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Dichromium(II) Compounds Containing 2-Phenylbenzoic Acid (biphCO$_2$H): [Cr$_2$(O$_2$Cbiph)$_4$]$_2$ and Cr$_2$(O$_2$Cbiph)$_4$(THF)$_2$

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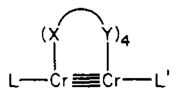
The reaction of dichromium tetraacetate with 2-phenylbenzoic acid, biphCO$_2$H, in presence of *n*-butyllithium in THF, gives red, crystalline Cr$_2$(O$_2$Cbiph)$_4$(THF)$_2$ (**1**). The reaction also occurs in toluene, and from the deep red solution red crystalline [Cr$_2$(O$_2$Cbiph)$_4$]$_2$·4C$_7$H$_8$ (**2**) is precipitated upon cooling. Both of these compounds have been fully characterized by X-ray crystallography; **1** crystallizes in space group $P2_1/n$ with cell dimensions a = 10.955 (2) Å, b = 17.771 (3) Å, c = 13.450 (3) Å, β = 103.58 (2)°, V = 2545 (2) Å^3, and Z = 2. Crystallographically centrosymmetric molecules with axially coordinated THF molecules are present in which the Cr–Cr and Cr–O(THF) distances are 2.316 (3) and 2.275 (6) Å, respectively. For compound **2** the space group is $C2/c$ with cell dimensions of a = 25.335 (2) Å, b = 19.233 (4) Å, c = 22.138 (3) Å, β = 103.28 (1)°, V = 10499 (5) Å^3, and Z = 4 for the tetranuclear formula unit. Aside from interstitial toluene molecules, the asymmetric unit is the dinuclear Cr$_2$(O$_2$Cbiph)$_4$ moiety. Pairs of these are linked by O→Cr bonds across a crystallographic inversion center. Thus, each Cr$_2$(O$_2$Cbiph)$_4$ moiety has one axial bond (Cr–Cr–O = 164.5 (1)°; Cr–O = 2.309 (5) Å) and one vacant axial position. The Cr–Cr quadruple bond distance is 2.348 (2) Å.

Introduction

In dichromium(II) compounds of the general type I, there



Ia: X-Y = PhNC(CH$_3$)O; L, L' absent
Ib: X-Y = (p-Me$_2$NPh)NC(CH$_3$)O; L = THF; L' absent
Ic: X-Y = PhNC(CH$_3$)O; L = L' = THF
Id: X-Y = (2,6-xylyl)NC(CH$_3$)O; L = L' = py

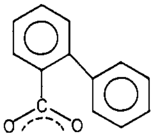
are two factors that must be principally responsible for determining the length of the Cr–Cr quadruple bond, namely, the nature of the bridging ligands, X–Y, and the nature of the axial ligands, L. It has already been convincingly demonstrated[1] that the axial ligands, simply in terms of their presence or absence, can exert a decisive influence in a series of compounds where a certain type of X–Y ligand is kept essentially invariant. Thus, the Cr–Cr bond length can be increased from 1.873 (4) in Ia to 2.006 (2) in Ib to 2.246 (2) in Ic to 2.354 (5) Å in Id.

In addition, the comparison of Ic with Id suggests that, in compounds with identical L and L′ ligands, a more basic axial ligand can increase the Cr–Cr distance.

The degree of control over the Cr–Cr distance exerted by the bridging ligands, X–Y, remains less clear. The results presented in this paper were obtained in our first attempt to answer the following specific question: If a tetrakis(carboxylato)dichromium(II) molecule with no axial coordination at all could be obtained, would the Cr–Cr distance be comparable to that in Ia or does the OC(R)O ligand inherently tend to give longer Cr–Cr bonds than the ArNC(R)O type ligand? It is well-known that all crystalline Cr$_2$(O$_2$CR)$_4$ compounds have axial ligands, either because separate additional axial ligands, e.g., R$_2$O, py, etc., are present or because the Cr$_2$(O$_2$CR)$_4$ molecules associate with one another, in infinite chains.[2,3]

The distances and angles in Cr$_2$(O$_2$CR)$_4$ molecules are such that it is not obvious how to design R groups that will fulfill all three of the following requirements: (1) access of separate axial ligands be prevented; (2) intermolecular association be prevented; (3) the unligated, unassociated compound form single crystals suitable for X-ray crystallographic investigation. The problem in achieving requirement 1 is very difficult but may perhaps be sidestepped with a Cr$_2$(O$_2$CR)$_4$ compound that is sufficiently soluble in a solvent that is quite incapable of being a ligand and may be crystallized therefrom. It is easier to imagine feasible R groups that would interfere with intermolecular association even though they cannot block access to the axial positions by suitably small, separate donor molecules. We have chosen this approach to the problem and report here two new compounds that have been prepared and characterized in our first attempt to obtain the desired result.

The ligand selected was the anion of 2-phenylbenzoic acid, biphCO$_2^-$ (II). It can be seen from scale models that the ortho phenyl groups are not going to prevent small to medium size ligands from reaching the axial positions of the dichromium unit. However, scale models do suggest that if four of these carboxylate groups are arranged on the Cr$_2^{4+}$ unit so that two ortho phenyl groups are directed toward each end, intermolecular association will be impossible. We therefore prepared Cr$_2$(O$_2$Cbiph)$_4$ in THF and obtained as expected, the bis THF adduct **1**. We then attempted the preparation in toluene and were successful in isolating Cr$_2$(O$_2$Cbiph)$_4$·2tol (**2**) as a crystalline solid. The structures of both compounds were then determined by X-ray crystallography.



