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The Crystal and Molecular Structure of Pentacarbonyl(2,2,4,4-tetramethyl-3-thietanone)chromium(0)

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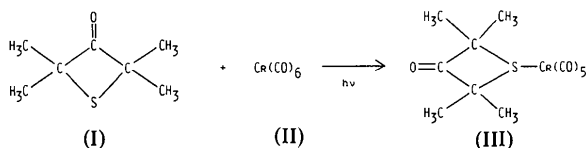
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Abstract

The crystal structure of the title compound, $C_{12}H_{12}CrO_6S$, $Cr(C_4H_8OS)(CO)_5$, has been determined at *ca* 120 K. The space group is $P2_1/c$, $Z = 4$, with $a = 13.154$ (2), $b = 6.4534$ (6), $c = 18.048$ (2) Å, $\beta = 101.43$ (1)°. 9499 reflections ($2\theta_{max} = 90^\circ$, $\lambda = 0.71069$ Å) contributed to the refinement of 229 variables to give $R = 0.049$ and $R_w = 0.052$. The complex displays approximate *m* molecular symmetry. The thietanone ligand, coordinated to the Cr through the S atom, $Cr-S = 2.4241$ (5) Å, displays similarities with the bonding geometry of cyclobutanone but the endocyclic bond angle about the carbonyl C atom is *ca* 10° larger and that about the S atom *ca* 11° smaller than their analogs in cyclobutanone.

Introduction

The title compound was prepared (Czauderna, 1976) by the following reaction:



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and the crystal structure determination was carried out to confirm that the product was indeed that of a substitution reaction rather than an oxidation–reduction reaction similar to that which gave rise to hexacarbonyl- $[\mu$ -(2,4-dimethyl-4-sulfido-2-penten-3-olato)- μ -O, μ -S]-diiron. The structure of the latter compound has been described previously (Jogun & Stezowski, 1979).

Experimental

Crystals of (III) were obtained from hexane by warming a solution containing a large number of fine needles until only a trace of solid remained and then cooling slowly to *ca* 240 K. The resultant crystals were large but not well formed; examination with polarized light established their probable singularity. A fragment *ca* 0.5 × 0.5 × 0.5 mm was sealed in a capillary and used for all crystallographic measurements. The space group is $P2_1/c$ with $Z = 4$; lattice parameters (at *ca* 120 K): $a = 13.154$ (2), $b = 6.4534$ (6), $c = 18.048$ (2) Å, $\beta = 101.43$ (1)°, resulted from a least-squares refinement (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)† with automatically centered 2θ values for 60 reflections in the angular range $40.0 < 2\theta < 53.7^\circ$ (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å).

† Unless otherwise stated this program system was used for all 175°9 (1)

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Intensities were measured in an ω -scan mode with a Syntex $P\bar{1}$ autodiffractometer equipped with a low-temperature device (Syntex LT-1) which maintained the crystal at *ca* 120 K. The scan range was 0.75° and the scan rate varied from 2.0 to $24.0^\circ \text{ min}^{-1}$; background radiation was measured on each side of the reflection center ($\Delta\omega = 1.0^\circ$) for one half the total scan time. Intensities were measured for 12 018 unique reflections ($2\theta_{\text{max}} = 90^\circ$, $\lambda = 0.71069 \text{ \AA}$), 7896 of which were classified as observed [$I > 2.0\sigma(I)$]. Three periodically measured reference reflections displayed neither systematic nor significant variations in their intensities. Data were corrected for Lorentz and polarization effects but not for absorption, $\mu = 0.78 \text{ mm}^{-1}$.

The structure was determined by the heavy-atom technique and refined by block-diagonal least-squares techniques with all parameters associated with one atom in a single block. All atomic coordinates, anisotropic thermal parameters for Cr, S, O and C, isotropic thermal parameters for H atoms and a single scale factor (229 variables) were refined with 9499 contributing reflections to give $R = 0.049$ and $R_w = 0.052$ where $w = [\sigma^2(F) + 0.0125|F| + 0.0001|F|^2]^{-1}$; the e.s.d. of an observation of unit weight is 1.2.

