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Bis-π-cyclopentadienyltungsten(IV)(bis-μ-benzenethiolato)metal(0) Tetracarbonyls $(\pi\text{-}C_5H_5)_2W(\mu\text{-}SC_6H_5)_2M(CO)_4$, M = Cr, Mo, or W

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The three complexes are monoclinic, $B2/b$, isomorphous and isostructural: (i) $C_{26}CrH_{20}O_4S_2W$, $a=17{\cdot}85$ (3), $b=18{\cdot}23$ (3), $c=15{\cdot}83$ (3) Å, $\gamma=112{\cdot}8$ (3)°, $D_m=1{\cdot}87$, $D_c=1{\cdot}90$ g cm^{-3}, $Z=8$; (ii) $C_{26}H_{20}MoO_4S_2W$, $a=18{\cdot}07(3)$, $b=18{\cdot}33(3)$, $c=16{\cdot}23(3)$ Å, $\gamma=112{\cdot}6(3)°$, $D_m=1{\cdot}98$, $D_c=2{\cdot}00$ g cm^{-3}, $Z=8$; (iii) $C_{26}H_{20}O_4S_2W_2$, $a=17{\cdot}90$ (3), $b=18{\cdot}37$ (3), $c=15{\cdot}93(3)$ Å, $\gamma=112{\cdot}3(3)°$, $D_m=2{\cdot}26$, $D_c=2{\cdot}27$ g cm^{-3}, $Z=8$. Patterson methods were used to determine the structures from linear diffractometer intensity measurements. Final R 0·075 (Cr), 0·070 (Mo), and 0·090 (W). The positions of all atoms except hydrogen were determined. Deviations from expected values in bond lengths and angles were not significant. The molecules do not have intramolecular metal–metal bonds.

Introduction

Crystals were prepared by Dias & Green (1969). The crystal system and approximate cell dimensions were determined from Weissenberg (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å) and precession photographs (Mo $K\alpha$, $\lambda=0{\cdot}7107$ Å) and from single-crystal diffractometry. Systematic extinctions [hkl, $k=2n+1$; $hk0$, $h=2n+1$ ($k=2n+1$)] indicated space groups Bb or $B2/b$. Since $Z=8$, $B2/b$ (C_{2h}^6, No. 15, first setting) was assumed and later confirmed by the successful completion of the structure analyses.

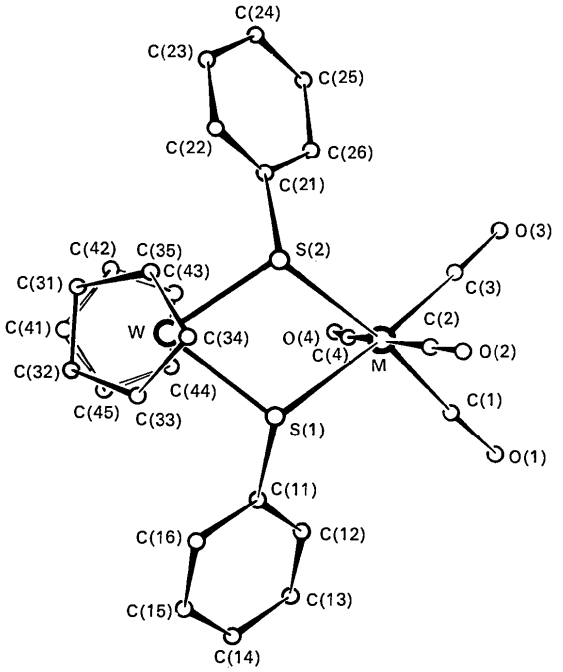

Fig. 1. A molecule of bis-π-cyclopentadienyltungsten(IV)-(bis-μ-benzenethiolato)chromium(0) tetracarbonyl seen projected onto the best plane of the WS_2Cr ring. Similar projections of the molybdenum and tungsten compounds are not noticeably or significantly different.

