Inorganica Chimica Acta, 27 (1978) 75–78

An Unusual, Trinuclear, Mixed-Valence Reaction Product of Dicyclopentadienylchromium with Trifluoroacetic Acid: Bis(cyclopentadienyl)hexakis(trifluoroacetato)trichromium

F. A. COTTON and G. W. RICE

Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

Received July 11, 1977

The reaction of dicyclopentadienylchromium, $(\eta^5\text{-}C_5H_5)_2Cr$, with CF_3COOH leads to various products, among which we have identified the compound $(C_5H_5)_2(CF_3CO_2)_6Cr_3$. It consists of centrosymmetric molecules in which two $(\eta^5\text{-}C_5H_5)Cr(III)$ moieties flank a central Cr(II) ion. The Cr(III) species are each united to the Cr(II) by three bridging CF_3CO_2 groups, two of which are bidentate while the third employs only one of its oxygen atoms as a bridging atom. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule placed on a center of symmetry. The unit cell dimensions are: a = 9.581(2), b = 10.214(2), c = 9.332(2)Å; α = 94.75(2), β = 101.74(2), γ = 112.31(2)°; V = 814.2(7)Å^3, and d_X = 1.97 g/cm^3.

Introduction

The chemistry of dicyclopentadienylchromium, Cp_2Cr, is already known to be very complex [1]. In this laboratory it has recently been observed that Cp_2Cr constitutes a useful starting material for the preparation of $Cr_2(O_2CR)_4$ compounds [2]. In an effort to employ this type of reaction, in which $(\eta^5\text{-}C_5H_5)_2Cr$ is allowed to react directly with RCOOH, to prepare $Cr_2(O_2CCF_3)_4$ we have found that several products are formed, in proportions depending on conditions. One of these has been shown by X-ray crystallography to be an unusual trinuclear, mixed valence ($2Cr^{III} + Cr^{II}$) compound with the formula $(\eta^5\text{-}C_5H_5)_2Cr_3(CF_3CO_2)_6$. In this report we describe the preparation and characterization of this substance.

Experimental

Bis(cyclopentadienyl)chromium(II) was prepared by the method of Wilkinson, *et al.* [3], from NaC_5H_5 and $CrCl_3$. A reaction apparatus was constructed, comprising two septum-stoppered vertical glass tubes connected by a 10 mm fine porosity frit. The apparatus was provided with an argon atmosphere and charged with toluene solutions of Cp_2Cr (0.2g, 1.1 mmol) and CF_3CO_2H (0.2 ml, 3.5 mmol) in the respective tubes. The reaction occurred *via* slow gaseous diffusion of the acid, through the dry frit, into the chromocene solution, which slowly changed in color from red to dark blue. After one week, the liquids were removed by syringe, leaving a purple product composed of quite large blocky crystals. These were covered with degassed mineral oil for handling. Selected specimens were coated with epoxy cement and mounted in glass capillaries.

X-ray Data Collection and Structure Solution

Preliminary examination of the crystals revealed that most were severely fractured. The crystal selected for data collection had dimensions of 0.4 X 0.5 X 0.5 mm and rather broad, though unsplit, omega scans (full width at half maximum = 0.4°). Data were collected on a Syntex $P\bar{1}$ automated diffractometer with a graphite crystal monochromator in the incident beam. Centering and indexing of 15 intense reflections according to a routine procedure [4] yielded a triclinic cell with the dimensions a = 9.581(2), b = 10.214(2), c = 9.332(2) Å; α = 94.75(2), β = 101.74(2), γ = 112.31(2)°; V = 814.2(7)Å^3; d_x = 1.97 g/cm^{-3} for Z = 1 and a formula weight of 964.28.

The 2134 unique reflections with $0° < 2\theta < 45°$ included 1532 reflections, for which $F_o^2 > 3\sigma(F_o^2)$, that were considered observed and used in the refinement. The intensities of three standard reflections measured after every 97 reflections were used to correct the data for crystal decay, with a maximum correction of 10%. Lorentz and polarization corrections were applied [5], but absorption correction was unnecessary (μ = 11.99 cm^{-1}).

