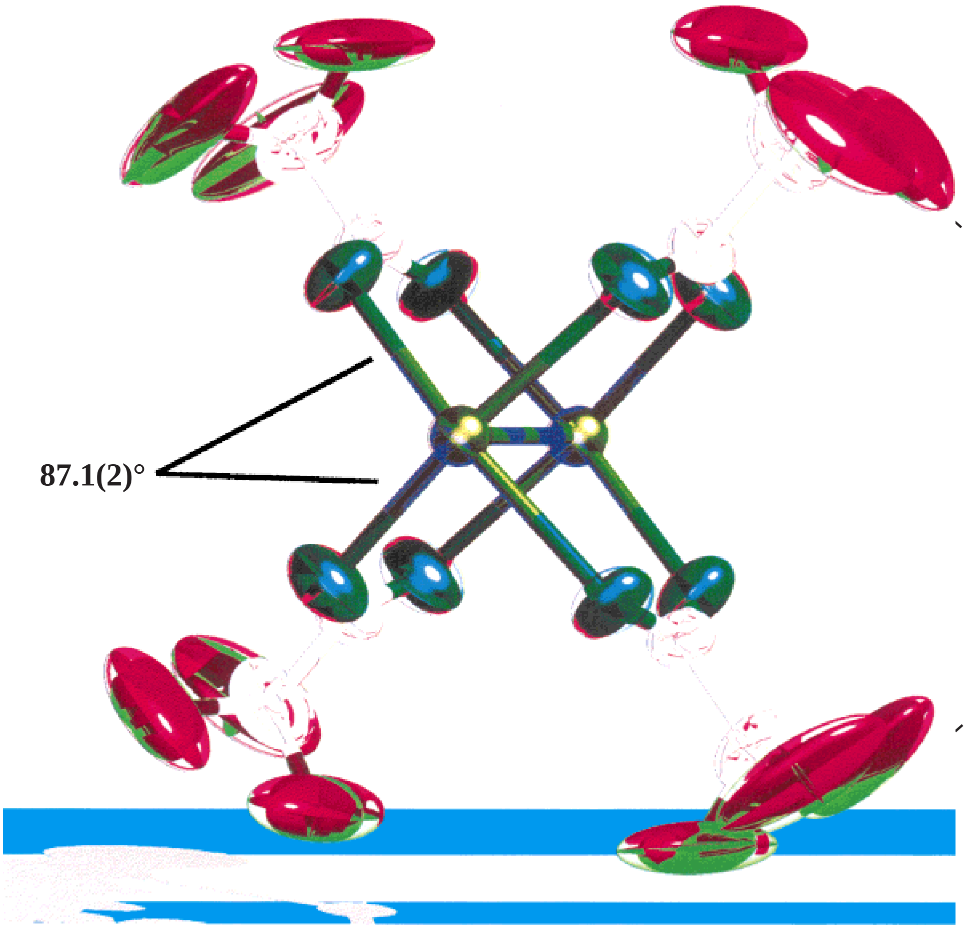
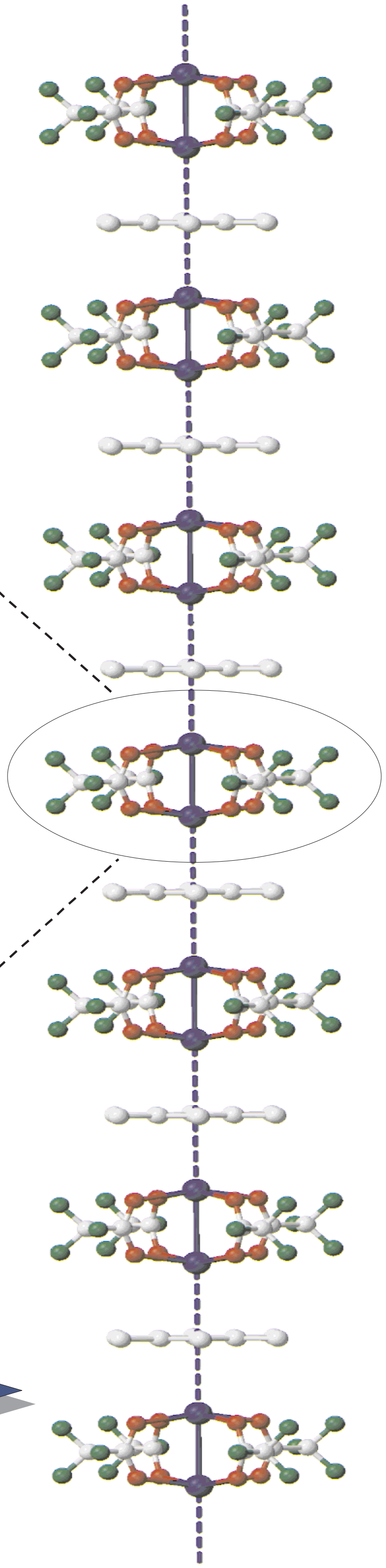
Coordination sphere of the dimetal unit in the bismuth(II) trifluoroacetate molecule:
the packing forces on the indicated periphery lead to the given deviation from the ideal tetragonal-prismatic arrangement in the crystal.





