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Structure Determination of Non-Linear Metallocenes. IV. The Crystal and Molecular Structure of Benzene-1,2-dithiolene-di-(π-cyclopentadienyl)tungsten(VI)

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The chelate complex $(C_5H_5)_2WS_2C_6H_4$ crystallizes in the orthorhombic crystal system. The cell dimensions are $a = 16{\cdot}088$, $b = 11{\cdot}148$ and $c = 7{\cdot}735$ Å; the space group is *Pnma* and $Z = 4$. The coordination polyhedron around the tungsten atom, defined by the cyclopentadienyl ring centroids and the sulphur atoms, is a distorted tetrahedron of nearly C_{2v} symmetry. The $S_2C_6H_4$ plane is inclined to the WS_2 plane at an angle of 8°. One of the two cyclopentadienyl rings occupies statistically the two possible positions with respect to the space-group symmetry (mirror plane).

Introduction

Of the series of 'dithiolene chelates', those with en-1,2-dithiolene ligands and also two π-cyclopentadienyl ligands bound to the central metallic atom are an important group. Although there are many metallocene dithiolene chelates, only a few of the crystal structures are known (McCleverty, 1968). From these analyses it appears that the geometry around the central metallic atom is disturbed from C_{2v} symmetry, as proposed by McCleverty (1968), to C_s or C_1 symmetry. Köpf (1961) postulates a different endithiolene-dithio-α-dicetene mesomery depending on whether the complexes are formed with metals of the fourth or the sixth subgroup; as was pointed out by Ballhausen & Dahl (1961), they have different φ_0 orbitals.

The work described in this paper is part of a contribution to a better knowledge of these complexes.

Experimental

Yellow-orange crystals were kindly supplied by Köpf (Berlin), for a crystal structure analysis. The cell parameters were obtained from the least-squares refinement of 25 strong reflexions found by the 'peak-hunting program' provided with the Philips PW 1100 automatic four-circle diffractometer. The crystallographic data are given in Table 1.

Table 1. *Crystal data*

Orthorhombic crystal symmetry
Systematic absences $0kl$: $k+l=2n+1$, $hk0$: $h=2n+1$
Space group: *Pnma* or $Pn2_1a$

$a = 16{\cdot}088 \pm 0{\cdot}008$ Å	$V = 1387{\cdot}26$ Å^3
$b = 11{\cdot}148 \pm 0{\cdot}007$	$Z = 4$
$c = 7{\cdot}735 \pm 0{\cdot}005$	$d_{\text{meas}} = 2{\cdot}16\text{g cm}^{-3}$ (in KI/H_2O solution)
M.W. 454·27	$d_{\text{cal}} = 2{\cdot}18\text{g cm}^{-3}$

$F(000) = 864$
$\lambda = 0{\cdot}7107$ Å (Mo $K\alpha$)
Graphite monochromator

2082 independent reflexions were measured with a 2θ–ω scan. Each reflexion was measured in a 60 s scan with a scan rate of 0·02° s^{-1}; the stationary background was measured at both ends of the scan for 10 s. Two reference reflexions were checked every hour for intensity stability and for crystal orientation, but no appreciable variation was observed. Lorentz and polarization corrections were computed for each reflexion, but no absorption correction was applied. A reflexion was considered as unobserved and set to zero when $I_{hkl} \le 2{*}\sigma(I_{hkl})$, $[\sigma(I_{hkl}) = \sqrt{(B_1 + B_2 + I_{\text{peak}})}]$. All the computation was carried out on the IBM 370/145 (150 kbytes) of our department and the TR 4 computer of the Zentralen Rechenanlage der Universität Marburg. The programs used were from the X-RAY 70 system or our own programs. The atomic form factors used in this work were those from Hanson, Herman, Lea & Skillman (1964) for the neutral atoms of tungsten and sulphur, and from Allmann (1967) for carbon. Corrections for anomalous dispersion were carried out for the tungsten atom, $\Delta f' = -1{\cdot}17$ and $\Delta f'' = 6{\cdot}99$ (Cromer, 1965).