An E-map was generated using as a starting phase set the one with the highest figure of merit produced by program MULTAN [5] from an input of 282 reflections with E values greater than 1.5. Though poorly defined for the light atoms, the E-map yielded the two chromium positions, and in particular

TABLE I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations.

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr1	0.0[b]	0.0	0.0	0.0108(2)	0.0082(2)	0.0102(2)	0.0074(3)	0.0086(3)	0.0019(3)
Cr2	−0.2054(1)	0.2009(1)	0.1521(1)	0.0099(1)	0.0074(1)	0.0114(1)	0.0076(2)	0.0058(2)	0.0020(2)
F11	0.3939(7)	0.3651(8)	0.3629(9)	0.0199(9)	0.0263(10)	0.0473(16)	0.014(1)	−0.031(2)	−0.014(2)
F12	0.2836(7)	0.4918(8)	0.3896(9)	0.0201(10)	0.0370(10)	0.0708(17)	0.001(2)	0.009(2)	−0.078(2)
F13	0.3541(10)	0.4782(9)	0.2093(9)	0.0483(17)	0.0425(13)	0.0350(14)	−0.067(2)	−0.022(2)	0.037(2)
F21	−0.3669(6)	−0.1985(6)	0.3594(6)	0.0261(7)	0.0269(7)	0.0375(8)	0.029(1)	0.043(1)	0.042(1)
F22	−0.2512(9)	−0.3066(6)	0.2698(8)	0.0984(15)	0.0151(6)	0.0574(11)	0.052(1)	0.119(2)	0.037(0)
F23	−0.1366(7)	−0.1529(8)	0.4547(7)	0.0275(11)	0.0440(11)	0.0318(9)	0.017(2)	0.011(2)	0.054(1)
F31	−0.2599(7)	−0.0063(6)	−0.3246(6)	0.0360(10)	0.0231(7)	0.0144(7)	0.028(1)	0.002(1)	−0.006(1)
F32	−0.3748(6)	0.1345(7)	−0.3389(7)	0.0238(7)	0.0429(11)	0.0235(10)	0.041(1)	−0.005(2)	0.000(2)
F33	−0.1578(8)	0.1914(8)	−0.3952(6)	0.0336(10)	0.0426(12)	0.0163(7)	0.027(2)	0.018(1)	0.025(2)
O11	0.1526(5)	0.1890(5)	0.1278(5)	0.0112(6)	0.0096(5)	0.0147(7)	0.0059(9)	0.008(1)	−0.0017(10)
O12	0.0226(5)	0.2852(5)	0.2446(5)	0.0105(6)	0.0120(6)	0.0135(7)	0.0084(8)	0.004(1)	−0.0022(11)
O21	−0.0815(5)	−0.0778(5)	0.1716(5)	0.0158(6)	0.0113(5)	0.0143(6)	0.0139(8)	0.015(1)	0.0066(10)
O22	−0.2478(5)	0.0133(5)	0.2248(5)	0.0171(6)	0.0103(5)	0.0164(7)	0.0148(8)	0.015(1)	0.0105(10)
O31	−0.1938(5)	0.1214(4)	−0.0456(5)	0.0141(6)	0.0082(5)	0.0109(6)	0.0085(8)	0.007(1)	0.0035(9)
O32	−0.0745(7)	0.3305(6)	−0.1145(7)	0.0261(10)	0.0113(6)	0.0243(9)	0.0104(12)	0.022(1)	0.0111(13)
C11	0.1397(7)	0.2804(7)	0.2128(7)	0.0107(8)	0.0086(7)	0.0109(9)	0.006(1)	0.003(1)	0.005(1)
C12	0.2934(8)	0.4046(8)	0.2957(10)	0.0124(10)	0.0078(8)	0.0213(13)	0.004(1)	0.005(2)	0.001(2)
C21	−0.1834(7)	−0.0720(7)	0.2310(7)	0.0123(8)	0.0079(7)	0.0096(8)	0.007(1)	0.005(1)	0.002(1)
C22	−0.2402(8)	−0.1877(7)	0.3253(8)	0.0170(9)	0.0117(8)	0.0166(10)	0.016(1)	0.014(2)	0.013(2)
C31	−0.1558(8)	0.2050(7)	−0.1400(8)	0.0146(9)	0.0108(7)	0.0141(10)	0.013(1)	0.010(2)	0.010(1)
C32	−0.2388(9)	0.1283(9)	−0.3007(9)	0.0192(10)	0.0224(11)	0.0131(10)	0.025(2)	0.012(2)	0.015(2)
C 1	−0.2404(9)	0.3996(8)	0.1379(13)	0.0210(10)	0.0097(8)	0.0427(19)	0.018(1)	0.034(2)	0.016(2)
C 2	−0.3732(9)	0.2890(8)	0.0467(10)	0.0231(11)	0.0187(9)	0.0228(14)	0.030(1)	0.016(2)	0.016(2)
C 3	−0.4433(8)	0.1937(8)	0.1357(9)	0.0127(9)	0.0158(9)	0.0187(12)	0.016(1)	0.010(2)	0.007(2)
C 4	−0.3593(8)	0.2427(9)	0.2815(9)	0.0200(9)	0.0229(10)	0.0191(12)	0.031(1)	0.019(2)	0.010(2)
C 5	−0.2292(9)	0.3759(9)	0.2860(12)	0.0211(10)	0.0246(10)	0.0320(18)	0.036(1)	−0.003(2)	−0.028(2)

