.009
C(4)	-0.3151	-0.0382	0.2581	0.012	0.010	0.010
C(5)	-0.3537	0.0466	0.2049	0.011	0.011	0.010
C(6)	-0.2992	0.0599	0.1343	0.010	0.010	0.009
C(7)	0.0395	0.1439	0.1455	0.013	0.014	0.011
C(8)	0.1424	0.1639	0.1135	0.014	0.013	0.011
C(9)	0.1357	0.2720	0.0686	0.011	0.010	0.011
C(10)	0.0251	0.3220	0.0745	0.018	0.011	0.013
C(11)	-0.0347	0.2369	0.1246	0.011	0.012	0.010
N(12)	-0.0288	0.2092	-0.0601	0.007	0.007	0.007
O(13)	-0.0625	0.2767	-0.1097	0.007	0.008	0.007
S	-0.1471	0.0092	0.0250	0.002	0.002	0.002
Cr	0.0141	0.1366	0.0193	0.001	0.001	0.001

reproduced here. The atomic co-ordinates and positional standard deviations are in Table 1, the temperature factors in Table 2, and the interatomic distances and valency angles in Table 3. The arrangement of atoms in the molecule as viewed along the *b*-axis is shown in Figure 1. The dimeric molecule is associated with a crystallographic centre of symmetry, and the $(\text{CrS})_2$

TABLE 2

Anisotropic temperature factors ($10^4 b_{ij}$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	33	56	20	-6	8	6
C(2)	91	83	24	18	32	8
C(3)	106	127	25	-18	32	18
C(4)	101	96	34	-47	51	-1
C(5)	85	108	36	-14	52	-12
C(6)	58	97	33	14	33	11
C(7)	139	216	24	-175	3	-49
C(8)	138	161	37	53	-68	-69
C(9)	108	132	40	-148	18	-92
C(10)	225	69	49	21	-59	-38
C(11)	80	208	45	-20	29	-156
N(12)	51	70	27	-4	10	10
O(13)	78	135	39	32	-7	74
S	33	60	19	11	8	-1
Cr	41	51	17	-2	6	-9

TABLE 3

Interatomic distances (Å) and angles (degrees), with standard deviations in parentheses

Intramolecular distances			
Cr-S	2.317 (0.002)	C(5)-C(6)	1.40 (0.014)
Cr-S'	2.315 (0.002)	C(7)-C(8)	1.35 (0.019)
Cr-Cr	2.950 (0.002)	C(7)-C(11)	1.36 (0.018)
Cr-N	1.662 (0.007)	C(8)-C(9)	1.38 (0.016)
Cr-C(7)	2.231 (0.011)	C(9)-C(10)	1.40 (0.020)
Cr-C(8)	2.253 (0.013)	C(10)-C(11)	1.43 (0.018)
Cr-C(9)	2.187 (0.011)	N(12)-O(13)	1.19 (0.010)
Cr-C(10)	2.167 (0.012)	C(1) ... C(7)	3.34
Cr-C(11)	2.197 (0.011)	C(1) ... C(11)	3.29
C(1)-S	1.783 (0.008)	C(1) ... N'	3.56
C(1)-C(2)	1.37 (0.012)	C(2) ... C(7)	3.54
C(1)-C(6)	1.38 (0.013)	C(2) ... N'	3.56
C(2)-C(3)	1.42 (0.014)	C(2) ... O'	3.42
C(3)-C(4)	1.36 (0.016)	C(6) ... C(11)	3.62
C(4)-C(5)	1.36 (0.015)	C(10) ... O	3.42
Valency angles			
S-Cr-S'	100.9 (0.1)	C(2)-C(3)-C(4)	120.5 (0.9)
S-Cr-Cr'	50.4 (0.1)	C(3)-C(4)-C(5)	119.7 (1.0)
S-Cr-N	92.9 (0.3)	C(4)-C(5)-C(6)	121.1 (1.0)
N-Cr-Cr'	102.4 (0.3)	C(1)-C(6)-C(5)	119.5 (0.9)
N-Cr-S'	103.0 (0.3)	C(8)-C(7)-C(11)	110.7 (1.1)
Cr'-Cr-S'	50.5 (0.1)	C(7)-C(8)-C(9)	108.2 (1.2)
Cr-N-O	169.9 (0.7)	C(8)-C(9)-C(10)	108.4 (1.1)
Cr-S-Cr'	79.1 (0.1)	C(9)-C(10)-C(11)	105.6 (1.0)
Cr-S-C(1)	115.2 (0.3)	C(7)-C(11)-C(10)	107.1 (1.1)
C(1)-S-Cr'	118.2 (0.3)	N-Cr-Cp*	122.2
C(2)-C(1)-C(6)	119.9 (0.8)	S-Cr-Cp	120.2
C(2)-C(1)-S	125.6 (0.7)	S'-Cr-Cp	113.8
C(6)-C(1)-S	114.4 (0.6)	Cr'-Cr-Cp	135.3
C(1)-C(2)-C(3)	119.4 (0.9)		

* Cp refers to the centre of the cyclopentadienyl ring.

Intermolecular distances (≤ 3.80 Å)

O ... C(5) _{II}	3.49	C(4) ... C(11) _I	3.75
C(8) ... O _{II}	3.52	C(5) ... C(11) _I	3.76
O ... C(6) _{II}	3.56	C(10) ... C(4) _{III}	3.77
C(2) ... C(6) _I	3.62	C(5) ... C(5) _{VI}	3.78
C(9) ... O _{II}	3.65	C(6) ... C(10) _I	3.78
C(9) ... C(4) _{III}	3.67	C(7) ... C(7) _V	3.78
C(4) ... C(8) _{IV}	3.69	C(8) ... C(3) _{III}	3.78
C(3) ... C(5) _I	3.72	C(9) ... S _{II}	3.80
C(2) ... C(5) _I	3.73		

The subscripts refer to the positions:

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

¹¹ Personal communication from Dr. G. R. Knox.

¹² O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1966, 1095.

unit is therefore planar. A view of the molecule projected on to the $(\text{CrS})_2$ plane is shown in Figure 2.

