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Two in one: the bismuth bromido clusters in $[Bi_6Cp*_6Br_9][Bi_7Br_{24}]$

Abstract: The reaction of $[FeCp*(CO)_2]_2$ in CH_2Cl_2 with $BiBr_3$ in a 1:1 molar ratio gave the novel bismuth compound $[Bi_6Cp*_6Br_9][Bi_7Br_{24}]$ (**1**), which is composed of a cationic and an anionic bismuth bromido cluster: the cation is based on a hexanuclear bismuth $\{Bi_6\}$-octahedron and the anion showing the first heptanuclear bismuth-bromido cluster within the class of bromido bismuthates.

Keywords: crystal structure; bismuth bromide; pentamethylcyclopentadienyl; polynuclear clusters.

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Introduction

Bismuth halides are well known to form diverse coordination polymers and anionic complexes as a result of their high Lewis acidity (Clegg et al., 1992, 1993; Wang et al., 1997; Erbe et al., 2010; Mansfeld et al., 2013). Thus, addition of sources for Br^- to bismuth bromide results in the formation of polybromido bismuthates of different stoichiometry (Robertson et al., 1967; McPherson and Meyers, 1968; Lazarini, 1977a,b). The structures are based on single or associated distorted octahedra, whereby association via corners, edges, and even faces was reported. For example, Ahmed et al. have prepared a variety of monomeric and oligomeric anions by the reaction between $BiBr_3$ with tetraphenylphosphonium bromide (Ph_4PBr) (Ahmed et al., 2001a,b), including $[Bi_2Br_9]^{3-}$, $[Bi_2Br_8(CH_3COCH_3)_2]^{2-}$ and $[Bi_6Br_{22}]^{4-}$. Additional representative examples of polybromidobismuthate ions are $[BiBr_5]^{2-}$, $[Bi_2Br_{10}]^{4-}$, and $[Bi_4Br_{16}]^{4-}$ (Norman, 1998). Diverse cations were used to stabilize such bromido bismuthates, e.g., $[Ph_4P]^+$ (Ahmed et al., 2001a,b), $[Me_3HP]^+$ (Clegg et al., 1991), $[Me_2NH_2]^+$, $[Et_2NH_2]^+$, and even $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ (Norman, 1998).

We report on the synthesis and structure of $[Bi_6Cp*_6Br_9][Bi_7Br_{24}]$ (**1**), containing heptanuclear $[Bi_7Br_{24}]^{3-}$, which is not reported for bismuth bromido complexes. The iodide analog was only recently described by Monakhov et al. as anionic part of the crystal structure of $[Bi(OAc)_2(thf)_4]_3[Bi_7I_{24}]$, which was obtained by the reaction of BiI_3 with $[Pd(OAc)_2]$ (Monakhov et al., 2012). However, the first report on $[Bi_7I_{24}]^{3-}$ dates back to 1996, but details on synthesis and structure were not given (Carmalt et al., 1996). In addition to the anionic cluster in **1**, a cationic bismuth complex with Cp*Bi moieties is observed in the solid state. To date, there are only a few examples reported in the literature containing Cp*Bi moieties. For example, $BiCp*Br_2$ (**A**) was reported by Jutzi and Schwartzen in 1989, prepared from metallic bismuth and 5-bromopentamethyl-1,3-cyclopentadiene. Recently, the single crystal X-ray structure analysis of **A** was reported (Monakhov et al., 2011). Another example is $[Al(\eta^5\text{-}Cp*)_2\{Bi(\eta^5\text{-}Cp*)\}(\mu\text{-}AlI_4)(AlI_4)_2]*2C_7H_8$ (**B**), which was obtained upon reaction of $(AlCp*)_4$ with BiI_3 in toluene (Üffing et al., 1999). The structure of **B** reveals in the solid state a chain of Cp*Bi units bridged by tetraiodoaluminate ions. Ionic bismuth halido clusters similar to **1** were reported recently (Monakhov et al., 2011). The reaction between BiX_3 (X=Cl, Br) and LiCp* gave compounds such as $[Bi_6Cp*_5Cl_{12}][Bi_2Cl_7(thf)_2]$ and $[\{Bi_5Cp*_5Br_9\}\{BiBr_4\}]_2$. The title compound $[Bi_6Cp*_6Br_9][Bi_7Br_{24}]$ (**1**) represents another example within the family of these novel organobismuth halido clusters.