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The Cr(1) position is fixed by the symmetry of the space group.

TABLE II. Interatomic Distances and Angles for $(\eta^5\text{-}C_5H_5)_2(CF_3CO_2)_6Cr_3$.

Distances, Å		Angles, Deg.		Angles, Deg.	
Cr(1)–Cr(2)	3.717(1)^{a}	Cr(2)–Cr(1)–O(11)	68.8(1)	O(11)–Cr(1)–O(11)	180^{b}
Cr(1)–O(11)	2.013(4)	Cr(2)–Cr(1)–O(21)	67.3(1)	O(21)–Cr(1)–O(21)	180^{b}
Cr(1)–O(21)	2.014(4)	Cr(2)–Cr(1)–O(31)	30.7(1)	O(31)–Cr(1)–O(31)	180^{b}
Cr(1)–O(31)	2.584(4)	Cr(1)–Cr(2)–O(12)	66.9(1)	O(11)–Cr(1)–O(21)	93.1(2)
Cr(2)–O(12)	1.985(4)	Cr(1)–Cr(2)–O(22)	68.1(1)	O(11)–Cr(1)–O(31)	86.0(1)
Cr(2)–O(22)	2.008(4)	Cr(1)–Cr(2)–O(31)	41.4(1)	O(21)–Cr(1)–O(31)	90.7(1)
Cr(2)–O(31)	1.995(4)	Cr(1)–Cr(2)–CENT	165.5^{c}	O(12)–Cr(2)–O(22)	95.4(2)
Cr(2)–C(1)	2.190(7)	Cr(1)–O(31)–Cr(2)	107.9(2)	O(12)–Cr(2)–O(31)	96.1(2)
Cr(2)–C(2)	2.229(7)	O(12)–Cr(2)–CENT	121.9^{c}	O(22)–Cr(2)–O(31)	92.9(2)
Cr(2)–C(3)	2.226(6)	O(22)–Cr(2)–CENT	119.4^{c}	C(n)–Cr(2)–C(n ± 1)	36.0–38.1^{d}
Cr(2)–C(4)	2.221(7)	O(31)–Cr(2)–CENT	124.1^{c}	C(n)–Cr(2)–C(n ± 2)	61.3–62.6^{d}
Cr(2)–C(5)	2.205(7)				
O(11)–C(11)	1.233(7)	Cr(1)–O(11)–C(11)	133.7(4)	O(11)–C(11)–O(12)	130.2(5)
O(12)–C(11)	1.235(7)	Cr(1)–O(21)–C(21)	135.1(4)	O(21)–C(21)–O(22)	129.6(5)
O(21)–C(21)	1.234(6)	Cr(1)–O(31)–C(31)	107.6(4)	O(31)–C(31)–O(32)	127.6(6)
O(22)–C(21)	1.242(7)	Cr(2)–O(12)–C(11)	136.8(4)	O(11)–C(11)–C(12)	114.9(5)
O(31)–C(31)	1.287(7)	Cr(2)–O(22)–C(21)	134.5(4)	O(12)–C(11)–C(12)	114.9(6)
O(32)–C(31)	1.193(7)	Cr(2)–O(31)–C(31)	119.8(4)	O(21)–C(21)–C(22)	115.4(5)
C(11)–C(12)	1.527(8)			O(22)–C(21)–C(22)	115.0(5)
C(21)–C(22)	1.532(8)			O(31)–C(31)–C(32)	112.3(6)
C(31)–C(32)	1.531(10)			O(32)–C(31)–C(32)	120.0(6)
C(12)–F(11)	1.256(8)	C(11)–C(12)–F(11)	113.8(6)	F(11)–C(12)–F(12)	105.6(8)
C(12)–F(12)	1.239(8)	C(11)–C(12)–F(12)	115.7(6)	F(11)–C(12)–F(13)	105.6(8)
C(12)–F(13)	1.230(9)	C(11)–C(12)–F(13)	110.0(6)	F(12)–C(12)–F(13)	104.3(8)
C(22)–F(21)	1.284(7)	C(21)–C(22)–F(21)	113.8(5)	F(21)–C(22)–F(22)	110.7(7)
C(22)–F(22)	1.237(8)	C(21)–C(22)–F(22)	112.9(6)	F(21)–C(22)–F(23)	104.4(6)
C(22)–F(23)	1.320(8)	C(21)–C(22)–F(23)	109.3(6)	F(22)–C(22)–F(23)	105.0(7)
