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π-ARENE COMPLEXES

I. THE CRYSTAL AND MOLECULAR STRUCTURES OF π-BENZENEDICARBONYL-1,3-DITHIANECHROMIUM(0) AND π-METHYLBENZOATEDICARBONYL-1,3-DITHIANECHROMIUM(0)

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Summary

The π-arene complexes π-benzenedicarbonyl-1,3-dithianechromium(0) and π-methylbenzoatedicarbonyl-1,3-dithianechromium(0) were studied by single crystal X-ray diffraction. These complexes have different conformations with the $Cr(CO)_2[\overline{S(CH_2)_3SCH_2}]$ fragment in a near eclipsed orientation relative to the planar η^6-methylbenzoate ligand and in a staggered orientation in relation to the carbon atoms of the benzene ring. Internal parameters are in good agreement for both structures and a noticeable feature is the very short Cr–S bond distances of 2.346(3) and 2.354(2) Å.

Introduction

Single crystal X-ray analyses were carried out for a number of complexes of the type: $Cr(\eta^6\text{-}C_6H_5R)(CO)_2L$ (R = H, L = CO [1], L = $C(OMe)C_6H_5$ [2]; R = COOMe, L = CO [3], L = CS [4], L = CSe [5], L = PF_3 [6], L = PPh_3 [7], L = $CNBu^t$ [8] and L = $CNCOC_6H_5$ [9]).

The effect of substituents R in the π-arene ring on the conformation of the molecule and of L on the bonding properties of the ligands are well known for these and similar compounds. No example of a thioether as ligand in such systems has been reported. As part of an ongoing study of the reactivity of coordinated sulphur ligands we have recently synthesized π-arenedicarbonylthioetherchromium(0)

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compounds and hereby wish to report on the crystal structures of $[Cr(\eta^6\text{-}C_6H_5R)(CO)_2\{S(CH_2)_3SCH_2\}]$, (I, R = H; II, R = COOMe) [10–12].

Experimental

Synthesis of $[Cr(\eta^6\text{-}C_6H_5R)(CO)_2\{S(CH_2)_3SCH_2\}]$ *(I, R = H; II, R = COOMe)*

Starting materials were obtained from Strem Chemicals and $[Cr(\pi\text{-arene})(CO)_3]$ prepared according to the published procedures [13,14]. All the experiments were carried out in an inert atmosphere and solvents were freshly dried and distilled under nitrogen. Irradiation of $[Cr(\eta^6\text{-}C_6H_5R)(CO)_3]$ (5 mmol) and 1,3-dithiane (5 mmol) in methanol (200 ml) for 3 h, followed by removal of the solvent in vacuo, yielded a brown residue. Chromatography on silica (−20 °C) with ether/hexane (1/1) gave two red and two yellow bands, which were separated, collected and concentrated. The two yellow bands, identified as $Cr(CO)_5[S(CH_2)_3SCH_2]$ and $Cr(\eta^6\text{-}C_6H_5R)(CO)_3$, were followed by the main product, the first red band, yielding the desired π-arene dithiane complex. Pure $[Cr(\eta^6\text{-}C_6H_6)(CO)_2\{S(CH_2)_3SCH_2\}]$ (I) and $[Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2\{S(CH_2)_3SCH_2\}]$ (II) were obtained in high yields after recrystallization from ether/pentane (−30 °C), m.p. 106 °C (decomposition) (I) and 92 °C (II).

Data collection and structure determination

Suitable single crystals of both I and II were identified by standard photographic techniques. Intensity measurements were made using Mo-K_α radiation (λ 0.7107 Å, graphite monochromator) on a Philips PW 1100 four circle diffractometer in the ω–2θ mode with $3 \leqslant \theta \leqslant 23°$. The crystal data and details of the structure analysis are listed in Table 1. The measured reflections were corrected for background and

