444 *Inorg. Chem.* **2011**, *50*, 444–450
DOI: 10.1021/ic101168b

Inorganic Chemistry
Article

Molecular Conductors with a 8-Hydroxy cobalt Bis(dicarbollide) Anion

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Received June 10, 2010

Molecular conductors based on the 8-hydroxy cobalt bis(dicarbollide) anion, (TMTTF)[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**1**), (BMDT-TTF)[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$) (1′,2′-$C_2B_9H_{11}$)] (**2**), and (BEDT-TTF)[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**3**), were synthesized, and their crystal structures and electrical conductivities were determined. Compounds **2** and **3** are isostructural to the corresponding radical-cation salts of the parent cobalt bis(dicarbollide). All of the radical-cation salts prepared were found to be semiconductors. The relative stability of the rotation conformers of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion was estimated using DFT/BP86 quantum chemical calculations.

Introduction

The cobalt bis(dicarbollide) anion occupies a unique position among all metallacarboranes because of its extraordinarily high thermal and chemical stability, low nucleophilicity, inorganic superacid behavior, and ease of modification through substitution of hydrogen atoms.[1] These properties have made cobalt bis(dicarbollide) and its derivatives appropriate for use as extractants of radionuclides from nuclear waste,[2,3] doping agents in conducting organic polymers,[4,5] and ion-selective electrodes[6] as well as boron-rich carriers for boron neutron capture therapy[7] and HIV protease inhibitors.[8] Crystal design and engineering is another field of potential application of bis(dicarbollide) complexes. Crystal engineering is a topic of intense research interest and holds promise for revolutionizing materials design and synthesis.

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(1) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818–1819. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Hove, D. V.; Pilling, R. L.; Pitts, A. D.; Reinjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879–896. (c) Sivaev, I. B.; Bregadze, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 783–805 and references cited therein.

(2) (a) Rais, J.; Grüner, B. In *Ion Exchange and Solvent Extraction*; Marcus, Y., Sengupta, A. K., Eds.; Marcel Dekker Inc.: New York, 2004; Vol. *17*; pp 243−334. (b) Grüner, B.; Mikulašek, L.; Bača, J.; Cisařova, I.; Böhmer, V.; Danila, C.; Reinoso-Garcia, M. M.; Verboom, W.; Reinhoudt, D. N.; Casnati, A.; Ungaro, R. *Eur. J. Org. Chem.* **2005**, 2022–2039. (c) Reinoso-Garcia, M. M.; Janczewski, D.; Reinhoudt, D. N.; Verboom, W.; Malinowska, E.; Pietrzak, M.; Hill, C.; Bača, J.; Grüner, B.; Selucky, P.; Grüttner, C. *New J. Chem.* **2006**, *30*, 1480–1492. (d) Mikulašek, L.; Grüner, B.; Dordea, C.; Rudzevich, V.; Böhmer, V.; Haddaoui, J.; Hubscher-Bruder, V.; Arnaud-Neu, F.; Časlavsky, J.; Selucky, P. *Eur. J. Org. Chem.* **2007**, 4772–4783. (e) Selucky, P.; Rais, J.; Lučanikova, M.; Grüner, B.; Kvičalova, M.; Fejfarova, K.; Cisařova, I. *Radiochim. Acta* **2008**, *96*, 273–284.

(3) (a) Romanovskiy, V. N.; Smirnov, I. V.; Babain, V. A.; Todd, T. A.; Law, J. D.; Herbst, R. S.; Brewer, K. N. *Solvent Extr. Ion Exch.* **2001**, *19*, 1–21. (b) Luther, T. A.; Herbst, R. S.; Peterman, D. R.; Tillotson, R. D.; Garn, T. G.; Babain, V. A.; Smirnov, I. V.; Stoyanov, E. S.; Antonov, N. G. *J. Radioanal. Nucl. Chem.* **2006**, *267*, 603–613. (c) Herbst, R. S.; Luther, T. A.; Peterman, D. R.; Babain, V. A.; Smirnov, I. V.; Stoyanov, E. S. In *Nuclear Waste Management*; Wang, P. W., Zachry, T., Eds.; ACS Symposium Series 943; American Chemical Society: Washington, DC, 2006; pp 171−185.

(4) (a) Teixidor, F.; Viñas, C.; Demonceau, A.; Nuñez, R. *Pure Appl. Chem.* **2003**, *75*, 1305–1313 and references cited therein. (b) Gentil, S.; Crespo, E.; Rojo, I.; Friang, A.; Viñas, C.; Teixidor, F.; Grüner, B.; Gabel, D. *Polymer* **2005**, *46*, 12218–12225. (c) Crespo, E.; Gentil, S.; Viñas, C.; Teixidor, F. *J. Phys. Chem. C* **2007**, *111*, 18381–18386.

(5) Fabre, B.; Hao, E.; LeJeune, Z. M.; Amuhaya, E. K.; Barriere, F.; Garno, J. C.; Vicente, M. G. H. *ACS Appl. Mater. Interfaces* **2010**, *2*, 691–702.

(6) (a) Krondak, M.; Volf, R.; Kral, V. *Collect. Czech. Chem. Commun.* **2001**, *66*, 1659–1664. (b) Titsch, J.; Krondak, M.; Volf, R.; Grüner, B.; Kral, V. *Chem. Listy* **2005**, *99*, 186–189.