The Cr-Cr distance of 2.950 Å leads to a single-bond covalent radius of 1.475 Å for Cr^{I} (in assessing the metal oxidation level, we regard the nitrosyl donor as NO^+), not significantly different from the Cr^0 radius of 1.48 Å which Cotton and Richardson deduced from the average

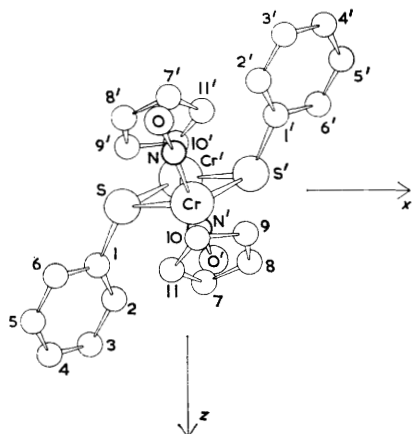


FIGURE 1 The molecular structure, viewed in projection along the b -axis

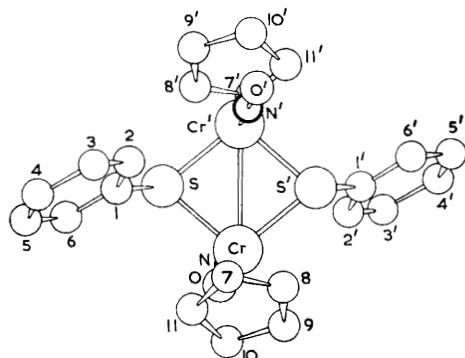


FIGURE 2 Projection of the molecule on to the $(\text{CrS})_2$ plane

Cr-N distance of 2.185 Å in diethylenetriaminechromium tricarbonyl.¹³ The average Cr-C(cyclopentadienyl) distance of 2.21 Å is close to the corresponding distance of 2.20 Å in cyclopentadienyldinitrosylchromium chloride¹² and to the average Cr-C(sp^2) bond lengths in tricarbonylchromiumbenzene (2.22 Å),¹⁴ methyl tricarbonylchromiumbenzoate (2.22 Å),¹ tricarbonylchromiumdihydrophenanthrene (2.22 Å),¹⁵ the tricarbonylchromium deri-

¹³ F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

¹⁴ M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.

¹⁵ K. W. Muir, G. Ferguson, and G. A. Sim, *Chem. Comm.*, 1966, 465.

¹⁶ W. A. C. Brown, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (B)*, 1966, 504.

¹⁷ M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.

¹⁸ O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1966, 822.

¹⁹ O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1967, 228.

²⁰ F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

vative of the diphenylketen-ethoxyacetylene adduct (2.23 Å),¹⁶ tricarbonylchromiumhexamethylbenzene (2.23 Å),¹⁷ tricarbonylchromiumphenanthrene (2.24 Å),¹⁵ tricarbonylchromiumanisole (2.24 Å),¹⁸ and tricarbonylchromium-*o*-toluidine (2.25 Å).¹⁹ These distances are larger than the metal-nitrogen single-bond distance by amounts which can reasonably be attributed to the greater single-bond radius of carbon, and it is likely that the chromium-arene bonds in these complexes have little, if any, double-bond character. A like deduction can be made about molybdenum-hydrocarbon bonds in a variety of complexes, for the average Mo-C bonding distances of 2.34 Å in $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ ²⁰ and $\text{C}_{10}\text{H}_8\text{Mo}_2(\text{CO})_6$,²¹ 2.33 Å in $(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{PMe}_2)(\text{CO})_4$,²² 2.36 Å in $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7$,²³ and $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{Me}]_2$,²⁴ and 2.37 Å in $[\text{Pr}^{\text{I}}(\text{Me})_2\text{C}_{10}\text{H}_5]\text{Mo}_2(\text{CO})_6$ ²⁵ and $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$ ²⁶ are slightly longer than the average Mo-N distance of 2.32 Å in diethylenetriaminemolybdenum tricarbonyl.²⁷ The mean Mo-C bond length of 2.29 Å in $(\text{C}_5\text{H}_5)_2\text{MoH}_2$ ²⁸ is somewhat shorter than these distances, but in the absence of strongly π -bonding ligands such as CO back-donation from metal d_π orbitals to the antibonding π^* orbitals of the hydrocarbon should be more important. In accord with this, the Cr-C distance in dibenzenechromium (2.15 Å)²⁹ is significantly shorter than the Cr-C distances cited earlier, and differs from the Mo-C distance in $(\text{C}_5\text{H}_5)_2\text{MoH}_2$ by an amount (0.14 Å) which is identical with the difference between the metal-nitrogen distances in diethylenetriaminechromium tricarbonyl¹³ and the corresponding molybdenum complex,²⁷ and hence with the difference in radii of Cr^0 and Mo^0 . The molybdenum single-bond radius of about 1.62 Å which is indicated by the Mo-N distance of 2.32 Å in diethylenetriaminemolybdenum tricarbonyl is supported by Mo-Mo separations of 3.22 Å in $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$,²⁰ 3.24, 3.25 Å in $\text{C}_{10}\text{H}_8\text{Mo}_2(\text{CO})_6$,^{21,25} 3.26 Å in $(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{PMe}_2)(\text{CO})_4$,²² and 3.27 Å in $[\text{Pr}^{\text{I}}(\text{Me})_2\text{C}_{10}\text{H}_5]\text{Mo}_2(\text{CO})_6$;²⁵ moreover, the Mo-CH₃ bond length in $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{Me}]_2$ is 2.38 Å.²⁴

Figure 3 shows the environment of the chromium atom, viewed in projection down a line perpendicular to its cyclopentadienyl ring. The geometric features of the chromium co-ordination are related to those of $[\text{C}_5\text{H}_5\text{MoS}(\text{O})]_2$ ³⁰ and $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$,⁹ and differ from the metal co-ordination in the seven-co-ordinate complexes $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7$,²³ $(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{PMe}_2)(\text{CO})_4$,²² and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$.²⁰ The carbon-carbon bond lengths

²¹ J. S. McKechnie and I. C. Paul, *Chem. Comm.*, 1967, 747.

²² R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

²³ M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213.

²⁴ P. H. Bird and M. R. Churchill, *Chem. Comm.*, 1967, 705.

²⁵ M. R. Churchill and P. H. Bird, *Chem. Comm.*, 1967, 746.

²⁶ J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, 1966, **88**, 5927.

²⁷ F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

²⁸ M. Gerloch and R. Mason, *J. Chem. Soc.*, 1965, 296; S. C. Abrahams and A. P. Ginsberg, *Inorg. Chem.*, 1966, **5**, 500.

²⁹ A. Haaland, *Acta Chem. Scand.*, 1965, **19**, 41; F. Jellinek, *J. Organometallic Chem.*, 1963, **1**, 43; E. Keulen and F. Jellinek, *ibid.*, 1966, **5**, 491.

³⁰ D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 3721.

in the cyclopentadienyl ring vary from 1.35 to 1.43 Å, and the deviation of the ring from five-fold symmetry is associated with an approximate vertical mirror plane which passes through C(10) and the midpoint of C(7)–C(8). Distortions of complexed cyclopentadienyl rings are common, and are generally rationalized in terms of the lack of cylindrical symmetry around the metal atom removing the degeneracy of the e_1 molecular orbitals of the

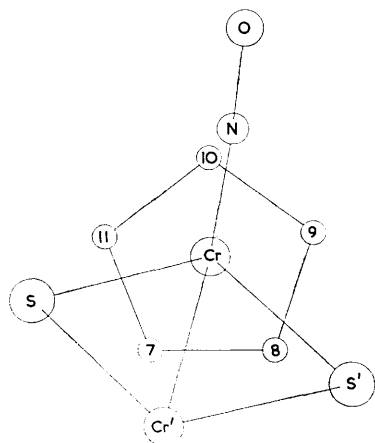


FIGURE 3 The co-ordination of the chromium atom in $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SC}_6\text{H}_5]_2$, viewed perpendicularly to the cyclopentadienyl ring

cyclopentadienyl ring.³¹ The chromium–carbon bond lengths range from 2.17 to 2.25 Å, and the variation is symmetrical with respect to the approximate symmetry plane of the cyclopentadienyl ring; the two longest chromium–carbon bonds [Cr–C(7), 2.23 Å; Cr–C(8), 2.25 Å] are associated with the shortest carbon–carbon bond [C(7)–C(8), 1.35 Å]. The approximate mirror plane of the cyclopentadienyl ring is not symmetrically oriented with respect to the sulphur and nitrogen ligands of the chromium atom, but this deviation from an idealized geometry presumably has a steric, rather than an electronic, origin (cf. ref. 7).