2724 (layers $hk0$–11) for Cr, 2702 (layers $hk0$–15) for Mo, 2576 (layers $hk0$–15) for W, independent reflexions with $I>3\sigma$ were measured on a Hilger & Watts linear diffractometer modified to scan peak and background, with Mo $K\alpha$ radiation [$\mu=57$ (Cr), 57 (Mo), 104 cm^{-1} (W)]. An empirical (North, Phillips & Mathews, 1968) absorption correction was applied to the measurements on $C_{26}H_{20}O_4S_2W_2$.

In each case the unsharpened Patterson function gave the metal atom positions and the metal-atom-phased F_o synthesis those of the sulphur atoms. The positional and isotropic temperature parameters of these atoms were refined by full-matrix least-squares methods and the light atoms (other than hydrogen) were located from subsequent difference syntheses. This model was then refined, first with isotropic, then anisotropic thermal parameters with a large-block approximation to the normal matrix. The final R indices were 0·075 (Cr), 0·070 (Mo), and 0·090 (W) and the weighting schemes had the form $w=\{1+[(|F_o|-a)/b]^2\}^{-1}$ for Cr ($a=40$, $b=50$) and for Mo ($a=60$, $b=65$); but for W, $\sqrt{w}=1$ if $|F_o|\leq 121$, otherwise $\sqrt{w}=121/|F_o|$. The scattering factors and corrections for the real part of the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). Rollett & Ford's (1970) Algol system was used for all calculations.

The observed structure amplitudes and the structure factors calculated from the final atomic parameters listed in Table 1 are available.* Standard deviations of the atomic parameters and of the bond distances and angles (Table 2) were obtained from the leading diagonal terms of the variance–covariance matrix.

* These have been deposited with the British Library Lending Division as Supplementary Publication No SUP 30481 (52 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters*

The standard deviations in parentheses refer to the least significant digit of the preceding number. The temperature factor T is given by $T=\exp\{-2\pi^2[U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*]\}$.

(*a*) $C_{26}CrH_{20}O_4S_2W$ (positional parameters $\times 10^4$, $U_{ij}\times 10^3$)