TABLE 1

CRYSTAL DATA AND DETAILS OF THE STRUCTURE ANALYSIS

Molecular formula	$CrC_{12}H_{14}S_2O_2$ (I)	$CrC_{14}H_{16}S_2O_4$ (II)
a (Å)	22.014(9)	12.991(7)
b (Å)	7.403(6)	9.278(6)
c (Å)	8.264(5)	7.001(6)
α (°)	90.0	90.57(1)
β (°)	98.64(1)	102.06(1)
γ (°)	90.0	105.76(1)
V (Å^3)	1331.50	792.19
Space group	$P2_1/n$	$P1$
Z	4	2
D_c (kg dm^{-3})	1.53	1.66
$F(000)$	632	316
μ(Mo-K_α) mm^{-1}	10.8	9.1
N (measured)	2030	2245
N (unobserved)	726	852
R_w $(= (\Sigma w\Delta F^2/\Sigma wF_o^2)^{1/2}, w = \sigma^{-2}(F_0))$	0.046	0.050
R $(= \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_0\rvert)$	0.079	0.067
Res. background (e Å^{-3})	0.59	0.50

for Lorentz and polarization effects only. Accurate cell parameters were obtained from the diffractometer settings for 25 reflections. The structures were solved uneventfully and refined by full-matrix least-squares techniques using the program SHELX [15] with $\sigma^{-2}(F)$ weights. All the hydrogen atoms were placed in calculated positions and included in the refinements with common isotropic thermal parameters, riding upon the associated carbon atoms. All the non-hydrogen atoms were refined anisotropically. Scattering factors for chromium(0) were taken from the literature [16]. Fractional atomic coordinates, interatomic distances and bond angles

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ($\times 10^3$) FOR THE NON-HYDROGEN ATOMS FOR I AND II

	x/a	y/b	z/c	U_{eq}
Complex I				
Cr	8400(1)	1500(2)	950(1)	33(0)
C(1)	8418(3)	1801(10)	3137(8)	38(3)
O(1)	8418(2)	1978(8)	4535(5)	62(3)
C(2)	8557(3)	−873(11)	1393(9)	49(4)
O(2)	8637(3)	−2399(8)	1707(8)	78(4)
C(3)	7784(4)	3817(13)	436(9)	57(5)
C(4)	8200(4)	3903(11)	−637(10)	55(5)
C(5)	8288(3)	2433(13)	−1612(9)	50(4)
C(6)	7962(4)	902(12)	−1572(9)	55(5)
C(7)	7529(4)	759(13)	−450(10)	66(5)
C(8)	7444(3)	2252(17)	543(9)	57(5)
S(1)	9454(1)	2142(3)	1086(2)	40(0)
C(9)	9603(3)	4205(10)	2245(10)	55(4)
S(2)	10396(1)	4816(4)	2661(3)	77(1)
C(10)	10685(4)	2885(13)	3814(10)	79(6)
C(11)	10573(3)	1125(12)	2918(10)	66(5)
C(12)	9892(3)	622(10)	2547(9)	50(4)
Complex II				
Cr	2307(1)	7903(2)	1923(2)	35(0)
C(1)	2868(8)	7865(12)	4475(17)	52(6)
O(1)	3261(6)	7791(10)	6143(12)	80(6)
C(2)	3696(8)	8109(11)	1575(13)	41(6)
O(2)	4574(5)	8178(9)	1406(11)	74(5)
C(3)	763(7)	7955(11)	−69(14)	40(5)
C(4)	1392(8)	7407(11)	−1132(14)	43(6)
C(5)	1787(8)	6199(11)	−498(15)	48(6)
C(6)	1523(8)	5489(11)	1151(16)	50(6)
C(7)	993(7)	6061(10)	2289(15)	41(5)
C(8)	518(7)	7291(10)	1649(13)	32(5)
C(9)	−166(7)	7906(12)	2675(15)	41(6)
O(3)	−466(5)	8979(8)	2228(10)	53(4)
O(4)	−420(5)	7092(7)	4172(10)	56(4)
C(10)	−1114(9)	7608(13)	5201(17)	68(7)
S(1)	2602(2)	10513(3)	2184(4)	43(1)
C(11)	2973(8)	11228(9)	−59(13)	41(6)
S(2)	3303(3)	13210(3)	−61(5)	70(2)
C(12)	4471(8)	13695(12)	1919(16)	59(7)
C(13)	4233(8)	13154(10)	3907(15)	45(6)
C(14)	3897(8)	11422(11)	3842(14)	55(6)