II

Experimental Section

All reactions and manipulations were performed under an atmosphere of nitrogen with dried, degassed tetrahydrofuran (THF) or toluene as solvents. Anhydrous chromium acetate, Cr$_2$(O$_2$CCH$_3$)$_4$, was prepared by the method reported by Ocone and Block.[4] Chromocene, Cp$_2$Cr (Cp = C$_5$H$_5$), was prepared by the method of King.[5] The Cp$_2$Cr was purified by sublimation under vacuum (50–80 °C, 10^{-3} cmHg). 2-Phenylbenzoic acid, biphCOOH, and n-butyllithium were purchased from Aldrich and used without further purification.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(O_2Cbiph)_4(THF)_2$ (1)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.5032 (2)	0.9776 (1)	0.0814 (1)	2.85 (6)	2.15 (7)	2.61 (6)	0.17 (8)	0.19 (6)	−0.05 (7)
O(1)	0.6683 (6)	0.9781 (4)	−0.0713 (5)	2.6 (3)	3.3 (3)	3.1 (3)	0.1 (3)	0.4 (3)	0.4 (3)
O(2)	0.3235 (6)	1.0625 (4)	−0.0865 (5)	3.5 (3)	2.8 (3)	3.4 (3)	0.8 (3)	0.6 (3)	0.8 (3)
O(3)	0.5788 (6)	1.0757 (4)	0.1417 (5)	3.5 (3)	2.7 (4)	2.5 (3)	−0.8 (3)	0.2 (3)	−0.4 (3)
O(4)	0.5729 (7)	1.1176 (4)	−0.0153 (6)	4.2 (4)	2.6 (3)	3.5 (4)	0.0 (3)	0.2 (3)	0.2 (3)
O(5)	0.4987 (8)	0.9286 (5)	0.2368 (6)	7.0 (5)	3.7 (4)	3.3 (3)	−0.3 (4)	1.8 (3)	0.7 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.277 (1)	1.0545 (6)	−0.0099 (8)	3.2 (2)	C(32)	0.606 (1)	1.2623 (7)	0.0532 (9)	4.0 (3)
C(2)	0.596 (1)	1.1256 (6)	0.0817 (8)	2.9 (2)	C(33)	0.635 (1)	1.3366 (8)	0.0861 (10)	4.8 (3)
C(11)	0.145 (1)	1.0826 (7)	−0.0184 (8)	3.3 (2)	C(34)	0.698 (1)	1.3505 (8)	0.1884 (10)	5.1 (3)
C(12)	0.110 (1)	1.1232 (7)	0.0611 (9)	3.6 (3)	C(35)	0.735 (1)	1.2899 (7)	0.2563 (9)	4.3 (3)
C(13)	−0.022 (1)	1.1395 (7)	0.0477 (10)	4.5 (3)	C(36)	0.708 (1)	1.2146 (7)	0.2243 (8)	3.3 (2)
C(14)	−0.109 (1)	1.1186 (8)	−0.0399 (10)	4.7 (3)	C(41)	0.753 (1)	1.1560 (7)	0.3026 (9)	3.8 (3)
C(15)	−0.072 (1)	1.0798 (8)	−0.1179 (10)	5.4 (3)	C(42)	0.827 (1)	1.0968 (7)	0.2817 (9)	4.2 (3)
C(16)	0.058 (1)	1.0640 (7)	−0.1078 (9)	4.3 (3)	C(43)	0.877 (1)	1.0458 (8)	0.3615 (10)	5.2 (3)
C(21)	0.198 (1)	1.1485 (7)	0.1528 (9)	3.9 (3)	C(44)	0.852 (1)	1.0523 (8)	0.4597 (10)	5.3 (3)
C(22)	0.303 (1)	1.1925 (8)	0.1466 (10)	5.2 (3)	C(45)	0.781 (1)	1.1119 (9)	0.4782 (11)	6.0 (4)
C(23)	0.384 (1)	1.2199 (9)	0.2397 (12)	7.0 (4)	C(46)	0.729 (1)	1.1654 (8)	0.3993 (10)	5.1 (3)
C(24)	0.359 (1)	1.2000 (10)	0.3335 (12)	7.4 (4)	C(51)	0.499 (1)	0.9771 (9)	0.3211 (11)	6.4 (4)
C(25)	0.258 (2)	1.1600 (11)	0.3386 (14)	9.3 (5)	C(52)	0.510 (2)	0.9230 (12)	0.4126 (15)	10.1 (6)
C(26)	0.172 (1)	1.1305 (9)	0.2472 (12)	6.5 (4)	C(53)	0.477 (2)	0.8453 (11)	0.3644 (14)	8.2 (5)
C(31)	0.642 (1)	1.2020 (6)	0.1222 (8)	2.9 (2)	C(54)	0.445 (1)	0.8565 (8)	0.2515 (10)	5.1 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

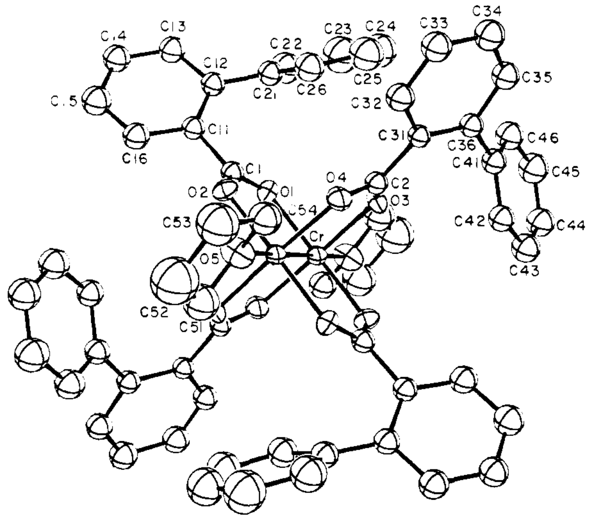

Figure 1. $Cr_2(O_2Cbiph)_4(THF)_2$ molecule (1). Atoms are represented by their thermal vibration ellipsoids scaled to enclose 40% of the electron density. The atom numbering scheme is defined; unnumbered atoms are related through the inversion center to numbered ones.