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
W	2295·7 (3)	3048·8 (3)	1711·3 (4)	13 (0·2)	27 (0·2)	23 (0·6)	−4 (0·4)	−7 (0·4)	16 (0·3)
Cr	4113 (1)	3957 (1)	3298 (2)	17 (1)	32 (1)	28 (2)	2 (2)	−6 (2)	12 (1)
S(1)	2787 (2)	2816 (2)	3113 (3)	20 (1)	30 (1)	27 (3)	6 (3)	−5 (3)	14 (2)
S(2)	3312 (2)	4337 (2)	2237 (3)	22 (1)	30 (1)	29 (3)	1 (3)	−8 (3)	14 (2)
C(1)	4560 (8)	3596 (9)	4144 (12)	17 (6)	52 (8)	29 (14)	0 (13)	−3 (11)	10 (11)
C(2)	3639 (8)	4340 (8)	4154 (12)	28 (7)	39 (6)	34 (14)	8 (13)	8 (13)	25 (11)
C(3)	4987 (9)	4916 (9)	3399 (11)	36 (8)	44 (7)	19 (14)	−26 (12)	−16 (13)	29 (11)
C(4)	4741 (8)	3610 (9)	2536 (12)	20 (6)	53 (8)	25 (13)	−3 (13)	−13 (12)	29 (11)
O(1)	4869 (8)	3384 (9)	4684 (10)	45 (7)	84 (9)	49 (12)	42 (15)	1 (13)	52 (12)
O(2)	3402 (9)	4599 (8)	4717 (9)	89 (11)	71 (8)	33 (12)	−8 (14)	19 (16)	88 (15)
O(3)	5556 (8)	5500 (7)	3496 (11)	35 (7)	51 (7)	93 (14)	−3 (14)	−9 (13)	1 (10)
O(4)	5177 (8)	3453 (9)	2139 (11)	39 (7)	93 (10)	69 (14)	−52 (16)	−16 (14)	74 (14)
C(11)	2734 (6)	1822 (5)	3238 (10)	32 (7)	21 (5)	39 (14)	4 (10)	3 (12)	23 (9)
C(12)	3384 (6)	1679 (6)	3587 (13)	17 (6)	47 (8)	73 (16)	2 (15)	−8 (14)	36 (11)
C(13)	3293 (7)	903 (6)	3762 (12)	42 (9)	45 (8)	46 (15)	18 (15)	5 (16)	48 (13)
C(14)	2558 (8)	265 (6)	3616 (13)	49 (10)	43 (8)	49 (16)	12 (15)	15 (17)	39 (14)
C(15)	1919 (7)	405 (6)	3237 (14)	34 (9)	70 (11)	73 (12)	41 (20)	20 (18)	50 (16)
C(16)	1999 (6)	1184 (6)	3087 (11)	28 (7)	39 (6)	28 (13)	4 (12)	1 (12)	21 (10)
C(21)	3827 (6)	5012 (7)	1424 (9)	24 (7)	35 (6)	39 (13)	1 (12)	−3 (12)	33 (10)
C(22)	3369 (6)	5233 (8)	839 (10)	33 (8)	48 (8)	54 (16)	30 (15)	11 (16)	47 (12)
C(23)	3751 (8)	5827 (9)	245 (11)	52 (10)	56 (9)	54 (18)	19 (18)	2 (19)	38 (15)
C(24)	4597 (8)	6172 (10)	203 (11)	79 (14)	65 (11)	42 (19)	13 (19)	−5 (23)	55 (19)
C(25)	5055 (7)	5953 (12)	792 (13)	32 (9)	83 (13)	79 (21)	36 (24)	27 (20)	16 (16)
C(26)	4671 (6)	5360 (11)	1386 (12)	33 (9)	78 (12)	39 (17)	44 (19)	8 (16)	25 (15)
C(31)	1148 (10)	3218 (11)	1137 (11)	28 (9)	128 (19)	78 (22)	58 (29)	−21 (20)	98 (22)
C(32)	899 (9)	2447 (8)	1507 (12)	13 (7)	54 (9)	116 (23)	−53 (20)	8 (17)	6 (12)
C(33)	1046 (9)	2538 (8)	2370 (11)	25 (7)	59 (9)	48 (17)	50 (17)	0 (15)	36 (13)
C(34)	1417 (9)	3357 (9)	2549 (10)	28 (8)	86 (13)	65 (18)	−37 (21)	2 (16)	82 (16)
C(35)	1487 (9)	2779 (7)	1785 (11)	26 (8)	58 (9)	57 (18)	19 (16)	−13 (14)	58 (14)
C(41)	2203 (8)	2464 (8)	469 (9)	43 (8)	57 (8)	6 (13)	−2 (13)	−4 (14)	51 (13)
C(42)	2845 (8)	3192 (8)	377 (9)	52 (9)	68 (9)	11 (12)	3 (13)	12 (13)	68 (14)
C(43)	3480 (7)	3186 (7)	922 (10)	27 (7)	48 (7)	26 (14)	8 (13)	15 (12)	33 (11)
C(44)	3203 (8)	2437 (7)	1333 (10)	29 (7)	36 (6)	45 (14)	−9 (13)	−6 (13)	27 (10)
C(45)	2406 (6)	1985 (6)	1041 (10)	9 (5)	42 (6)	55 (15)	−11 (13)	4 (12)	32 (9)

(*b*) $C_{26}H_{20}MoO_4S_2W$ (positional parameters $\times 10^4$, $U_{ij}\times 10^2$)