Results and discussion

Atomic coordinates* are given in Table 1; a stereoscopic projection (Johnson, 1971) with atom labels is presented in Fig. 1. Selected bond distances, bond angles and dihedral angles are contained in Tables 2–4.

(III) may be thought of as consisting of two components of different molecular symmetry; the thietanone ligand can adopt a maximum of C_{2v} symmetry and the $\text{Cr}(\text{CO})_5$ moiety C_{4v} . The maximum molecular symmetry for the complex, C_{2v} , can be

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34355 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

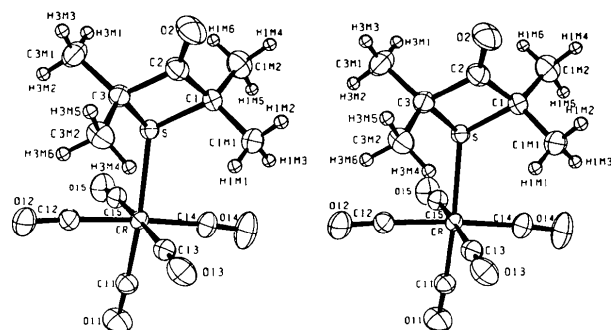


Fig. 1. A stereoscopic view of (III) showing the numbering scheme.

Table 1. Fractional atomic coordinates ($\times 10^4$)

Cr	1762.5 (1)	3148.0 (2)	4387.5 (1)
S	3042.1 (2)	4460.6 (4)	3707.4 (1)
C(11)	840 (1)	2567 (2)	1 (1)
O(11)	293 (1)	2966 (2)	409 (1)
C(12)	2823 (1)	1926 (2)	5126 (1)
O(12)	3427 (1)	3826 (2)	594 (1)
C(13)	1519 (1)	547 (2)	3875 (1)
O(13)	8662 (1)	3977 (2)	1421 (1)
C(14)	632 (1)	4258 (2)	3658 (1)
O(14)	-78 (1)	4820 (2)	3231 (1)
C(15)	8049 (1)	4289 (2)	5066 (1)
O(15)	7951 (1)	2818 (2)	4705 (1)
C(1)	2866 (1)	4255 (2)	2648 (1)
C(1M1)	2006 (1)	2806 (3)	2265 (1)
C(1M2)	7190 (1)	1375 (3)	2733 (1)
C(2)	3933 (1)	3209 (2)	2761 (1)
C(3)	4194 (1)	2820 (2)	3615 (1)
C(3M1)	5220 (1)	3783 (3)	4010 (1)
C(3M2)	4122 (1)	525 (2)	3798 (1)
O(2)	4441 (1)	2782 (2)	2296 (1)
H(1M1)	2055 (17)	1428 (35)	2514 (12)
H(1M2)	2075 (16)	2613 (37)	1737 (12)
H(1M3)	1351 (18)	3453 (38)	2272 (13)
H(1M4)	7190 (17)	1198 (37)	3297 (12)
H(1M5)	7854 (17)	2036 (35)	2676 (12)
H(1M6)	6610 (18)	2173 (37)	2489 (13)
H(3M1)	5254 (15)	5279 (34)	3878 (11)
H(3M2)	5281 (18)	3643 (36)	4548 (12)
H(3M3)	5788 (18)	3064 (35)	3850 (13)
H(3M4)	3446 (16)	-73 (37)	3574 (12)
H(3M5)	4682 (17)	-196 (35)	3624 (12)
H(3M6)	4283 (17)	298 (39)	4365 (12)

Table 2. Bond distances (\AA) between Cr, S, O and C atoms

Bond distances tabulated on the same line are for chemically equivalent bonds related by C_s molecular symmetry.

