Acta Cryst. (1980). B**36**, 2054–2059

The Structures of (η^{12}-[3.3]Paracyclophane)chromium(I) Triiodide and Hexafluorophosphate

BY N. E. BLANK AND M. W. HAENEL

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, *D*-4330 *Mülheim a.d. Ruhr, Federal Republic of Germany*

AND A. R. KORAY, K. WEIDENHAMMER AND M. L. ZIEGLER*

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, *D*-6900 *Heidelberg, Federal Republic of Germany*

(*Received* 1 *December* 1979; *accepted* 24 *March* 1980)

Abstract

The crystal structures of (η^{12}-[3.3]paracyclophane)-chromium(I) triiodide (I) [$C_{18}H_{20}Cr^+.I_3^-$, monoclinic, $P2_1/c$, a = 7·482 (2), b = 7·642 (2), c = 16·701 (3) Å, β = 102·90 (2)°, Z = 2] and the hexafluorophosphate (II) [$C_{18}H_{20}Cr^+.PF_6^-$, tetragonal, $P4/mbm$, a = b = 11·385 (4), c = 6·580 (3) Å, Z = 2] have been determined. The final R values are 0·057 and 0·083 for (I) and (II) respectively. The [3.3]paracyclophane cations in (I) and (II) show the two benzene rings in the eclipsed configuration.

Introduction

Cyclophane chemistry has been a matter of wide interest during the last two decades. It is therefore not surprising that, in view of the existence of dibenzene-chromium and related compounds, efforts have been made to place a metal atom inside cyclophane skeletons. It was not until recently (Elschenbroich, Möckel & Zenneck, 1978) that the synthesis of (η^{12}-[2.2]paracyclophane)chromium(0) (III) and (η^{12}-[3.3]paracyclophane)chromium(0) (IV) (Koray, Ziegler, Blank & Haenel, 1979; Benn, Blank, Haenel, Klein, Koray, Weidenhammer & Ziegler, 1980) as the first species of this class was reported. (IV) is extremely air-sensitive in solution so that a characterization by means of X-ray analysis was impossible; the same seems to be the case with (III). Contrarily, the I_3^- (I) and PF_6^- (II) salts of (η^{12}-[3.3]paracyclophane)-chromium(I) are air-stable (Koray, Ziegler, Blank & Haenel, 1979) and it was for this reason that we determined the crystal and molecular structures of (I) and (II). In addition, such questions as how does the cyclophane skeleton change when a metal atom is incorporated or how bent will the benzene rings be were of interest to us.

Rotation and Weissenberg photographs (Cu $K\alpha$ radiation) showed the crystals to be monoclinic (I) and tetragonal (II) and provided rough lattice constants. Exact lattice parameters were calculated by least squares (Berdesinski & Nuber, 1966) from diffractometrically determined θ values of 60 (I) and 36 (II) selected reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (AED, Mo $K\alpha$, θ–2θ scans, five-value method). Reflections with $I < 2{\cdot}568\sigma(I)$ were not considered. 1511 (I) and 273 (II) independent intensities remained for calculation. These were corrected for Lorentz and polarization factors. Absorption corrections were omitted, the size of the

Table 1. *Crystal data of* (I) *and* (II)

	$C_{18}H_{20}Cr^+.I_3^-$ (I)	$C_{18}H_{20}Cr^+.PF_6^-$ (II)
a (Å)	7·482 (2)	11·385 (4)
b (Å)	7·642 (2)	11·385 (4)
c (Å)	16·701 (3)	6·580 (3)
β (°)	102·90 (2)	
d_o (Mg m^{-3})	2·54	1·74
d_c	2·493	1·687
Z	2	2
V (Å^3)	930·82	852·89
M_r	699·07	433·32
F(000)	410	306
Independent intensities	1511	273
$2\theta_{max}$, $2\theta_{min}$ (°)	$59{\cdot}87 \geq 2\theta \geq 5{\cdot}00$	$61{\cdot}45 \geq 2\theta \geq 5{\cdot}06$
μ(Mo $K\alpha$) (mm^{-1})	5·6645	0·8602
Space group	$P2_1/c$	$P4/mbm$
λ(Mo $K\alpha$) (Å)	0·7107	0·7107
Systematic absences	$0k0$: $k = 2n + 1$ $h0l$: $l = 2n + 1$	$0kl$: $k = 2n + 1$
Crystal size (mm)	0·2 × 0·2 × 0·3	0·1 × 0·2 × 0·4
R_{iso}	0·104	0·112
R_{aniso}	0·057	0·083

---

* To whom correspondence should be addressed.