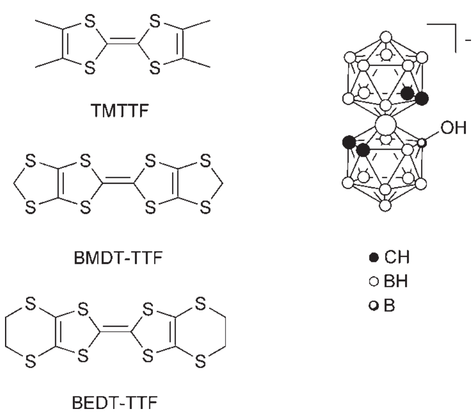
(7) (a) Sivaev, I. B.; Bregadze, V. I. *Eur. J. Inorg. Chem.* **2009**, 1433–1450. (b) Sivaev, I. B.; Semioshkin, A. A.; Bregadze, V. I. *Appl. Radiat. Isot.* **2009**, *67*, S91–S93 and references cited therein.

(8) (a) Cigler, P.; Kožišek, M.; Řezačova, P.; Otwinowski, Z.; Pokorna, J.; Plešek, J.; Grüner, B.; Dolečkova-Marešova, L.; Masa, M.; Sedlaček, J.; Bodem, J.; Kräusslich, H.-G.; Kral, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 15394–15399. (b) Kožišek, M.; Cigler, P.; Lepšik, M.; Fanfrlik, J.; Řezačova, P.; Brynda, J.; Pokorna, J.; Plešek, J.; Grüner, B.; Šaškova, K. G.; Vaclavikova, J.; Kral, V.; Konvalinka, J. *J. Med. Chem.* **2008**, *51*, 4839–4843. (c) Řezačova, P.; Pokorna, J.; Brynda, J.; Kožišek, M.; Cigler, P.; Lepšik, M.; Fanfrlik, J.; Řezač, J.; Šaškova, K. G.; Sieglova, I.; Plešek, J.; Šicha, V.; Grüner, B.; Oberwinkler, H.; Sedlaček, J.; Kräusslich, H.-G.; Hobza, P.; Kral, V.; Konvalinka, J. *J. Med. Chem.* **2009**, *52*, 7132–7141.

An essential step along the path to predicting solid structures from the substituent groups on the chemical species of interest is to more clearly elucidate the factors that govern the noncovalent assembly of molecules or ions into their ultimate solid-state architectures. The auto-organization of crystal lattices of molecular and ionic species through secondary interactions has been recognized for many years. Nevertheless, the real chemical significance of secondary bonds (or secondary interactions) has become evident relatively recently.[9] Although most of the research in crystal engineering has been performed in the field of organic chemistry, the use of organometallic or coordination complexes as building blocks allows one to obtain compounds with novel solid-state properties such as magnetism, conductivity, redox, luminescent, etc. Thus, organometallic crystal engineering of molecular materials has become a rapidly developing research field.[10]

The tetrathiafulvalene-based radical-cation salts with organometallic counterions have been intensively investigated over the last 2 decades and characterized by the diversity of their crystal structures and physical properties.[11] Because conductivity in these materials occurs via a π-electron-donor network made up of stacks or sheets of closely packed radical cations, crystal packing of radical cations is a crucial parameter determining the transport properties of molecular conductors. As far as radical-cation salts are two-component systems, their structures and properties depend strongly on the nature of the anions, which determine the character of particular structures. The iron group metal bis(1,2-dicarbollide) complexes $[3,3'\text{-M}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (M = Fe, Co, Ni) have been proposed as counterions for the synthesis of new radical-cation-based molecular materials.[12] Substitution of hydrogen atoms for various atoms and groups in these complexes opens practically unlimited perspectives of their modification.[13] As a result, the metallacarborane anions with a variety of volumes and charges can be prepared. Moreover, an introduction of substituents which are capable of hydrogen-bond formation provides important strategy for molecular design to control the molecular arrangement in organometallic crystals.[14] Recently, we demonstrated that the introduction of bromine[15] or iodine[16] substituents into the open face of the dicarbollide ligand of cobaltacarborane complexes can result in the formation of layered-structure molecular conductors with infinite-length chains of anions due to CH···XB (X = Br, I) intermolecular hydrogen bonds.

Scheme 1. Structures of Tetrathiafulvalene and Cobalt Bis(dicarbollide) Derivatives



In this contribution, we present the results of a study of the effect of the hydroxy substituent on the crystal structure and electrical conductivity of tetrathiafulvalene-derived radical-cation salts [tetramethyltetrathiafulvalene (TMTTF), bis(methylenedithio)tetrathiafulvalene (BMDT-TTF), and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF); Scheme 1)] of a cobalt bis(dicarbollide) anion as well as the quantum chemical calculations of the relative stability of the rotation conformers of the $[8\text{-HO-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ anion.

Results and Discussion

Bis(dicarbollide) complexes of transition metals can play an active role in the formation of the crystal structures of molecular conductors depending on the mutual orientation of the dicarbollide ligands.[12] The asymmetry of the charge distribution in the dicarbollide ligand (a positive charge on the *CH* hydrogen atoms and the most negative charge on the opposite side of the pentagonal ligand face) results in a rather high dipole moment (5.4 D) of the bis(dicarbollide) anion in a cisoid conformation and a null dipole moment in a transoid conformation.[17] In the case of unsubstituted bis(dicarbollide) complexes, the difference in energy of the rotational conformers and the corresponding rotation barriers is rather low.[18,19] As a result, easy rotation of the dicarbollide ligands could result in stabilization of different conformations of the anion in the solid state. The difference in the rotational conformer energy could be enlarged by the substitution of hydrogen atoms in the dicarbollide ligand for different atoms

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(9) (a) *Crystal Engineering: from Molecules and Crystals to Materials*; Braga, D., Grepioni, F., Orpen, A. G., Eds.; NATO Science Series C: Mathematical and Physical Sciences; Kluwert Academic Publishers: Dordrecht, The Netherlands, 1999; Vol.*538*, p 512. (b) Braga, D.; Grepioni, F.; Desiraju, G. P. *Chem. Rev.* **1998**, *98*, 1375–1406. (c) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138. (d) Braga, D. *J. Chem. Soc., Dalton Trans.* **2000**, 3705–3713. (e) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (f) Braga, D.; Brammer, L.; Champness, N. R. *CrystEngComm* **2005**, *7*, 1–19.