Table II. Bond Distances (Å) in $Cr_2(O_2Cbiph)_4(THF)_2$ (1)

Cr–Cr′	2.316 (3)	C(21)–C(26)	1.40 (1)
Cr–O(1)	2.012 (5)	C(22)–C(23)	1.44 (1)
Cr–O(2)	2.014 (5)	C(23)–C(24)	1.39 (2)
Cr–O(3)	2.017 (5)	C(24)–C(25)	1.34 (2)
Cr–O(4)	2.000 (6)	C(25)–C(26)	1.46 (2)
Cr–O(5)	2.275 (6)	C(31)–C(32)	1.41 (1)
O(1)–C(1)	1.26 (1)	C(31)–C(36)	1.41 (1)
O(2)–C(1)	1.26 (1)	C(32)–C(33)	1.41 (1)
O(3)–C(2)	1.24 (1)	C(33)–C(34)	1.40 (1)
O(4)–C(2)	1.28 (1)	C(34)–C(35)	1.41 (1)
O(5)–C(51)	1.42 (1)	C(35)–C(36)	1.42 (1)
O(5)–C(54)	1.44 (1)	C(36)–C(41)	1.48 (1)
C(1)–C(11)	1.51 (1)	C(41)–C(42)	1.39 (1)
C(2)–C(31)	1.50 (1)	C(41)–C(46)	1.40 (1)
C(11)–C(12)	1.42 (1)	C(42)–C(43)	1.41 (1)
C(11)–C(16)	1.39 (1)	C(43)–C(45)	1.42 (1)
C(12)–C(13)	1.45 (1)	C(44)–C(45)	1.37 (1)
C(12)–C(21)	1.44 (1)	C(45)–C(46)	1.44 (1)
C(13)–C(14)	1.38 (1)	C(51)–C(52)	1.544 (17)
C(14)–C(15)	1.39 (1)	C(52)–C(53)	1.533 (19)
C(15)–C(16)	1.43 (1)	C(53)–C(54)	1.489 (16)
C(21)–C(22)	1.41 (1)		

Preparation of $Cr_2(O_2Cbiph)_4$·2THF (1). $Cr_2(O_2CCH_3)_4$ (2.15 g, 6.3 mmol) and 2-phenylbenzoic acid (5.00 g, 25.4 mmol) were placed in a round-bottom flask containing 100 mL of THF and 80 mL of a 1.6 M hexane solution of *n*-butyllithium. After being stirred overnight, the solution was filtered and subsequently refrigerated to give red crystals of $Cr_2(O_2Cbiph)_4$·2THF. The yield was 452 mg.

Preparation of $Cr_2(O_2Cbiph)_4$·2tol (2). Cp_2Cr (0.2 g, 1.1 mmol) and biphCOOH (0.87 g, 4.4 mmol) were placed in a round-bottom flask containing 50 mL of toluene. An immediate reaction occurred, giving a deep red solution. Red crystals of $Cr_2(O_2Cbiph)_4$·2tol precipitated upon cooling to −10 °C. The yield was 160 mg.

X-ray Studies. Compound 1. A red-orange crystal with approximate dimensions of 0.10 × 0.15 × 0.15 mm was coated with epoxy cement, attached to a glass fiber, and mounted on an Enraf-Nonius CAD-4F automated diffractometer. Procedures used to collect and process data for this compound (and compound **2**) were essentially the same as reported previously.[6] Indexing on 25 intense centered reflections in the range 25° ≤ 2θ ≤ 45° gave a monoclinic unit cell with dimensions a = 10.955 (2) Å, b = 17.771 (3) Å, c = 13.450 (3) Å, β = 103.58 (2)°, and V = 2545 (2) Å^3. This volume is consistent with $Z = 2$. Systematic absences of $h0l$ with $h + l \neq 2n$ and $0k0$ with $k \neq 2n$ indicated the space group $P2_1/n$. With use of Mo Kα radiation (λ = (0.7107 73 Å), 3439 reflections were collected in the range of 0° ≤ 2θ ≤ 45°; the 1586 reflections having $I > 3\sigma(I)$ were used to solve and refine the structure. The low linear absorption coefficient of 5 cm^{-1} made an absorption correction unnecessary.

The position of the Cr atom was located by the direct-methods program MULTAN.[7] Refinement of this position gave discrepancy indices of

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

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.55$$

The remaining 35 atoms were located by subsequent refinement and difference Fourier maps.

Final refinement on positional parameters, anisotropic thermal parameters for the Cr and O atoms, and isotropic thermal parameters for the remaining atoms gave discrepancy indices of R_1 = 0.081 and R_2 = 0.102. The estimated standard deviation of an observation of

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(6) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(7) All computing to solve and refine the structure was carried out on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, with the Enraf-Nonius structure determination package with some local modifications.

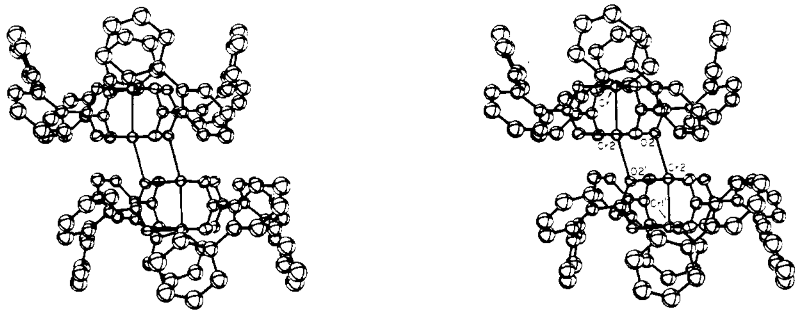

Figure 2. ORTEP stereographic representation of $[Cr_2(O_2Cbiph)_4]_2$ (**2**).