The single-bond covalent radius of sulphur is 1.04 Å,³² and the length of a chromium–sulphur single bond should therefore be close to 2.52 Å. The actual Cr–S bridging distances are 2.315 and 2.317 Å, and the contraction of 0.20 Å suggests some degree of π -bonding. In the case of the iron complexes $[\text{EtSFe}(\text{CO})_3]_2$,⁴ $[\text{MeSFe}_2(\text{CO})_6]_2\text{S}$,³³ $[\text{SFe}(\text{CO})_3]_2$,⁶ and $[\text{EtSFe}(\text{NO})_2]_2$,⁸ the quantities $d(\text{Fe–Fe})/2 + 1.04 \text{ Å} - d(\text{Fe–S})$ are 0.05, 0.05, 0.09, and 0.13 Å, respectively, and it thus appears that the Fe–S bridging bonds in these complexes may have less double-bond character than the Cr–S bridging bonds in $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SC}_6\text{H}_5]_2$; this distinction may

derive from the iron atoms' carrying several ligands (the CO or NO groups) and the chromium atom only one ligand (the NO group) to which extensive π -donation can occur. An explanation of this sort may account for the mean Mo–P bond distance in $(\text{EtP})_5\text{Mo}(\text{CO})_4$, 2.523 Å,³⁴ being appreciably longer than the distance in $\{\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\}_2\text{H}(\text{PMe}_2)$, 2.42 Å.²² Coleman and Dahl⁷ noted that the Co–P and Ni–P bond lengths in $(\text{C}_5\text{H}_5\text{CoPPh}_2)_2$ and its Ni analogue, 2.16 and 2.15 Å, respectively, are shorter than Co–SC₂H₅ distances of 2.21–2.26 Å in a number of cobalt carbonyl complexes,³⁵ and inferred that for these first-row transition metals there is greater π -bonding associated with a bridging PR₂ group than with a bridging SR group. The average Co–C(cyclopentadienyl) distance of 2.05 Å in $(\text{C}_5\text{H}_5\text{CoPPh}_2)_2$ suggests a Co radius in the neighbourhood of 1.30 Å, which is close to half the Co–Co distance in the complex, viz., 1.28 Å. (Co–Co distances in other complexes indicate metal radii in the range 1.23–1.32 Å.^{3,35,36}) Since Pauling's covalent radius for phosphorus is 1.10 Å, the apparent shortening of the Co–P bonds in $(\text{C}_5\text{H}_5\text{CoPPh}_2)_2$ is around 0.2 Å, similar to the estimated contraction of the Cr–S bonds in $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SPh}]_2$. On the basis of a molybdenum radius of 1.62 Å, the Mo–P bond lengths in $(\text{EtP})_5\text{Mo}(\text{CO})_4$ ³⁴ and $\{\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\}_2\text{H}(\text{PMe}_2)$ ²² are shorter than single-bond distances by 0.20 and 0.30 Å, respectively.

The Cr–S–Cr' angle, 79°, is close to M–X–M' angles of 77° in $[\text{C}_5\text{H}_5\text{MoS}(\text{O})]_2$,³⁰ 85° in $\{\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\}_2\text{H}(\text{PMe}_2)$,²² 80° in $\text{Mn}_2\text{H}(\text{PPh}_2)(\text{CO})_8$,³⁷ 73° in $(\text{C}_5\text{H}_5\text{CoPPh}_2)_2$,⁷ and 74° in $[\text{EtSFe}(\text{NO})_2]_2$.⁸ The angle at the bridging phosphorus atom in $(\text{C}_5\text{H}_5\text{NiPPh}_2)_2$ is appreciably larger (102°), but this molecule lacks a metal–metal bond. The S–Cr–S' angle (101°) is close to the average S–Mo–S' angle of 103° in $[\text{C}_5\text{H}_5\text{MoS}(\text{O})]_2$, and distinctly larger than the P–Co(or Ni)–P' angles of 84° and 78° in $(\text{C}_5\text{H}_5\text{CoPPh}_2)_2$ and its Ni analogue.

The Cr–N bond length of 1.66 Å is shorter than the average Cr–N distance of 1.71 Å in cyclopentadienyl-dinitrosylchromium chloride. A metal–nitrosyl bond of 1.66 Å is encountered also in $\text{K}_3\text{Mn}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$,³⁸ and in that compound the average Mn–C(*sp*) bond length is 1.98 Å; in $\text{Mn}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2$, on the other hand, the Mn–N bond length is longer (1.73 Å) and the Mn–C(*sp*) distances are notably shorter (1.75 and 1.78 Å),³⁹ reflecting the marked superiority in π -acceptor capacity of CO relative to CN[–]. In $[\text{EtSFe}(\text{NO})_2]_2$ the Fe–N distance is 1.67 Å. The Cr–N(*sp*³) distance in

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diethylenetriaminechromium tricarbonyl is 2.19 Å,¹³ and on decreasing this distance by 0.06 Å to allow for the change from sp^3 to sp hybridisation we obtain 2.13 Å as a reasonable estimate of a standard Cr-N(sp) single-bond distance. The actual metal-nitrosyl bond length in $[C_5H_5Cr(NO)SPh]_2$ is 0.47 Å shorter than this predicted value, and the bond order must therefore appreciably exceed unity. The Cr-C(sp) bond lengths in the arenechromium tricarbonyls and in diethylenetriaminechromium tricarbonyl average about 1.82 Å, and the Cr-N bond in $[C_5H_5Cr(NO)SPh]_2$ is shorter than this by an amount (0.16 Å) which is appreciably greater than the difference of about 0.06 Å in the radii of nitrogen and carbon atoms. Since the Cr-C distance in diethylenetriaminechromium tricarbonyl has been estimated⁴⁰ to correspond to a bond order of 1.7, we conclude that the chromium-nitrosyl bond must approximate to a double bond.