Determination and refinement of the structure

All reflexions were used in the computation of the three-dimensional Patterson synthesis, from which the positions of the metal, the sulphur and the three adjacent carbon atoms were obtained. The rest of the structure was found from a difference Fourier synthesis computed with the above-mentioned atomic positions.

The refinement of the parameters of the molecule was carried out by full-matrix least-squares methods. Up to this stage the refinement was carried out for both of the space groups (*cf.* Table 1). However, the acentric space group $Pn2_1a$ had to be rejected because further refinement was impossible ($R = 0{\cdot}073$). There were large discrepancies between the C–C distances in the benzene ring (1·29–1·54 Å), and it was impossible to locate the atomic positions for reasonable cyclopentadienyl rings. In addition to the above results the intensity statistics had values very close to the theoretical values for a centrosymmetric structure. From this we deduced that the space group was *Pnma*. In the initial stages of the refinement all the atoms were given isotropic temperature factors; later they were given anisotropic temperature factors. The value minimized is of the form $\sum(w|F_o| - k|F_c|)^2$, where k is the scale factor and w is the weight ($w = 1/\sigma^2$, initially $w = 1{\cdot}0$; during the last cycles of refinement $\sigma = 4{\cdot}75$ for $|F_o| = 0$, $\sigma = 19/|F_o|$ for $|F_o| < 19$ and $\sigma = 0{\cdot}0575 F_o$ for $F_o \geq 19$). After the last cycle of refinement the shifts were less than 20% of the standard deviation, the R value was then 0·060 (R_w 0·085). $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = \sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2$. The results of the structure determination and refinement are summarized in Tables 2–6 and Figs. 1–3.

Table 3. *Interatomic distances and angles in the crystal structure of* $(C_5H_5)_2WS_2C_6H_4$

W—S	2·421 (2) Å
S—C(1)	1·753 (8)
C(1)–C(1′)	1·42 (2)
C(1)–C(2)	1·39 (1)
C(2)–C(3)	1·41 (2)
C(3)–C(3′)	1·40 (3)
W—C(4)	2·31 (1)
W—C(5)	2·33 (1)
W—C(6)	2·32 (2)
W—C(7)	2·23
W—C(8)	2·29
W—C(9)	2·32
C(4)–C(5)	1·44 (2)
C(5)–C(6)	1·33 (2)
C(6)–C(6′)	1·44 (4)
S—W—S	82·3 (3)°
W—S—C(1)	108·3 (5)
S—C(1)–C(1′)	120 (1)
C(2)–C(1)–C(1′)	120 (1)
C(1)–C(2)–C(3)	120 (1)
C(2)–C(3)–C(3′)	120 (1)
C(5)–C(4)–C(5′)	108 (2)
C(4)–C(5)–C(6)	106 (2)
C(5)–C(6)–C(6′)	110 (2)

Table 2. *Atomic and thermal parameters*

	x	*y*	*z*
W	0·47570 (3)	¼	0·29567 (5)
S	0·38737 (14)	0·1072 (2)	0·1480 (3)
C(1)	0·3218 (5)	0·1864 (7)	0·0075 (10)
C(2)	0·2712 (4)	0·1243 (9)	−0·1064 (12)
C(3)	0·2194 (6)	0·1872 (13)	−0·2219 (12)
C(4)	0·3696 (13)	¼	0·4975 (24)
C(5)	0·4195 (10)	0·1456 (13)	0·5292 (16)
C(6)	0·4935 (12)	0·1855 (16)	0·5787 (19)
C(7)	−0·4452	¼	0·0588
C(8)	−0·4145	0·1456	0·1811
C(9)	−0·3828	0·2088	0·2941