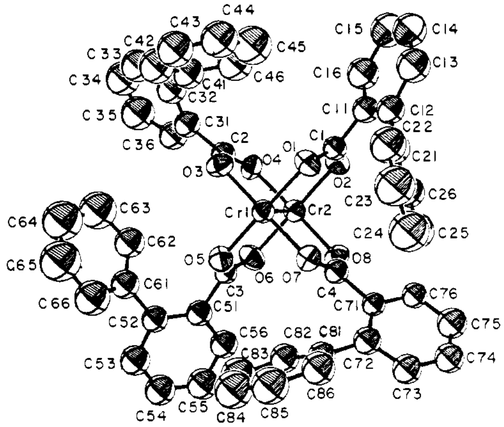

Figure 3. One $Cr_2(O_2Cbiph)_4$ component of compound **2**. Atoms are represented by their ellipsoids of thermal vibration scaled to 40% of the electron probability density and numbered in accord with Tables IV–VI. Atoms in the other half of **2** are related by an inversion center (cf. Figure 2) and identified by corresponding primed labels.

unit weight after the final least-squares cycle was 2.00. A final difference map revealed only peaks presumably assocated with hydrogen atoms; these were not refined.

Compound 2. A red crystal with approximate dimensions of 0.30 × 0.30 × 0.45 mm was coated with epoxy cement, attached to a glass fiber, and mounted on the CAD-4F diffractometer. Indexing on 25 intense reflections in the range $25° \le 2\theta \le 45°$ produced a unit cell in the monoclinic system with the dimensions a = 25.335 (2) Å, b = 19.233 (4) Å, c = 22.138 (3) Å, β = 103.28 (1)°, and V = 10 499 (5) Å^3. This volume is consistent with $Z = 8$ for the dinuclear molecule. Systematic absences of hkl with $h + k \neq 2n$ and $h0l$ with $l \neq 2n$ indicate the space groups $C2/c$ or Cc.

A total of 9363 unique reflections between $0° < 2\theta \le 50°$ was collected as previously described, and those 3148 reflections having $I > 3\sigma(I)$ were used to solve and refine the structure.

Statistical tests indicated the space group to be the centric one, $C2/c$. The positions of the two Cr atoms were located by the direct-methods program MULTAN.[7]

The remaining 60 atoms in the molecular unit and a toluene molecule in the lattice consisting of seven atoms were found by subsequent refinement and difference Fourier maps. After final refinement, a difference Fourier map revealed several large peaks that could not be associated as "ghosts" of the heavy metal atoms or with hydrogen atoms. Attempted refinement as C atoms reduced the discrepancy indices and the estimated standard deviation of an observation of unit weight. Therefore it was assumed a disordered toluene was present in the lattice, and refinement proceeded with this assumption. Final refinement on the positional parameters, anisotropic thermal parameters for the Cr and O atoms, and isotropic thermal parameters for all other atoms gave discrepancy indices of $R_1 = 0.084$ and $R_2 = 0.098$ with an estimated standard deviation of an observation of unit weight of 2.34.

A final difference map revealed peaks associated with hydrogen atoms, which were not refined.

Results and Discussion

$Cr_2(O_2Cbiph)_4(THF)_2$ (1). The atomic positional and thermal parameters are listed in Table I, and the molecular structure is depicted in Figure 1 which also defines the atomic labels. Tables II and III present the interatomic distances and angles. The molecule resides on a crystallographic inversion center, and its structure is similar to those of most other $Cr_2(O_2CR)_4L_2$ molecules.[3] The Cr–Cr distance for compounds with alkyl or aryl R groups and L ligands which are oxygen or nitrogen donors is, approximately, from 2.28 to 2.37 Å. Thus, the present value of 2.316 (3) Å is within the established range. Similarly, previously reported distances from the Cr atoms to axial oxygen atoms are mostly in the range 2.27–2.34 Å, and the present value of 2.275 (6) Å is again within the established range. The same is true for all other distances and angles.

The structure of **1** is qualitatively as well as quantitatively as expected. The biphCO_2 ligands are so arranged that two of the ortho phenyl groups are directed toward one end and the other two toward the other end, the whole configuration being in conformity with the presence of a crystallographic inversion center at the midpoint of the Cr–Cr bond. Also, as

Table III. Bond Angles (Deg) in $Cr_2(O_2Cbiph)_4(THF)_2$ (1)

Cr′–Cr–O(1)	88.9 (2)	C(11)–C(12)–C(13)	116.7 (8)
–O(2)	88.4 (2)	–C(21)	124.1 (8)
–O(3)	90.1 (2)	C(11)–C(16)–C(15)	120.2 (9)
–O(4)	87.3 (2)	C(12)–C(11)–C(16)	121.5 (8)
–O(5)	176.2 (2)	C(12)–C(13)–C(14)	121.4 (9)
O(1)–Cr–O(2′)	177.0 (2)	C(12)–C(21)–C(22)	120.6 (9)
–O(3)	88.7 (2)	–C(26)	118.1 (9)
–O(4′)	90.9 (2)	C(13)–C(14)–C(15)	121 (1)
–O(5)	89.5 (2)	C(13)–C(12)–C(21)	119.3 (8)
O(2′)–Cr–O(3)	88.9 (2)	C(14)–C(15)–C(16)	118.8 (9)
–O(4′)	90.4 (2)	C(21)–C(22)–C(23)	119 (1)
–O(5)	93.3 (2)	C(21)–C(26)–C(25)	117 (1)
O(3)–Cr–O(4′)	177.3 (2)	C(22)–C(23)–C(24)	120 (1)
O(5)	93.3 (2)	C(22)–C(21)–C(26)	121.2 (9)
O(4′)–Cr–O(5)	89.3 (2)	C(23)–C(24)–C(25)	121 (1)
Cr–O(1)–C(1)	119.1 (5)	C(24)–C(25)–C(26)	122 (1)
Cr′–O(2)–C(1)	119.4 (5)	C(31)–C(32)–C(33)	119.9 (9)
Cr–O(3)–C(2)	117.8 (5)	C(31)–C(36)–C(35)	117.9 (8)
Cr′–O(4)–C(2)	120.7 (5)	–C(41)	126.2 (8)
Cr–O(5)–C(51)	120.2 (6)	C(32)–C(31)–C(36)	121.4 (8)
Cr–O(5)–C(54)	124.3 (5)	C(32)–C(33)–C(34)	119.7 (9)
O(1)–C(1)–O(2)	124.0 (8)	C(36)–C(41)–C(42)	120.1 (8)
O(3)–C(2)–O(4)	124.0 (8)	–C(46)	118.1 (9)
O(1)–C(1)–C(11)	118.2 (8)	C(33)–C(34)–C(35)	120 (1)
O(2)–C(1)–C(11)	117.7 (8)	C(34)–C(35)–C(36)	121.2 (9)
O(3)–C(2)–C(31)	119.9 (8)	C(35)–C(36)–C(41)	115.9 (8)
O(4)–C(2)–C(31)	116.1 (8)	C(41)–C(42)–C(43)	118.2 (9)
C(1)–C(11)–C(12)	122.5 (8)	C(41)–C(46)–C(45)	119 (1)
–C(16)	116.0 (8)	C(42)–C(43)–C(44)	122 (1)
C(2)–C(31)–C(32)	115.4 (7)	–C(41)–C(46)	121.6 (9)
–C(36)	123.0 (8)	C(43)–C(44)–C(45)	118 (1)
		C(44)–C(45)–C(46)	121 (1)
		O(5)–C(51)–C(52)	104 (1)
		O(5)–C(54)–C(53)	104.7 (9)
		C(51)–O(5)–C(54)	110.7 (8)
		C(51)–C(52)–C(53)	105 (1)
		C(52)–C(53)–C(54)	107 (1)