The metal-nitrosyl grouping departs from linearity by a highly significant amount, and the Cr-N-O angle (170°) is very close to the average Cr-N-O angle in cyclopentadienyldinitrosylchromium chloride (169°). In $[Co(NO)_2Cl]_2$ ⁴¹ and $[EtSFe(NO)_2]_2$ ⁸ the average metal-nitrosyl angles are 166 and 167°, respectively, and in $CsFe_4S_3(NO)_7 \cdot H_2O$ the deviations from linearity extend to 20°.⁴² The Co-N-O angle in $Co(NO)(S_2CNMe_2)_2$ is 127°,⁴³ whereas the Fe-N-O angle in $Fe(NO)(S_2CNEt_2)_2$ is $174 \pm 4^\circ$.⁴⁴ The metal-nitrosyl groupings in $Mn(NO)(CO)_2(PPh_3)_2$ ³⁹ and $Na_2Fe(CN)_5NO \cdot 2H_2O$ ⁴⁵ do not depart significantly from linearity, and the microwave rotational spectrum of C_5H_5NiNO demonstrates that this nickel-nitrosyl grouping is strictly linear.⁴⁶ In view of the proximity of the nitrosyl group to the phenyl group of the SC_6H_5 bridge it is not possible to exclude a steric mechanism for the departure from 180° of the Cr-N-O angle in $[C_5H_5Cr(NO)SPh]_2$, but we hope that our studies of related molecules containing different bridging ligands will enable us to differentiate between steric and electronic origins for the non-linearity of the metal-nitrosyl grouping.

The phenyl group of the SC_6H_5 bridging ligand is wedged between the nitrosyl and cyclopentadienyl groups on the same side of the $(CrS)_2$ ring, with the benzene plane inclined at 35° to the plane through the atoms C(1), S, S', and C(1'). The enlargement beyond 120° of the angle C(2)C(1)S, 126°, with concomitant reduction of the angle C(6)C(1)S, 114°, serves to displace the phenyl group away from the cyclopentadienyl ring, and the C(2) ... C(7) and C(2) ... C(11) distances are 3.54 and 3.93 Å, respectively. The sulphur-carbon bond length (1.78 Å) is identical with the sum of the

radii appropriate to sulphur (1.04 Å) and sp^2 -carbon (0.74 Å),⁴⁷ and is in good agreement with S-C(sp^2) distances in orthonitric acid (1.774 Å),⁴⁸ di-*p*-chlorophenyl sulphone (1.765 Å),⁴⁹ and β -sulphanilamide (1.750 Å).⁵⁰

The arrangement of molecules in the crystal is shown in projection along the *b*-axis in Figure 4. The intermolecular contacts are listed in Table 3 and contain no

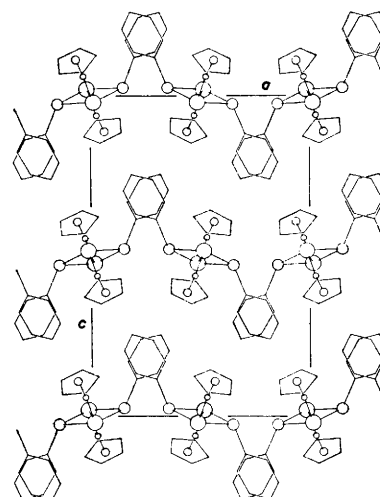


FIGURE 4 The crystal structure viewed in projection along the *b*-axis

unusual feature. Table 4 shows the displacement of the atoms from the benzene and the cyclopentadiene plane.

TABLE 4

Displacements (Å) of the atoms from (a) the benzene plane and (b) the cyclopentadienyl plane

(a)		(b)	
C(1)	−0.03	C(7)	0.01
C(2)	−0.01	C(8)	−0.01
C(3)	0.01	C(9)	0.01
C(4)	0.00	C(10)	0.00
C(5)	0.01	C(11)	0.00
C(6)	−0.01	Cr	1.86
S	0.02		

EXPERIMENTAL

Crystal Data.—*trans*-Di- μ -phenylthio-dinitrosylbis-(π -cyclopentadienyl)chromium(I), $C_{22}H_{20}Cr_2N_2O_2S_2$, $M = 512.6$. Orthorhombic, $a = 11.75$, $b = 10.44$, $c = 17.51$ Å, $U = 2148$ Å³, $Z = 4$, $D_c = 1.584$ g. cm.^{−3}, $F(000) = 1048$. Space group *Pbcn* (D_{2h}^{14}). Absorption coefficient for Mo- K_α X-radiation ($\lambda = 0.7107$ Å), $\mu = 12.6$ cm.^{−1}, and for Cu- K_α X-radiation ($\lambda = 1.5418$ Å), $\mu = 106$ cm.^{−1}.

Crystallographic Measurements.—The unit-cell dimensions

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TABLE 5

Measured and calculated values of the structure factors. Indices h and k are given at the head of each section, and are followed by values of l , $|F_0|$, and F_c .