TABLE 3

BOND LENGTHS (Å) (with e.s.d.'s) FOR THE NON-HYDROGEN ATOMS FOR I AND II

Bond	Lenghts	
	I	II
C(1)–Cr	1.816(6)	1.788(11)
C(2)–Cr	1.817(8)	1.830(9)
C(3)–Cr	2.187(7)	2.204(8)
C(4)–Cr	2.214(7)	2 195(9)
C(5)–Cr	2.205(6)	2.172(9)
C(6)–Cr	2.205(6)	2.203(9)
C(7)–Cr	2.156(6)	2.171(8)
C(8)–Cr	2.154(7)	2.203(8)
S(1)–Cr	2.355(2)	2.346(3)
O(1)–C(1)	1.162(6)	1.183(10)
O(2)–C(2)	1.167(7)	1.156(9)
C(3)–C(4)	1.369(9)	1.397(11)
C(3)–C(8)	1.389(10)	1.412(11)
C(4)–C(5)	1.384(9)	1.394(11)
C(5)–C(6)	1.345(9)	1.394(12)
C(6)–C(7)	1.431(10)	1.404(11)
C(7)–C(8)	1.406(10)	1.427(10)
S(1)–C(9)	1.807(6)	
S(2)–C(9)	1.785(6)	
S(1)–C(12)	1.818(6)	
S(2)–C(10)	1.782(8)	
C(10)–C(11)	1.500(9)	
C(11)–C(12)	1.529(8)	
C(8)–C(9)		1.472(11)
O(3)–C(9)		1.186(9)
O(4)–C(9)		1.342(9)
O(4)–C(10)		1.436(10)
S(1)–C(11)		1 817(8)
S(2)–C(11)		1.771(8)
S(1)–C(14)		1.812(9)
S(2)–C(12)		1.779(9)
C(12)–C(13)		1.548(12)
C(13)–C(14)		1.544(11)

are listed in Tables 2 to 4. Ortep drawings of I and II as viewed along the Cr–arene bond perpendicular to the benzene rings are shown in Fig. 1.

Some of the relevant bond lengths and infrared data for the complexes [Cr(η^6-(C_6H_5COOMe)$(CO)_2L$] (L = CS, CSe, CO, PPh_3, $CNBu^t$ and $\overline{S(CH_2)_3SCH_2}$) are tabulated in Table 5. Tables of thermal parameters and structure factors may be obtained from the authors.

Results and discussion

A feature relating to the geometry of these structures is that the dithiane ligand in II is in a near eclipsed position in relation to the arene carbon atoms but in a staggered conformation in relation to the arene carbon atoms in I. In the case of II