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Cr_2(O_2Cbiph)_4]_2 \cdot 4tol$ (2)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.33829 (7)	0.3349 (1)	0.41114 (8)	3.46 (7)	4.46 (9)	3.72 (7)	−0.04 (8)	0.84 (6)	−0.23 (8)
Cr(2)	0.26590 (7)	0.2689 (1)	0.43034 (8)	3.62 (7)	4.03 (8)	3.73 (7)	−0.20 (8)	0.87 (6)	0.04 (8)
O(1)	0.3657 (3)	0.3459 (4)	0.5023 (3)	4.0 (3)	5.3 (4)	4.2 (3)	−1.4 (3)	1.1 (3)	0.2 (3)
O(2)	0.2977 (2)	0.2829 (3)	0.5245 (3)	3.4 (3)	4.5 (4)	3.7 (3)	−1.1 (3)	0.3 (3)	−0.2 (3)
O(3)	0.3789 (3)	0.2448 (4)	0.4135 (3)	3.4 (3)	5.4 (4)	5.5 (4)	0.5 (3)	1.0 (3)	0.6 (3)
O(4)	0.3096 (3)	0.1828 (3)	0.4315 (3)	4.5 (3)	4.4 (4)	5.0 (3)	0.4 (3)	2.1 (3)	0.0 (3)
O(5)	0.3086 (3)	0.3231 (4)	0.3207 (3)	4.3 (3)	5.0 (4)	3.8 (3)	−0.3 (3)	1.0 (3)	−0.3 (3)
O(6)	0.2395 (3)	0.2606 (4)	0.3379 (3)	4.5 (3)	6.2 (4)	4.0 (3)	−0.9 (3)	1.1 (3)	0.5 (3)
O(7)	0.2925 (2)	0.4197 (3)	0.4093 (3)	3.9 (3)	3.5 (3)	5.0 (3)	−0.4 (3)	1.3 (3)	0.2 (3)
O(8)	0.2238 (2)	0.3561 (3)	0.4275 (3)	3.0 (3)	4.5 (4)	5.1 (3)	0.2 (3)	1.0 (3)	0.4 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.3424 (4)	0.3178 (6)	0.5412 (5)	4.3 (3)	C(55)	0.1542 (5)	0.3186 (7)	0.1575 (6)	7.6 (4)
C(2)	0.3563 (4)	0.1875 (6)	0.4217 (5)	4.6 (3)	C(56)	0.1827 (5)	0.3078 (6)	0.2206 (5)	5.8 (3)
C(3)	0.2645 (4)	0.2908 (5)	0.3033 (4)	3.8 (2)	C(61)	0.3244 (5)	0.2590 (7)	0.2005 (6)	6.2 (3)
C(4)	0.2451 (4)	0.4134 (6)	0.4183 (5)	4.2 (3)	C(62)	0.3399 (5)	0.2044 (7)	0.2416 (6)	6.9 (3)
C(11)	0.3686 (4)	0.3259 (6)	0.6097 (5)	4.8 (3)	C(63)	0.3921 (7)	0.1763 (8)	0.2475 (8)	10.3 (5)
C(12)	0.3875 (5)	0.3923 (6)	0.6326 (5)	5.6 (3)	C(64)	0.4271 (7)	0.2008 (9)	0.2134 (8)	11.3 (5)
C(13)	0.4209 (6)	0.3934 (7)	0.6961 (6)	8.1 (4)	C(65)	0.4129 (7)	0.2581 (9)	0.1770 (8)	11.0 (5)
C(14)	0.4296 (5)	0.3326 (7)	0.7270 (6)	7.7 (4)	C(66)	0.3586 (6)	0.2907 (8)	0.1655 (7)	8.7 (4)
C(15)	0.4114 (6)	0.2698 (8)	0.7067 (6)	8.5 (4)	C(71)	0.2123 (4)	0.4773 (5)	0.4228 (4)	3.9 (2)
C(16)	0.3766 (5)	0.2639 (7)	0.6413 (6)	7.2 (3)	C(72)	0.2147 (4)	0.5379 (6)	0.3867 (5)	4.8 (3)
C(21)	0.3765 (5)	0.4550 (6)	0.6009 (5)	6.2 (3)	C(73)	0.1855 (5)	0.5971 (6)	0.3972 (5)	5.8 (3)
C(22)	0.4201 (6)	0.5063 (8)	0.6002 (6)	8.1 (4)	C(74)	0.1551 (5)	0.5949 (7)	0.4428 (6)	6.3 (3)
C(23)	0.4064 (6)	0.5669 (8)	0.5704 (7)	9.6 (4)	C(75)	0.1519 (5)	0.5347 (7)	0.4768 (6)	7.0 (3)
C(24)	0.3553 (6)	0.5880 (8)	0.5396 (7)	9.9 (5)	C(76)	0.1802 (4)	0.4741 (6)	0.4663 (5)	4.7 (3)
C(25)	0.3122 (6)	0.5392 (8)	0.5422 (6)	8.5 (4)	C(81)	0.2420 (4)	0.5416 (6)	0.3341 (5)	5.4 (3)
C(26)	0.3231 (5)	0.4769 (7)	0.5700 (5)	6.4 (3)	C(82)	0.2331 (5)	0.4865 (7)	0.2908 (5)	5.8 (3)
C(31)	0.3876 (4)	0.1208 (6)	0.4165 (5)	5.3 (3)	C(83)	0.2565 (5)	0.4901 (8)	0.2357 (6)	8.0 (4)
C(32)	0.4437 (5)	0.1161 (7)	0.4411 (6)	6.7 (3)	C(84)	0.2861 (6)	0.5508 (8)	0.2292 (6)	8.8 (4)
C(33)	0.4684 (6)	0.0518 (8)	0.4302 (6)	8.2 (4)	C(85)	0.2963 (6)	0.6024 (8)	0.2738 (6)	8.7 (4)
C(34)	0.4370 (6)	−0.0003 (8)	0.3970 (6)	8.9 (4)	C(86)	0.2735 (5)	0.6011 (7)	0.3278 (6)	7.0 (3)
C(35)	0.3820 (6)	0.0045 (8)	0.3694 (6)	9.1 (4)	C(105)	0.4474 (6)	0.3775 (9)	0.4136 (7)	9.6 (4)
C(36)	0.3556 (5)	0.0689 (7)	0.3835 (6)	6.7 (3)	C(101)	0.5821 (9)	0.5115 (13)	0.6250 (9)	16.5 (8)
C(41)	0.4765 (5)	0.1684 (7)	0.4782 (6)	6.4 (3)	C(102)	0.4143 (8)	0.4651 (10)	0.3220 (9)	13.5 (6)
C(42)	0.5235 (6)	0.1891 (8)	0.4592 (6)	8.2 (4)	C(103)	0.4281 (11)	0.4067 (13)	0.3000 (12)	19.5 (9)
C(43)	0.5543 (6)	0.2421 (8)	0.4983 (7)	9.3 (4)	C(106)	0.4372 (7)	0.4364 (10)	0.4331 (8)	12.7 (6)
C(44)	0.5430 (6)	0.2701 (8)	0.5487 (7)	9.3 (4)	C(104)	0.4447 (8)	0.3577 (10)	0.3523 (9)	13.5 (6)
C(45)	0.4969 (6)	0.2470 (8)	0.5692 (7)	9.9 (5)	C(111)	0.5783 (14)	0.4729 (18)	0.5771 (15)	26.3 (13)
C(46)	0.4635 (6)	0.1966 (8)	0.5318 (6)	8.1 (4)	C(200)	0.5215 (11)	0.9976 (14)	0.2609 (17)	22.9 (10)
C(51)	0.2380 (4)	0.2927 (6)	0.2346 (5)	4.7 (3)	C(201)	0.4357 (14)	0.0760 (17)	0.6840 (15)	25.7 (13)
C(52)	0.2674 (5)	0.2844 (6)	0.1892 (5)	5.4 (3)	C(202)	0.5129 (15)	0.0914 (16)	0.7216 (14)	28.2 (15)
C(53)	0.2377 (5)	0.2925 (7)	0.1247 (6)	6.9 (3)	C(203)	0.5705 (12)	−0.0124 (17)	0.3049 (13)	23.0 (11)
C(54)	0.1836 (5)	0.3098 (7)	0.1128 (6)	7.5 (4)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Bond Lengths (Å) in $[Cr_2(O_2Cbiph)_4]_2 \cdot 4tol$ (**2**)