0567-7408/80/092054-06$01.00

crystals used for intensity measurements being smaller than the optimum thickness [t_{opt}(I) = 0·35 mm, t_{opt}(II) = 2·33 mm]. The crystal data for both compounds are listed in Table 1.

Since (I) has $Z = 2$, the $C_{18}H_{20}Cr^+$ cation and the I_3^- anion have to be centrosymmetric. The structure was solved by Patterson and Fourier syntheses. Refinement with isotropic and anisotropic temperature factors resulted in $R = 0{\cdot}104$ and $R = 0{\cdot}057$ respectively. A difference map allowed the location of all H atoms. Their coordinates were refined independently with one constant thermal parameter for all (U = 7·1 Å^2).* Table 2 shows the atomic coordinates. Bond and other distances and bond angles of (I) are given in Figs. 1, 2 and 3; the packing of the unit cell is shown in Fig. 4.

(II) also has $Z = 2$ for the tetragonal unit cell. As the general equivalent positions are 16-fold, the Cr, P, F, one ring C, and the methylene C atoms have to occupy special positions. For the last the special positions are eightfold, which means that for the central methylene C atom there are eight positions but only four C atoms, *i.e.* this C atom is statistically distributed. Only the second ring C atom occupies a general equivalent position.

The two other possible space groups (noncentrosymmetric, $P\bar{4}b2$ and $P4bm$) could be excluded by statistical tests (Stewart, Kundell & Baldwin, 1970) and by the course of the structure determination. All non-hydrogen atoms were determined from Patterson and Fourier syntheses and refined with anisotropic

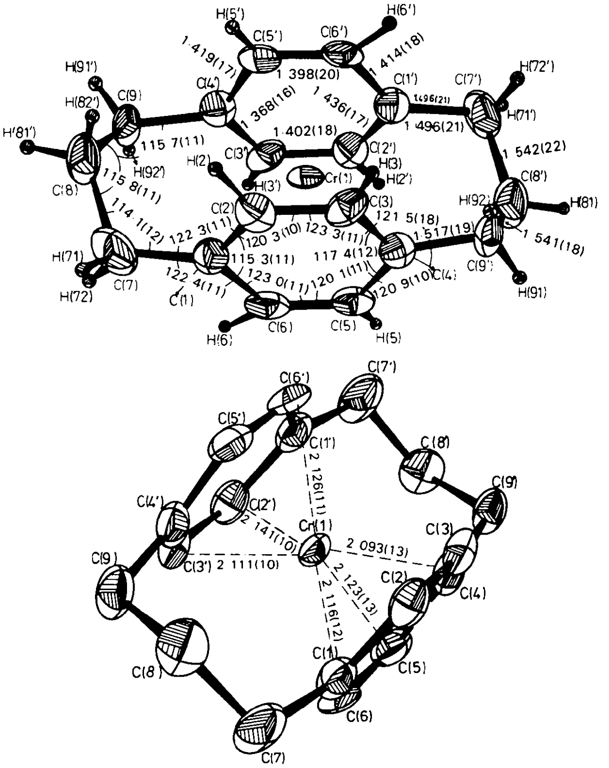

Fig. 1. *ORTEP* drawings (Johnson, 1965) of the cation of (I) with the atom numbering, bond angles (°) and bond distances (Å). 50% probability ellipsoids are displayed.

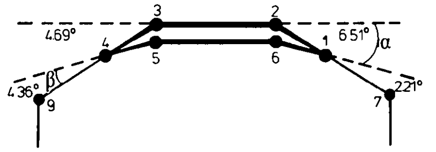

Fig. 2. Out-of-plane distortion of the aromatic rings.

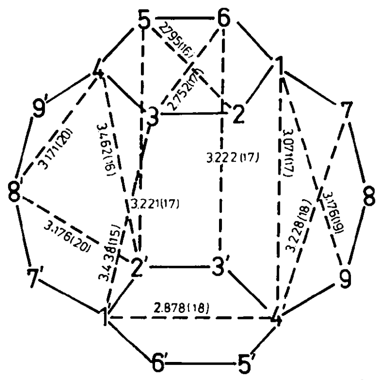

Fig. 3. Non-bonded intramolecular contacts (Å) in (I).