$[Bi_2(O_2CCF_3)] \cdot C_{12}H_{18}$:
a one-dimensional coordination copolymer of a main group element compound with hexamethylbenzene.

Further details on this arene adduct of the first reduced main group element carboxylate are discussed on the following pages.

$[Bi_2(O_2CCF_3)_4] \cdot C_6Me_6$—Arene Adduct of a Reduced Main Group Element Carboxylate with Paddle Wheel Structure**

Walter Frank,* Vera Reiland, and Guido J. Reiß

Dedicated to Professor Otto J. Scherer
on the occasion of his 65th birthday

In the course of the development of bonding models for systems containing isolated metal–metal bonds, transition metal complexes with tetragonal-prismatic coordination and among these especially the transition metal carboxylates with "paddle wheel structure" have played an outstanding role.[1] Remarkably hitherto no corresponding main group element species within this class of compounds have been presented. On the whole very few examples of carboxylato groups functioning as bridging ligands at element–element bonds have been observed in the field of the representative elements: $B_3H_6(O_2CR)$,[2a] $Ga_2(CH(SiMe_3)_2)_2(O_2CR)_2$,[2b] and $Ph_4Sn_2(O_2CR)$.[2c] In our work on the chemistry and coordination chemistry of bismuth(III) trifluoroacetate and its π-arene complexes we isolated the title compound **1** which contains the first reduced main group element carboxylate as part of a one-dimensional coordination copolymer with hexamethylbenzene.

$[Bi_2(O_2CCF_3)_4] \cdot C_6Me_6$ **1**

Dark red crystals of **1** were obtained by an as yet unclarified route by thermolysis of bismuth(III) trifluoroacetate[3] in the presence of hexamethylbenzene in a sealed glass tube. The crystals, which are remarkably stable when exposed to air, were characterized by elemental analysis, mass spectrometry, and a crystal structure determination.[4] These crystals are negligibly soluble in arenes and in donor solvents. In the mass spectrum (electron impact) the peak corresponding to the highest mass observed is attributed to $[Bi_2(O_2CCF_3)_4]$. In addition the signals related to the members of the series $[Bi_2(O_2CCF_3)_n]^+$ with $n = 3-0$ are present. Although the Bi atoms of the complex are held together by both the Bi–Bi bond and the bridging ligands, signals related to the series $[Bi(O_2CCF_3)_n]^+$ with $n = 2-0$ are observed as well.