TABLE 4

BOND ANGLES (°) (with e.s.d.'s) FOR THE NON-HYDROGEN ATOMS

Atoms	Angles	
	I	II
C(2)–Cr–C(1)	86.7(3)	86.3(4)
S(1)–Cr–C(1)	93.0(2)	92.3(3)
S(1)–Cr–C(2)	91.6(2)	91.8(3)
S(1)–Cr–C(3)	115.4(3)	83.0(2)
S(1)–Cr–C(4)	88.4(2)	99.6(3)
S(1)–Cr–C(5)	87.1(2)	134.7(3)
S(1)–Cr–C(6)	111.9(2)	161.9(2)
S(1)–Cr–C(7)	150.2(2)	131.6(2)
S(1)–Cr–C(8)	152.6(3)	96.7(2)
O(1)–C(1)–Cr	178.6(5)	177.0(9)
O(2)–C(2)–Cr	177.3(7)	176.6(9)
C(4)–C(3)–Cr	72.9(4)	71.2(5)
C(8)–C(3)–Cr	70.0(4)	71.3(5)
C(8)–C(3)–C(4)	120.0(8)	120.5(9)
C(3)–C(4)–Cr	70.8(4)	71.8(5)
C(5)–C(4)–Cr	71.4(4)	70.5(5)
C(5)–C(4)–C(3)	120.4(7)	120.1(9)
C(4)–C(5)–Cr	72.1(4)	72.3(5)
C(6)–C(5)–Cr	72.3(4)	72.7(6)
C(6)–C(5)–C(4)	121.8(7)	120.5(9)
C(5)–C(6)–Cr	72.2(4)	70.2(5)
C(7)–C(6)–Cr	69.0(4)	70.0(5)
C(7)–C(6)–C(5)	119.3(7)	120.2(9)
C(6)–C(7)–Cr	72.7(4)	72.5(5)
C(8)–C(7)–Cr	70.9(4)	72.2(5)
C(8)–C(7)–C(6)	118.7(7)	119.5(8)
C(3)–C(8)–Cr	72.7(4)	71.3(5)
C(7)–C(8)–Cr	71.0(4)	69.7(5)
C(7)–C(8)–C(3)	119.9(7)	118.9(8)
C(9)–S(1)–Cr	107.2(2)	
C(12)–S(1)–Cr	109.1(2)	
C(12)–S(1)–C(9)	97.8(3)	
S(2)–C(9)–S(1)	114.3(4)	
C(10)–S(2)–C(9)	99.2(4)	
C(11)–C(10)–S(2)	114.4(5)	
C(12)–C(11)–C(10)	113.2(6)	
C(11)–C(12)–S(1)	112.9(5)	
C(9)–C(8)–Cr		131.4(6)
C(9)–C(8)–C(3)		117.6(8)
C(9)–C(8)–C(7)		123.5(8)
O(3)–C(9)–C(8)		124.4(9)
O(4)–C(9)–C(8)		111.6(8)
O(4)–C(9)–O(3)		124.0(9)
C(10)–O(4)–C(9)		114.4(7)
C(11)–S(1)–Cr		107.3(3)
C(14)–S(1)–Cr		110.9(3)
C(14)–S(1)–C(11)		97.4(4)
S(2)–C(11)–S(1)		113.5(5)
C(12)–S(2)–C(11)		99.4(5)
C(13)–C(12)–S(2)		114.2(6)
C(14)–C(13)–C(12)		110.3(7)
C(13)–C(14)–S(1)		114.6(7)

the dithiane ligand is *ortho* to the ester group and has moved slightly towards the ester group whereas in the case of $L = PF_3$ the ligand has moved away from the ester group [6]. The torsion angle described by S(1)–Cr–X–C(8) (X = centre of arene ring) is −57.2°. The same phenomenon has been observed for $L = CNBu^t$ [8], although the movement in that case is much larger.

The arene ring in II is more puckered than in I as indicated by the deviation from planarity (C(5), C(6), C(7): −0.009, 0.011, −0.006 Å in I; −0.017, 0.029, −0.023 Å in II), with C(6) bending towards and C(5) and C(7) bending away from the Cr atom, as could be expected.

Although the distance from the Cr atom to the mean plane of the arene ring (Table 5) is somewhat shorter than that found for L = CS and L = CO [3,4], the average Cr–C(arene) distances do not differ significantly for $L = CNBu^t$, PPh_3 and $\overline{S(CH_2)_3SCH_2}$ [7,8]. The Cr–C(arene) distances seem to be insensitive to variation of the substituent R on the arene ring, the average Cr–C(arene) distance being 2.189(9) Å in I and 2.191(9) Å in II.

There are significant differences in both Cr–C and C–O bond lengths in II, whereas these distances are almost identical in I. Although Cr–C(1) is the shorter Cr–C(O) bond (1.788(11) Å) (II) and C(1)–O(1) the longer C–O bond (1.183(10) Å), the Cr–O(1) and Cr–O(2) distances are almost identical at 2.970 and 2.985 Å respectively (2.978 and 2.983 Å for I).

The effects of varying the ligand L in complexes of the type $[Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2L]$ on the Cr–C(O) distances, bond angles and $\nu(CO)$ frequencies are given in Table 5. Substitution of a carbonyl by a weaker π-acceptor ligand gives rise to the shortening of the Cr–C(O) distance. A clear trend is the shortening of Cr–C(O) distances in the order CS, CO > $CNBu^t$ > PPh_3 > $\overline{S(CH_2)_3SCH_2}$. This correlates well with the infrared frequencies observed and is in accordance with the accepted bonding properties of these ligands [17]. An interesting aspect of distortions around the $Cr(CO)_2\{\overline{S(CH_2)_3SCH_2}\}$-tripod in I and II is the S–Cr–C(O)

