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Isolation of Planar Four-Membered Aromatic Systems by Using Confined Spaces of Cobalt Pentaaryl[60]fullerene Complexes

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S *Supporting Information*

ABSTRACT: As a new class of neutral closed-shell aromatic four-membered ring systems, CoE_3 (E = S, Se) was constructed inside the bowl-shaped space of pentaaryl[60]fullerene. X-ray crystallographic analysis of $CoS_3(\eta^5\text{-}C_{60}Ar_5)$ revealed that the CoS_3 unit is planar, and DFT calculations suggested an aromatic 6π-electron system. Steric protection by the pentaaryl[60]fullerene ligand is critical for isolation and characterization of the aromatic hetero cobaltacyclobutane. Unique reactivity of the CoS_3 unit was demonstrated by disruption of 6π-conjugation with abstraction of the sulfur atom, affording a dimer, $[CoS_2(\eta^5\text{-}C_{60}Ar_5)]_2$. This work provides new insight into the aromaticity of four-membered ring systems and advances the understanding of aromatic organometallic compounds.

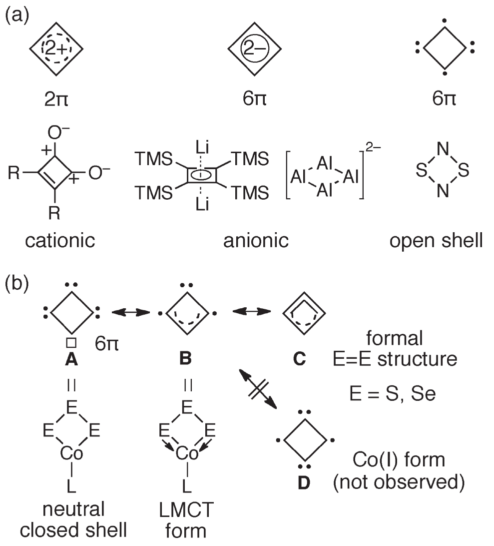

Figure 1. Aromatic four-membered rings and their electronic structures. (a) Previous examples. (b) A cyclic cobalt trichalcogenide complex and its electronic structure (only lone pairs perpendicular to the CoE_3 plane are shown). L is a bowl-shaped ligand.

Aromaticity,[1] one of the most useful concepts in chemistry, enables the stability of cyclic compounds to be predicted without complex analysis or calculation; however, the extent to which this concept can be applied keeps expanding. Toward that end, considerable efforts have been made to prepare unconventional cyclic heavy-atom analogues of aromatic organic compounds,[2] exotic aromatic species,[3] and aromatic metal clusters.[4] However, research into small cyclic compounds is still lacking, and our understanding of the strain and orbital overlap in such systems is limited. In particular, the synthetic accessibility of four-membered rings is low, owing to the low stability of species that satisfy the Hückel $4n + 2$ rule: highly reactive dication,[5] dianion,[6] or biradical[5b,7] species are usually required in the case of 2π or 6π conjugated systems (Figure 1a). Hence, although many theoretical studies[8] have been reported, experimental studies are scarce.

In previous studies on reactive aromatic compounds,[5−7] the steric hindrance of bulky protecting groups such as trialkyl silyl groups has often been exploited, but such a conventional approach is insufficient for aromatic compounds to which bulky substituents cannot be attached. On the other hand, the use of bowl- or cage-shaped confined spaces is a promising approach for isolation of reactive species.[9] Here, we report the synthesis and full characterization of novel four-membered aromatic systems consisting of planar cobalt trichalcogenide compounds, protected inside a bowl-shaped confined space of pentaaryl[60]fullerene.[10] The isolated cyclic CoE_3 (E = S, Se) substance is neutral and has a closed shell. Cyclic CoE_3 represents a new class of 6π aromaticity based on the conjugation of three lone pairs of the chalcogenides and one vacant d-orbital of the cobalt atom (Figure 1b).