Cr(1)–Cr(2)	2.348 (2)	C(11)–C(12)	1.42 (1)	C(42)–C(43)	1.44 (1)	C(74)–C(75)	1.39 (1)
–O(1)	1.990 (5)	–C(16)	1.38 (1)	C(43)–C(44)	1.33 (1)	C(75)–C(76)	1.42 (1)
–O(3)	2.010 (5)	C(12)–C(13)	1.47 (1)	C(44)–C(45)	1.41 (1)	C(81)–C(82)	1.41 (1)
–O(5)	1.983 (5)	–C(21)	1.39 (1)	C(45)–C(46)	1.42 (1)	–C(86)	1.42 (1)
–O(7)	1.996 (5)	C(13)–C(14)	1.35 (1)	C(51)–C(52)	1.39 (1)	C(82)–C(83)	1.48 (1)
Cr(2)–O(2)	2.072 (5)	(14)–C(15)	1.33 (1)	–C(56)	1.39 (1)	C(83)–C(84)	1.41 (1)
–O(4)	1.989 (5)	C(15)–C(16)	1.51 (1)	C(52)–C(53)	1.46 (1)	C(84)–C(85)	1.38 (1)
–O(6)	2.009 (5)	C(21)–C(22)	1.48 (1)	–C(61)	1.49 (1)	C(85)–C(86)	1.44 (1)
–O(8)	1.980 (5)	–C(26)	1.43 (1)	C(53)–C(54)	1.38 (1)	C(101)–C(102)	1.24 (4)
–O(2′)	2.309 (5)	C(22)–C(23)	1.34 (1)	C(54)–C(55)	1.38 (1)	–C(106)	1.61 (3)
C(1)–O(1)	1.272 (8)	C(23)–C(24)	1.38 (1)	C(55)–C(56)	1.43 (1)	–C(111)	1.28 (3)
–O(2)	1.296 (8)	C(24)–C(25)	1.45 (1)	C(61)–C(62)	1.39 (1)	C(102)–C(103)	1.30 (2)
–C(11)	1.52 (1)	C(25)–C(26)	1.35 (1)	–C(66)	1.42 (1)	C(103)–C(104)	1.48 (2)
C(2)–O(3)	1.274 (9)	C(31)–C(32)	1.40 (1)	C(62)–C(63)	1.41 (1)	C(104)–C(105)	1.39 (2)
–O(4)	1.252 (8)	–C(36)	1.38 (1)	C(63)–C(64)	1.37 (1)	C(105)–C(106)	1.26 (2)
–C(31)	1.53 (1)	C(32)–C(33)	1.43 (1)	C(64)–C(65)	1.36 (1)	C(200)–C(200′)	1.09 (5)
C(3)–O(5)	1.257 (8)	–C(41)	1.44 (1)	C(65)–C(66)	1.48 (1)	C(200)–C(202)	1.91 (4)
–O(6)	1.254 (8)	C(33)–C(34)	1.38 (1)	C(71)–C(72)	1.422 (9)	C(200)–C(203)	1.40 (3)
–C(51)	1.52 (1)	C(34)–C(35)	1.39 (1)	–C(76)	1.396 (9)	C(201)–C(203)	1.26 (5)
C(4)–O(7)	1.267 (8)	C(35)–C(36)	1.47 (1)	C(72)–C(73)	1.41 (1)	C(202)–C(202′)	1.54 (5)
–O(8)	1.263 (8)	C(41)–C(42)	1.41 (1)	–C(81)	1.49 (1)		
–C(71)	1.500 (9)	–C(46)	1.41 (1)	C(73)–C(74)	1.40 (1)		