0, 0	6 147.5	132.4	9 47.7	-51.6	9 59.6	56.0	3, 4	3 36.7	-37.8		
4 62.9	67.4	7 58.7	-62.0	11 41.6	-42.7	11 32.8	35.9	4 74.3	-76.4		
6 53.8	54.2	8 64.5	-67.5	13 43.5	-43.0	12 25.6	28.3	5 8.8	-17.3		
8 150.2	153.0	9 95.7	-91.9	15 29.9	-31.9	13 37.4	42.6	6 53.0	-53.2		
14 16.5	-39.4	11 62.7	-60.7	17 31.3	-26.9	15 44.2	45.6	7 91.5	-93.9		
16 18.5	-34.6	13 54.2	-50.8	19 23.2	-19.9	17 33.5	31.2	9 79.7	-78.5		
18 48.7	-48.0	14 26.2	-23.6	1, 10		19 19.5	19.3	11 14.4	16.2		
20 55.2	-55.0	15 65.5	-62.9	8 19.2	19.5	2, 7		12 15.0	16.2		
22 52.9	-58.2	16 28.5	-31.1	10 16.2	17.8	3 26.8	27.7	13 15.6	-17.5		
24 34.5	-34.9	17 46.8	-45.8	1, 11		5 25.2	24.3	14 32.3	33.4		
26 29.9	-27.7	18 30.8	-29.9	0 27.0	-25.6	6 28.2	29.1	15 16.8	-14.9		
0, 2	2 89.5	-70.1	19 22.6	-18.9	2 35.0	-34.4	8 24.1	24.3	16 17.4	19.3	
3 121.1	-110.9	20 33.1	-35.2	22 30.6	-27.8	9 17.5	-21.3	0 87.6	-79.4		
4 154.2	143.2	22 30.6	-27.8	24 26.7	-23.6	10 23.7	26.0	1 13.1	12.0		
5 36.6	26.6	24 26.7	-23.6	1, 15		12 16.4	17.5	2 107.7	-107.7		
6 99.7	92.5	1, 2	0 23.8	25.3	2 23.9	23.4	0 32.9	35.1	3 34.4	35.5	
7 71.2	-81.8	2 174.3	156.8	2 23.9	23.4	2, 0	2 35.1	36.7	4 40.3	-46.0	
8 41.9	45.5	3 28.0	26.6	4 30.8	33.8	3 14.5	-12.9	5 98.3	95.2		
9 119.4	-119.4	4 73.8	64.9	6 85.6	80.3	4 35.8	35.5	6 42.7	-45.2		
11 145.3	-146.2	6 26.2	23.9	10 34.0	36.9	5 21.0	-23.9	7 70.9	73.1		
13 52.1	-54.3	7 26.7	-18.4	14 20.7	20.5	6 46.0	47.0	8 48.2	-53.7		
14 34.4	-34.2	8 34.3	35.7	16 13.0	-15.1	7 21.7	-20.7	9 71.5	71.6		
15 71.7	-80.0	10 55.2	56.0	22 16.2	-19.0	8 33.8	34.0	10 37.5	-39.6		
16 26.4	-30.7	12 40.5	44.6	24 21.1	-27.4	9 22.6	-23.1	11 27.5	28.2		
17 38.8	-42.3	15 19.5	20.7	2, 1	4 60.8	62.0	11 16.8	11 27.5	28.2		
18 36.7	-34.8	0 125.4	-114.8	4 60.8	62.0	15 21.4	-16.4	12 20.1	20.5		
19 17.0	-18.4	2 21.8	28.7	5 56.5	-55.3	2 30.8	31.8	13 76.8	68.1		
20 17.6	-20.0	3 52.7	-49.2	6 56.5	-55.3	3 16.6	18.8	14 23.6	26.8		
0, 4	0 9.1	5.9	4 62.5	-64.1	10 37.9	37.9	3 16.6	15 52.8	52.7		
1 15.9	19.9	6 94.1	-84.0	12 37.9	37.9	10 24.4	27.0	16 38.6	37.5		
3 33.2	-31.1	7 47.3	-45.2	14 36.0	37.2	12 18.0	23.3	17 39.9	38.0		
4 89.1	-86.6	8 51.9	-54.4	2, 2	0 282.0	-258.7	2 32.8	18 27.0	30.4		
5 38.5	-36.7	9 64.4	-64.4	1 87.3	-70.2	1 13.4	-18.7	19 19.7	18.7		
6 103.2	-93.2	11 46.3	-46.6	2 53.1	-51.0	2 26.9	-32.7	20 28.7	27.2		
7 44.6	-42.2	13 39.0	-41.2	3 24.9	12.5	3 16.6	-18.7	22 24.9	24.1		
8 20.1	-23.4	14 19.1	-17.8	4 41.6	35.7	4 27.3	-29.8	1 39.6	40.3		
9 45.3	42.1	15 28.2	-28.7	5 47.8	-52.1	6 34.1	-34.8	3 31.4	30.7		
11 26.3	25.8	1, 4	1 27.4	28.5	6 16.0	17.5	8 24.9	5 20.3	23.6		
12 54.6	-51.3	2 25.0	26.2	7 73.0	-67.7	9 32.6	-28.5	6 13.6	10.0		
13 44.9	48.8	3 18.1	-15.2	8 56.6	-55.3	11 21.4	-24.1	8 11.8	10.4		
0, 6	0 91.1	89.3	4 39.7	38.9	9 125.1	-123.4	13 15.8	2 27.5	23.9		
2 111.0	110.8	8 49.1	49.7	11 68.0	-71.7	11 21.4	-24.1	4 36.4	36.2		
3 46.6	48.4	9 30.3	35.6	12 22.3	20.8	6 20.9	21.1	5 28.7	29.6		
4 69.1	76.1	10 75.3	69.1	13 94.6	-88.9	8 21.4	24.4	6 37.7	37.5		
5 75.1	73.5	12 48.3	50.6	15 50.6	-52.3	10 19.1	20.0	7 24.4	25.9		
6 46.5	44.6	16 25.9	24.7	17 43.3	-39.5	2 26.3	-28.0	8 25.0	24.4		
7 47.7	50.5	17 15.5	-12.9	19 25.5	-22.2	0 30.4	-30.8	9 38.4	40.6		