(10) Coronado, E.; Gimenez-Saiz, C.; Marti-Gastaldo, C. In *Engineering of Crystalline Materials Properties*; Novoa, J. J., Braga, D., Addadi., L., Eds.; NATO Science for Peace Security Series B: Physics and Biophysics;Springer Scientific: Dordrecht, The Netherlands, 2008; pp173−191.

(11) (a) Geiser, U.; Schlueter, J. A. *Chem. Rev.* **2004**, *104*, 5203–5242. (b) Schlueter, J. A. In *Conducting and Magnetic Organometallic Molecular Materials*; Topics in Organometallic Chemistry; Fourmigue, M., Ouahab, L., Eds.; Springer-Verlag: Berlin, 2009; Vol. *27*; pp 1−33.

(12) (a) Yan, Y.-K.; Mingos, D. M. *Chem. Soc. Rev.* **1995**, 203. (b) Bregadze, V.; Sivaev, I.; Lobanova, I.; Kazheva, O.; Alexandrov, G.; Kravchenko, A.; Starodub, V.; Buravov, L.; Titov, L.; Dyachenko, O. *J. Chem. Sci.* **2010**, *122*, 37.

(13) Bregadze, V. I.; Timofeev, S. V.; Sivaev, I. B.; Lobanova, I. A. *Russ. Chem. Rev.* **2004**, *73*, 470.

(14) (a) Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **2000**, 3745. (b) Brammer, L. *Chem. Soc. Rev.* **2004**, *33*, 476. (c) Fourmigue, M.; Batail, P. *Chem. Rev.* **2004**, *104*, 5379.

(15) Kazheva, O.; Alexandrov, G.; Kravchenko, A.; Starodub, V.; Lobanova, I.; Sivaev, I.; Bregadze, V.; Buravov, L.; Dyachenko, O. *Solid State Sci.* **2008**, *10*, 1734–1739.

(16) Kazheva, O. N.; Alexandrov, G. G.; Kravchenko, A. V.; Starodub, V. A.; Lobanova, I. A.; Sivaev, I. B.; Bregadze, V. I.; Titov, L. V.; Buravov, L. I.; Dyachenko, O. A. *J. Organomet. Chem.* **2009**, *694*, 2336–2342.

(17) Juarez-Perez, E. J.; Nuñez, R.; Viñas, C.; Sillanpää, R.; Teixidor, F. *Eur. J. Inorg. Chem.* **2010**, 2385–2392.

(18) Bühl, M.; Hnyk, D.; Machaček, J. *Chem.—Eur. J.* **2005**, *11*, 4109–4120.

(19) (a) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849–1851. (b) Hawthorne, M. F.; Ramachandran, B. M.; Kennedy, R. D.; Knobler, C. B. *Pure Appl. Chem.* **2006**, *78*, 1299–1304. (c) Bühl, M.; Holub, J.; Hnyk, D.; Machaček, J. *Organometallics* **2006**, *25*, 2173–2181.

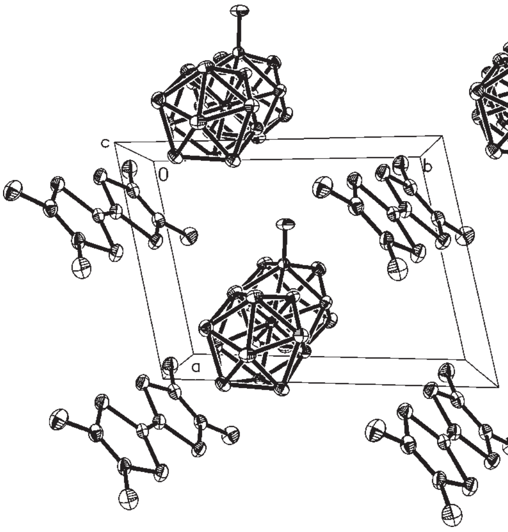

Figure 1. Fragment of the crystal structure of **1**.

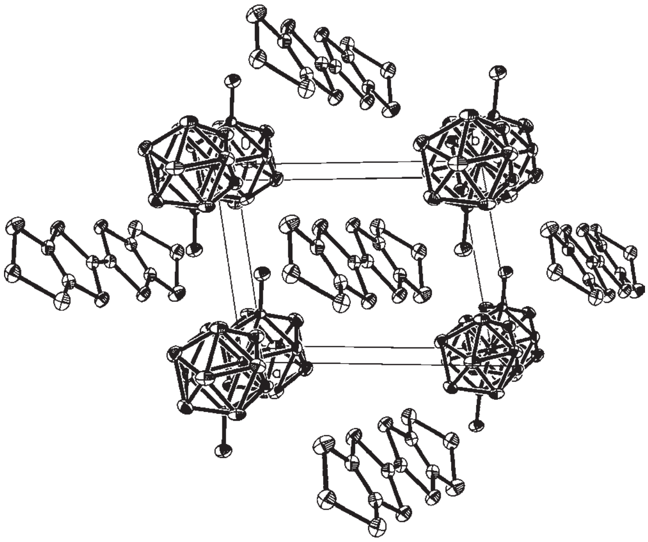

Figure 2. Fragment of the crystal structure of **2**.