W	2295·8 (4)	3063·7 (4)	1700·6 (5)	1·68 (3)	2·91 (3)	2·54 (4)	−0·48 (8)	−1·35 (7)	1·70 (5)
Mo	4143 (1)	3974 (1)	3314 (1)	2·50 (7)	3·65 (8)	2·89 (10)	0·72 (7)	−1·15 (14)	1·46 (13)
S(1)	2758 (3)	2818 (3)	305 (3)	2·2 (2)	3·0 (2)	3·7 (4)	0·5 (4)	−0·4 (3)	1·1 (3)
S(2)	3288 (3)	4344 (3)	2209 (3)	2·9 (2)	2·8 (2)	3·2 (3)	0·2 (4)	−1·1 (4)	1·1 (4)
C(1)	4637 (11)	3570 (12)	4204 (15)	2 (1)	4 (1)	6 (2)	2 (2)	0 (2)	4 (2)
C(2)	3655 (12)	4394 (13)	4238 (16)	3 (1)	4 (1)	5 (2)	−1 (2)	−4 (2)	4 (2)
C(3)	5071 (15)	4954 (13)	3430 (15)	6 (1)	4 (1)	1 (1)	1 (2)	−2 (2)	−2 (2)
C(4)	4816 (12)	3614 (14)	2492 (18)	2 (1)	6 (1)	6 (2)	−1 (2)	−4 (2)	2 (2)
O(1)	4909 (10)	3387 (13)	4737 (13)	3 (1)	11 (2)	5 (1)	8 (2)	1 (2)	5 (2)
O(2)	3415 (12)	4648 (13)	4789 (14)	8 (1)	10 (2)	5 (2)	−4 (2)	2 (2)	11 (2)
O(3)	5621 (12)	5548 (12)	3504 (17)	6 (1)	6 (1)	10 (2)	−3 (2)	−2 (2)	−3 (2)
O(4)	5239 (10)	3460 (12)	2079 (12)	4 (1)	10 (1)	5 (1)	−4 (2)	0 (2)	8 (2)
C(11)	2678 (7)	1822 (7)	3254 (12)	3 (1)	2 (1)	4 (1)	5 (2)	5 (2)	5 (1)
C(12)	3336 (8)	1678 (8)	3551 (16)	4 (1)	4 (1)	7 (2)	−1 (2)	−3 (2)	5 (2)
C(13)	3259 (10)	909 (9)	3724 (18)	5 (1)	5 (2)	7 (2)	−4 (3)	1 (3)	3 (2)
C(14)	2534 (10)	276 (8)	3583 (17)	4 (1)	6 (2)	8 (2)	0 (2)	1 (2)	5 (2)
C(15)	1888 (10)	418 (8)	3253 (19)	4 (1)	3 (1)	7 (2)	1 (3)	−1 (3)	1 (2)
C(16)	1968 (8)	1188 (8)	3071 (14)	3 (1)	3 (1)	4 (2)	0 (2)	0 (2)	1 (2)
C(21)	3796 (8)	5016 (11)	1390 (13)	3 (1)	4 (1)	6 (2)	2 (2)	−1 (2)	2 (2)
C(22)	3345 (8)	5263 (13)	841 (14)	4 (1)	4 (1)	6 (2)	1 (2)	−2 (2)	3 (2)
C(23)	3732 (11)	5815 (13)	232 (13)	8 (2)	4 (1)	7 (2)	1 (2)	−1 (3)	6 (3)
C(24)	4566 (11)	6196 (18)	245 (19)	5 (2)	10 (2)	6 (3)	6 (3)	−2 (3)	−3 (3)
C(25)	5016 (9)	5924 (23)	770 (21)	5 (2)	13 (3)	6 (3)	10 (5)	−1 (3)	1 (4)
C(26)	4629 (8)	5363 (16)	1374 (16)	3 (1)	7 (2)	6 (2)	7 (3)	3 (2)	3 (2)
C(31)	1168 (13)	3226 (14)	1117 (11)	3 (1)	13 (3)	7 (2)	9 (4)	2 (2)	8 (3)
C(32)	888 (10)	2460 (11)	1484 (12)	1 (1)	8 (2)	6 (2)	−5 (2)	−3 (1)	4 (1)
C(33)	1043 (12)	2561 (11)	2324 (13)	2 (1)	8 (2)	11 (3)	12 (4)	6 (3)	6 (3)
C(34)	1412 (12)	3380 (12)	2494 (11)	3 (1)	8 (2)	4 (2)	−5 (3)	−3 (2)	5 (3)
C(35)	1490 (12)	3789 (9)	1744 (13)	4 (1)	5 (1)	4 (1)	0 (2)	−3 (2)	3 (2)
C(41)	2231 (10)	2437 (12)	466 (14)	3 (1)	6 (1)	6 (2)	−1 (2)	0 (2)	4 (2)