8 37.1	36.3	21 15.8	-18.9	21 15.8	-18.9	5 15.5	18.5	10 26.3	30.3		
9 48.7	44.5	0 25.7	-28.5	2, 3	1 55.8	-48.3	6 15.6	11 15.5	17.1		
11 24.9	18.4	1 39.0	42.6	3 36.0	36.3	5 15.6	-17.0	12 27.8	29.8		
13 26.5	28.2	3 30.5	61.8	4 96.0	80.7	7 15.8	19.9	13 37.8	39.6		
15 30.5	28.7	5 29.3	29.5	5 96.0	80.7	3, 0	0 36.7	3 9	-32.2		
16 26.5	-27.5	7 24.0	56.3	6 68.7	64.3	4 57.5	-58.2	3 18.6	-19.1		
17 27.4	28.8	9 27.9	58.3	4 68.7	64.3	46 47.0	46.0	4 16.2	-13.9		
18 25.2	-25.5	10 17.7	-22.0	6 34.3	33.0	10 17.6	-17.5	5 13.4	-16.9		
19 18.4	25.9	11 64.7	63.0	7 23.9	-24.7	12 11.3	10.3	6 19.2	-22.2		
20 18.9	-20.9	12 23.2	-26.2	8 64.5	69.9	3, 1	2 29.5	7 21.8	-22.1		
21 19.5	19.2	13 34.0	35.8	9 22.3	-21.6	8 18.2	22.1	8 19.8	-22.0		
22 20.0	-20.8	15 36.4	41.2	10 89.4	80.2	9 88.8	-83.5	9 22.6	-24.9		
0, 8	0 88.2	94.4	17 27.5	29.9	12 54.8	54.5	6 15.8	11 29.9	-35.1		
2 84.6	86.8	19 20.7	21.9	14 32.8	36.7	7 72.2	-70.4	13 15.6	-16.3		
3 23.6	-22.4	1, 6	1 40.3	40.3	16 21.2	18.1	8 18.2	14 16.0	14.8		
4 80.5	73.5	4 41.9	39.8	2, 4	0 130.3	-118.1	9 88.8	15 16.4	-17.0		
5 31.3	-37.2	5 36.2	37.7	2 149.0	-139.1	11 56.2	-57.4	3, 10	8 18.2	18.3	
6 69.7	65.7	6 23.4	25.6	4 122.4	-112.2	13 55.8	-54.1	3, 11	0 83.7	-79.6	
7 61.5	-64.4	8 21.4	21.6	5 42.6	-44.1	14 39.5	39.5	2 53.6	-52.3		
8 55.3	54.7	10 29.4	31.3	6 100.9	-101.1	15 55.0	-51.8	4 42.5	-44.3		
9 33.8	-31.9	11 19.2	-17.4	7 16.7	19.0	17 34.4	-35.9	6 26.5	-31.5		
11 25.0	-26.0	12 24.2	25.4	8 51.2	-52.7	3, 2	1 41.0	8 22.2	-20.0		
13 23.5	-27.8	1, 7	0 131.8	126.3	9 41.9	42.7	2 36.1	3, 13	7 24.4	24.1	
14 29.6	-30.1	2 103.2	97.3	10 24.4	-28.6	4 58.4	54.5	7 24.9	29.2		
15 24.8	-28.5	4 66.4	69.6	15 26.4	27.5	6 55.1	55.2	9 28.6	29.1		
16 18.0	-22.8	6 62.9	65.3	16 27.4	29.9	7 58.7	-55.2	11 18.6	24.4		
18 26.8	-24.8	8 58.8	62.5	18 29.4	33.5	9 17.2	-22.4	13 18.6	24.4		
20 34.6	-36.3	10 33.9	35.4	20 27.2	28.4	12 16.3	16.1	15 19.1	24.7		
22 29.7	-30.1	12 24.2	25.4	22 23.6	26.5	14 15.4	14.3	4, 0	4 39.2	41.5	
0, 10	3 22.1	-22.6	14 20.1	16.5	24 25.0	24.4	0 159.0	-151.9	6 22.0	29.0	
5 47.6	-43.7	6 28.4	-27.7	16 28.4	-27.7	2, 5	1 69.8	-68.5	8 66.0	68.5	
7 37.7	-33.9	18 27.4	26.5	20 22.5	-24.7	3 31.9	-31.9	12 23.5	22.1		
11 39.1	-42.2	22 27.4	-28.4	22 27.4	-28.4	4 26.5	26.5	14 20.0	22.7		
13 36.4	-33.7	24 20.3	-22.2	4 26.5	26.5	0 144.5	-133.3	2 29.7	-35.5		
15 30.1	-33.2	1, 8	7 38.6	38.1	7 38.6	38.1	7 60.7	57.9	3 63.3	-73.4	
0, 14	0 27.7	27.7	4 16.0	19.3	8 39.9	42.0	8 53.1	-54.1	4 21.1	-26.3	
2 27.8	33.6	6 16.5	19.1	5 20.9	24.4	10 63.7	60.6	5 72.8	-73.5		
4 19.8	21.8	10 20.7	21.8	12 30.1	33.8	12 22.7	-21.6	6 49.2	-47.0		
1, 0	4 66.3	-65.7	12 18.8	20.1	14 16.1	14.8	13 17.5	-21.0	7 23.8	-25.9	
6 28.2	36.3	0 38.7	41.8	0 36.8	35.3	15 23.2	-21.1	8 58.1	-60.3		
8 59.9	66.1	1 13.7	-14.0	2 22.1	25.1	16 34.0	32.6	10 40.5	-45.1		
10 53.5	60.3	2 21.7	23.7	3 19.9	21.4	18 42.2	38.6	12 33.4	-36.8		
12 29.1	36.2	3 27.7	-28.3	3 34.9	40.1	19 21.9	-17.9	14 38.4	-40.0		
14 13.0	14.7	4 27.9	25.7	4 30.8	36.1	20 39.2	40.4	17 22.7	24.6		
1, 1	4 90.8	99.3	5 37.4	-40.7	5 58.3	63.0	22 34.1	32.2	18 21.5	-21.7	
5 41.7	-38.2	7 46.0	-47.9	6 18.6	21.5	24 31.4	31.1	4, 2	0 98.5	-114.2	
				7 77.2	76.3	26 19.1	19.4	2 64.0	-72.7	0 38.8	-39.5
										2 46.8	-45.3