and groups, resulting in stabilization of definite conformers.[20,21] Earlier we found that the introduction of bromine or iodine atoms in the open pentagonal face of the dicarbollide ligand (positions 8 and 8′ of the cobaltacarborane skeleton) favors the formation of intermolecular hydrogen bonds participating in the formation of the crystal supramolecular architecture.[15,16] At the same time, the halogen introduction results in stabilization of the transoid conformation due to the formation of intramolecular $CH\cdots XB$ ($X = Br, I$) hydrogen bonds, locking ligand rotation. The aim of this work was to study the effect of the hydroxy group as a classical hydrogen-bond-forming substituent on the rotational mobility of the dicarbollide ligands in a cobalt bis(dicarbollide) anion and the formation of the crystal structures of tetrathiafulvalenium salts of the $[8\text{-HO-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ anion.

Single crystals of the 1:1 radical-cation salts (TMTTF)$[8\text{-HO-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**1**), (BMDT-TTF)$[8\text{-HO-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**2**), and (BEDT-TTF)$[8\text{-HO-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**3**) were prepared by electrochemical anodic oxidation of the corresponding π donors in the presence of $(Me_4N)[8\text{-HO-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$.

Compound **1** represents the first example of a tetramethylthiafulvalenium salt with a metallacarborane anion. In the crystal structure of **1**, the TMTTF$^{\bullet+}$ radical cations and the cobaltacarborane anions alternate along the *ab* diagonal to form mixed stacks (Figure 1). Based on the known correlation between the bond lengths in the TMTTF skeleton and the charge-transfer degree in TMTTF complexes,[22] the donor charge was determined to be 1+, which is in good agreement with the overall compound stoichiometry and 3+ metal oxidation degree in the cobaltacarborane anion.

Compounds **2** and **3** were found to be isostructural with the corresponding radical-cation salts of the parent cobaltacarborane, (BMDT)$[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$[23] and (BEDT)-$[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$.[24] The crystal structure of **2** is similar to that of **1**, with the BMDT-TTF$^{\bullet+}$ radical cations and the cobaltacarborane anions alternating along the *ab* diagonal (Figure 2). Bond lengths in the BMDT-TTF skeleton are typical for compounds with 1+ donor charge and the overall compound stoichiometry.[25] In the crystal structure of **3**, the BEDT-TTF$^{\bullet+}$ radical cations and the cobaltacarborane anions form layers, alternating along the *b* axis (Figure 3). The BEDT-TTF$^{\bullet+}$ radical cations in the layers form bonded pairs possessing an inversion center. The distance between the averaged planes of the radical cations in the pairs is 3.66 Å, and shortened $S(3)\cdots S(6)$ [3.395(1) Å] and $S(4)\cdots S(5)$ [3.459(4) Å] distances (the sum of the van der Waals radii is 3.68 Å[26]) were found between the BEDT-TTF$^{\bullet+}$ cations in the pairs. The radical cations in the pairs are fully eclipsed. No intermolecular interactions between the pairs were revealed. Bond lengths in the BEDT-TTF skeleton are in good agreement with the 1+ donor charge and the overall compound stoichiometry.[27] The metallacarboranes in the anionic layer are arranged in a parquet-like manner (Figure 3).

It was shown earlier that crystal packing in the radical-cation salts of the iron group bis(dicarbollide) complexes depends strongly on the mutual orientation of the dicarbollide ligands, producing transoid and cisoid rotational conformers with different dipole moments (Scheme 2). All earlier studied tetrafulvalenium salts of the 8,8′-dihalogen derivatives of the cobalt bis(dicarbollide) anion with the same radical cations were found to be isostructural. In all of these compounds, the anions adopt a transoid conformation, which is stabilized by the formation of $CH\cdots XB$ intramolecular hydrogen bonds.[15,16] As expected, a change of halogens for smaller hydroxy groups

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(20) (a) Nuñez, R.; Tutusaus, O.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Chem.—Eur. J.* **2005**, *11*, 5637–5647. (b) Rojo, I.; Teixidor, F.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Chem.—Eur. J.* **2003**, *9*, 4311–4323.

(21) Kennedy, R. R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **2009**, *48*, 9377–9384.

(22) Katayama, C.; Honda, M.; Kumagai, H.; Tanaka, J.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2272–2278.

(23) Kazheva, O. N.; Alexandrov, G. G.; Kravchenko, A. V.; Starodub, V. A.; Sivaev, I. B.; Lobanova, I. A.; Bregadze, V. I.; Buravov, L. I.; Dyachenko, O. A. *J. Organomet. Chem.* **2007**, *692*, 5033–5043.

(24) Kazheva, O. N.; Chekhlov, A. N.; Alexandrov, G. G.; Buravov, L. I.; Kravchenko, A. V.; Starodub, V. A.; Sivaev, I. B.; Bregadze, V. I.; Dyachenko, O. A. *J. Organomet. Chem.* **2006**, *691*, 4225–4233.

(25) Nigrey, P. J.; Duesler, E.; Wang, H. H.; Williams, J. M. *Acta Crystallogr.* **1987**, *C43*, 1073–1075.

(26) Zefirov, Yu. V. *Crystallogr. Rep.* **1997**, *42*, 865–886.

(27) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973–1974.