Table 2. *Final atomic fractional coordinates of* (I) *for the* I ($\times 10^5$), Cr, C ($\times 10^4$) *and* H ($\times 10^3$) *atoms*

	x	*y*	*z*
I(1)	377 (16)	91350 (16)	93049 (7)
I(2)	0	0	0
Cr	$\frac{1}{2}$	0	$\frac{1}{2}$
C(1)	4083 (15)	2250 (16)	4288 (7)
C(2)	2637 (15)	975 (17)	4148 (7)
C(3)	2119 (14)	160 (17)	4813 (7)
C(4)	2911 (15)	529 (16)	5615 (7)
C(5)	4198 (16)	1920 (15)	5770 (8)
C(6)	4735 (17)	2753 (15)	5116 (9)
C(7)	4900 (20)	2934 (19)	3609 (9)
C(8)	5763 (20)	1513 (21)	3160 (8)
C(9)	7451 (16)	591 (19)	3689 (7)
H(2)	197 (19)	56 (19)	354 (9)
H(3)	167 (19)	−68 (19)	476 (9)
H(5)	479 (19)	215 (19)	622 (8)
H(6)	626 (19)	361 (19)	519 (9)
H(71)	388 (19)	342 (20)	321 (9)
H(72)	620 (19)	384 (19)	376 (9)
H(81)	632 (20)	183 (20)	275 (9)
H(82)	477 (20)	66 (20)	289 (9)
H(91)	780 (19)	8 (22)	332 (9)
H(92)	798 (20)	103 (20)	390 (9)

---

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35291 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters to $R = 0·083$.* We were not able to locate the H atoms either from difference maps or with the help of a model. The atomic coordinates of (II) are listed in Table 3; bond and other distances and angles are shown in Fig. 5 and Table 4.

All calculations were performed on Siemens 301 (Anorganisch-Chemisches Institut, Heidelberg) and IBM 370/168 (Rechenzentrum der Universität Heidelberg) computers with local versions of XRAY 70 (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964). The atom numbering corresponds to that in the figures.

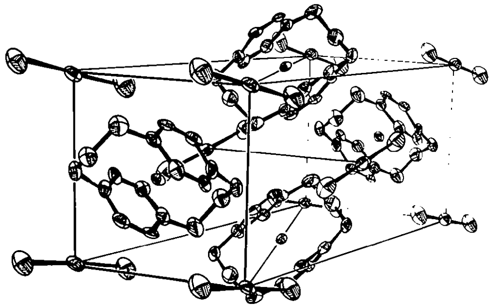

Fig. 4. Packing of the unit cell of (I).

Table 3. *Final atomic fractional coordinates* (×10⁴) *of* (II)

	x	y	z
Cr	0	½	½
P	0	0	0
F(1)	0	0	2186 (31)
F(2)	1219 (10)	529 (11)	0
C(1)	5831 (18)	831 (18)	2657 (28)
C(2)	4690 (8)	1197 (8)	2583 (17)
C(3)	6822 (18)	1822 (18)	3027 (25)
C(4)	7556 (28)	1643 (28)	½

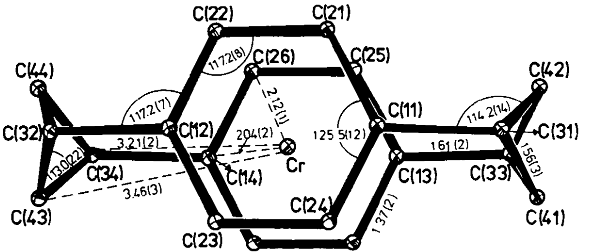

Fig. 5. *ORTEP* drawing of the cation of (II) with the atom numbering, bond angles (°) and bond distances (Å).

Discussion

In Fig. 1 an *ORTEP* plot of the cation $C_{18}H_{20}Cr^{+}$ of (I) is given. Some closest intermolecular approaches between the cations and the I_3^{-} anions are depicted in Table 5 and Fig. 6.