Cr-S	2.4241 (5)		
Cr-C(11)	1.857 (2)		
	<i>1.861*</i>		
Cr-C(12)	1.899 (1)	Cr-C(14)	1.919 (1)
	<i>1.901</i>		<i>1.924</i>
Cr-C(13)	1.913 (1)	Cr-C(15)	1.917 (1)
	<i>1.915</i>		<i>1.920</i>
C(11)-O(11)	1.156 (2)		
	<i>1.159</i>		
C(12)-O(12)	1.147 (2)	C(14)-O(14)	1.145 (2)
	<i>1.149</i>		<i>1.149</i>
C(13)-O(13)	1.147 (2)	C(15)-O(15)	1.144 (2)
	<i>1.150</i>		<i>1.147</i>
S-C(1)	1.885 (1)	S-C(3)	1.883 (1)
C(1)-C(2)	1.533 (2)	C(3)-C(2)	1.532 (2)
C(1)-C(1M1)	1.524 (2)	C(3)-C(3M2)	1.525 (2)
	<i>1.530</i>		<i>1.535</i>
C(1)-C(1M2)	1.526 (2)	C(3)-C(3M1)	1.527 (2)
	<i>1.533</i>		<i>1.530</i>
C(2)-O(2)	1.204 (2)		
	<i>1.216</i>		

* Values in italics are bond distances corrected for riding motion (Busing & Levy, 1964; Busing, Martin & Levy, 1964).

achieved only if both mirror symmetry operators of the unique ligand spatially coincide with analogous symmetry operators of the $\text{Cr}(\text{CO})_5$ moiety. The resultant conformation would minimize intramolecular steric repulsion between the ligand and the equatorial CO groups of the $\text{Cr}(\text{CO})_5$ moiety, but would require all atoms bonded to the S atom to be coplanar. It can be seen from Fig. 1 that this condition is not fulfilled and that the conformation is of lower than C_{2v} symmetry. The σ_C value (Jogun & Stezowski, 1979) obtained from the dihedral angles in Table 4, $3 \cdot 3^\circ$, is consistent with a structure that displays a good approximation to mirror symmetry.

The bonding parameters are also indicative of local mirror symmetry. Further, the bond distances for all chemically equivalent bonds are very similar but there are some significant differences in the bond angles. These differences are readily explained in terms of steric interaction between methyl groups C(1M1) and C(3M2) with the carbonyl groups of the equatorial plane of the octahedral coordination polyhedron.

Table 3. Bond angles ($^\circ$) between Cr, S, O and C atoms

SCrC(11)	172.20 (5)		
SCrC(12)	90.78 (5)	SCr(14)	92.52 (5)
SCrC(13)	97.37 (4)	SCrC(15)	85.81 (5)
C(11)CrC(12)	87.37 (6)	C(11)CrC(14)	89.57 (6)
C(11)CrC(13)	90.22 (6)	C(11)CrC(15)	86.60 (7)
C(12)CrC(13)	90.26 (6)	C(12)CrC(15)	89.71 (6)
C(12)CrC(14)	176.40 (6)	C(13)CrC(15)	176.82 (6)
C(13)CrC(14)	87.86 (6)		
C(14)CrC(15)	92.00 (6)		
C(1)SCr	122.09 (4)	C(3)SCr	120.01 (5)
C(1)SC(3)	79.04 (6)		
SC(1)C(2)	88.3 (1)	SC(3)C(2)	88.4 (1)
SC(1)C(1M1)	115.7 (1)	SC(3)C(3M2)	116.2 (1)
SC(1)C(1M2)	112.3 (1)	SC(3)C(3M1)	112.5 (1)
C(1M1)C(1)C(2)	111.6 (1)	C(3M2)C(3)C(2)	111.4 (1)
C(1M2)C(1)C(2)	114.6 (1)	C(3M1)C(3)C(2)	113.9 (1)
C(1M1)C(1)C(1M2)	112.4 (1)	C(3M1)C(3)C(3M2)	112.4 (1)
C(1)C(2)O(2)	128.9 (1)	C(3)C(2)O(2)	128.2 (1)
C(1)C(2)C(3)	102.9 (1)		
CrC(11)O(11)	177.0 (1)		
CrC(12)O(12)	176.6 (1)	CrC(14)O(14)	175.9 (1)
CrC(13)O(13)	177.3 (1)	CrC(15)O(15)	176.0 (1)