Under the conditions described here **1** crystallizes in the monoclinic space group $C2/m$. $Bi_2(O_2CCF_3)_4$ and C_6Me_6 molecules acting as η^6 bridging ligands on both sides build up chains along [010] (Figure 1).[5] Both components occupy special positions of crystallographic point group symmetry $2/m$. The distance between the metal atom and the plane of the arene ligand (3.053(2) Å) is slightly shorter than in $[Me_6C_6(BiCl_3)_2]$[6a] (3.07 Å) and significantly longer than in the cationic complex $[Me_6C_6BiCl_2][AlCl_4]$ (2.62 Å).[6b] The Bi–Bi distance of 2.947(1) Å is significantly shorter in **1** than in $(Me_3Si)_4Bi_2$ (3.035(3) Å),[7a] 2,2′,5,5′-tetramethyldibismole (2.9905(5) Å),[7b] and the three structurally characterized modifications of Ph_4Bi_2 (2.984(2)–2.990(2) Å).[7c–e] It is just 5% longer than in Tbt_2Bi_2 (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)(2.8206(8) Å),[8] which recently was presented as a compound containing a Bi–Bi double bond. The Bi–O distances of 2.387(6) and 2.417(7) Å are comparable to the shorter ones in $Bi(O_2CCF_3)_3 \cdot HO_2CCF_3$,[3b] which exhibits a Bi–O distance spectrum ranging from 2.26(3) to 2.91(3) Å. If the center of the arene is considered to be a coordination site, the Bi atoms are six-coordinate. The geometry of the coordination sphere reflects the insufficient span of the carboxylato ligands with respect to the length of a Bi–Bi bond. The coordination sphere (Figure 2) does not show any gap interpretable in the sense of a stereochemically active lone pair of electrons, an extremely rare situation in the coordination chemistry of bismuth(III) complexes with oxygen donor ligands.[9]

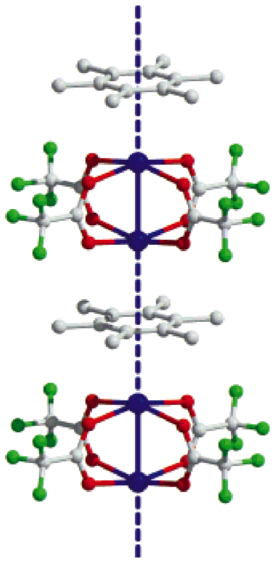


Figure 1. Segment of the one-dimensional coordination-polymeric arrangement of bismuth(II) trifluoroacetate and hexamethylbenzene molecules in the crystal of **1**; Bi atoms are shown blue, F atoms green, O atoms red, and C atoms gray. The distances Bi–Bi and Bi–arene$_{center}$ which are characteristic intercepts on the "supramolecular axis" are very similar (2.9466(11) and 3.053(2) Å, respectively). The distances between the Bi atom and the three crystallographically independent ring C atoms are 3.354(4), 3.357(4), and 3.358(3) Å.

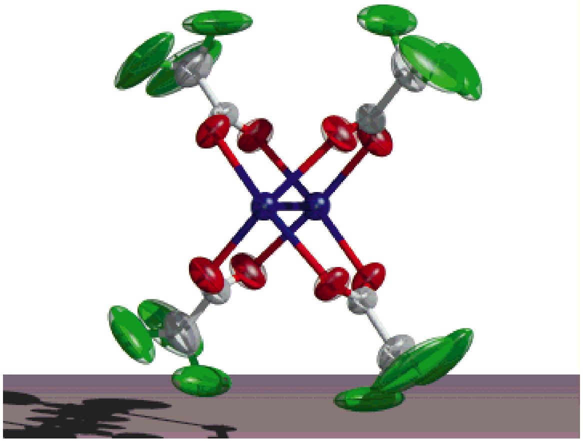


Figure 2. Structure of the $Bi_2(O_2CCF_3)_4$ molecule having C_{2h} point group symmetry in the crystal of **1**; anisotropic displacement ellipsoids are drawn at the 50% probability level; color coding as in Figure 1. The representation of the CF_3 groups indicates their high mobility.

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In addition to the red needles described we obtained small orange plates of another modification of **1** under different reaction conditions. Furthermore, the red phase slowly changes into a yellow one at low temperature. Thus investigations on the phase relations as well as efforts to solve the formation mechanism of **1** are in progress.

