Crystal data

$[Co(C_5H_7O_2)_2(NO_2)$-$(C_6H_7N)]$
M_r = 396.29
Orthorhombic
Pnma
a = 13.451 (3) Å
b = 14.746 (3) Å
c = 9.402 (3) Å
V = 1864.9 (8) Å^3
Z = 4
D_x = 1.411 Mg m^{-3}
D_m not measured

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 14.3–15.0°
μ = 0.953 mm^{-1}
T = 299 K
Needle
0.9 × 0.1 × 0.1 mm
Dark red

Data collection

Rigaku AFC-5 diffractometer
ω scans
Absorption correction: by integration (Coppens, Leiserowitz & Rabinovich, 1965)
$T_{\min}$ = 0.885, $T_{\max}$ = 0.926
2815 measured reflections
2815 independent reflections

1955 reflections with $|F_o| > 3\sigma(|F_o|)$
$\theta_{\max}$ = 30.0°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on *F*
R = 0.048
wR = 0.041
S = 1.20
1955 reflections
140 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\max}$ = 0.047
$\Delta\rho_{\max}$ = 0.66 e Å^{-3}
$\Delta\rho_{\min}$ = −0.47 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Co1	0.62470 (3)	1/4	0.60300 (4)	0.0308 (1)
O2	0.5457 (1)	0.1646 (1)	0.6993 (2)	0.0402 (5)
O3	0.7033 (1)	0.1645 (1)	0.5063 (2)	0.0410 (5)
O4	0.7464 (2)	0.3215 (1)	0.8068 (2)	0.0783 (8)
N5	0.7172 (2)	1/4	0.7565 (3)	0.0418 (9)
N6	0.5268 (2)	1/4	0.4427 (2)	0.0335 (8)
C7	0.5519 (2)	0.0790 (2)	0.6811 (2)	0.0468 (8)
C8	0.6191 (2)	0.0359 (1)	0.5935 (3)	0.0538 (8)
C9	0.6923 (2)	0.0789 (2)	0.5159 (3)	0.0464 (8)
C10	0.4775 (3)	0.0256 (2)	0.7670 (3)	0.071 (1)
C11	0.7671 (3)	0.0249 (2)	0.4336 (4)	0.081 (1)
C12	0.5560 (2)	1/4	0.3060 (3)	0.043 (1)
C13	0.4913 (3)	1/4	0.1932 (4)	0.053 (1)
C14	0.3913 (3)	1/4	0.2238 (4)	0.059 (1)
C15	0.3600 (3)	1/4	0.3616 (4)	0.060 (1)
C16	0.4294 (2)	1/4	0.4698 (4)	0.045 (1)
C17	0.5314 (5)	1/4	0.0411 (5)	0.097 (3)

Table 2. *Selected geometric parameters (Å, °)*

Co1—O2	1.880 (2)	Co1—N6	2.001 (3)
Co1—O3	1.880 (2)	O4—N5	1.220 (3)
Co1—N5	1.905 (3)		
O2—Co1—O2$^{\rm i}$	84.1 (1)	O3—Co1—N5	89.9 (1)
O2—Co1—O3	95.8 (1)	O3—Co1—N6	90.3 (2)
O2—Co1—O3$^{\rm i}$	179.8 (1)	N5—Co1—N6	179.6 (2)
O2—Co1—N5	90.2 (1)	Co1—N5—O4	120.2 (2)
O2—Co1—N6	89.5 (2)	O4—N5—O4$^{\rm i}$	119.5 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Positions of all H atoms were calculated geometrically and restrained to maintain the C—H distance at 0.96 Å.

Data collection: *AFC/MSC Diffractometer Control Software* (Rigaku Corporation, 1993). Cell refinement: *AFC/MSC Diffractometer Control Software*. Data reduction: local programs. Program(s) used to solve structure: *CRYSTAN-GM* (Edwards *et al.*, 1996). Program(s) used to refine structure: *CRYSTAN-GM*. Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1185). Services for accessing these data are described at the back of the journal.