Results and discussion

The pentamethylcyclopentadienyl-substituted bismuth bromido compound $[Bi_6Cp*_6Br_9][Bi_7Br_{24}]$ (**1**) was obtained by the reaction of $[FeCp*(CO)_2]_2$ in CH_2Cl_2 with $BiBr_3$. Based on a recently reported synthesis protocol formation of $[Bi\{FeCp*(CO)_2\}Br_2]$ (**C**) was expected (Wójcik et al., 2012). However, most likely as a result of a lower concentration used, compound **C** did not crystallize, and the title

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$$[\text{FeCp}^*(\text{CO})_2]_2 + \text{BiBr}_3 \longrightarrow [\text{Bi}\{\text{FeCp}^*(\text{CO})_2\}\text{Br}_2] + [\text{FeCp}^*(\text{CO})_2\text{Br}] \quad (\text{Eq. 1})$$

$$[\text{Bi}\{\text{FeCp}^*(\text{CO})_2\}\text{Br}_2] \xrightarrow[-\ \text{"Fe(CO)}_2\text{"}]{} \text{BiCp}^*\text{Br}_2 \quad (\text{Eq. 2})$$

$$6\ \text{BiCp}^*\text{Br}_2 + 7\ \text{BiBr}_3 \longrightarrow [\text{Bi}_6\text{Cp}^*{}_6\text{Br}_9][\text{Bi}_7\text{Br}_{24}]\ (\mathbf{1}) \quad (\text{Eq. 3})$$

Scheme 1 Proposed reaction scheme for the formation of compound **1**.

compound **1** was isolated instead. The mechanism of formation of **1** might be explained by the reaction sequence shown in Scheme 1. In the first step, **C** is formed, which converts into $BiCp^*Br_2$ (**A**) by the formal loss of "$Fe(CO)_2$" (Eq. 1, 2). Reaction of **A** with unreacted $BiBr_3$ (Eq. 3) gave the title compound **1**, in analogy to the reaction between BiX_3 (X=Cl, Br) and Cp*Li as described recently for similar Cp*–substituted bismuth halides (Monakhov et al., 2011). Monakhov et al. observed the formation of a mixture of $BiCp^*Br_2$ (**A**) and $[\{Bi_5Cp^*{}_5Br_9\}\{BiBr_4\}]_2$ upon reaction of LiCp* with $BiBr_3$. Our attempts to synthesize compound **1** either starting from this reaction mixture with appropriate stoichiometry for **1** or directly from **A** by addition of LiCp* were not successful so far. The ^{1}H NMR spectrum of compound **1** in $CDCl_3$ shows one singlet resonance at δ 1.77 assigned to the Cp* ligands, suggesting a η^5-coordination mode.

The title compound $[Bi_6Cp^*{}_6Br_9][Bi_7Br_{24}]$ (**1**) crystallizes in the trigonal space group *R*-3 with the lattice parameters a=22.731(5) Å, b=22.731(5) Å, c=19.515(5) Å, V=8732(4) Å^3 and Z=3 (crystallographic data are provided in Table 1). Selected bond lengths and angles are listed in Table 2, the structure of the cation is shown in Figure 1 and the structure of the anion in Figure 2.