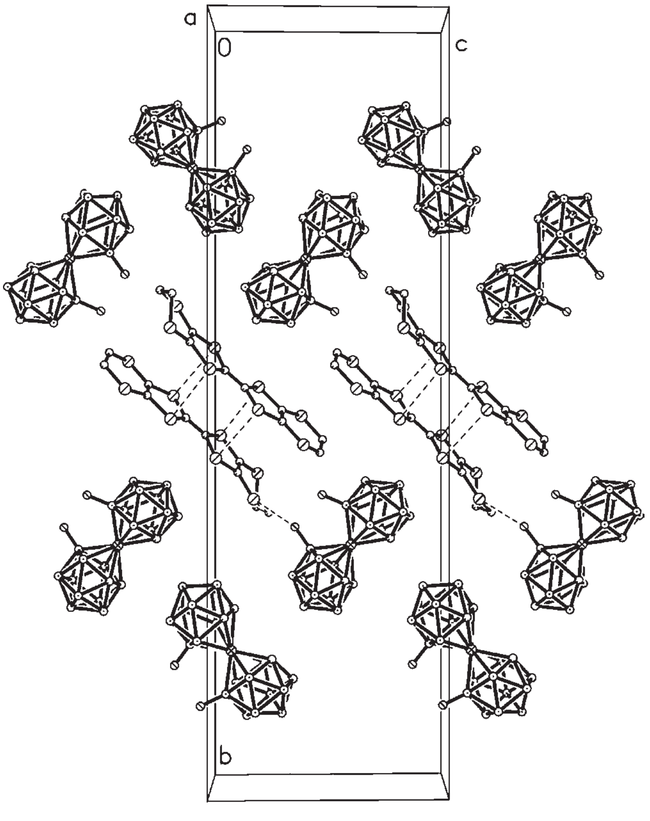
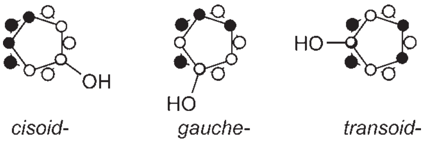


Figure 3. Fragment of the crystal structure of **3**.

Scheme 2. Mutual Orientation of the Dicarbollide Ligands in the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] Anion



could prevent the formation of strong intramolecular hydrogen bonds, keeping the possibility of the formation of intermolecular bonds. Therefore, a study of the conformation mobility of the dicarbollide ligands in the hydroxy derivative was of a special interest. It should be noted that the structure of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion has not been reported.

The distances from the cobalt atom to the pentagonal bonding face of the dicarbollide ligands in **1**−**3** are equal to 1.46−1.48 Å, which is typical for cobalt(III) bis(dicarbollide) salts. The Co−C and Co−B distances in **1** are 2.041(4)−2.071(3) and 2.065(4)−2.125(3) Å, respectively. Practically the same bond lengths for Co−C(1′) [2.071(3)] and Co−B(7′) [2.071(4)] indicate disorder of the boron and carbon atoms over the positions B(7′) and C(1′) with approximately equal occupancy, which corresponds to a mixture of the cisoid and gauche conformers. The C_2B_3 faces are nearly parallel (the dihedral angle is 2.5°). In the anion layer, the CH···OB intermolecular hydrogen bonds connect the cobaltacarborane anions into infinite-length chains (Figure 4). In the structure of **2**, the hydroxy substituent in the cobaltacarborane anion is disordered between two dicarbollide ligands. The Co−C and Co−B distances in **2** are 2.054(2)−2.075(2) and 2.059(3)−2.103(2) Å, respectively, which correspond to disorder of the carbon and boron atoms and a mixture of the transoid and gauche conformers. As in the structure of **1**, the cobaltacarborane anions in the structure of **2** combined into infinite-length chains through the CH···OB intermolecular hydrogen bonds. The Co−C and Co−B distances in **3** are 2.040(2)−2.048(2) and 2.082(2)−2.115(2) Å, respectively. The dicarbollide ligands are mutually rotated by 36°, producing a cisoid conformation of the anion. The pentagonal bonding faces are nearly parallel (the dihedral angle is 2.6°).

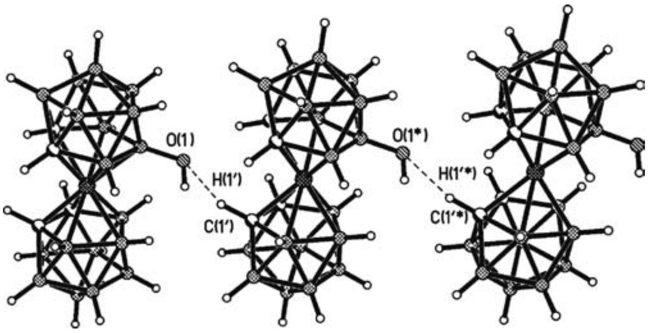


Figure 4. Anion chains in the structure of **1**. Parameters of the intermolecular hydrogen bond are O(1)−H(1′) 2.50 Å, O(1)···C(1′) 3.173(4) Å, and O(1)−H(1′)···C(1′) 118°.

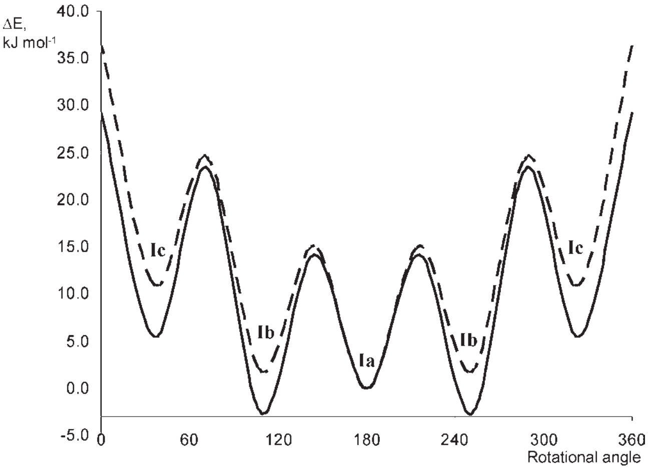


Figure 5. Calculated energies of [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (solid line) and [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ (dashed line) conformers as a function of the rotation angle [B(8)′−Co−B(10)−B(8) dihedral angle].