Experimental Section

catena-Poly{[tetrakis(μ-trifluoroacetato-$\kappa O,\kappa O'$)dibismuth($Bi-Bi$)]-μ-η^6-hexamethylbenzene} (**1**): A mixture of $Bi(O_2CCF_3)_3$[3b] (0.010 g, 0.18 mmol) and freshly sublimed hexamethylbenzene (0.020 g, 0.12 mmol) in a sealed Duran glass tube was heated to 100 °C in an aluminum block oven. Small light yellow plates of $Bi(O_2CCF_3)_3 \cdot 0.5\,C_{12}H_{18}$ which initially grew at the glass surface disappeared in the course of several weeks, while dark red needles of **1** grew (0.019 g, 20.5 % isolated; a yellow-gray residue remained). Elemental analysis calcd for ($M_r = 1032.30$) (%): C 23.1, H 1.7; found: C 22.1, H 1.8; MS (EI, 70 eV, 1.0 mA, QT = 220 °C): *m/z* (%): 870 (9) $[(\mathbf{1} - C_{12}H_{18})^+]$, 757 (24) $[(Bi_2(O_2CCF_3)_3)^+]$, 644(7) $[(Bi_2(O_2CCF_3)_2)^+]$, 531(6) $[(Bi_2(O_2CCF_3))^+]$, 435 (8) $[(Bi(O_2CCF_3)_2)^+]$, 418 (6) $[Bi_2^+]$, 322(19) $[(Bi(O_2CCF_3))^+]$, 209 (50) $[Bi^+]$, 162 (57) $[C_{12}H_{18}^+]$, 147 (100) $[C_{11}H_{15}^+]$.

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[4] $C_{20}H_{18}Bi_2F_{12}O_8$, $M_r = 1032.30$; crystal dimensions: $0.02 \times 0.02 \times 0.1$ mm^3, monoclinic, space group $C2/m$, $a = 19.963(4)$, $b = 9.053(2)$, $c = 9.040(2)$ Å, $\beta = 109.22(3)°$, $Z = 2$, $V = 1542.7(6)$ Å^3, $\rho_{calcd} = 2.222$ Mg m^{-3}, $T = -10 \pm 1$ °C, $2\theta_{max} = 52.1°$, STOE-IPDS, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 5558 measured, 1397 unique, and 1321 observed reflections with $I > 2\sigma(I)$, LP correction ($\mu = 11.50$ mm^{-1}), Patterson method and ΔF synthesis, minimization of $\Sigma w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.0599\,P)^2]$ where $P = (F_o^2 + 2\,F_c^2)/3$, 114 refined paramters, $R_1 = 0.0367$, $wR_2 = 0.0850$; $\Delta\rho_{max}/\Delta\rho_{min}$ +1.18/−1.37 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102011. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Cooperative Hydrogen Bonding and Enzyme Catalysis**

Hong Guo* and Dennis R. Salahub*

Understanding the structural basis for stabilization of transition states in enzyme-catalyzed reactions is of fundamental importance. Such knowledge would help to improve existing enzymes and to design new ones.[1, 2] High-resolution structures have revealed important features at enzyme active sites.[3, 4] However, identification of the key factors responsible for the catalysis has proven to be difficult[5, 6] owing to the complexity of interactions that obscure the underlying mechanisms. This is the case for stabilization of transition states involving α helices, for example. Although the ability of the helices to stabilize negatively charged reaction intermediates and transition states has been well established,[2, 3, 7] the origin of the charge stabilization is still uncertain.[3, 5]

Here we report results of density functional calculations which reveal a large cooperative effect induced by the interaction of an anion with a peptide hydrogen bond network, directly or through an imidazole (Im) molecule. The major contribution to this cooperativity consists of nonadditive, many-body effects that can not be reflected by the pair-wise interactions of the charged ligand with the individual peptide units involved, and that are closely associated with the presence of the hydrogen-bond network. The increase of the cooperative effect on going from a neutral to a negatively charged ligand is sufficiently large that it could make an important contribution to the catalysis by stabilizing the charge formation along the reaction pathway in the enzyme-catalyzed reactions. The mechanism proposed here, based on the enhancement of cooperative hydrogen bonding, provides a consistent interpretation for both the wide occurrence of helices at enzyme active sites[3] and phosphate (sulfate) binding sites[7] as well as their absence in some instances.[8–11]

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