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Structure of the Chromium(III) Salt $[Cp^*_2Cr]^+[Cp^*CrCl_3]^-$

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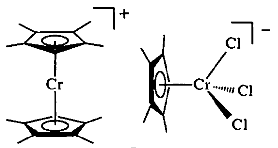
Abstract

The title compound, bis(η^5-pentamethylcyclopentadienyl)chromium(III) trichloro(η^5-pentamethylcyclopentadienyl)chromium(III), $[Cr(C_{10}H_{15})_2][CrCl_3(C_{10}H_{15})]$, is a salt consisting of discrete anionic $[\{\eta^5\text{-}C_5(CH_3)_5\}CrCl_3]^-$ and cationic $[\{\eta^5\text{-}C_5(CH_3)_5\}_2Cr]^+$ chromium(III) species. The anion adopts a 'three-legged piano-stool' structure, whereas the cation displays a

staggered orientation of the C_5 rings and approximates to D_{5d} local symmetry. The Cr—C distances range from 2.177 (5) to 2.208 (4) Å in the cation and from 2.234 (4) to 2.265 (5) Å in the anion; Cr—Cl distances in the anion fall in the range 2.320 (1)–2.331 (1) Å.

Comment

In the course of our work on the synthesis of inorganometallic clusters of chromium and molybdenum (Ho *et al.*, 1995; Aldridge, Fehlner & Shang, 1997), we have been using pentamethylcyclopentadienyl metal halides (such as $[Cp^*CrCl]_2$ and $[Cp^*MoCl_2]_2$; Cp* is pentamethylcyclopentadienyl) as the metal-containing precursors in highly selective routes to boron-rich species of the type M_2B_x (x = 3, 4 or 5). The reaction of one such cluster, $(Cp^*Cr)_2B_4H_8$, with reagents containing a B—Cl bond (*e.g.* $BHCl_2.SMe_2$, $BCl_3.SMe_2$ and $PhBCl_2$) has been investigated and shown to involve cluster degradation. In the case of the reaction with $PhBCl_2$, cluster breakdown was shown to proceed with regeneration of Cr—Cl bonds and the title compound, $[Cp^*_2Cr]^+[Cp^*CrCl_3]^-$, (I), was isolated in *ca* 50% yield.



(I)

The structure consists of discrete $[Cp^*_2Cr]^+$ and $[Cp^*CrCl_3]^-$ ions. The $[Cp^*_2Cr]^+$ cation displays a staggered orientation of the two Cp* rings, in contrast to the eclipsed conformation observed for the same cation in the salt $[Cp^*_2Cr]^+[TCNE]^-$ (Miller *et al.*, 1993), but similar to that found in the iron analogue $[Cp^*_2Fe]^+[TCNE]^-$ (Miller *et al.*, 1987) (TCNE is tetracyanoethenide). The mean Cr—C bond length [2.193 (5) Å] is similar to that found in the TCNE salt (2.197 Å), although the range of values is much narrower [2.177 (5)–2.208 (4) Å as opposed to 2.137–2.278 Å] for the staggered species. The differing conformational geometries are also reflected in the slightly shorter Cr–(ring centroid) distance for the title compound [1.83 (5) *versus* 1.87 Å]. Presumably the staggered orientation allows closer interaction of each ring with the metal centre. The Cr–(ring centroid) distance is only slightly different from that found for the chromium(II) species Cp^*_2Cr (1.797 Å; Bottomley *et al.*, 1991), reflecting the formal removal of a single electron from an essentially non-bonding e_{2g} orbital.

The anionic species $[Cp^*CrCl_3]^-$ represents a rare example of a crystallographically characterized $CpMX_3$ trihalide species (M = Cr, Mo or W) with a 'three-legged piano-stool' structure. Interestingly, the Cl—Cr—Cl angles (and Cr—Cl bond lengths) show little difference from those reported for $Li[CpCrCl_3]$ [91.3 (2)–95.7 (2)° and 2.211 (18)–2.322 (18) Å, respectively; Müller & Krausse, 1972], despite the greater steric demands of the permethylated Cp* ligand.