As a result, the mutual orientation of the dicarbollide ligands in the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion was found to be different in all of the structures studied. A brief analysis of the literature data on the structure of the related alkoxy derivatives [8-RO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ revealed that the cisoid conformation is prevailing in structures with alkali-metal cations because of their inclusion in B−O···M^+···H−B coordination with participation of the both dicarbollide ligands.[28−31] On the contrary, the transoid conformation was found in structures without

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(28) Plešek, J.; Grüner, B.; Heřmanek, S.; Bača, J.; Mareček, V.; Jänchenova, J.; Lhotsky, A.; Holub, K.; Selucky, P.; Rais, J.; Cisařova, I.; Časlavsky, J. *Polyhedron* **2002**, *21*, 975–986.

(29) Teixidor, F.; Pedrajas, J.; Rojo, I.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Sivaev, I.; Bregadze, V.; Sjöberg, S. *Organometallics* **2003**, *22*, 3414–3423.

(30) Llop, J.; Masalles, C.; Viñas, C.; Teixidor, T.; Sillanpää, R.; Kivekäs, R. *Dalton Trans.* **2003**, 556–561.

(31) Farras, P.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C.; Grüner, B.; Cisařova, I. *Inorg. Chem.* **2008**, *47*, 9497–9508.

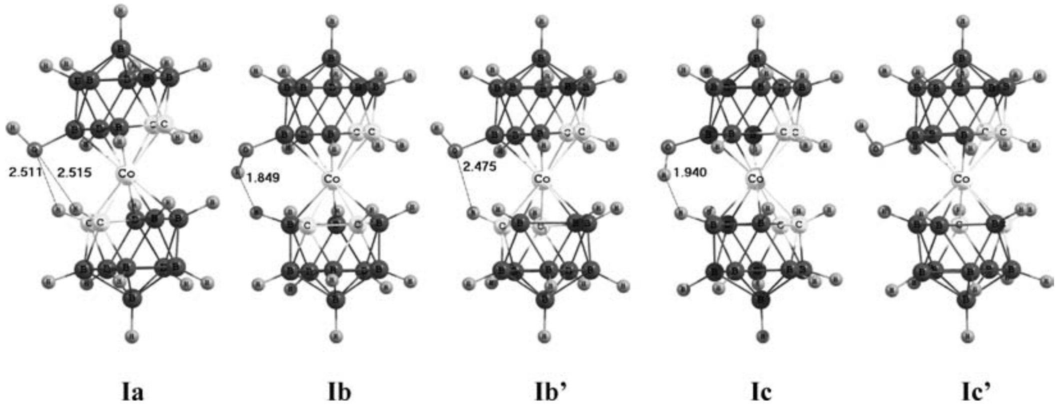

Figure 6. Optimized geometry of the rotational conformers of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] anion calculated by the DFT/BP86 method.

anion–cation interactions.[32–35] These results demonstrate the high rotational flexibility of the dicarbollide ligands in hydroxy and alkoxy derivatives of the cobalt bis(dicarbollide) anion.

The calculated energy difference between the rotational conformers of an unsubstituted cobalt bis(dicarbollide) anion was found to be rather low (approximately 10–12 kJ/mol), and the corresponding interconversion barriers are low as well.[17] In this study, the DFT/BP86 method was used to estimate the relative stability of the rotation conformers of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion. As in the case of the parent cobalt bis(dicarbollide) anion, three local energy minima corresponding to the mutual rotation of the dicarbollide ligands by 180° (**Ia**, transoid), 108° (**Ib**, gauche), and 36° (**Ic**, cisoid) were found (Figure 5). Opposite to the parent cobaltacarborane, the gauche conformation in the hydroxy derivative is slightly more stable than the transoid and cisoid ones (by 2.7 and 8.2 kJ mol^{-1}, respectively). This difference can be explained by the formation of intramolecular hydrogen bonds between the hydroxy group of one dicarbollide ligand and the CH/BH groups of the other one (Figure 6). Intramolecular hydrogen bonds in all three rotamers were identified by (3, −1) critical points for corresponding contacts in the framework of Bader's "atoms in molecule" (AIM) theory.

In rotamer **Ia**, two weak classical CH···O hydrogen bonds are responsible for stabilization of the transoid conformation, whereas in rotamers **Ib** and **Ic**, the formation of OH···HB dihydrogen bonds takes place. For the gauche conformation, an additional minimum with a rotated outside OH group and a weak classical CH···O hydrogen bond was found (Figure 5, **Ib**′). This rotamer is somewhat less stable than rotamer **Ib** stabilized by the formation of a nonclassical dihydrogen bond (by 9.7 kJ mol^{-1}). Comparing the relative energies of rotamers **Ib** and **Ib**′ and the energies of their hydrogen bonds, one could say that a change of the Co–B(8)–O–H dihedral angle from ~0 to 180° (inside–outside rotation) is unfavorable itself and, probably, is one of reasons for the higher stability of rotamer **Ib**. The cisoid conformation also has a minimum similar to that corresponding to rotamer **Ic**′ with a rotated outside OH group and without any stabilization due to intramolecular hydrogen bonds. It is not surprising that rotamer **Ic**′ has much higher energy than the dihydrogen-bond-stabilized conformer **Ic** ($\Delta E_{\mathbf{Ic'}-\mathbf{Ic}}$ = +16.3 kJ mol^{-1}).