TABLE 5 (Continued)

2	39.5	-39.6	6	42.3	45.4	8	18.1	-19.2	2	12.9	-11.6	2	24.5	23.7	5	30.2	-31.2
6	38.1	-39.6	8	44.3	49.0	6	6.7	63.5	4	11.6	12.9	5	10.4	-11.2	5	68.0	72.3
8	17.0	-20.3	11	33.8	31.3	2	57.1	55.9	5	29.8	-27.9	4	54.1	53.6	7	33.0	-37.7
4, 12			5			3	21.7	20.6	7	30.2	-26.4	4	20.7	-21.7	8	30.8	34.2
0	32.7	-32.1	1	30.3	-29.9	4	42.7	44.2	8	22.5	-21.3	6	63.6	58.8	9	22.4	-24.5
2	32.8	-31.3	3	19.4	-19.9	5	38.2	41.8	9	52.7	-52.8	8	68.5	68.5	10	20.4	16.6
4	29.7	-25.5	4	19.6	-20.0	6	28.3	26.9	10	33.1	-35.2	10	56.7	55.8	12	18.3	18.6
5	21.1	20.5	5	37.2	-35.6	7	14.5	14.6	11	23.1	-24.0	12	48.4	46.0	14	28.3	27.7
7	15.2	18.6	6	32.0	-29.5	8	35.5	36.5	13	21.8	-24.3	14	48.7	46.2	16	18.7	16.6
9	31.2	24.8	8	55.5	-55.0	9	34.4	34.2	15	13.6	-17.8	16	28.3	30.7			
11	22.7	22.1	10	43.8	-43.1	11	24.9	23.9	16	14.1	-15.7	18	14.3	16.9	0	52.6	-49.3
13	23.4	19.6	12	43.1	-37.7	13	31.7	31.6	17	14.6	-18.8				2	60.0	-58.1
15	21.0	19.8	14	32.1	-30.1	14	12.7	-11.6	18	15.1	-17.5	0	37.9	-45.4	4	50.2	-52.7
4, 14			16	18.0	-16.9	15	15.1	14.5				2	24.2	-27.5	6	38.8	-39.6
9	21.0	17.6				16	15.5	-15.2	2	17.1	19.3	4	18.2	-18.6	7	25.8	-29.0
5, 0			0	32.5	32.9	17	19.6	18.8	4	22.2	23.1	6	11.3	-13.9	8	24.8	-26.0
4	47.1	-50.4	5	30.0	-27.0	18	14.3	-16.9	6	21.9	18.9	8	43.8	-42.6	11	20.2	-16.4
6	102.4	-107.9	7	34.6	-32.2	19	14.7	-13.8	7	14.4	13.5	9	16.5	13.4	16	15.5	13.2
8	100.8	-98.2	9	35.8	-31.5	20	15.1	-11.7	8	31.8	33.0	10	43.1	-23.7	18	16.7	16.4
10	62.4	-65.0	11	23.6	-21.6	21	15.6	-13.5	9	22.1	24.5						
12	69.3	-70.4	13	21.4	-24.5	22	16.0	-15.7	10	55.2	51.7	1	60.3	60.1	1	9.3	9.0
14	48.0	-50.7	15	25.8	-21.2				12	35.2	33.7	3	39.0	34.5	2	18.8	20.1
16	36.9	-42.2	17	23.5	-19.3	6, 7			4	26.8	26.0	4	20.0	23.4	3	15.3	13.9
5, 1						6	33.9	-34.2	5	27.0	26.4	5	21.6	21.2	4	29.1	29.1
2	73.7	72.7	1	34.8	-35.7	10	46.2	-40.8				6	39.3	38.0	5	19.4	22.5
3	30.5	-30.8	3	15.7	-22.2	12	45.5	-42.8	0	21.0	20.5	7	40.6	41.1	6	45.8	47.3
4	43.9	44.8				14	37.2	-37.2	2	19.1	17.2	8	42.0	41.9	8	56.2	59.5
5	21.4	-23.1	0	28.7	-30.0	16	25.4	-23.6	4	19.9	21.1	9	17.4	16.7	10	61.0	63.4
6	49.1	47.5	2	33.2	-37.2				5	32.3	30.3	10	48.5	44.9	12	53.2	53.2
7	35.7	-34.8	4	29.1	-28.4	6, 8			7	30.8	30.3	12	32.4	32.0	14	44.4	43.5
8	22.8	24.4	6	21.0	-19.8				14	23.5	18.1	14	34.7	32.8	16	29.7	29.0
9	46.0	-46.6				0	55.9	54.7	11	28.0	26.7	16	26.2	24.4			
10	25.7	26.7	4	124.6	117.7	2	62.9	63.3	13	20.0	27.8	19	10.9	-14.9	9, 5		
11	60.5	-63.4	6	85.9	89.3	4	53.7	52.1	15	24.8	22.6						
13	49.8	-49.7	8	36.1	39.8	5	13.0	-12.7				8, 6			0	38.7	39.1
15	41.1	-41.8	10	14.9	15.9	6	41.8	42.9	1	44.2	44.9	2	29.8	32.8	2	29.8	32.8
17	24.9	-24.8	14	14.3	-15.0	7	35.6	-31.9	2	12.9	-12.1	3	24.7	28.8	4	41.1	-40.8
5, 2			16	19.7	-23.3	8	16.8	19.1	4	26.1	26.7	5	19.2	20.5	5	21.1	19.2
1	52.1	-47.0	18	31.9	-32.9	9	18.6	-18.6	5	29.3	30.4	6	14.8	12.9	6	14.3	-12.9
2	20.8	-19.1	20	36.1	-37.0	11	29.4	-28.5	7	21.8	19.7	7	17.4	19.1	7	24.0	25.5
3	48.3	-47.7	22	32.3	-33.2	13	18.9	-20.9	0	62.2	61.4	8	21.2	16.7	9	28.8	28.5
5	49.8	-51.0	24	18.4	-20.4	14	11.2	-11.7	2	77.6	75.9	11	23.2	21.4	11	23.9	22.5
6	53.4	-55.1	26	21.7	-22.9	15	16.2	-16.9	4	81.2	78.1	13	18.6	17.7	13	27.6	26.1
7	26.2	-28.7				16	16.7	-17.0	6	50.1	51.2	15	19.8	17.2	15	22.3	18.2
8	47.1	-44.4	3	36.7	-41.0	20	25.4	-21.9	8	18.0	16.2	17	16.8	19.8			
9	32.5	-33.8	4	43.7	-47.5	22	16.7	-17.3	16	19.4	-21.8	19	15.7	15.6	9, 6		
10	43.9	-43.9	5	68.1	-65.4				18	20.4	-23.9				1	64.1	59.2
12	40.9	-40.0	6	53.0	-51.9	1	39.2	-40.2	22	22.6	-21.4	1	24.1	25.1	3	40.7	40.1
14	24.4	-24.5	7	43.2	-40.8	3	28.0	-30.6	20	17.6	-22.5	3	15.5	17.1	5	29.9	29.0
16	21.6	-21.6	8	79.0	-85.0	4	19.4	-20.6				4	11.1	11.4	6	23.4	23.9
17	27.5	22.9	9	7.1	-7.8	5	22.0	-23.6	1	15.1	-16.4	5	9.8	12.5	8	20.9	17.8
5, 3			10	36.0	-40.3	6	34.5	-37.1	7	19.7	-16.6	6	18.2	19.4	9, 7		
0	127.9	-116.6	12	31.1	-33.8	7	16.0	-15.4	8	16.5	-16.2				0	19.8	21.1
1	22.6	22.2	14	34.1	-37.3							5	12.5	14.9	2	15.5	14.9
2	74.3	-74.4	15	16.4	14.4	5	20.9	-19.6				6	18.2	19.4	4	15.8	-14.1
4	102.5	-97.2	16	32.8	-35.2	5	30.3	-27.3	0	22.8	20.8	0	33.9	34.0	8	20.3	24.3
5	69.5	-64.8	17	20.5	22.5	9	24.7	-22.4	2	26.5	27.4	1	11.6	-14.8	10	17.1	20.3
6	49.8	-50.7	19	17.5	15.8	11	22.9	-24.7	3	18.9	-23.8	2	34.1	36.4			
7	55.5	-52.7				13	25.3	-22.3	4	27.0	25.7	3	16.7	-15.9	9, 11		
8	38.2	-34.4	6, 2			15	23.2	-23.1	5	27.3	-25.8	4	34.7	36.7	0	28.6	-26.4
9	14.2	-14.3	0	54.2	51.9	17	18.3	-14.5	6	19.5	18.5	5	17.1	-19.8	2	23.5	-22.3
11	15.6	-20.9	3	24.4	-22.9				7	31.4	30.2	6	21.3	20.8	4	20.6	-23.0
12	16.2	-16.2	4	30.3	26.8	0	18.1	17.7	8	38.5	-36.2	8	15.6	15.5	9, 12		
13	23.9	-26.2	5	49.5	-52.4	0	18.1	17.7	9	38.5	-36.2	10	20.6	-19.6	1	21.4	21.9
15	21.2	-24.0	6	17.2	-16.0	2	22.2	21.8	11	40.1	-34.7	11	21.5	20.7	10, 0		
17	16.1	-15.1	7	43.5	-44.8	4	18.3	18.4	13	35.4	-30.4	13	14.3	-15.2	8	24.2	24.7
18	20.5	21.1	8	68.8	-66.6				15	20.3	-19.3				12	11.7	10.9
5, 4			9	68.8	-66.6	4	44.8	-45.9				1	16.5	-16.8	14	12.8	13.2
1	13.0	-13.3	11	76.1	-70.8	6	55.1	-52.9	8	15.1	18.2	3	15.5	-15.9	16	16.1	16.8
4	17.2	-20.0	12	12.0	-14.2	8	22.5	-21.5				6	17.3	14.6			
6	21.5	-21.1	13	37.5	-41.8	10	14.7	-16.4	4	102.3	98.4	8	16.5	15.0	3	25.8	-28.0
7	22.4	20.5	14	22.6	-24.0	14	28.2	-28.9	6	57.2	57.9	10	14.0	13.4	5	20.2	-22.5
10	31.0	-30.2	15	40.8	-43.8				10	19.6	16.9	14	10.8	9.3	6	15.0	-14.5
5, 5			16	14.1	-15.0	2	121.3	115.7	16	22.4	-21.1				7	19.2	-20.6
3	45.3	50.5	17	29.4	-32.3	3	51.7	-52.8	18	26.1	-25.4	1	17.4	16.6	8	23.2	-21.4
4	54.7	-57.2	4	77.2	76.4	4	77.2	76.4	20	18.3	-20.0	6	29.3	27.9	9	21.8	-20.7
5	29.8	27.1	5	25.5	-30.3	5	25.5	-30.3	22	13.8	-17.2	8	28.1	23.6	11	11.2	-7.6
6	28.4	-25.0	6	77.1	74.6	6	77.1	74.6	24	16.9	-18.5	10	24.5	21.0	12	16.7	-15.8
7	52.2	55.3	8	33.4	34.6	8	33.4	34.6				12	22.6	22.4	14	12.9	-15.2
9	48.0	48.1	9	44.1	-45.1	9	44.1	-45.1	3	26.3	-27.9	14	21.9	22.9	16	16.1	-14.6
11	47.7	47.5	11	42.6	-43.7	11	42.6	-43.7	5	35.9	-34.3						
12	17.4	-16.8	13	36.3	-37.8	13	36.3	-37.8	7	18.3	-21.9	1, 8, 13			0	17.6	-18.5
13	29.5	32.1	14	21.9	-20.0	14	21.9	-20.0	8	26.3	31.1	3	13.8	17.6	2	35.6	-36.8
15	44.7	42.9	15	20.9	-23.8	15	20.9	-23.8	5	14.8	-12.3	4	14.0	15.1	4	60.3	-62.3
17	26.7	-26.9	16	33.6	-33.8	16	33.6	-33.8	7	18.0	-19.6	6	16.4	13.8			