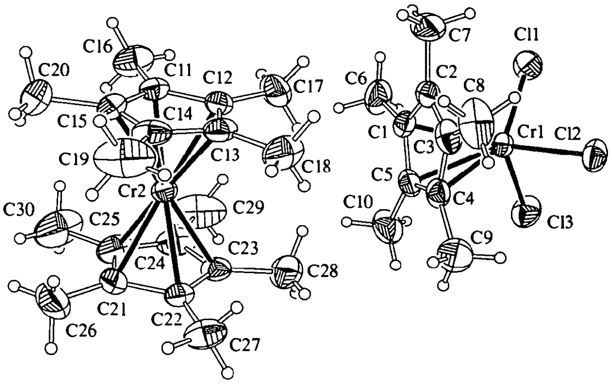


Fig. 1. The molecular structure of the title salt showing 40% probability displacement ellipsoids.

Experimental

Synthesis was carried out by the reaction of $(Cp^*Cr)_2B_4H_8$ and $PhBCl_2$ (molar ratio 1:1.2) in toluene solution for 72 h at 328 K under an argon atmosphere. The green precipitate so formed was separated from the supernatant, washed thoroughly with toluene and recrystallized by slow diffusion of hexane into a tetrahydrofuran solution.

Crystal data

$[Cr(C_{10}H_{15})_2][CrCl_3(C_{10}H_{15})]$
M_r = 616.01
Monoclinic
$P2_1/c$
a = 12.602 (2) Å
b = 13.0428 (10) Å
c = 19.074 (3) Å
β = 94.289 (7)°
V = 3126.4 (7) Å^3
Z = 4
D_x = 1.309 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13–14°
μ = 0.968 mm^{-1}
T = 293 (2) K
Bar
0.33 × 0.18 × 0.13 mm
Very dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.84, T_{max} = 0.88
5736 measured reflections
5480 independent reflections

4242 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = -22 \rightarrow 22$
3 standard reflections every 200 reflections intensity decay: 12.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 1.153$
5477 reflections
317 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 5.8729P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.290$ e Å^{-3}
$\Delta\rho_{\min} = -0.256$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0002 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cr1—C4	2.234 (4)	Cr1—Cl1	2.3308 (14)
Cr1—C1	2.250 (4)	Cr2—C25	2.177 (5)
Cr1—C2	2.253 (4)	Cr2—C24	2.182 (5)
Cr1—C5	2.262 (4)	Cr2—C21	2.185 (5)
Cr1—C3	2.265 (5)	Cr2—C23	2.193 (4)
Cr1—Cl3	2.3195 (14)	Cr2—C22	2.208 (4)
Cr1—Cl2	2.3208 (14)		
Cl3—Cr1—Cl2	95.02 (6)	Cl2—Cr1—Cl1	97.92 (6)
Cl3—Cr1—Cl1	98.34 (6)		

Most of the non-H atoms were located by direct methods and the remainder were found in difference Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference syntheses. In the final refinement, the positions of the H atoms were idealized with a riding model which imposed geometric constraints on the positional parameters of the H atoms used in the refinement [C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$].

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1067). Services for accessing these data are described at the back of the journal.

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First Hg$^{\rm II}$–ω-Thiocaprolactam Complex

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Abstract

The X-ray crystal structure of bis(1-azacycloheptane-2-thione-*S*)dichloromercury(II), $[{\rm HgCl_2(C_6H_{11}NS)_2}]$, is reported, which is the first structurally characterized complex of ω-thiocaprolactam with a heavy metal. The molecule exhibits disymmetric Hg—Cl distances of 2.480 (2) and 2.613 (2) Å, while the two organic fragments are coordinated with identical Hg—S bond lengths of 2.496 (2) Å.

Comment

Solvent extraction of heavy metals such as Hg$^{\rm II}$ is important from the point of view of environmental protection problems. Extracting reagents containing sulfur as a donor atom are particularly effective and selective for Hg$^{\rm II}$ (Bromberg, Lewin & Warshawsky, 1993; Inoue, Yasukawa & Miura, 1994; Zuo & Muhammed, 1995). On the other hand, 2-thioxohexamethyleneimine (ω-thiocaprolactam) has been tested as an analytical reagent (Sikorska-Tomicka, 1984, 1985). The syntheses, crystal structure determinations and reactivities of several of its complexes have been reported with Cu$^{\rm I}$

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