Novel cobalt trichalcogenide complexes were synthesized by thermal reaction of a cobalt dicarbonyl complex $Co(\eta^5\text{-}C_{60}Ar_5)(CO)_2$ (**1**)[11] with elemental sulfur or selenium (Scheme 1). The reactions proceeded without formation of other polychalcogenides, selectively affording thermally stable, green trichalcogenide complexes $CoE_3(\eta^5\text{-}C_{60}Ar_5)$ (**2**: E = S; **3**: E = Se) in good yields.[12] This observation implies that specific stabilization effects are involved in the formation of the tetraatomic systems. The unambiguous structure of the cobalt trichalcogenide unit was determined for compound **2a** by X-ray single-crystal crystallographic analysis of **2a**$\cdot(C_6H_6)_{2.5}$ and **2a**$\cdot(C_8H_{10})_2$ (Figure 2). In the crystal packing of **2a**$\cdot(C_6H_6)_{2.5}$, C−H/π coordination was found between C_6H_6 and the four-membered CoS_3 ring (Figure 2b), while *p*-xylene was not located in the $C_{60}Ar_5$-space because of its steric bulkiness (Figure S1, Supporting Information [SI]). The CoS_3 units in both cocrystals were found to have a planar, nearly square structure with Co−S

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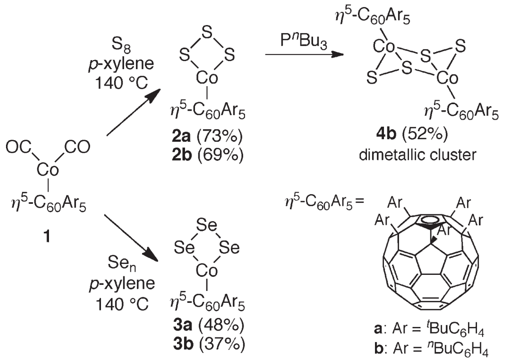
Scheme 1



bond lengths of 2.12−2.15 Å and S−S bond lengths of 2.01−2.03 Å. As determined from the crystal structure, the metal center is a coordinatively unsaturated 16-electron Co^{III} species (Figure 1b, form **A**).[13] In addition to the large contribution from form **A**, the clearly shorter Co−S bond length in comparison with those of other cobalt polysulfide complexes, whose bond lengths are 2.23−2.25 Å (Figure S3, SI),[14] indicates that there are considerable contributions of LMCT interactions in form **B**.[15] We also can expect plausible small contributions from form **C**, which is a formal S═S bond structure.[16] We can rule out form **D** containing Co(I) species and open shell structure on the sulfur atoms, because the compound is ESR-silent. Thus, cyclic 6π-electron aromatic conjugation, consisting of three lone pairs on the sulfur atoms and one unoccupied d-orbital on the cobalt atom, was found to make the dominant contribution to the four-membered CoS_3 ring structure. The planarity of the ring and high selectivity of formation are in good agreement with aromaticity. More direct evidence of aromaticity was obtained with the unusual downfield-shift of ^1H NMR signals of five aryl groups. In compound **2a**, the signal due to ortho protons of the aryl groups was observed at 8.32 ppm. This value is quite a large shift from those of previously reported η^5- and η^1-$C_{60}Ar_5$ metal complexes[17] which show the value in the range from 7.5 to 7.9. We ascribe this downfield-shift to the diatropic ring current in the central CoS_3 ring.

Next, we investigated the electronic properties of these aromatic four-membered rings in detail. The low reduction potential of the CoS_3 unit in this compound supports the main contribution from form **A**: the first reduction potential of **2b** at −1.09 V (vs Fc/Fc^+) is ascribed to the electron-deficient Co^{III} atom, while the second reduction wave at −1.54 V is assigned to one-electron reduction of the pentaaryl[60]fullerene ligand (Figure 3b). The electron-donating nature of the trisulfide ligand was confirmed from the oxidation waves at 0.62 and 0.91 V (Figure 3a). A charge transfer band from the ligands (sulfur atoms) to the metal atom (LMCT band; green color, λ = 667 nm for **2b**, Figure S2, SI)[15] was observed to show good agreements with the above discussion. Selenium analogue **3** showed similar electrochemical (Figures 3a and 3b) and photophysical (Figure S2, SI) properties as **2**, suggesting that **3** has aromatic character similar to that of **2**.

