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CRYSTAL AND MOLECULAR STRUCTURE OF $Cr(CO)_5(SCMe_2)$, A THIOKETONE COMPLEX *

BARBARA A KARCHER and ROBERT A JACOBSON *

Ames Laboratory-ERDA and Department of Chemistry, Iowa State University Ames, Iowa 50011 (U S A)

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Summary

The crystal structure of $Cr(CO)_5(SCMe_2)$ has been determined by three-dimensional single crystal X-ray analysis The compound crystallizes in the monoclinic space group $P2_1/a$ with a = 10 468(8), b = 11 879(5), c = 9 575(6) Å and β = 108 14(9)° Least squares refinement of 1435 reflections resulted in a final conventional crystallographic discrepancy factor of R = 0 075 The coordination around the chromium atom is essentially octahedral, the Cr—C distance opposite the Me_2CS group is significantly shorter, 1 835(12) Å, than the remaining Cr—C distances (averaging 1 898(2) Å) The C=S distance is 1 618(8) Å while the Cr—S—C angle is 120 8(4)°, and the chromium atom deviates from the plane described by the Me_2CS moiety by only 0 2 Å

Introduction

Few metal complexes of thioketones have been reported since most thioketones are unstable and polymerize rapidly Recently Gingerich and Angelici [13], as reported in the previous article, have succeeded in preparing complexes of the type $M(CO)_5(S{=}CR_2)$ in which the thioketone was stabilized by coordination to the metal atom, where M = Cr, Mo, or W, and R = Me, Et or Ph. In order to more accurately characterize the coordination of a thioketone to a metal, we decided to carry out a single crystal X-ray investigation of $Cr(CO)_5(S{=}CMe_2)$

Experimental

Crystal data $CrSO_5C_8H_6$, mol wt 266 19, monoclinic $P2_1/a$, a = 10 468(8), b = 11 879(5), c = 9 575(6) Å, β = 108 14(9)°, V = 1131 50 Å^3, ρ_c = 1 562 g

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cm^{-3}, $Z = 4$, Mo-K_α ($\lambda = 0.70954$ Å), $\mu = 12.38$ cm^{-1}

Crystals were obtained from R J. Angelici and R.G W Gingerich and a nearly spherical crystal of diameter 0.2 mm was wedged into a Lindeman glass capillary and mounted on a four-circle diffractometer. Initial ω-oscillation photographs were taken and these verified that the crystal was indeed single Fourteen reflections were selected from these photographs and their approximate positions were input into our automatic indexing program [1] The reduced cell and reduced cell scalars that resulted indicated monoclinic symmetry Subsequent ω-oscillation Polaroid photographs taken around each of the three cell axes in turn verified the $2/m$ Laue symmetry as well as the reciprocal lattice spacings predicted by the program

Accurate unit cell parameters and their standard deviations were obtained by a least squares fit to the $\pm 2\theta$ values of eleven independent high angle reflections measured on a previously aligned four-circle diffractometer.

Collection and reduction of X-ray intensity data Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson [2] The diffractometer is interfaced to a PDP-15 computed in a real-time mode and is equipped with a scintillation counter Graphite reflected-beam monochromated Mo-K_α radiation ($\lambda = 0$ 70954 Å) was used for data collection. Within a sphere of $2\theta \leqslant 50°$ ($\sin \theta/\lambda = 0$ 595 Å^{-1}), all data in the hkl and $hk\bar{l}$ octants were measured using an ω-stepscan technique

As a general check on crystal and electronic stability, the intensities of three standard reflections were remeasured every 75 reflections These standard reflections were not observed to vary to any significant degree during the entire period of data collection In all 2224 reflections were recorded in this manner Examination of the data revealed the following systematic absences $h0l$ when $h = 2n+1$ and $0k0$ when $k = 2n+1$ These absences uniquely determine the space group as $P2_1/a$

The intensity data were corrected for Lorentz and polarization effects, but absorption corrections were not deemed necessary, the maximum and minimum transmission factors were 0 906 and 0 862, respectively. The estimated variance in each intensity was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.03\ C_T)^2 + (0\ 03\ C_B)^2$$

where C_T and C_B represent the total and background counts, respectively, and the factor 0 03 represents an estimate of non-statistical errors The estimated deviations in the structure factors were calculated by the finite difference method [3] After correction, 1435 reflections with $I_o > 3\sigma(I_o)$ were retained for use in the structure solution and refinement During the later stages of the investigation it was discovered that six large reflections suffered from secondary extinction effects These effects were corrected via the approximation $I_o' = I_o/(1 + gI_c)$ where an average value for g, 1 9315 × 10^{-5}, was determined using the ten largest I_o's