C(32)–F(31)	1.304(9)	C(31)–C(32)–F(31)	114.0(6)	F(31)–C(32)–F(32)	108.2(7)
C(32)–F(32)	1.306(8)	C(31)–C(32)–F(32)	110.0(6)	F(31)–C(32)–F(33)	106.0(7)
C(32)–F(33)	1.337(8)	C(31)–C(32)–F(33)	111.3(7)	F(32)–C(32)–F(33)	107.0(6)
C(1)–C(2)	1.39(1)	C(5)–C(1)–C(2)	108.4(7)		
C(2)–C(3)	1.40(1)	C(1)–C(2)–C(3)	107.9(7)		
C(3)–C(4)	1.37(1)	C(2)–C(3)–C(4)	109.9(7)		
C(4)–C(5)	1.44(1)	C(3)–C(4)–C(5)	107.1(7)		
C(5)–C(1)	1.41(1)	C(4)–C(5)–C(1)	106.7(7)		

[a] Metal–metal bonding is *not* implied. [b] Value is required by symmetry. [c] CENT is the centroid of the $(\eta^5\text{-}C_5H_5)$ ring. [d] Maximum and minimum values for angles involving $(\eta^5\text{-}C_5H_5)$ atoms.

indicated the unexpected presence of Cr(1) upon the origin. Refinement of the position of Cr(2) in two cycles of least squares gave discrepancy indices

$$R_1 = \Sigma||F_o|-|F_c||/|F_o| = 0.45$$

$$R_2 = [\Sigma w(||F_o|-|F_c||)^2/\Sigma w|F_o|^2]^{1/2} = 0.54$$

The function minimized during all least-squares refinements was $\Sigma w(|F_o|-|F_c|)^2$, where the weighting factor, w, equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for *p* in the calculation of σ [5].

The remainder of the model was built up in three successive difference Fourier map/least squares refinement sequences. Anisotropic refinement of all 28 non-hydrogen atoms was quite slow and required seven full-matrix least squares cycles to obtain convergence. The final discrepancy indices were R_1 = 0.056 and R_2 = 0.074, while the error in an observation of unit weight was 1.73. A final difference Fourier map had no peaks larger than 0.9 electrons/Å^3. The six largest peaks were so disposed as to form a second set of fluorine atoms bonded to C(12) and C(22), indicating that partial disordering of those six fluorines contribute to their very large temperature factors. No such peaks were found near C(32). Additional weak peaks were found where the cyclopentadienyl protons are expected, but no attempt was made to include these in the model. A table (7 pages) of observed and calculated structure factors is available upon request to F.A.C.