The shortest intermolecular C···C distance is 3·4 Å; the shortest C···H and H···H contacts are 3·0 and 2·9 Å respectively, which correspond approximately to the sums of the van der Waals radii. The geometry of the cation is shown in Figs. 1, 2, 3 and 4. Bonding parameters concerning the H atoms are listed in Table 6.

As in the uncomplexed ligand, [3.3]paracyclophane (V), the aromatic rings are bent out of the planar conformation but the deformation angle α (Fig. 2) is less than in (V) (6·4°). Gantzel & Trueblood (1965) consider that in (V) the difference in β at the two ends of the molecule is due to the parallel displacement of

Table 5. *Some contact distances* (Å) *in* (I)

I(2)–C(1)	4·10 (1)	I(1)–C(1)	4·16 (1)
–C(2)	4·08 (1)	–C(2)	4·14 (1)
–C(3)	4·06 (1)	–C(3)	4·22 (1)
–C(4)	4·06 (1)	–C(4)	4·18 (1)
–C(5)	3·91 (1)	–C(5)	4·18 (1)
–C(6)	3·90 (1)	–C(6)	4·33 (1)
–C(7)	4·30 (1)	–C(7)	4·50 (1)
–C(9)	4·23 (1)	–C(9)	4·21 (1)

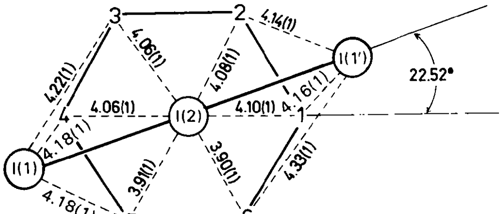

Fig. 6. Contact distances (Å) between the I_3^{-} anion and the benzene rings in (I).

Table 4. *Bond lengths* (Å) *and angles* (°) *of* (II)

Atoms C(11)–C(14), C(21)–C(28), C(31)–C(34), and C(41)–C(42) (Fig. 5) are crystallographically equivalent.

Cr–C(14)	2·04 (2)	P–F(1)	1·44 (2)	C(13)–C(28)	1·37 (2)	C(11)–C(13)	3·08 (3)	C(31)–C(41)	1·56 (3)
Cr–C(26)	2·12 (1)	P–F(2)	1·51 (1)	C(13)–C(33)	1·61 (2)	C(27)–C(28)	1·43 (1)		

C(3)–C(1)–C(2)	117·2 (7)	F(1)–P–F(1)	180·0	F(1)–P–F(2)	90·0	F(2)–P–F(2)	180·0 and 90·0
C(2)–C(1)–C(2)	125·5 (12)	C(21)–C(22)–C(12)	117·2 (8)	C(11)–C(31)–C(42)	114·2 (14)		

---

* See previous footnote.

Table 6. *Bond distances* (Å) *and angles* (°) *involving* H *atoms in* (I)

C(2)–H(2)	1·08 (14)	C(7)–H(71)	0·97 (13)	C(9)–H(91)	0·82 (16)
C(3)–H(3)	0·72 (15)	–H(72)	1·18 (14)	–H(92)	0·57 (14)
C(5)–H(5)	0·80 (13)	C(8)–H(81)	0·91 (16)		
C(6)–H(6)	1·30 (15)	–H(82)	1·01 (14)		
C(1)–C(2)–H(2)	122 (8)	C(2)–C(3)–H(3)	120 (12)	C(4)–C(5)–H(5)	123 (11)
C(3)–C(2)–H(2)	118 (8)	C(4)–C(3)–H(3)	113 (11)	C(6)–C(5)–H(5)	116 (11)
C(5)–C(6)–H(6)	124 (6)	H(71)–C(7)–H(72)	114 (11)	H(91)–C(9)–H(92)	116 (19)
C(1)–C(6)–H(6)	110 (7)	H(81)–C(8)–H(82)	105 (12)	H(91)–C(9)–C(4)	116 (12)
H(92)–C(9)–C(4)	95 (16)	H(81)–C(8)–C(9)	96 (9)	H(91)–C(9)–C(8)	99 (10)
H(92)–C(9)–C(8)	117 (15)	H(81)–C(8)–C(7)	119 (10)	H(82)–C(8)–C(9)	113 (8)
H(71)–C(7)–C(1)	106 (9)	H(71)–C(7)–C(8)	106 (9)	H(82)–C(8)–C(7)	109 (9)
H(72)–C(7)–C(1)	120 (7)	H(72)–C(7)–C(8)	96 (8)		

the two benzene rings. For (I) not only differences in β but also differences in α are observed (Fig. 2). As the parallel displacement of the rings in (I) lies within the borderline of significance we are not sure if differences in α or β can be traced to parallel displacement. The C—C—C angle at C(9) in (I) is about 2·0° larger than at C(7), a fact which in (V) (115·9 and 113·6°) has been related to the displacement of the rings too. For electronic reasons, in (I) the aromatic rings are almost ideally eclipsed.