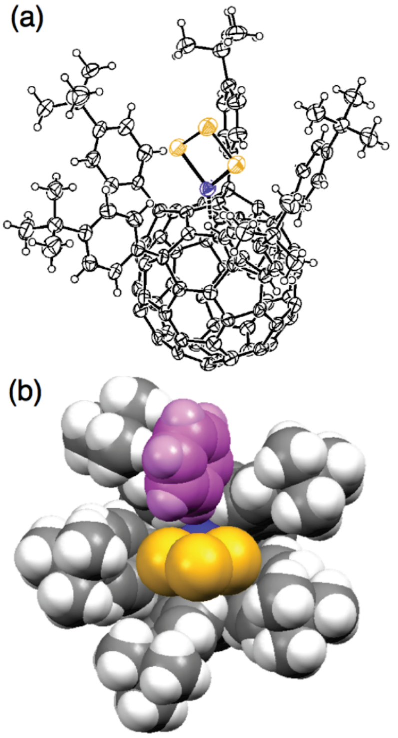


Figure 2. (a) ORTEP drawing of the crystal structure of $\mathbf{2a}\cdot(C_6H_6)_{2.5}$ with 50% probability (solvent molecules omitted for clarity). (b) Space-filling drawing of **2a**, showing coordination of C_6H_6 (pink) to CoS_3.

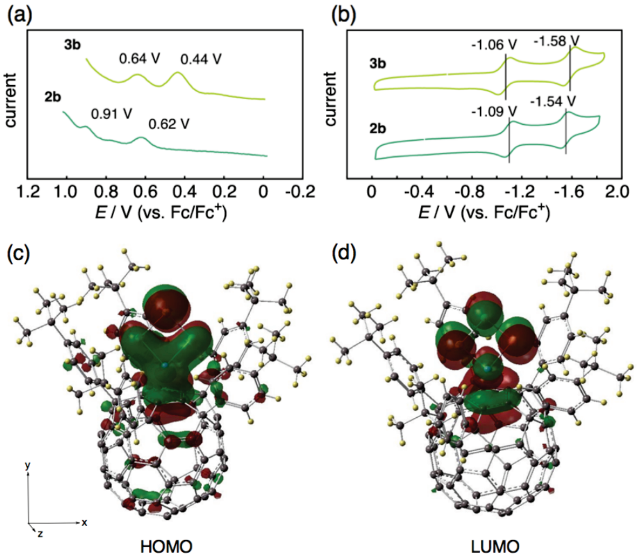


Figure 3. (a) Differential pulse voltammograms of **2b** and **3b** in CH_2Cl_2 (TBAP as supporting electrolyte). (b) Cyclic voltammograms of **2b** and **3b** under the same conditions. (c,d) Frontier orbitals of **2a** (B3LYP, Co: LANL2DZ, others: 6-31G*).

Complementing the experimental studies, DFT calculations were conducted to investigate the characteristic electronic structures of the cobalt trichalcogenides. Cobalt trisulfide complex **2a** was used to examine the nature of the aromatic molecular orbitals (Figure 3c and d, and Figure S7 [SI]). As a result, one d_{yz}-orbital on Co and three axial lone pairs on the sulfur atoms were observed for both the HOMO and LUMO. This result fairly well explains the LMCT from the occupied π-orbital of a sulfur atom to the vacant d_{yz}-orbital of the cobalt atom. This charge transfer interaction can be regarded as a part of cyclic d−π conjugation. The large negative NICS(1)[18] value of −12 also supports the presence of aromaticity in the four-membered ring. In addition, a clear evidence

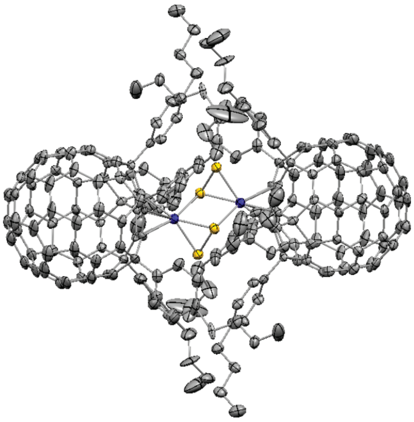


Figure 4. Crystal structure of **4b** with thermal ellipsoid plotted at 30% probability (hydrogen atoms and solvent molecules are omitted for clarity).

of π-aromaticity was obtained in NICS-scan calculations[19] for an out-of-plane component (NICS$_{zz}$), which showed respectable negative values (up to −8) at 1−2 Å above the CoS$_3$ plane, indicating the magnetic shielding from aromatic π-electrons of the CoS$_3$ ring (Figure S4, SI).