Solution and refinement

The position of the chromium atom was obtained from an analysis of a sharpened three-dimensional Patterson function. All other non-hydrogen atoms were found by successive structure factor [4] and electron density map calculations [5]. Analysis of an electron density difference map also revealed some small residual electron density near the carbon. Methyl hydrogen atoms were therefore added such as to complete the tetrahedron around the carbon and best fit the residual electron density. The C—H distances were set equal to 1 0 Å, and all isotropic thermal parameters for hydrogen were fixed at 4 0 $Å^2$

Refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms by a full-matrix least-squares procedure minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, yielded a final crystallographic discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0 075. The final weighted discrepancy factor, $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, was 0.11

Description of the structure and discussion

A computer-generated perspective drawing [6] of $Cr(CO)_5(SCMe_2)$ is shown in Fig 1, and the more important bond distances and angles ae given in Tables 1 and 2, respectively *

The coordination around the chromium is basically octahedral, the C—Cr—C angles ranging from 88 5(3) to 90 9(3)° The sulfur atom however is slightly displaced from the octahedral position, forming S—Cr—C angles of 85 3(3), 87.8(3), 94.6(3) and 95.8(4)° with C(2), C(1), C(4) and C(3), respectively (Table 3) This distortion appears to be due to a steric effect arising from repulsion between the C(8) methyl group and the adjacent carbonyl groups, the shortest contacts being 3 357 and 3 584 Å (Table 2)

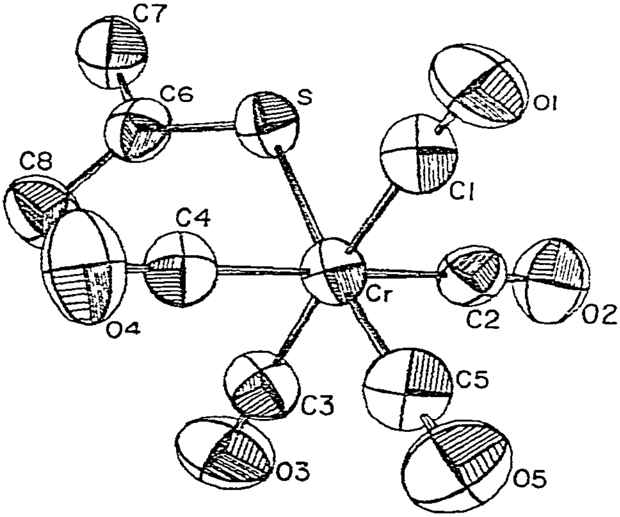

Fig 1 A computer-generated perspective drawing of $Cr(CO)_5(SCMe_2)$ excluding the hydrogen atoms

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* The table of structure factors has been deposited as NAPS Document No 2987 (8 pages) Order from ASIS/NAPS c/o Microfiche Publications, P O Box 3513, Grand Central Station, New York, N Y, 10017 A copy may be secured by citing the document number remitting $5 for photocopies or $ 3 for microfiche Advance payment is required Make checks payable to Microfiche Publications

TABLE 1a

FINAL ATOMIC POSITIONAL PARAMETERS (represented in fractional unit cell coordinates)

Atom	x	y	z
Cr	0 29805(13)	0 11028(9)	0 17649(13)
S	0 1753(2)	0 0848(2)	0 3455(2)
C(1)	0 1303(9)	0 1160(6)	0 0245(9)
O(1)	0 0337(7)	0 1181(5)	—0 0737(7)
C(2)	0 2981(8)	—0 0485(7)	0 1661(8)
O(2)	0 3012(7)	—0 1456(5)	0 1579(7)
C(3)	0 4706(10)	0 1026(7)	0 3187(10)
O(3)	0 5753(7)	0 0957(6)	0 4002(9)
C(4)	0 2997(9)	0 2706(7)	0 1891(9)
O(4)	0 2988(8)	0 3662(6)	0 1941(8)
C(5)	0 3821(10)	0 0343(10)	0 0343(10)
O(5)	0 4331(9)	0 1233(6)	—0 0553(9)
C(6)	0 2247(9)	0 1431(6)	0 5061(8)
C(7)	0 1516(13)	0 1162(9)	0 6146(12)
C(8)	0 3385(12)	0 2217(10)	0 5605(11)
H(17)	0 1191	0 1867	0 6480
H(27)	0 2128	0 0750	0 7002
H(37)	0 0720	0 0665	0 5652
H(48)	0 3077	0 3005	0 5437
H(58)	0 3836	0 2086	0 6689
H(68)	0 4068	0 2063	0 5079