The dihedral angles C(4′)C(9)C(8)/C(7)C(8)C(9) and C(1)C(7)C(8)/C(7)C(8)C(9) are 57·0 and 66·6° [(V): 65, 70°] respectively (Table 7), so that as in (V) the conformation of the trimethylene bridges is similar to that in *gauche-n*-butane, the angles there being 63° (Bonham & Bartell, 1959).

The aromatic rings are folded about the C(1)—C(4) axis (see Fig. 1*a* for bond angles) and, as mentioned above, C(1) and C(4) are bent towards the Cr atom. The latter is true also for the ring H atoms (Table 7), their average deviation from the C(2)C(3)C(5)C(6) plane being 0·10 Å. As in (V) (0·08 Å), this slight displacement is just significant. The explanation that in (V) this displacement is due to repulsion between π electrons and C—H bonding electrons (Gantzel & Trueblood, 1965) also seems acceptable for (I), though it might only be a consequence of the torsion about the ring C—C bonds to C(1) and C(4) (Gantzel & Trueblood, 1965). The latter explanation is consistent with the observation that the deformation angle α and the displacement of the ring H atoms in (I) and (V) is about the same.

The average aromatic bond distance in (I) is 1·406 (19) Å, which is within 1σ of the corresponding value in (V) [1·389 (1) Å].

The bonding parameters of the trimethylene bridges do not show any peculiarities: they are within 1σ in good agreement with (V) and other related distances. This is valid for the distances between tetrahedral as well as for those between tetrahedral and trigonal C atoms. The distances of the Cr atom from the planes *P*1 and *P*2 (Table 7) are 1·58 and 1·61 Å respectively, *i.e.* the distance between the two aromatic rings (3·16 and 3·22 Å) is comparable to the values found in dibenzenechromium (Förster, Albrecht, Dürselen & Kurras, 1969), dibenzenechromium iodide (3·18 Å; Morosin, 1974) and in the free ligand (V). In the latter, the distances between the two aromatic rings are about 3·10 Å (involving all six C atoms) and 3·266 Å (involving only the four C atoms to which the H atoms are attached). As in (V), the aromatic rings are closer than in ferrocene (3·34 Å) but are more distant than in ditoluenechromium iodide (3·06 Å; Starovskii & Struchkov, 1961). A discussion of the H atom parameters does not seem reasonable in view of the relatively high e.s.d.'s; they are, nevertheless, in the range of known values (Table 6).

The counterion to $C_{18}H_{20}Cr^+$ is a discrete symmetric I_3^- anion. The central I(2) occupies a centre of symmetry; therefore, the bond angle in the I_3^- unit has to be 180°. The I—I lengths are 2·913 (1) Å, which is consistent with those reported elsewhere (Nolte, Singleton & van der Stock, 1978, and references therein). The angle between the plane *P*2 [C(2), C(3), C(5), C(6); Table 7] and the line I(1)—I(2)—I(1′) is 1·60°, the perpendicular distance of I(2) from that plane being 3·73 Å (Table 7). A similar distance (3·69 Å) is found in 5,10-diethyl-5,10-dihydrophenazinium triiodide (Keller, Moroni, Nöthe, Scherz & Weiss, 1978). The packing in the unit cell is shown in Fig. 4.

The Cr atom and the two central I(2) atoms of the I_3^- units which are situated above and below the aromatic rings of the $C_{18}H_{20}Cr^+$ cation form a line which is almost perpendicular (87·0°) to the plane of the aromatic C atoms. The arrangement of the I_3^- unit relative to the benzene rings is given schematically in Fig. 6.