Table 1 (*cont.*)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(42)	2853 (12)	3184 (10)	422 (12)	6 (1)	4 (1)	3 (1)	−3 (2)	−2 (2)	6 (2)
C(43)	3464 (9)	3195 (10)	947 (13)	4 (1)	4 (1)	4 (1)	1 (2)	1 (2)	6 (2)
C(44)	3205 (10)	2453 (10)	1361 (11)	3 (1)	5 (1)	3 (1)	−5 (2)	−1 (2)	4 (2)
C(45)	2431 (11)	1998 (10)	1074 (13)	4 (1)	6 (2)	5 (2)	−7 (2)	0 (2)	1 (2)

(*c*) $C_{26}H_{20}O_4S_2W_2$ (positional parameters $\times 10^3$, $U_{ij} \times 10^2$)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	229·0 (1)	306·1 (1)	170·8 (1)	1·88 (5)	3·71 (7)	4·78 (8)	−0·52 (13)	−1·58 (11)	2·39 (9)
W(2)	413·7 (1)	397·7 (1)	331·3 (1)	1·80 (6)	3·90 (7)	4·82 (8)	0·08 (14)	−1·15 (10)	1·89 (10)
S(1)	276·5 (4)	282·3 (5)	310·6 (5)	2·3 (3)	3·9 (4)	5·0 (5)	0·3 (6)	−0·5 (5)	2·4 (6)
S(2)	328·3 (4)	434·2 (5)	221·6 (6)	2·3 (3)	4·3 (4)	6·3 (6)	1·4 (7)	−1·4 (7)	2·4 (6)
C(1)	460 (2)	358 (2)	426 (2)	1 (1)	6 (2)	8 (3)	4 (4)	−2 (3)	1 (2)
C(2)	364 (2)	438 (2)	429 (3)	4 (2)	3 (2)	11 (3)	−2 (4)	4 (4)	3 (3)
C(3)	507 (2)	497 (2)	342 (2)	5 (2)	2 (1)	4 (2)	−2 (2)	0 (3)	0 (2)
C(4)	480 (2)	360 (2)	245 (3)	1 (1)	2 (1)	9 (3)	−5 (3)	−4 (3)	1 (2)
O(1)	491 (2)	339 (2)	475 (2)	5 (2)	13 (3)	9 (2)	−1 (4)	−2 (3)	12 (4)
O(2)	344 (2)	469 (2)	478 (2)	9 (2)	14 (3)	9 (3)	2 (5)	−1 (4)	19 (5)
O(3)	560 (2)	560 (2)	346 (2)	6 (2)	10 (3)	7 (2)	−4 (4)	1 (4)	4 (4)
O(4)	524 (2)	346 (2)	208 (3)	4 (2)	12 (3)	10 (3)	−4 (5)	0 (3)	9 (4)
C(11)	272 (1)	186 (1)	326 (2)	2 (1)	3 (1)	4 (2)	2 (3)	2 (2)	2 (2)