Resonance in the CoS$_3$ ring was studied by using second-order perturbation theory to estimate the structure of a model compound, CpCoS$_3$ (Figures S5 and S6, SI). The donor−acceptor stabilization from the p$_z$-orbital on the sulfur atoms (lone pair) to the d$_{yz}$-orbital on Co (vacant d-orbital) was estimated to be 22.5 kcal/mol (form B in Figure 1b). In addition, resonance stabilization from one S═S bond (form C in Figure 1b) was estimated to be 4.1 kcal/mol. In our analysis, the degree of π-electron delocalization in the CoS$_3$ ring was comparable to that in a thiophene as a representative sulfur-containing aromatic molecule (SI).

The uniqueness of this CoE$_3$ system can also be seen through a comparison with previously reported MS$_3$ complexes (M = Ti and Re).[20] Because these complexes have coordinatively saturated metal centers or nonplanar MS$_3$ rings, the systems are not aromatic. In contrast, the present cobalt C$_{60}$Ar$_5$ compounds have a sterically confined space, which rigorously excludes highly coordinating compounds; this allows isolation of coordinatively unsaturated CoS$_3$ species. When an ordinary cyclopentadienyl derivative, CpCo(CO)$_2$, is used for a reaction with elemental sulfur under the same conditions, the reaction gives a mixture of oligomerized Co−S clusters such as Cp$_4$Co$_4$S$_4$.[21] A less bulky C$_{60}$Me$_5$ derivative, Co(η^5-C$_{60}$Me$_5$)(CO)$_2$, did not afford the corresponding CoS$_3$ complex, suggesting the importance of the bowl-shaped confined space.

Unique reactivity of the CoS$_3$ unit was also demonstrated by intentionally disrupting the 6π conjugation. From trisulfide complex **2b**, one sulfur atom was abstracted by reaction with one equivalent of P^{n}Bu$_3$ in toluene at room temperature. The product was a cluster complex **4b**, which we postulate to be the dimerization product of the most likely intermediate CoS$_2$(C$_{60}$Ar$_5$) (Scheme 1, Figures 4 and S8 [SI]). A nonaromatic coordinatively unsaturated CoS$_2$ complex, generated in situ, is highly unstable and readily dimerizes to achieve an 18-electron configuration. From X-ray crystallographic analysis of **4b**·(C$_7$H$_8$)$_2$, the geometry of the Co$_2$S$_4$ moiety was found to be essentially the same as that of Cp*$_2$Co$_2$S$_4$,[14b] but the Co−Co distance was elongated (3.47 Å vs 3.38 Å), likely owing to steric repulsion of the bulky C$_{60}$Ar$_5$ ligands. It is noteworthy that a small change at the substituents on the phenyl groups, from ^{n}Bu (**2b**) to ^{t}Bu (**2a**), strongly affected the reactivity: the more bulky trisulfide complex **2a** did not react with P^{n}Bu$_3$ at all, showing the tunability of the bowl-shaped confined spaces. These results also demonstrate that trisulfide complexes can be used as starting materials for precise syntheses of metal−sulfur clusters.

In conclusion, by utilizing the bowl-shaped confined space of pentaaryl[60]fullerene, we successfully prepared a series of 6π-electron cobalt trichalcogenide complexes, which are neutral four-membered aromatic species. The following evidence supports the conclusion that these four-membered rings are aromatic: (1) high planarity of the four-membered ring, (2) short Co−S bond distances, (3) high stability and excellent selectivity in formation of complexes, (4) strongly delocalized 6π-electron molecular orbitals with high resonance energies, (5) a large negative NICS(1) value, and (6) severe destabilization upon disruption of the 6π-electron structure. The findings reported here will advance the understanding of exotic aromatic compounds and open new avenues of materials science research on interesting π-electron systems

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures, spectral data, details of DFT studies on model compound, and crystallographic data for **2a** and **4b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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