As can be seen from the e.s.d.'s (Table 3), the structure determination of the PF_6^- salt (II) is less accurate than that of (I). This is mainly due to the poor quality of the crystals and to the low number of observed reflections (273), but possibly also to the

Table 7. *Least-squares planes and lines in* (I) *with displacements of atoms from the planes* (Å) *in parentheses*; *e.s.d.'s are in square brackets*

*P*1: C(1) (−0·05) [0·04], C(2) (0·03), C(3) (0·02), C(4) (−0·04), C(5) (0·02), C(6) (0·03)
*P*2: C(2) (0·001) [0·0007], C(3) (−0·001), C(5) (0·001), C(6) (−0·001)
*P*3: C(1), C(2), C(6)
*P*4: C(3), C(4), C(5)
*P*5: C(7), C(8), C(9)
*P*6: C(1) (0·000) [0·0003], C(4) (0·000), C(1′) (0·000), C(4′) (0·000)
*P*7: H(2) (0·04) [0·06], H(3) (−0·05), H(5) (0·06), C(6) (−0·05)
*P*8: C(4) (−0·003) [0·01], C(5) (0·005), C(6) (−0·006), C(1) (0·003)
*P*9: C(4) (−0·003) [0·005], C(3) (0·005), C(2) (−0·005), C(1) (0·002)
*P*10: C(4′), C(9), C(8)
*P*11: C(1), C(7), C(8)
*P*12: C(2) (0·001) [0·001], C(5) (−0·001), C(2′) (0·001), C(5′) (−0·001)
*L*1: I(1), I(2), I(1′)
*L*2: C(4′), C(9)
*L*3: C(1), C(7)
*L*4: I(2), Cr
*L*5: C(1), C(4)
*L*6: C(2), C(5)

Distances (Å) of some atoms from the least-squares planes (approximate e.s.d.'s: *Pn*—I and *Pn*—Cr 0·01–0·02 Å, *Pn*—C 0·02 Å, *Pn*—H 0·1–0·2 Å)

*P*1—Cr	−1·58	*P*1—I(2)	3·76	*P*2—C(1)	−0·09
*P*2—Cr	−1·61	*P*2—I(2)	3·73	*P*2—C(4)	−0·06
*P*3—Cr	−1·68				
*P*2—H(2)	−0·02	*P*2—H(3)	−0·16	*P*2—H(5)	−0·07
*P*2—H(6)	−0·15				

Angles between planes and lines respectively (°); that is the acute angle between the planes; for a plane and a line the angle is to the normal of the plane [approximate e.s.d.'s: *P*(carbon)/*P*(carbon) 1–2°, *P*(carbon)/*P*(hydrogen) 5–10°].

*P*1/*P*2	0·4	*P*1/*P*3	6·1	*P*2/*P*3	6·5	*P*1/*P*4	5·1
*P*2/*P*4	4·7	*P*3/*P*4	11·2	*P*5/*P*1	89·8	*P*5/*P*2	89·5
*P*5/*P*3	85·0	*P*5/*P*4	85·5	*P*6/*P*1	89·7	*P*6/*P*2	89·7
*P*6/*P*3	89·7	*P*6/*P*4	89·7	*P*6/*P*5	58·3	*P*7/*P*1	1·5
*P*7/*P*2	1·2	*P*7/*P*3	7·6	*P*7/*P*4	3·7	*P*7/*P*5	88·8
*P*7/*P*6	89·3	*P*8/*P*2	3·4	*P*8/*P*7	4·1	*P*5/*P*10	57·0
*L*3/*P*4	76·6	*L*3/*L*1	24·6	*L*3/*L*2	17·8	*P*5/*P*11	66·6
*L*4/*P*1	3·0	*L*4/*P*2	3·0	*L*4/*P*3	7·1	*L*4/*P*4	5·7
*L*1/*P*1	88·4	*L*1/*P*2	88·8	*L*1/*P*3	82·8	*L*1/*P*4	86·9
*L*2/*P*1	80·6	*L*2/*P*2	81·0	*L*2/*P*3	74·5	*L*2/*P*4	85·6
*L*2/*L*1	23·8	*L*3/*P*1	81·7	*L*3/*P*2	81·3	*L*3/*P*3	87·8
*L*4/*P*5	88·8	*L*4/*P*6	86·7				
*L*5/*L*6	60·4	*L*5/*L*1	22·6	*L*6/*L*1	37·8		

statistical distribution of the central C atoms of the trimethylene bridges.