Table 2 (*cont.*)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	3·87 (3)	3·83 (3)	3·48 (3)		0·37 (3)	
S	4·6 (1)	3·7 (1)	5·1 (2)	−0·1 (1)	−0·3 (1)	0·0 (1)
C(1)	3·9 (5)	4·0 (6)	4·3 (5)	−0·0 (5)	0·7 (5)	−0·6 (5)
C(2)	3·7 (5)	5·2 (7)	5·1 (6)	−0·3 (5)	0·0 (6)	−0·3 (6)
C(3)	4·4 (7)	6·8 (10)	5·4 (7)	−0·2 (7)	−0·2 (6)	−0·3 (7)
C(4)	7 (1)	13 (3)	5 (1)		3 (1)	
C(5)	11 (2)	8 (1)	5 (1)	−1 (1)	1 (1)	1 (1)
C(6)	11 (2)	11 (2)	6 (1)	3 (1)	3 (1)	1 (1)
C(7)	2	30	3		2	
C(8)	3	3	8	0	3	0
C(9)	3	12	4	0	2	0

Discussion

Fig. 1 shows a projection of the molecule viewed in the [010] direction, with the atomic numbering and the angles between the different molecular planes in the molecule. A stereographic drawing of the molecule in the [001] direction is given in Fig. 3.

The final atomic parameters are given in Table 2. The interatomic distances and angles computed with these parameters are shown in Table 3. Table 4 gives the normal equations of the planes. In Table 5 the weight analysis of the observed and calculated structure factors in the last cycle of refinement is given. The comparison between observed and calculated structure factors after refinement is given in Table 6.

Table 4. *Normal equations of selected planes and related angles in the crystal structure of* $(C_5H_5)_2WS_2C_6H_4$

No.	plane
1:	S–W–S
2:	S–benzene–S
3:	cp ring (normal)
4:	cp ring (statistical)
5:	W–cp(1)–S/S
6:	W–cp(2)–S/S

Plane equations

1: $10{\cdot}080X - 0{\cdot}000Y - 6{\cdot}023Z - 3{\cdot}013 = 0$

2: $11{\cdot}729X + 0{\cdot}174Y - 6{\cdot}293Z - 3{\cdot}773 = 0$

3: $-4{\cdot}894X - 0{\cdot}078Y + 7{\cdot}368Z - 1{\cdot}835 = 0$

4: $14{\cdot}037X - 0{\cdot}285Y - 3{\cdot}774Z - 7{\cdot}494 = 0$

5: $0{\cdot}000X + 11{\cdot}148Y - 0{\cdot}000Z - 2{\cdot}787 = 0$

6: $0{\cdot}000X + 11{\cdot}148Y + 0{\cdot}000Z - 2{\cdot}787 = 0$

Planes	Angle
1–2	8·1°
1–3	21·1
1–4	22·0
1–5	90·0
1–6	90·0
2–3	29·1
2–4	14·2
3–4	43·1

Table 5. *Weight analysis of the observed and calculated structure factors*

$\langle F_o \rangle$	$\langle F_c \rangle$	Number of reflexions in this interval	$\langle \Delta F \rangle$	$\langle w\Delta F^2 \rangle$	R
0·0	2·0	172	0·07	0·01	0·000
6·6	5·1	224	1·87	0·66	0·200
10·0	8·4	173	2·00	1·64	0·127
13·0	12·1	175	1·64	2·28	0·086
16·0	15·7	166	1·39	2·36	0·069
18·9	18·8	153	1·31	2·72	0·063
22·4	22·7	177	1·42	1·82	0·057
27·4	27·6	162	1·56	1·66	0·053
34·2	34·4	152	1·80	1·29	0·049
45·1	44·8	151	2·19	1·36	0·041
62·1	61·5	154	2·58	1·31	0·042
90·9	89·4	153	3·84	1·05	0·040
158·9	154·9	72	6·41	0·82	0·043