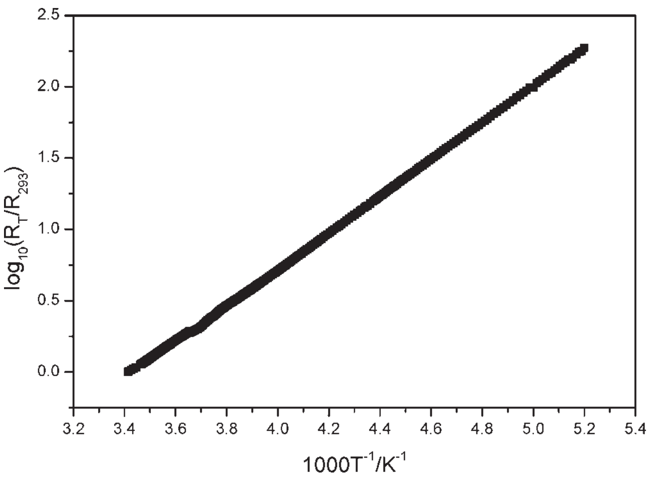

Figure 7. Temperature dependence of resistance for a single crystal of **3**.

The barriers for both the OH group and the dicarbollide ligand rotations are not high; the highest transition state is +31.9 kJ mol^{-1} relative to the most stable **Ib** conformer (see the Supporting Information for details), and it is slightly lower than the rotational barriers for the parent cobalt bis(dicarbollide) (+36.3 kJ mol^{-1}). In general, a small difference in the energy of rotamers **Ia**–**Ic** should result in a strong effect of the crystal surroundings upon conformation of the cobaltacarborane anion in the solid state. It should be noted that including one of the oxygen lone pairs in the formation of intermolecular hydrogen bonds in the solid state will result in the breakage of one of the intramolecular hydrogen bonds in rotamer **Ia** and some destabilization of the transoid conformation and, as a consequence, in the growth of parts of the cisoid and gauche conformers. The calculation results are in good agreement with the conformation flexibility of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion in the solid state.

The conductivity studies of the tetrathiafulvalenium salts demonstrated that all are semiconductors. The room temperature conductivities σ_{293} of **1** and **2** are 6 × 10^{-8} and 1.5 × 10^{-7} Ω^{-1} cm^{-1}, respectively. The activation energy of **3**,

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(32) Sivaev, I. B.; Starikova, Z. A.; Sjöberg, S.; Bregadze, V. I. *J. Organomet. Chem.* **2002**, *649*, 1–8.

(33) Grüner, B.; Mikulašek, L.; Bača, J.; Cisařova, I.; Böhmer, V.; Danila, C.; Reinoso-Garcia, M. M.; Verboom, W.; Reinhoudt, D. N.; Casnati, A.; Ungaro, R. *Eur. J. Org. Chem.* **2005**, 2022–2039.

(34) Hao, E.; Zhang, M.; E, W.; Kadish, K. M.; Fronczek, F. R.; Courtney, B. H.; Vicente, M. G. H. *Bioconjugate Chem.* **2008**, *19*, 2171–2181.

(35) Selucky, P.; Rais, J.; Lučanikova, M.; Grüner, B.; Kvičalova, M.; Fejfarova, K.; Cisařova, I. *Radiochim. Acta* **2008**, *96*, 273–284.

Table 1. Crystal Data and Structure Refinement for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{14}H_{34}B_{18}CoOS_4$	$C_{12}H_{25}B_{18}CoOS_8$	$C_{14}H_{29}B_{18}CoOS_8$
fw	600.16	695.31	723.36
cryst syst	triclinic	triclinic	monoclinic
space group	$P1$ (No. 1)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	6.9897(5)	6.949(1)	6.7512(5)
b/Å	9.8046(6)	9.484(1)	38.284(3)
c/Å	11.3083(7)	11.930(2)	11.6564(8)
α/deg	71.833(1)	73.484(2)	90
β/deg	84.732(1)	78.815(2)	91.846(2)
γ/deg	76.728(1)	78.014(2)	90
U/Å^3	716.50(8)	729.7(2)	3011.2(4)
Z	1	1	4
λ/Å	0.71073	0.71073	0.71073
D_{calc}/Mg m^{-3}	1.39	1.58	1.60
μ/mm^{-1}	0.903	1.175	1.142
no. of reflns collected	8689	7194	32350
no. of indep reflns	7752	3307	8768
no. of reflns with $F_o > 4\sigma(F_o)$	6949	2009	7258
no. of param refined	341	229	487
$2\theta_{max}$/deg	63.74	54.96	62.62
R [$F^2 > 2\sigma(F^2)$], wR(F^2)	0.031, 0.078	0.048, 0.077	0.046, 0111

E_a, was found to be 0.25 eV. The room temperature conductivity σ_{293} is $7 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ (Figure 7), which is close to that of the BEDT-TTF salt of parent cobaltacarborane (BEDT-TTF)-[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] ($\sigma_{293} = 5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$).[23]

Conclusions

In this study, the effect of the hydroxy group on the rotational mobility of the dicarbollide ligands in a cobalt bis(dicarbollide) anion was studied using quantum chemical calculations and X-ray diffraction analysis of tetrathiafulvalenium salts of the [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion. Opposite to halogen substituents, the introduction of the hydroxy group at position 8 of the cobalt bis(dicarbollide) anion does not increase the rotation energy barriers of the dicarbollide ligands, which results in saving of the general structure motif of the parent radical-cation salts with some extension of the crystal lattice. These results shed new light on the role of different substituents in the stabilization of rotational conformers of cobalt bis(dicarbollide) and should be taken into account in the design of molecular material based on them.