Nevertheless, the cation $C_{18}H_{20}Cr^+$ of (II) shows in the main the same features as in (I). For crystallographic reasons the two aromatic rings in the cations have to be exactly eclipsed, *i.e.* there is no parallel displacement as in the free ligand (V).

Table 8. *Least-squares planes and lines in* (II) *with displacements of atoms from the planes* (Å) *in parentheses*; *e.s.d.'s are in square brackets*

*P*1: C(11) (−0·03) [0·03], C(21) (0·02), C(22) (0·02), C(12) (−0·03), C(23) (0·02), C(24) (0·02)
*P*2: C(21), C(22), C(23), C(24)
*P*3: C(11), C(21), C(24)
*P*4: C(12), C(22), C(23)
*P*5: C(31), C(41), C(33)
*P*6: C(11), C(12), C(13), C(14)
*P*7: C(32), C(44), C(34)
*P*8: C(11), C(21), C(22), C(12)
*P*9: C(11), C(24), C(23), C(12)
*P*10: C(11), C(31), C(41)
*P*11: C(13), C(33), C(41)
*P*12: C(21), C(23), C(25), C(27)
*L*2: C(11), C(31)
*L*3: C(12), C(32)
*L*5: C(11), C(12)
*L*6: C(21), C(23)

Distances (Å) of some atoms from the least-squares planes; e.s.d 's are in the range 0·01–0·02 Å

*P*1—Cr	−1·57	*P*2—Cr	−1·59	*P*2—C(11)	−0·05
*P*2—C(12)	−0·05	*P*3—Cr	−1·64	*P*2—C(31)	−0·304

Angles between planes and lines respectively (°); that is the acute angle between the planes; for a plane and a line the angle is to the normal of the plane; e.s.d.'s are in the range 1·0–1·5°.

*P*1/*P*2	0·0	*P*1/*P*3	4·5	*P*2/*P*3	4·5	*P*1/*P*4	4·5
*P*2/*P*4	4·5	*P*3/*P*4	8·9	*P*5/*P*1	90·0	*P*5/*P*2	90·0
*P*5/*P*3	86·2	*P*5/*P*4	86·2	*P*6/*P*1	90·0	*P*6/*P*2	90·0
*P*6/*P*3	90·0	*P*6/*P*4	90·0	*P*6/*P*5	58·6	*P*5/*P*7	0·1
*P*8/*P*2	2·3	*P*5/*P*10	68·2	*P*9/*P*11	60·9		
*L*2/*P*2	80·9			*L*2/*P*3	85·4	*L*2/*P*4	76·4
*L*3/*P*1	80·9	*L*3/*P*2	80·9	*L*3/*P*3	76·4	*L*3/*P*4	85·3
*L*3/*L*2	18·3	*L*5/*L*6	59·5				

There are no intermolecular C···H and C···C contacts shorter than the sum of the van der Waals radii. The same is true for C···F contacts, the shortest being 3·41 (1) Å [C(2)···F(2)]. H···F interactions cannot be discussed, as we were unable to locate the H atoms, but considerations based on a model show that the shortest H···F contacts between the ring H and the four equatorial F atoms must be about 2·5–2·8 Å. This is clearly shorter than the sum of the van der Waals radii, ranging from 3·15 to 3·30 Å (Bondi, 1964; Allinger, 1968). This strongly suggests H···F interactions and resembles to some extent the distorted PF_6^- anion in $NaPF_6.H_2O$ where 1·58 Å (F atoms having Na^+ neighbours) and 1·73 Å (F atoms having H_2O neighbours at 2·90 Å) were found (Bode & Teufer, 1956). The short H···F contact distances for the equatorial F atoms could possibly explain the different P—F distances: 1·51 (1) Å for the P—F_{eq} and 1·44 (2) Å for the two axial bonds, the F_{ax}···H contacts excluding van der Waals or hydrogen bonding. But it may be that the differences in the P—F lengths are only a consequence of the relatively inaccurate structure determination (P—F lengths are equal within 3σ).

As in (I) and (V), the ring C atoms to which the methylene bridges are bonded are bent towards the Cr atom (Table 8). Although the conformation of the [3.3]paracyclophane skeleton in (I) is unequivocally the chair conformation, in (II) owing to the statistical distribution of C(4) we cannot say whether we have the chair and/or the boat form.