Table 4. Selected dihedral angles ($^\circ$)

C(12)CrSC(1)	135.18 (7)	C(14)CrSC(3)	-139.26 (6)
C(13)CrSC(1)	44.82 (7)	C(13)CrSC(3)	-51.09 (6)
C(14)CrSC(1)	-43.35 (7)	C(12)CrSC(3)	39.27 (6)
C(15)CrSC(1)	-135.17 (7)	C(15)CrSC(3)	128.92 (6)
C(13)CrSC(2)	-4.10 (6)		
CrSC(1)C(1M1)	-13.2 (1)	CrSC(3)C(3M2)	15.5 (1)
CrSC(1)C(1M2)	117.6 (1)	CrSC(3)C(3M1)	-116.1 (1)
CrSC(1)C(2)	-126.4 (1)	CrSC(3)C(2)	128.6 (1)
C(3)SC(1)C(2)*	-7.8 (1)	C(1)SC(3)C(2)	7.8 (1)
SC(1)C(2)C(3)	9.6 (1)	SC(3)C(2)C(1)	-9.6 (1)
C(1M1)C(1)C(2)O(2)	72.1 (2)	C(3M2)C(3)C(2)O(2)	-71.6 (2)
C(1M2)C(1)C(2)O(2)	-57.0 (2)	C(3M1)C(3)C(2)O(2)	56.8 (2)

* The 3-thietanone ring system is not planar. The distances of the atoms from the mean plane fit to them are S 0.1103 (6), C(1) -0.088 (2), C(3) -0.089 (2), C(2) -0.012 (2), and O(2) 0.079 (2) Å. The standard deviation from the mean plane is 0.093 Å.

The thietanone ligand is a heteroatom analog of cyclobutanone. The infrared absorptions assigned to the carbonyl group of 2,2,4,4-tetramethyl-3-thietanone, 1780 cm^{-1} (Czuderna, 1976), and for free 3-thietanone, 1780 cm^{-1} (Mayer & Funk, 1961), are similar to that of cyclobutanone, 1791 cm^{-1} (Zbinden & Hall, 1960). The bond distances for common bonds in complexed (I) are identical within experimental error with those reported by Shirrell & Williams (1975) for 2,2,4,4-tetramethyl-3-methylenecyclobutanone. This structure therefore supports their conclusion that there is little interaction between the p electrons of the C atoms of the carbonyl and methylene groups in the structure.

It is interesting to compare the bonding geometry of (I) in (III) with the bonding parameters reported for cyclobutanone from microwave studies (Scharpen & Laurie, 1968; Stigliani, Laurie & Scharpen, 1976) (Table 5). The comparable bond distances are equal to within experimental precision but the endocyclic bond angles for the carbonyl C atom differ by nearly 10° . Surprisingly, the bond angles about the C_α atoms [C(1) and C(3) in (III)] are the same as those in cyclobutanone; the CSC angle is 11° smaller than the analogous angle in cyclobutanone. The stretching frequency of the thietanone carbonyl group in (III), and probably that in free thietanones as well, differs significantly from the expected value in view of the C(1)C(2)C(3) bond angle. The observed frequency would be expected to correspond to a bond angle of *ca* 97° based on the usual linear relationship between stretching frequency and bond angle (see, for example, Fig. 4 in Brauman & Laurie, 1968). These authors have indicated that anharmonicity, perhaps strain-induced in (III), may cause deviations from the usual linear bond angle-frequency relationship.