$\langle \sin\theta/\lambda \rangle$	$\langle \lvert F_o \rvert \rangle$	$\langle \lvert F_c \rvert \rangle$	Number of reflexions in this interval	$\langle \Delta F \rangle$	$\langle w\Delta F^2 \rangle$	R
0·22	98·1	95·4	153	6·40	4·11	0·065
0·33	65·9	64·3	154	2·65	1·31	0·039
0·40	47·4	46·5	154	2·12	1·59	0·045
0·45	39·1	38·2	158	1·94	1·63	0·050
0·49	33·1	32·4	161	1·75	1·37	0·053
0·52	28·2	27·5	162	1·66	1·63	0·059
0·55	22·9	23·0	171	1·28	0·95	0·056
0·58	18·7	18·9	168	1·27	0·96	0·068
0·61	16·5	16·6	156	1·24	0·93	0·075
0·63	15·1	15·2	172	1·39	1·29	0·096
0·66	13·0	13·2	166	1·16	0·88	0·090
0·68	11·4	11·4	181	1·40	1·34	0·123
0·70	9·9	10·1	126	1·37	1·24	0·130

According to the parameters listed in Table 5, it seems unlikely that there are systematic errors in the data, so that in the discussion which follows such errors can be neglected.

The molecule itself possesses the mirror symmetry of the space group (Fig. 2). This feature was also observed by Kutoglu & Köpf (1970) in the structure $(C_5H_5)_2MoS_2C_6H_4$. The special position of the molecule defines the absolute $C_s = m$ symmetry. The possible $C_{2v} = mm2$ symmetry is not satisfied because of the folding of the molecule along the S–S axis, as is shown in Fig. 1.

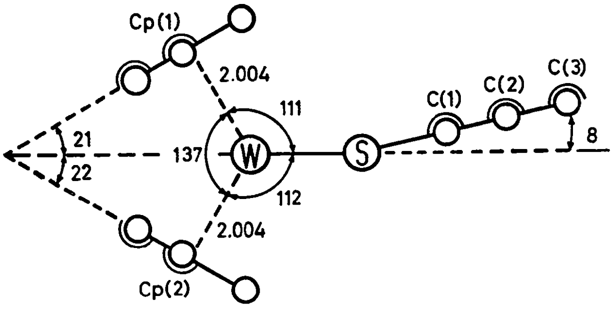

Fig. 1. Profile of the molecule $(C_5H_5)_2WS_2C_6H_4$ viewed in the [010] direction.

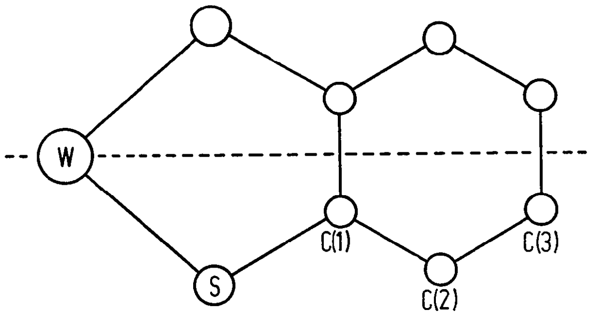

Fig. 2. Idealized representation of the chelate part and the normal cyclopentadienyl ring of $(C_5H_5)_2WS_2C_6H_4$ with regard to the mirror plane of the space group.

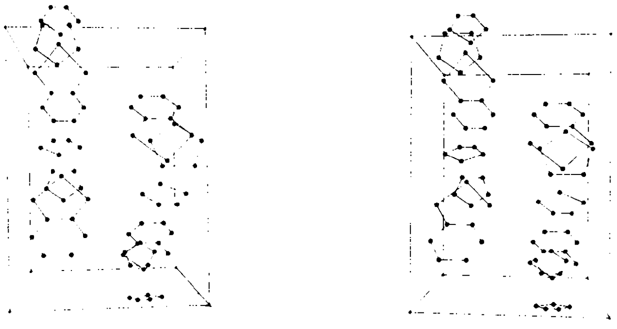

Fig. 3. Stereographic drawing of the molecular packing in the crystal.