The average C—C distance within the aromatic ring, 1·39 (2) Å, agrees with that found in (I) and (V). 2·07 (2) Å is the corresponding value for the Cr—C_{ring} distances, which is only within 2σ significantly shorter than the 2·12 (1) Å in (I). Table 8 shows the distance from the Cr atom to the least-squares planes $P1$ and $P2$ to be 1·57 and 1·59 Å respectively, which compare well with the parameters for (I) and (V).

References

Allinger, N. L. (1968). *J. Am. Chem. Soc.* **90**, 1199–1210.

Benn, R., Blank, N. E., Haenel, M. W., Klein, I., Koray, A. R., Weidenhammer, K. & Ziegler, M. L. (1980). *Angew. Chem.* **92**, 45–46.

Berdesinski, W. & Nuber, B. (1966). *Neues Jahrb. Mineral. Abh.* **104**, 113–146.

Bode, H. & Teufer, G. (1956). *Acta Cryst.* **9**, 825–826.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bonham, R. A. & Bartell, L. S. (1959). *J. Am. Chem. Soc.* **81**, 3491–3496.

Elschenbroich, Ch., Möckel, R. & Zenneck, U. (1978). *Angew. Chem.* **90**, 560.

Förster, E., Albrecht, G., Dürselen, W. & Kurras, E. (1969). *J. Organomet. Chem.* **19**, 215–217.

Gantzel, P. K. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 958–968.

Hanson, H., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Keller, H. J., Moroni, W., Nöthe, D., Scherz, M. & Weiss, J. (1978). *Z. Naturforsch. Teil B*, **33**, 838–842.

Koray, A. R., Ziegler, M. L., Blank, N. E. & Haenel, M. W. (1979). *Tetrahedron Lett.* pp. 2465–2466.

Morosin, B. (1974). *Acta Cryst.* B**30**, 838–839.

Nolte, M. J., Singleton, E. & van der Stock, E. (1978). *Acta Cryst.* B**34**, 1684–1687.

Starovskii, O. V. & Struchkov, Yu. T. (1961). *Zh. Strukt. Khim.* **2**, 162–172.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1980). B**36**, 2059–2063

The Structure of Tris(2,4-pentanedionato)indium(III)

By Gus J. Palenik and K. R. Dymock

Center for Molecular Structures, Department of Chemistry, University of Florida, Gainesville, Florida 32611, *USA*

(*Received* 19 *April* 1979; *accepted* 5 *March* 1980)

Abstract

The crystal and molecular structure of tris(2,4-pentanedionato)indium(III), or [In(acac)$_3$], has been determined by three-dimensional X-ray diffraction methods. Crystals of orthorhombic [In(acac)$_3$], [In($C_5H_7O_2$)$_3$], $C_{15}H_{21}InO_6$, space group $Pbca$, have unit-cell dimensions a = 15·576 (4), b = 13·724 (5) and c = 16·855 (5) Å. Since the compound is isomorphous with [Fe(acac)$_3$], the parameters for the latter compound were used as starting parameters for a least-squares refinement. The final R was 0·034 for the 1516 reflections used in the analysis. The average In—O distance is 2·132 (8) Å. The dimensions of the acac ligands are similar to those reported for other acac complexes. The O···O bite of 2·905 (8) Å is less than the O···O nonbonded contact of 3·053 (85) Å, the usual case in orthorhombic [M(acac)$_3$] complexes. Plots of M—O distance *versus* ligand bite, M—O distance *versus* ionic radius and M—O distance *versus* the O···O nonbonded distance are given. The best correlation of the M—O distance is with ionic radius, which is not surprising if the interactions between M and ligand are mainly electrostatic.

Introduction

Acetylacetone (acac) forms complexes with most metallic elements. The crystal structures of a number of acac complexes have been determined by X-ray diffraction techniques. The tris complexes of trivalent metal ions are usually octahedral species and fall into either of two isomorphous groups. The [M(acac)$_3$] complexes with M = Al (Hon & Pfluger, 1973), Co (Kruger & Reynhardt, 1974; Hon & Pfluger, 1973),

0567-7408/80/092059-05$01.00