Results and Discussion

The positional and thermal parameters are listed in Table I, while the molecular structure and the atom

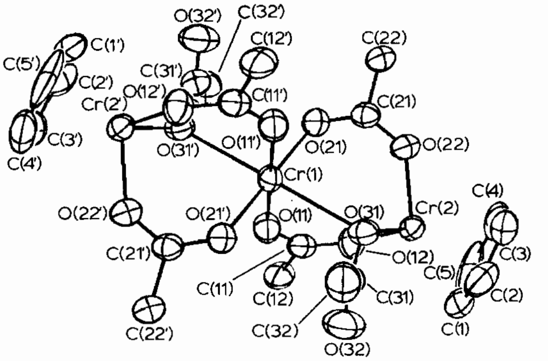

Figure 1. An ORTEP drawing of the $(\eta^5\text{-}C_5H_5)_2(CF_3CO_2)_6$-$Cr_3$ molecule. Thermal ellipsoids enclose 50% of the electron density. Fluorine atoms are omitted for clarity.

numbering scheme are illustrated in Figure 1. Pertinent bond lengths and angles are collected in Table II; this table also reports the Cr(1)–Cr(2) distance and several angles involving that vector, but there is no intent to imply any form of metal–metal bonding in the compound. Additionally, the coordination geometry about Cr(2) has been defined in terms of the centroid (CENT) of the η^5-C_5H_5 ring rather than in terms of the individual ring carbon atoms.

The chromium(II) atom, Cr(1), lies at the cell origin, which is an inversion center. Its coordination polyhedron is a tetragonally distorted octahedron with four short (2.01Å) and two long (2.58Å) Cr–O bonds. The coordination geometry of the chromium(III) atom, Cr(2), is essentially that of the previously known $[(\eta^5\text{-}C_5H_5)CrX_3]^-$ complexes [1]. There are three roughly orthogonal Cr–O bonds, with the remaining three coordination sites of the distorted octahedron filled by the cyclopentadienyl ring. The assignment of oxidation number +3 to Cr(2) is confirmed by the absence of a proton on O(32) as shown by the O(32)–C(31) and O(31)–C(31) distances, which indicate a double and a single C–O bond, respectively, rather than the uniform distances expected from delocalized π-bonding.

An interesting feature of the structure is the lack of planarity forced upon the Cr–O–C–O–Cr linkages by the large separation of the metal atoms. The known metal–metal bonded $Cr_2(O_2CR)_4$ complexes [2] invariably possess $Cr_2O_2C_2$ units which are essentially planar. The O_2C_2 skeletons of the three trifluoroacetato ligands in $(Cp)_2(CF_3CO_2)_6Cr_3$ are each planar within experimental error (as is the C_5H_5 ring), but the planes of the two bridging ligands are twisted with respect to the Cr(1)–Cr(2) axis. The twisting of the O(11, 12), C(11, 12) plane is readily evident from Figure 1. The displacements of Cr(1) and Cr(2) from this particular plane are –0.110(0) and 0.466(1)Å, respectively, while the corresponding displacements from the plane defined by O(21, 22) and C(21, 22) are 0.476(0) and –0.297(1)Å. These twisted chains add emphasis to the idea that a μ-carboxylato bridge is a flexible structural unit which imposes very few restraints upon the relative positions of the ligated metal ions.

Prior to the findings described here, the acidification of Cp_2Cr^{II} was known to follow one of two main courses: (i) Reaction with the halo acids HX in the presence of X^-, yielding $[CpCr^{III}X_3]^-$ in a redox process [1]; and (ii) simple displacement of the Cp moiety with the organic acids RCOOH, yielding the dinuclear complexes $Cr_2(O_2CR)_4$ [2]. A strong organic acid is evidently capable of following either the redox or the displacement pathway, and, as in the present instance, can lead to novel mixed oxidation-state products as well.

Acknowledgement

We thank the National Science Foundation for support.

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5 Computer programs used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, were those of the Enraf-Nonius structure determination package.