Blackwell & Lord (1975) have examined the far infrared spectrum of 3-thietanone and have concluded that the free molecule is planar in the gas phase. The ligand in (III) has not adopted such a conformation. The dihedral angles (Table 4) indicate a fold in the ligand ring that brings C(1M1) and C(3M2) closer to the equatorial plane. Whether or not the non-planarity of (I) in (III) is a result of complex formation or a property of the ligand is not determinable from the data available.

Table 5. Bonding parameters for cyclobutanone from microwave studies

Distances (Å)		Angles ($^\circ$) ^a	
C(1)-C(2) ^c	1.527 (3) ^a	C(2)C(1)C(2')	93.1 (3)
C(2)-C(3)	1.556 (1) ^a	C(1)C(2)C(3)	88.0 (3)
C(1)-O(1)	1.204 (6) ^b	C(4)C(3)C(2')	90.9 (2)

^a Scharpen & Laurie (1968). ^b Stigliani, Laurie & Scharpen (1976).

^c Conventional numbering scheme for a molecule assumed to have mirror symmetry.

Avirah, Cook & Malloy (1975) have reported an analysis of the microwave spectrum of 3-thietanone and have presented estimates for structural parameters. The values $C(1)-C(2) = 1.528$ (9) and $C(2)-O(2) = 1.224$ (18) Å (our numbering scheme) are in good agreement with those in the crystal. Their angle $C(1)C(2)C(3) = 100.5$ (8)° is somewhat smaller and their C—S distance 1.826 (13) is considerably shorter than that in (III). We suspect that their value is unrealistically short since the analogous C—C bond distance in cyclobutanone is 1.556 (1) Å (Table 5).

The Cr⁰ atom of (III) displays a reasonable approximation to octahedral coordination geometry. The deviations from ideality are largely traceable to the steric repulsions mentioned above. There is clear indication of a *trans* effect in the Cr—C(11) and C(11)—O(11) distances which are respectively shorter and longer than their analogs in the equatorial plane. The presence of such an effect may be taken as evidence that ligand (I) is a good electron donor (*n* electrons) but a rather poor π -electron acceptor. The equatorial Cr—C distances are very similar to those reported for Cr(CO)₆ at 78 K (Jost, Rees & Yelon, 1975); the equatorial C—O distances are slightly, but possibly significantly, longer. The average values for riding-motion-corrected coordinates are $\langle Cr-C \rangle_e = 1.915$ and $\langle C-O \rangle_e = 1.149$ for (III) and $\langle Cr-C \rangle = 1.918$ and $\langle C-O \rangle = 1.141$ Å for Cr(CO)₆.

Two methyl groups, C(1M1) and C(3M2), display short intermolecular contact distances to two carbonyl O atoms, O(14) and O(12), respectively [3.171 (2) and 3.376 (2) Å]. Since the Fe complex described in the previous paper displays a similar contact distance with no apparent affect on the bonding geometry of either atom involved, these contact distances probably do not contribute significantly to the differences in bond angles between these methyl groups and the other two. We assign the differences to intramolecular interactions.

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The Molecular and Crystal Structure of Bis[2-(aminomethyl)pyridine]platinum(II) Dichloride Monohydrate

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Abstract

[Pt(C₆H₈N₂)₂]Cl₂ · H₂O, [Pt(amp)₂]Cl₂ · H₂O [amp = 2-(aminomethyl)pyridine], forms monoclinic crystals

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with $a = 8.137$ (4), $b = 14.617$ (7), $c = 13.905$ (7) Å, $\beta = 110.66$ (4)°, $Z = 4$ and space group $P2_1/c$. The structure was refined by block-diagonal least-squares analysis to a conventional R factor of 0.031 and $R_w =$

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