C(12)	335 (2)	166 (3)	355 (2)	5 (2)	9 (3)	3 (2)	−1 (3)	0 (3)	9 (4)
C(13)	328 (2)	94 (2)	373 (3)	5 (2)	6 (2)	6 (2)	−1 (4)	0 (4)	6 (4)
C(14)	255 (3)	26 (3)	356 (3)	8 (3)	9 (3)	5 (3)	6 (4)	4 (4)	11 (5)
C(15)	193 (2)	38 (4)	322 (3)	1 (2)	21 (7)	7 (3)	−1 (7)	1 (3)	6 (5)
C(16)	199 (2)	121 (2)	306 (2)	5 (2)	2 (2)	4 (2)	0 (2)	0 (2)	−1 (2)
C(21)	378 (2)	502 (2)	142 (2)	5 (2)	2 (1)	4 (2)	2 (2)	−1 (3)	2 (3)
C(22)	335 (2)	524 (2)	82 (2)	6 (2)	6 (2)	2 (2)	1 (3)	−1 (3)	5 (4)
C(23)	371 (2)	574 (3)	22 (3)	5 (2)	5 (2)	8 (3)	4 (5)	−2 (4)	2 (3)
C(24)	461 (4)	621 (4)	24 (4)	1 (5)	10 (5)	7 (4)	6 (7)	−4 (7)	0 (7)
C(25)	503 (2)	591 (4)	83 (4)	3 (2)	10 (4)	15 (6)	8 (8)	8 (6)	1 (5)
C(26)	462 (2)	537 (3)	139 (3)	3 (2)	11 (4)	8 (3)	3 (6)	−1 (4)	−2 (4)
C(31)	120 (2)	328 (4)	116 (2)	5 (2)	19 (6)	4 (2)	8 (6)	3 (4)	18 (7)
C(32)	92 (2)	247 (4)	145 (4)	2 (2)	21 (7)	12 (5)	−21 (9)	0 (4)	12 (6)
C(33)	104 (2)	252 (3)	237 (3)	2 (1)	10 (3)	7 (3)	3 (5)	0 (3)	6 (4)
C(34)	139 (2)	337 (3)	251 (2)	5 (2)	9 (3)	7 (3)	4 (5)	4 (4)	9 (4)
C(35)	148 (2)	383 (2)	179 (2)	2 (1)	3 (1)	5 (2)	1 (3)	1 (2)	4 (2)
C(41)	224 (2)	249 (2)	46 (2)	2 (1)	5 (2)	6 (2)	2 (3)	1 (3)	2 (3)
C(42)	283 (2)	321 (3)	43 (2)	9 (2)	11 (4)	1 (2)	−7 (4)	−2 (3)	9 (5)
C(43)	349 (2)	321 (2)	97 (2)	2 (1)	7 (3)	4 (2)	−4 (3)	−1 (2)	3 (3)
C(44)	317 (2)	241 (3)	137 (3)	4 (2)	12 (3)	8 (3)	−14 (5)	−5 (3)	14 (4)
C(45)	241 (2)	198 (2)	113 (3)	1 (1)	6 (2)	15 (4)	−8 (5)	4 (4)	2 (3)