Experimental Section

Bis(methylenedithio)tetrathiafulvalene (BMDT-TTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Aldrich) were used as received. Tetramethyltetrathiafulvalene (TMTTF) was twice crystallized from CH_3CN. [Me_4N][8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] was prepared as previously described.[36] New radical-cation salts (TMTTF)[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**1**), (BMDT-TTF)[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**), and (BEDT-TTF)-[8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**3**) were grown by anodic oxidation of the corresponding tetrathiafulvalene derivatives in the presence of [Me_4N][8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] under an argon atmosphere. The crystals were grown by electrochemical crystallization under galvanostatic conditions in a standard two-electrode H-cell with platinum electrodes separated by a glass frit. The current applied was changed discretely by 0.05−0.10 mA day^{-1} from 0.10 to 1.50 mA. The period of crystal growth was 5−6 weeks.

Crystals of **1** were obtained from the [Me_4N][8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (8×10^{-3} M)−TMTTF (2.5×10^{-3} M) system using a 1,1,2-trichloroethane−acetonitrile mixture (12:1) as the solvent. Crystals of **2** were obtained from the [Me_4N][8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (8.5×10^{-3} M)−BMDT-TTF (2.5×10^{-3} M) system using 1,1,2-trichloroethane−acetonitrile (12:1) and dichloromethane−acetonitrile (12:1) mixtures as solvents. Crystals of **3** were obtained from the [Me_4N][8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (8.5×10^{-3} M)−BEDT-TTF (2×10^{-3} M) system using a dichloromethane−acetonitrile mixture (12:1) as the solvent.

X-ray Crystal Structure Determinations. X-ray diffraction studies of **1**−**3** were carried out on a Bruker SMART APEX2 CCD diffractometer using graphite-monochromated Mo Kα radiation (ω scanning). The structures were solved by direct methods followed by Fourier difference syntheses using *SHELXS-97* software[37] and refined by the full-matrix least-squares method in a anisotropic approximation for all non-hydrogen atoms using *SHELXL-97* software.[38] The reflection intensities were corrected for absorption using *APEX2* software.[39] The hydrogen atoms were located from difference Fourier maps or fixed in positions of ideal geometry. In the structure of **1**, the C(1) and B(7) as well as C(1′) and B(7′) atoms are disordered over two positions. In the structure of **2**, the C(1) and B(7) atoms are disordered over two positions with equal occupancy and the hydroxy group occupies two positions, 8 and 8′, with equal probability as well (statistical disorder). In the structure of **3**, the hydroxy group of the cobaltacarborane anion is disordered over two dicarbollide ligands (positions 8 and 8′) with occupancy factors of approximately 0.7 and 0.3. Details concerning the crystal data collection and refinement parameters for compounds **1**−**3** are summarized in Table 1. Selected bond lengths are listed in Tables S2−S4 in the Supporting Information. CCDC 759576, 759574, and 759575 (for **1**−**3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(36) Plešek, J.; Grüner, B.; Bača, J.; Fusek, J.; Cisařova, I. *J. Organomet. Chem.* **2002**, *649*, 181–190.

(37) Sheldrick, G. M. *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen: Göttingen, Germany, 1997.

(38) Sheldrick, G. M. *SHELXL-97, Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(39) *APEX2 Software Package*; Bruker AXS: Madison, WI, 2005.

Quantum Chemical Calculations. Quantum chemical calculations were carried out with the *GAUSSIAN 03* program package.[40] The BP86 hybrid density functional was applied.[41,42] The augmented Wachters' basis[43] and the 6-31G(d) basis were implemented to the cobalt atom and the cage carbon and boron atoms, respectively. The 6-31++G(d,p) basis was used for hydrogen and oxygen atoms. All isomers and transition states were fully optimized without any symmetry restriction. Transition states were identified by having one imaginary frequency in the Hessian matrix. Topological analysis of the electron-density distribution function $\rho(r)$ was performed using the *AIMALL* program package[44] based on the wave function obtained by the BP86 calculations. The energy of the hydrogen-bonding interaction was estimated using the correlation between the energy of the contact (E_{cont}) and the value of the potential energy density function $V(r)$ in (3, −1) critical point $E_{\mathrm{cont}} = {}^{1}/_{2}V(r)$.[45]

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (Grants 08-03-00668, 08-03-12043, 10-03-00698, and 10-03-00960), the Russian President Grant (Grant MK-1836.2009.3), and the Program of the Presidium of the Russian Academy of Sciences "Development of Methods of Synthesis of Chemical Compounds and Design of New Materials".

Supporting Information Available: Crystallographic data in CIF format for compounds **1**−**3**, atom designations for compounds **1**−**3** (Figures S1−S3), fragments of crystal packing of **2** and **3** (Figures S4 and S5), tables of selected bond distances and angles (Tables S1−S3), details of optimized rotation conformers and transition states for $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ and $[8\text{-HO-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (Tables S4−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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[40] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03*; Gaussian Inc.: Pittsburgh, PA, 2003.

[41] (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

[42] Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.

[43] (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033–1036. (b) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377–4384.

[44] Keith, T. A. *AIMALL*, version 09.11.29; 2009; aim.tkgristmill.com.

[45] (a) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170–173. (b) Espinosa, E.; Alkorta, I.; Rozas, I.; Elguero, J.; Molins, E. *Chem. Phys. Lett.* **2001**, *336*, 457–461.