Table 6. *Observed and calculated structure factors of* (C_5H_5)$WS_2C_6H_4$

[illegible]

Table 6 (*cont.*)

[illegible]

The fourfold neighbourhood of the central atom, a distorted tetrahedral one, is defined by the angle S–W–S = 82·3°. This value was predicted by Alcock (1967) in a modified Ballhausen-orbital schema. The angle defined by the two normals to the C_5H_5 planes is equal to 137°, which is similar to the value found in $(C_5H_5)_2MoS_2C_6H_4$ (Kutoglu & Köpf, 1970) but lies between the corresponding values for $(C_5H_5)_2MoH_2$ (Gerloch & Mason, 1965) and $(C_5H_5)_2MoS_2C_6H_3CH_3$ (Knox & Prout, 1969). The plane formed by the atoms of tungsten and sulphur nearly bisects the angle formed by the intersection of the two C_5H_5 planes (21 and 22°).

The tungsten–sulphur distance is 2·421 Å, in good agreement with the sum of the covalent atomic radii (W: 1·41; S: 1·04 Å) as given by Slater (1964).

The bond distance between the sulphur and the carbon atom [C(1)] of the tungsten ring is 1·753 Å; if the sum of the covalent radii (C = 0·77 Å for a single bond) of these atoms is taken, a distance of 1·8 Å is found, as in paraffinic substances like CH_3 SH. The observed shortening of the S–C distance, which is above the 3σ range ($3\sigma = 0·024$ Å), could be due to the fact that the partial double bonding of the benzene ligand is extended towards the sulphur atom, if other errors such as the systematic ones in the data are eliminated. The sulphur–sulphur distance (3·185 Å) in the chelate ring of the molecule results from this configuration.

The interatomic distances and angles in the benzene ring of the molecule are identical with the values normally found (average 1·39 Å and 120°). An interesting feature of this molecule is that one of the cyclopentadienyl rings is in a stable position, whereas the other one occupies statistically two possible orientations in the crystal. Therefore only the distances and angles of the first cyclopentadienyl ring are reported [C(4)–C(6)] in Table 3. The fivefold symmetry of this ring is disturbed in such a way that two C–C distances [C(4)–C(5) = 1·437 and C(6)–C(6′) = 1·439 Å] are longer and one [C(5)–C(6) = 1·326 Å] is shorter than the values expected for an aromatic ring like benzene (1·4 Å).

The variation in the C–C distances is of the order of 7σ. A considerable part of this discrepancy is probably a consequence of the atomic thermal vibrations, which influence the calculated bond distances. An underestimation of the standard deviations seems to be unlikely to have resulted from the calculation procedures. It is not clear why this differentiation rather than the expected equivalence of the C–C distances in the cyclopentadienyl ring is observed. However, the angles in this ring ligand (106, 108 and 110°) are close to the normal value of 108°.

The distances from the cyclopentadienyl ligands to the central atom are equal (2·004 Å). The carbon atoms of the undisturbed C_5H_5 ring are located 2·312, 2·331 and 2·322 Å from the tungsten atom; in the disordered ring these values are not regular but are still reasonable (2·322, 2·340 and 2·230 Å).

The molecular packing

The molecules lie on the mirror plane of the space group *Pnma* so that the centre of gravity of the molecule (± tungsten atom) occupies approximately the 4(*c*) position of the space group and the pseudo-parameters $\frac{1}{2},\frac{1}{4},\frac{1}{4}$. There is octahedral coordination of molecular packing around each of the molecules, where the ideal intermolecular distance is *ca.* $\frac{1}{2}$ of the identity period in the direction [100], and equal to 8·0 Å. The stereographic drawing of Fig. 3 shows the orientation of the molecule in the unit cell. All the intermolecular distances are greater than 4·0 Å.

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