TABLE 1b

FINAL ATOMIC THERMAL PARAMETERS [a]

Atom	Atomic temperature factors ×10^2					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	1 22(2)	0 66(1)	1 18(2)	—0 02(1)	0 24(1)	0 04(1)
S	1 37(3)	0 87(2)	1 30(3)	—0 10(2)	0 33(2)	—0 14(2)
C(1)	1 5(1)	0 82(6)	1 4(1)	0 05(7)	0 33(9)	0 06(7)
O(1)	1 52(9)	1 35(7)	1 9(1)	—0 09(6)	—0 04(8)	0 17(6)
C(2)	1 3(1)	0 85(7)	1 4(1)	0 02(7)	0 57(8)	0 05(6)
O(2)	2 3(1)	0 77(5)	2 4(1)	0 05(6)	0 7(1)	0 00(6)
C(3)	1 4(1)	0 91(7)	1 8(1)	—0 04(7)	0 3(1)	0 03(7)
O(3)	1 24(8)	1 71(8)	2 6(1)	0 09(6)	0 00(9)	0 17(8)
C(4)	1 5(1)	0 82(7)	1 51(1)	0 02(7)	0 34(9)	—0 08(7)
O(4)	3 1(2)	0 84(6)	2 6(1)	—0 19(7)	0 6(1)	—0 06(6)
C(5)	1 9(1)	0 92(7)	1 6(1)	0 03(8)	0 6(1)	0 31(7)
O(5)	2 3(1)	1 47(8)	2 2(1)	0 18(7)	1 1(1)	0 38(7)
C(6)	1 3(1)	0 80(6)	1 4(1)	0 18(7)	0 31(9)	0 02(6)
C(7)	1 9(2)	1 07(9)	1 9(2)	—0 12(10)	0 7(1)	—0 16(9)
C(8)	1 5(2)	1 3(1)	1 7(2)	—0 3(1)	0 2(1)	—0 2(1)
H(17)	400					
H(27)	400					
H(37)	400					
H(48)	400					
H(58)	400					
H(68)	400					

[a] The β_{ij} are defined by $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ If only the β_{11} column is listed this corresponds to an isotropic temperature factor

TABLE 2

SELECTED BOND DISTANCES (Å)

Cr—S	2 377(4)	S—C(6)	1 618(8)
Cr—C(1)	1 901(8)	C(6)—C(7)	1 497(17)
Cr—C(2)	1 889(8)	C(6)—C(8)	1 477(14)
Cr—C(3)	1 896(9)	C(4)—C(8)	3 584(15)
Cr—C(4)	1 905(8)	O(4)—C(8)	3 809(15)
Cr—C(5)	1 835(12)	C(3)—C(8)	3 357(17)
		O(3)—C(8)	3 621(17)
C(1)—O(1)	1 147(10)		
C(2)—O(2)	1 156(11)	O(1)—O(1) [a]	3 314
C(3)—O(3)	1 132(11)	O(1)—O(2) [a]	3 359
C(4)—O(4)	1 146(11)	C(1)—O(2) [b]	3 516
C(5)—O(5)	1 153(16)	O(1)—O(2) [b]	3 519
		C(5)—O(1) [c]	3 270
		C(5)—O(4) [c]	3 831
		O(1) [b]—C(1) [c]	3 377
		O(1) [b]—O(1) [c]	3 314

[a] Via symmetry operation (x, y, z) [b] Via symmetry operation ($\frac{1}{2}-x$, $\frac{1}{2}+y$ z) [c] Via symmetry operation ($1\frac{1}{2}+x$ $\frac{1}{2}-y$ z)

The Cr—C distance *trans* to the Me_2CS group is significantly shorter, 1 835(12) Å, than the remaining Cr—C distances (averaging 1 898(8) Å) Such a shortening has been observed in other metal carbonyl complexes when a CO group is *trans* to a poorly π-bonding ligand and can be attributed to a resultant increase in the π-bonding of the CO

The Cr—C equatorial distances compare quite well with those previously reported, namely, 1 90 Å in $(MeSCN)Cr(CO)_5$ [7], 1 88 Å in $(C_6H_5)_3PCr(CO)_5$ [8], and 1 903 Å in $Me_3PSCr(CO)_5$ [9]

The C—O distances are all essentially equal to within three standard deviations, averaging 1 146 Å The C=S distance 1 618(8) Å, is significantly shorter than the 1 71 Å distance found in ethylene thiourea [10] and thioacetamide [11], but longer than the 1 561 Å distance in HNCS [12]