expected, the two ortho phenyl groups at each end do not prevent the axial coordination of the medium size donor molecules.

$[Cr_2(O_2Cbiph)_4]_2$ (2). The atomic positional and thermal parameters for this structure are listed in Table IV. The structure is a dimer of dimers, and for it to be represented in

Table VI. Bond Angles (Deg) in $[Cr_2(O_2Cbiph)_4]_2 \cdot 4tol$ (**2**)

Cr(2)–Cr(1)–O(1)	88.8 (1)
–O(3)	86.9 (1)
–O(5)	89.4 (1)
–O(7)	88.3 (1)
Cr(1)–Cr(2)–O(2)	88.4 (1)
–O(4)	89.8 (1)
–O(6)	87.1 (1)
–O(8)	88.5 (1)
–O(2′)	164.5 (1)
O(1)–Cr(1)–O(3)	90.5 (2)
–O(5)	178.1 (2)
–O(7)	90.0 (2)
O(3)–Cr(1)–O(5)	90.0 (1)
–O(7)	175.1 (2)
O(5)–Cr(1)–O(7)	89.4 (2)
O(2)–Cr(2)–O(4)	90.5 (2)
–O(6)	175.6 (2)
–O(8)	90.3 (2)
–O(2′)	76.6 (2)
O(4)–Cr(2)–O(6)	90.1 (2)
–O(8)	178.1 (2)
–O(2′)	94.4 (2)
O(6)–Cr(2)–O(8)	89.1 (2)
–O(2′)	107.7 (2)
O(8)–Cr(2)–O(2′)	87.4 (2)
Cr(1)–O(1)–C(1)	122.2 (5)
–O(3)–C(2)	120.4 (5)
–O(5)–C(3)	118.1 (5)
–O(7)–C(4)	119.1 (5)
Cr(2)–O(2)–C(1)	117.9 (5)
–O(4)–C(2)	118.9 (6)
–O(6)–C(3)	119.4 (5)
–O(8)–C(4)	119.8 (5)
O(1)–C(1)–O(2)	122.6 (7)
–C(11)	117.9 (7)
O(2)–C(1)–C(11)	119.5 (7)
O(3)–C(2)–O(4)	124.0 (8)
–C(31)	117.2 (8)
O(4)–C(2)–C(31)	118.7 (8)
O(5)–C(3)–O(6)	125.7 (7)
–C(51)	117.0 (7)
O(6)–C(3)–C(51)	117.2 (7)
O(7)–C(4)–O(8)	124.3 (8)
–C(71)	119.4 (8)
O(8)–C(4)–C(71)	116.1 (7)
C(1)–C(11)–C(12)	119.0 (8)
–C(16)	113.5 (8)
C(11)–C(12)–C(13)	115.4 (8)
C(11)–C(12)–C(21)	126.1 (8)
C(11)–C(16)–C(15)	114.0 (9)
C(12)–C(11)–C(16)	127.0 (8)
C(12)–C(13)–C(14)	117 (1)
C(12)–C(21)–C(22)	121.2 (9)
–C(26)	123.6 (9)
C(13)–C(12)–C(21)	118.5 (9)
C(13)–C(14)–C(15)	128 (1)
C(14)–C(15)–C(16)	118 (1)
C(21)–C(22)–C(23)	118 (1)
C(21)–C(26)–C(25)	123.5 (9)
C(22)–C(21)–C(26)	115.1 (9)
C(22)–C(23)–C(24)	127 (1)
C(23)–C(24)–C(25)	115 (1)
C(24)–C(25)–C(26)	121 (1)
C(2)–C(31)–C(32)	121.5 (8)
–C(36)	113.3 (8)
C(31)–C(32)–C(33)	115.7 (9)
–C(41)	125.3 (9)
C(31)–C(36)–C(35)	118.7 (9)
C(32)–C(31)–C(36)	125.1 (9)
C(32)–C(33)–C(34)	119 (1)
C(32)–C(41)–C(42)	116.4 (9)
–C(46)	122.3 (9)
C(33)–C(32)–C(41)	118.8 (9)
C(33)–C(34)–C(35)	126 (1)
C(34)–C(35)–C(36)	115 (1)
C(41)–C(42)–C(43)	113 (1)
C(41)–C(46)–C(45)	122 (1)
C(42)–C(41)–C(46)	121 (1)
C(42)–C(43)–C(44)	127 (1)
C(43)–C(44)–C(45)	120 (1)
C(44)–C(45)–C(46)	117 (1)
C(3)–C(51)–C(52)	122.5 (7)
–C(56)	114.8 (7)
C(51)–C(52)–C(53)	117.1 (8)
–C(61)	125.1 (8)
C(51)–C(56)–C(55)	120.2 (8)
C(52)–C(51)–C(56)	122.6 (8)
C(52)–C(53)–C(54)	118.6 (8)
C(52)–C(61)–C(62)	118.5 (9)
–C(66)	117.1 (9)
C(53)–C(52)–C(61)	117.4 (8)
C(53)–C(54)–C(55)	125 (1)
C(54)–C(55)–C(56)	117 (1)
C(61)–C(62)–C(63)	118.1 (9)
C(61)–C(66)–C(65)	112 (1)
C(62)–C(61)–C(66)	124.4 (9)
C(62)–C(63)–C(64)	122 (1)
C(63)–C(64)–C(65)	119 (1)
C(64)–C(65)–C(66)	124 (1)
C(4)–C(71)–C(72)	122.5 (7)
–C(76)	115.4 (7)
C(71)–C(72)–C(73)	118.6 (7)
–C(81)	124.6 (7)
C(71)–C(76)–C(75)	118.3 (7)
C(72)–C(71)–C(76)	122.0 (7)
C(72)–C(73)–C(74)	119.4 (8)
C(72)–C(81)–C(82)	117.7 (8)
–C(86)	119.3 (8)
C(73)–C(72)–C(81)	116.5 (7)
C(73)–C(74)–C(75)	121.5 (9)
C(74)–C(75)–C(76)	120.0 (8)
C(81)–C(82)–C(83)	119.6 (8)
C(81)–C(86)–C(85)	115.9 (9)
C(82)–C(81)–C(86)	122.9 (8)
C(82)–C(83)–C(84)	116.5 (9)
C(83)–C(84)–C(85)	123 (1)
C(84)–C(85)–C(86)	122 (1)
C(102)–C(101)–C(106)	118 (2)
–C(111)	166 (2)
C(106)–C(101)–C(111)	75 (2)
C(101)–C(102)–C(103)	134 (2)
C(101)–C(106)–C(105)	109 (1)
C(102)–C(103)–C(104)	108 (2)
C(103)–C(104)–C(105)	122 (2)
C(104)–C(105)–C(106)	128 (1)
C(200′)–C(200)–C(201)	128 (3)
–C(202)	78 (2)
–C(203)	161 (5)
C(202)–C(200)–C(203)	101 (2)
C(202)–C(201)–C(203)	103 (3)
C(200)–C(203)–C(201)	98 (3)