The cation $[Bi_6Cp^*{}_6Br_9]^{3+}$ (**1a**) is comprised of six bismuth atoms located at the corners of an octahedron, eight μ_3-bromides cap the trigonal faces of the octahedral core, and one bromide located in the center of the Bi_6 octahedron showing μ_6-coordination. Six Cp* ligands are η^5-bonded to the bismuth atoms and comprise the periphery of the metal bromido cluster. The hexanuclear $\{Bi_6\}$ octahedron is a well known structural unit reported for bismuth oxido compounds (Sundvall, 1983; James et al., 1996; Whitmire et al., 2000; Mehring et al., 2006) and even $\{Bi_6O_9\}$ moieties with interstitial oxygen atoms are reported as part of larger structures (Miersch et al., 2013). However, to the best of our knowledge, $\{Bi_6X_9\}$ moieties (X=halogen) as reported here are rare. Similar arrangements are restricted to recently reported examples such as $[Bi_6Cp^*{}_5Cl_{12}]^+$ (Monakhov et al., 2011).

In **1a,** the bromine atoms Br1 and Br3 bridge three bismuth atoms while the interstitial atom Br2 is located in the center of the Bi_6 octahedron with symmetric coordination to the six bismuth atoms with a Bi1-Br2 distance of 3.1977(7) Å. The bond distances assigned to Bi1 are Bi1-Br1, 3.1276(12) Å, Bi1-Br3 3.1377(14) Å, and Bi1-Br3b 3.1606(13) Å. The distances between the carbon atoms in the Cp* ring and the Bi atom are similar and range from 2.521(10) to 2.565(12) Å, which indicates that the Cp* ligand is symmetrically bonded to the bismuth atom with η^5-coordination. The Bi-$Cp^*_{centroid}$ bond distance of 2.234(6) Å is similar to Bi-Cp* bond distances as reported for **B** (2.243 Å) (Üffing et al., 1999) and $[Bi_6Cp^*{}_5Cl_{12}]^+$ (2.250 Å) (Monakhov et al., 2011). The $[Bi_6Cp^*{}_6Br_9]^{3+}$ cluster might be described to be built from six Cp*Bi-based units as presented in Figure 3C.

The heptanuclear $[Bi_7Br_{24}]^{3-}$ (**1b**) anion is best described as being composed of seven distorted edge-sharing $BiBr_6$–octahedra connected by μ_2- and μ_3-bridging bromides with bond lengths in the range from 2.8585(13) Å to 2.9346(13) Å and 2.8631(11) Å to 3.3161(12) Å, respectively (Figure 3D), similar to previously reported $[Bi_7I_{24}]^{3-}$ (Monakhov et al., 2012). The terminal Bi–$Br_{terminal}$ bond distances amount to 2.6361(13) Å.

Table 1 Crystallographic data and structure refinement details for $[Bi_6Cp^*{}_6Br_9][Bi_7Br_{24}]$ (**1**).

Empirical formula	$C_{60}H_{90}Bi_{13}Br_{33}$
M (g mol^{-1})	6165.09
Temp (K)	100
λ (Å)	1.54184
Crystal system	Trigonal
Space group	*R*-3
a (Å)	22.731(5)
b (Å)	22.731(5)
c (Å)	19.515(5)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	8732(4)
Z	3
D_{calc} (g cm^{-3})	3.517
μ (Cu Kα) (mm^{-1})	51.214
F(000)	8052
Crystal size (mm)	0.05×0.05×0.05
Reflections collected	9303
Independent reflections	3022
R_{int}	0.0316
Data/restraints/parameters	3022/0/161
Goodness-of-fit on F^2	0.987
Final *R* indices [$I>2\sigma(I)$]	
R_1	0.0357
wR_2	0.0899
R indices (all data)	
R_1	0.0437
wR_2	0.0949
$\Delta\rho_{min}$ (e Å^{-3})	−1.720
$\Delta\rho_{max}$ (e Å^{-3})	1.890

Table 2 Selected interatomic distances [Å] and angles [°] for $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (**1**).