TABLE 5 (Continued)

0	10.9	4	3	10.9	10.1	2	23.5	-24.6	11	11.9	-11.4	18	19.9	13.4	8	27.4	-26.3
2	66.0	-66.5	4	15.7	-18.2	4	23.8	-24.9	13	13.1	-14.9	2	11.7	4	10	25.6	-24.2
12	66.5	-68.8	5	22.6	21.0	6	21.1	-19.9	14	13.6	14.9	2	17.3	17.0	12	14.5	-16.3
4	59.0	-62.1	7	19.4	19.0	10, 12	10.9	12.1	11, 2	11.1	32.3	7	17.4	16.5	14	18.9	-17.0
5	22.2	21.4	9	22.9	20.5	0	16.1	-17.2	3	46.1	-44.2	10	15.2	15.3	16	20.0	-19.2
6	32.0	-35.3	11	36.1	33.9	2	16.1	-16.8	5	35.3	-35.9	12	17.8	15.8	11, 7	11.7	
8	17.7	-19.1	13	28.4	25.2	11, 0	11.0		6	14.5	-18.4	11, 5	11.1	30.5	9	14.0	14.3
16	22.4	19.6	16	17.9	15.7	4	33.5	-32.0	7	21.9	-25.0	0	27.0	-30.5	11, 8	11.1	
18	25.6	23.3	10, 7	10.9		6	79.6	-78.5	9	19.0	-19.6	2	27.4	-30.2	1	28.2	-29.7
20	19.2	17.6	3	16.7	15.6	8	57.1	-54.3	10	15.3	-15.6	3	16.6	16.1	3	15.0	-12.1
22	14.4	19.4	6	12.4	-12.2	10	31.7	-34.3	12	18.0	-18.2	4	21.6	-23.6	4	11.8	-13.0
10, 5	10.9		8	18.3	-19.2	12	32.9	-35.2	14	16.9	-18.6	5	15.7	16.5	6	24.2	-23.9
1	40.2	39.1	10	22.2	-19.6	14	47.1	-45.6	17	15.5	15.0	6	21.3	-19.7	8	30.8	-31.4
3	32.4	34.5	12	16.6	-15.6	16	29.5	-29.3	0	43.2	-46.8	7	16.7	17.1	10	26.2	-24.7
5	27.0	27.6	14	17.5	-18.3	18	22.4	-18.3	11, 3	11.1	32.1	9	19.9	19.2	12	27.4	-26.2
7	20.3	21.6	16	22.6	-19.4	11, 1	11.1		2	45.5	-47.6	11	21.3	21.1	14	26.3	-25.7
8	23.0	21.3	10, 9	10.9		4	7.3	-8.0	13	19.1	18.2	15	15.4	15.7	16	17.4	-17.9
10	15.9	13.4	1	26.9	-22.5	5	16.0	-17.3	4	42.5	-41.8	17	16.4	11.1	11, 10	11.1	
12	13.2	15.7	3	19.2	-16.3	6	11.5	7.5	5	11.4	-11.6	1	27.7	32.1	1	18.6	-20.0
14	16.3	11.7	5	17.9	-14.6	7	13.3	-11.9	6	26.0	-26.2	3	20.0	24.0	3	17.1	-15.5
10, 6	10.9		10, 10	10.9		9	13.1	-11.3	8	18.8	-18.7	4	18.5	-17.9	5	15.6	-13.7
2	12.4	-15.2	0	26.2	-25.4	10	13.8	14.6	14	14.1	14.1	5	14.7	11.6	7	15.8	-13.0
												6	21.2	-20.1	11, 11	11.1	
															0	16.1	-19.4
															2	16.2	-19.8
															4	14.1	-15.7

were evaluated from precession photographs taken with Mo- K_{α} radiation. The intensity data were collected by means of equi-inclination Weissenberg photographs taken with Cu- K_{α} radiation (layers $0kl$ — $9kl$; 1535 independent reflexions with measurable intensities) and subsequently with Mo- K_{α} radiation (layers $0kl$ — $11kl$; 1225 independent reflexions with measurable intensities). Absorption corrections appropriate to a cylindrical crystal⁵¹ were applied to the Cu- K_{α} data, but in the case of the Mo- K_{α} data absorption was neglected. Values of $|F_0|$ were derived by the usual mosaic crystal formula. The exposure times served initially to place the various layers on a common relative scale. The absolute scale of each layer was adjusted during the early stages of the analysis by comparison of $\Sigma|F_0|$ and $\Sigma|F_c|$, but during the final stages of the least-squares refinement only the overall scale factor was varied.

Structure Analysis.—Since there are four molecules in the unit cell and the space group is $Pbcn$, the asymmetric crystal unit comprises half a molecule. Co-ordinates for the chromium and sulphur atoms were deduced from the three-dimensional Patterson synthesis, and an electron-density distribution, phased by these atoms, gave positions for the oxygen, nitrogen, and carbon atoms.

The initial least-squares adjustment of the positional and isotropic vibrational parameters of the atoms was accomplished with the Cu- K_{α} data. We used a modified version of the Gantzel, Sparks, and Trueblood UCLA full-matrix programme, and the weighting scheme adopted was

$\sqrt{w} = 1$ for $|F_0| < |F^*|$, $\sqrt{w} = |F^*|/|F_0|$ for $|F_0| > |F^*|$, where $|F^*|$ was assigned the value 35.0. When these calculations converged R had decreased to 14.4%.

Subsequent refinement of the atomic parameters was based on the Mo- K_{α} data, and a series of calculations in which isotropic temperature factors were retained reduced R to 10.2%. When anisotropic temperature factors were assigned to the chromium and sulphur atoms R decreased to 9.7%, and when anisotropic temperature factors were also adopted for the oxygen, nitrogen, and carbon atoms R fell to 6.8%. In these calculations $|F^*|$ was assigned the value 35.0. The atomic scattering factors employed in the structure-factor calculations were taken from 'International Tables'.⁵¹ The structure factors are listed in Table 5, and the atomic co-ordinates, vibrational parameters, molecular dimensions, and intermolecular separations are in Tables 1—3.

The calculations were performed on the IBM 7094 computer of the University of Illinois and the ICT 1905 computer of the University of Sussex. We thank Dr. G. R. Knox (University of Strathclyde) for material and discussions, and the U.S. National Science Foundation for financial support.

[8/111 Received, January 26th, 1968]

⁵¹ 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, Vol. III.