its entirety, a stereopair (Figure 2) is required. The two $Cr_2(O_2Cbiph)_4$ units are related by a center of inversion and are joined by two axial O–Cr bonds from Cr(2) to O(2)′ and Cr(2)′ to O(2). All of the ortho phenyl groups are directed away from the juncture and lie toward the two axial regions around Cr(1) and Cr(1)′. Figure 3 shows just one $Cr_2(O_2Cbiph)_4$ unit and defines the atomic numbering scheme. Tables V and VI list the bond distances and bond angles, respectively.

It is evident that in **2** our intention of obtaining a $Cr_2(O_2CR)_4$ species without any axial coordination has again been frustrated, or perhaps one may take the slightly more cheerful view that it has now been only half-frustrated. The way in which this has happened, though disappointing and not anticipated, is easily rationalized. Obviously, when all four ortho phenyl groups are directed toward one end of the $Cr_2(O_2Cbiph)_4$ unit, the other end is left quite free to engage in the kind of association through carboxylate oxygen bridging that in other unhindered $Cr_2(O_2CR)_4$ compounds leads to the formation of infinite chains, as observed when R = CH_3 and $C(CH_3)_3$. Apparently, the driving force for such oxygen bridging is great enough to stabilize the observed structure as compared to a more loosely packed one consisting of centrosymmetric, unassociated $Cr_2(O_2Cbiph)_4$ molecules. It appears that a still more elaborate R group that is individually capable of interfering with association *at both ends simultaneously* must be used to achieve our goal of observing completely discrete $Cr_2(O_2Cbiph)_4$ molecules.

The structure which has been adopted by **2** is, however, not without interest. The bond lengths and angles in the four-membered bridging group Cr(2)···O(2)′–Cr(2)′···O(2) are rather typical. The Cr(1)–Cr(2)···O(2)′ chain is slightly nonlinear, with an angle of 164.5 (1)°, which is usual. The interdimer, Cr(2)···O(2)′ distance, 2.309 (5) Å, is well within the normal range of axial Cr···O distances. Finally, the Cr(2)–O(2) distance, 2.072 (5) Å, is about 0.08 Å longer than the Cr–O distances where the oxygen atoms are not bridging. This, too, is quite usual.

The feature of **2** that is most interesting is the Cr–Cr distance, 2.348 (2) Å. This is within the range spanned by most of the $Cr_2(O_2CR)_4L_2$ compounds with aliphatic or aromatic R groups and axial ligands that are N or O donors. It is also between the values for the infinite-chain structures of $Cr_2(O_2CCH_3)_4$ and $Cr_2(O_2CCMe_3)_4$. A particularly significant comparison is with the Cr–Cr distance in **1**, where there is axial coordination at *both* ends of the Cr–Cr unit; in **2** where such coordination occurs, via bridging, at only *one* end, the Cr–Cr distance is longer.

It might have been expected that on proceeding from the situation in **1**, and many similar compounds, where there is axial coordination at both Cr atoms, to that in **2**, which has axial coordination at only one Cr atom, the Cr–Cr bond would be shorter. This is the kind of pattern clearly shown[1] for Ib and Ic. Evidently, $Cr_2(O_2CR)_4$ systems do not have such simple behavior. It may be noted that this unexpected result is not unlike that obtained with $Cr_2(O_2CCMe_3)_4$, which has two unusually long axial Cr···O distances but a Cr–Cr distance very similar to those found in other compounds with much shorter axial Cr···O distances.

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Registry No. **1**, 76173-80-3; **2**, 76173-82-5; $Cr_2(O_2CCH_3)_4$, 15020-15-2; Cp_2Cr, 1271-24-5.

Supplementary Material Available: Tables of observed and calculated structure factors for the two structures (21 pages). Ordering information is given on any current masthead page.