Table 2. *Interatomic distances and interbond angles with standard deviations in parentheses for* $(\pi\text{-}C_5H_5)_2W(\mu\text{-}SC_6H_5)_2M(CO)_4$

M =	Cr	Mo	W	M =	Cr	Mo	W
W——M	3·927 (5)	4·062 (3)	4·011 (2)	M——S(1)	2·490 (8)	2·606 (6)	2·59 (1)
W——S(1)	2·483 (7)	2·526 (5)	2·48 (1)	M——S(2)	2·472 (8)	2·621 (6)	2·57 (1)
W——S(2)	2·491 (7)	2·483 (6)	2·49 (1)	M——C(1)	1·81 (3)	1·99 (3)	1·99 (4)
W——C(31)	2·37 (5)	2·37 (3)	2·31 (5)	M——C(2)	1·87 (3)	2·04 (3)	2·06 (4)
W——C(32)	2·32 (4)	2·38 (3)	2·31 (4)	M——C(3)	1·84 (3)	1·94 (3)	1·96 (4)
W——C(33)	2·31 (4)	2·32 (4)	2·33 (5)	M——C(4)	1·91 (3)	2·08 (3)	2·10 (4)
W——C(34)	2·28 (4)	2·29 (3)	2·29 (5)	C(1)—O(1)	1·16 (4)	1·11 (4)	1·09 (6)
W——C(35)	2·32 (4)	2·32 (3)	2·38 (4)	C(2)—O(2)	1·16 (4)	1·17 (4)	1·10 (6)
W——C(41)	2·21 (3)	2·29 (3)	2·23 (7)	C(3)—O(3)	1·16 (4)	1·16 (4)	1·19 (6)
W——C(42)	2·30 (3)	2·28 (4)	2·23 (3)	C(4)—O(4)	1·12 (4)	1·21 (4)	1·09 (6)
W——C(43)	2·38 (3)	2·37 (4)	2·37 (5)	S(1)—C(11)	1·79 (3)	1·79 (2)	1·76 (3)
W——C(44)	2·37 (3)	2·38 (3)	2·37 (5)	S(2)—C(21)	1·77 (3)	1·81 (2)	1·76 (4)
W——C(45)	2·28 (3)	2·30 (3)	2·27 (8)	C(11)–C(12)	1·39 (4)	1·40 (3)	1·39 (6)
C(31)–C(32)	1·43 (5)	1·43 (3)	1·45 (7)	C(12)–C(13)	1·39 (5)	1·39 (4)	1·31 (7)
C(32)–C(33)	1·39 (5)	1·39 (3)	1·48 (7)	C(13)–C(14)	1·40 (4)	1·40 (4)	1·45 (7)
C(33)–C(34)	1·41 (5)	1·42 (3)	1·46 (7)	C(14)–C(15)	1·40 (5)	1·40 (4)	1·33 (10)
C(34)–C(35)	1·41 (5)	1·41 (3)	1·40 (6)	C(15)–C(16)	1·39 (5)	1·40 (4)	1·51 (8)
C(35)–C(31)	1·41 (5)	1·41 (3)	1·38 (7)	C(16)–C(11)	1·40 (4)	1·39 (4)	1·43 (5)
C(41)–C(42)	1·39 (4)	1·40 (3)	1·34 (8)	C(21)–C(22)	1·39 (4)	1·40 (3)	1·38 (5)
C(42)–C(43)	1·40 (4)	1·39 (3)	1·46 (6)	C(22)–C(23)	1·40 (5)	1·40 (3)	1·31 (6)
C(43)–C(44)	1·43 (4)	1·43 (3)	1·50 (7)	C(23)–C(24)	1·39 (6)	1·40 (4)	1·51 (8)
C(44)–C(45)	1·42 (4)	1·40 (3)	1·34 (10)	C(24)–C(25)	1·40 (5)	1·40 (5)	1·44 (10)
C(45)–C(41)	1·42 (4)	1·39 (3)	1·52 (11)	C(25)–C(26)	1·40 (5)	1·40 (5)	1·33 (9)

Table 2 (*cont.*)