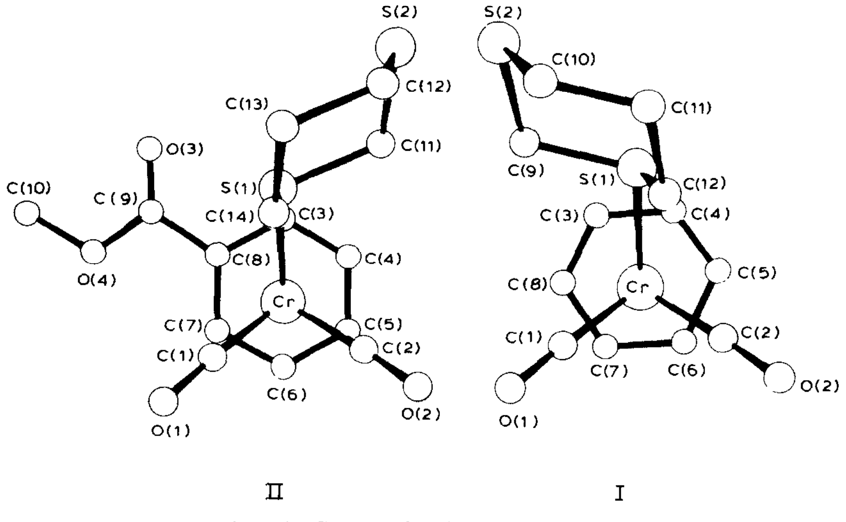

Fig. 1. I and II viewed along the Cr–arene bond perpendicular to the arene rings.

TABLE 5

BOND LENGTHS (Å), BOND ANGLES (°) AND CARBONYL FREQUENCIES (cm^{-1}) FOR SELECTED COMPLEXES: $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2L$

	Ligand L				
	CS	CO	$CNBu^t$	PPh_3	$S(CH_2)_3SCH_2$
Bond lengths					
Cr–C(arene)	2.226(3)	2.217(3)	2.204(5)	2.198(4)	2.191(9)
Cr–Mean plane (arene)	1.730(1)	1.714(1)	1.697(1)	1.695(1)	1.682(9)
Cr–C(O) [a]	1.849(3)	1.849(3)	1.833(4)	1.824(4)	1.809(11)
Bond angles					
(O)C–Cr–C(O)	90.8(1)	88.1 [a](1)	86.2(2)	85.3(1)	86.3(4)
(O)C–Cr–L [a]	85.7(1)	88.1(1)	90.5(2)	90.1(1)	92.0(3)
Ref.	4	3	8	7	
Infrared [b]					
ν(CO) [c]	1991	1994	1924	1923	1917
	1939	1928	1872	1871	1862
			(1708)		(1730)
ν(CO) [d]	1980	1978	1908		1883
	1935	1898	1856		1862
	(1720)		(1700)		(1689)
Ref.	4	21	8	4	10

[a] Average. [b] Values for COOMe are given below those for CO ligands in brackets. [c] Measured in CCl_4. [d] Measured on polycrystalline material (KBr).

angles which are significantly greater than 90° (91.6 and 93.0° for I; 91.8 and 92.3° for II).

The Cr–S bond distance of 2.355(2) and 2.346(3) Å (I and II respectively) are significantly shorter than those found for $[Cr(CO)_5\{S(Et)CH_2Ph\}]$ (2.459(2) Å) and $[Cr(CO)_4\{S(Et)CH_2CH_2SEt\}]$ (2.452(1) and 2.412(1) Å) [17,18]. These distances are consistent with the greater degree of carbonyl substitution and a stronger *trans* influence exerted by the arene ligand, resulting in increased π-interaction within the Cr–S bond. The puckering parameters calculated for the dithiane rings as described by Cremer and Pople [19] are as follows: θ 174.0 and 5.7°, ϕ 221.3 and 55.4° and Q 0.72 and 0.74 Å for I and II, respectively. This indicates that both dithiane rings have almost exclusively chair conformations but are less puckered on coordination than found in $[Fe(CO)_4\{\overline{S(CH_2)_3SCH_2}\}]$ [20].

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