Least-squares planes and deviations from these planes are given in Table 4 As can be seen from this table, the Me_2CS group shows no significant deviation from planarity and the chromium atom also essentially lies in this plane This would be in accord with a model which assumes sp^2 hybridization at the sulfur and inter action between the sulfur and the chromium via a lone pair in one of these hybrids The Cr—S—C(6) angle of 120 8(4)° is also in excellent agreement with

TABLE 3

SELECTED ANGLES (DEG)

S—CR—C(1)	87 8(3)	C(6)—S—Cr	120 8(4)
S—Cr—C(2)	85 3(3)	C(7)—C(6)—C(8)	114 7(8)
S—Cr—C(3)	95 8(4)		
S—Cr—C(4)	94 6(3)		
S—Cr—C(5)	173 9(2)		
O(1)—C(1)—Cr	175 5(10)	C(1)—Cr—C(2)	90 6(3)
O(2)—C(2)—Cr	178 0(10)	C(1)—Cr—C(4)	90 1(3)
O(3)—C(3)—Cr	177 5(10)	C(2)—Cr—C(3)	88 7(3)
O(4)—C(4)—Cr	178 7(8)	C(2)—Cr—C(4)	90 9(3)
O(5)—C(5)—Cr	179 4(13)		

TABLE 4

EQUATIONS OF LEAST SQUARES PLANES AND INTERPLANAR ANGLES

Plane I fitting (Cr—C(1)—C(2)—C(3)—C(4))
$0\ 7090\ X + 0\ 02899\ Y - 0\ 70671\ Z - 0\ 77433 = 0$

Atom	Distance from plane (Å)
Cr	—0 0390
C(1)	0 0224
C(2)	—0 0031
C(3)	0 0225
C(4)	—0 0027

Plane II fitting (Cr—S—C(3)—C(4)—C(5))
$0\ 067599\ X + -0\ 02144\ Y + 0\ 73659\ Z - 2\ 87378 = 0$

Atom	Distance from plane (Å)
Cr	0 0339
S	—0 0351
C(2)	0 0256
C(4)	0 0219
C(5)	—0 0463

Plane III fitting (Cr—S—C(1)—C(3)—C(5))
$-0\ 04078\ X + 0\ 99424\ Y - 0\ 09909\ Z - 1\ 31559 = 0$

Atom	Distance from plane (Å)
Cr	0 0408
S	—0 0361
C(1)	0 0234
C(3)	0 0202
C(5)	—0 0483

Plane IV fitting (S—C(6)—C(7)—C(8))
$0\ 53567\ X - 0\ 76966\ Y + 0\ 34737\ Z - 0\ 74726 = 0$

Atom	Distance from plane (Å)
S	0 0015
C(6)	—0 0046
C(7)	0 0014
C(8)	0 0016
Cr	0 1908

Plane V fitting (Cr—S—C(2)—C(4))
$0\ 65649\ X - 0\ 02119\ Y + 0\ 75403\ Z - 2.87810 = 0$

Atom	Distance from plane (Å)
Cr	0 0074
S	—0 0001
C(2)	—0 0036
C(4)	—0 0036

Interplanar Angles

Plane	Plane	Angle (deg)
I	II	87 51
I	III	85 98
I	IV	83 63
I	V	86 02
II	III	88 61
II	IV	50 61
III	IV	41 17

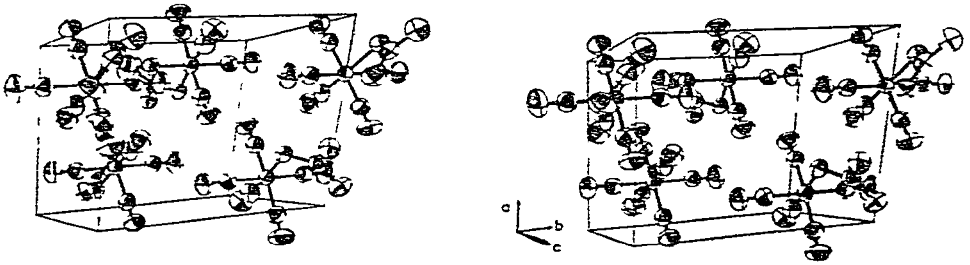

Fig 2 Unit cell stereograph of $Cr(CO)_5(SCMe_2)$

such a model In addition, this plane approximately bisects the angle between the planes formed by S, Cr, C(2), C(4), C(5) and S, Cr, C(1), C(3), C(5), indicating rotation about the Cr—S bond to minimize repulsive effects.

Unit cell packing is illustrated in Fig. 2 and no abnormally short contacts are present, the shortest intermolecular distance being 3 270 Å between O(1) and C(5) in adjacent molecules

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