C(26)–C(21)	1·39 (5)	1·39 (3)	1·39 (7)
S(1)—W——S(2)	71·7 (2)	72·6 (2)	72·8 (3)
S(1)—M——S(2)	71·9 (2)	69·1 (2)	69·7 (3)
S(2)—M——C(1)	172 (1)	172 (1)	169 (1)
C(1)—M——C(2)	86 (1)	86 (1)	82 (2)
C(2)—M——C(3)	86 (1)	86 (1)	86 (2)
C(3)—M——C(4)	89 (1)	87 (1)	89 (2)
S(1)—M——C(1)	101 (1)	103 (1)	101 (1)
S(2)—M——C(2)	90 (1)	91 (1)	92 (1)
C(1)—M——C(3)	87 (1)	86 (1)	87 (1)
C(2)—M——C(4)	171 (1)	170 (1)	171 (2)
S(1)—M——C(2)	89 (1)	89 (1)	89 (1)
S(2)—M——C(3)	99 (1)	102 (1)	101 (1)
C(1)—M——C(4)	87 (1)	87 (1)	91 (2)
S(1)—M——C(3)	170 (1)	170 (1)	170 (1)
S(2)—M——C(4)	98 (1)	97 (1)	96 (1)
S(1)—M——C(4)	98 (1)	99 (1)	97 (1)
M——S(1)—W	104·3 (3)	104·6 (2)	104·9 (3)
M——S(1)—C(11)	119·6 (9)	119·2 (7)	118 (1)
W——S(1)—C(11)	112·8 (9)	113·6 (7)	115 (1)
M——S(2)—W	104·6 (3)	105·4 (2)	104·9 (4)
M——S(2)—C(21)	119·2 (9)	119·0 (7)	119 (1)
W——S(2)—C(21)	113·9 (9)	113·2 (7)	115 (1)
M——C(1)—O(1)	178 (3)	175 (2)	175 (3)
M——C(2)—O(2)	175 (3)	176 (2)	171 (3)
M——C(3)—O(3)	177 (3)	179 (2)	175 (3)
M——C(4)—O(4)	173 (3)	171 (2)	169 (3)
C(31)–C(32)–C(33)	108 (3)	108 (3)	105 (4)
C(32)–C(33)–C(34)	108 (3)	109 (2)	102 (5)
C(33)–C(34)–C(35)	108 (3)	108 (2)	115 (5)
C(34)–C(35)–C(31)	108 (3)	108 (2)	103 (4)
C(35)–C(31)–C(32)	107 (3)	108 (2)	114 (4)
C(41)–C(42)–C(43)	107 (3)	109 (2)	108 (4)
C(42)–C(43)–C(44)	108 (3)	108 (2)	107 (4)
C(43)–C(44)–C(45)	108 (2)	107 (2)	104 (5)
C(44)–C(45)–C(41)	107 (2)	108 (2)	112 (5)
C(45)–C(41)–C(42)	110 (3)	108 (2)	111 (4)
C(11)–C(12)–C(13)	119 (3)	120 (3)	124 (3)
C(12)–C(13)–C(14)	121 (3)	120 (3)	123 (3)
C(13)–C(14)–C(15)	119 (3)	120 (3)	118 (4)
C(14)–C(15)–C(16)	119 (3)	120 (3)	120 (3)
C(15)–C(16)–C(11)	121 (3)	120 (3)	120 (4)
C(16)–C(11)–C(12)	120 (3)	120 (2)	115 (4)
S(1)—C(11)–C(12)	121 (2)	120 (1)	125 (3)
S(1)—C(11)–C(16)	119 (2)	121 (1)	119 (3)
C(21)–C(22)–C(23)	120 (3)	120 (3)	122 (3)
C(22)–C(23)–C(24)	120 (3)	120 (3)	121 (3)
C(23)–C(24)–C(25)	119 (3)	120 (3)	113 (4)
C(24)–C(25)–C(26)	120 (4)	120 (3)	120 (3)
C(25)–C(26)–C(21)	120 (4)	120 (3)	124 (4)
C(26)–C(21)–C(22)	120 (3)	120 (2)	118 (3)
S(2)—C(21)–C(22)	119 (2)	119 (1)	121 (3)
S(2)—C(21)–C(26)	122 (2)	120 (1)	121 (3)

Discussion

Dias & Green (1969) reported that metal–metal bonded complexes of the type $(\pi\text{-}C_5H_5)_2W$(or Mo) $(\mu\text{-}SC_6H_5)_2W$(or Mo or Cr) $(CO)_3$ were obtained from the reaction of $(\pi\text{-}C_5H_5)_2W$(or Mo) $S(C_6H_5)_2$ with Group VI metal hexacarbonyls. The crystal structures reported here are those of the supposed tricarbonyls which were investigated to study the variation of the metal–metal bond distance. The investigation showed the complexes to be the tetracarbonyls $(\pi\text{-}C_5H_5)_2W(\mu\text{-}SC_6H_5)_2M(CO)_4$. The bond distances and angles (Table 2) show that the molecules are remarkably similar and have the form of the representative molecule $C_{26}H_{20}CrO_4S_2W$ in Fig. 1. The bis-π-cyclopentadienyl system has the staggered conformation. The mean lengths of the normals to the π-cyclopentadienyl ligands at the atoms are 1·99 (Cr), 2·01 (Mo) and 1·99 Å (W) and the angles between the normals 131·5 (Cr), 134·6 (Mo) and 132·4° (W). In the bis-μ-benzenethiolato bridge the phenyl groups are *cis*, the internal angles in the WS_2M ring are contrary to the Dahl criteria for metal–metal bonding, and the lack of planarity of the ring is consistent with intramolecular steric repulsion. These and other observed deviations from expected values of bond distances and angles are not thought to be significant.

These results have been mentioned briefly in a preliminary publication by Cameron *et al.* (1971).

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