C(1)-Bi(1)	2.533(11)	Br(3)-Bi(1a)	3.1606(13)
C(2)-Bi(1)	2.521(10)	Br(4)-Bi(2)	2.8585(13)
C(3)-Bi(1)	2.538(11)	Br(4c)-Bi(2)	2.9346(13)
C(4)-Bi(1)	2.565(12)	Br(5)-Bi(2)	2.6361(13)
C(5)-Bi(1)	2.555(11)	Br(6)-Bi(2)	2.6083(13)
Br(1)-Bi(1)	3.1276(12)	Br(7)-Bi(2)	3.2171(12)
Br(2)-Bi(1)	3.1977(7)	Br(7c)-Bi(2)	3.3161(12)
Br(2)-Bi(1a)	3.1977(7)	Br(7)-Bi(3)	2.8631(11)
Br(3)-Bi(1)	3.1377(14)	Bi(1)-D_{Cp^*}	2.234(6)
Bi(1)-Br(2)-Bi(1c)	180.00(10)	Br(3)-Bi(1a)-Br(3a)	137.69(4)
Bi(1)-Br(2)-Bi(1a)	89.202(17)	Br(4)-Bi(2)-Br(5)	89.95(4)
Bi(1)-Br(2)-Bi(1b)	90.798(17)	Br(4)-Bi(2)-Br(6)	93.00(4)
Bi(1)-Br(1)-Bi(1a)	91.76(4)	Br(4)-Bi(2)-Br(4d)	177.11(4)
Bi(1)-Br(3)-Bi(1b)	92.60(3)	Br(4)-Bi(2e)-Br(5e)	91.76(4)
Bi(1)-Br(3)-Bi(1a)	90.54(3)	Br(4)-Bi(2e)-Br(6e)	89.06(4)
Bi(2)-Br(4)-Bi(2e)	104.51(4)	Br(4)-Bi(2)-Br(7)	84.70(3)
Bi(2)-Br(7)-Bi(3)	97.61(3)	Br(4)-Bi(2)-Br(7d)	93.23(3)
Br(1)-Bi(1)-Br(2)	69.83(3)	Br(5)-Bi(2)-Br(7)	169.14(4)
Br(1)-Bi(1)-Br(3)	138.99(4)	Br(6)-Bi(2)-Br(7)	91.28(4)
Br(1)-Bi(1)-Br(3b)	83.82(2)	Br(7)-Bi(3)-Br(7d)	90.18(3)
Br(3)-Bi(1)-Br(2)	69.15(3)	Br(7)-Bi(3)-Br(7f)	89.82(3)
Br(3b)-Bi(1)-Br(2)	68.87(2)	Br(7e)-Bi(3)-Br(7f)	180.0
Br(3)-Bi(1)-Br(3b)	81.67(2)		

D_{Cp^*}, Centroid of the Cp* ring.

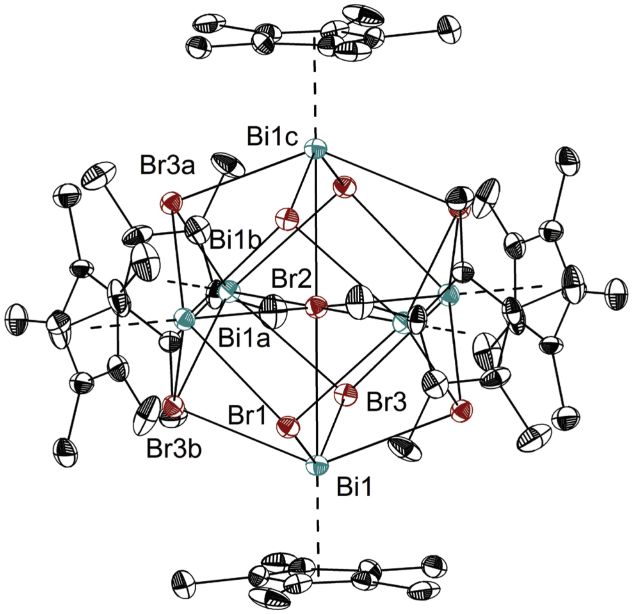

Figure 1 Thermal ellipsoid plot of the structure of the cationic part of **1**, $[Bi_6Cp^*_6Br_9]^{3+}$ (**1a**).
Thermal ellipsoids are set at 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry equivalent atoms are given by *a*: -x+y, 1-x, z; *b*=-1/3+y, 1/3-x+y, 1/3-z; *c*=2/3-x, 4/3-y, 1/3-z.

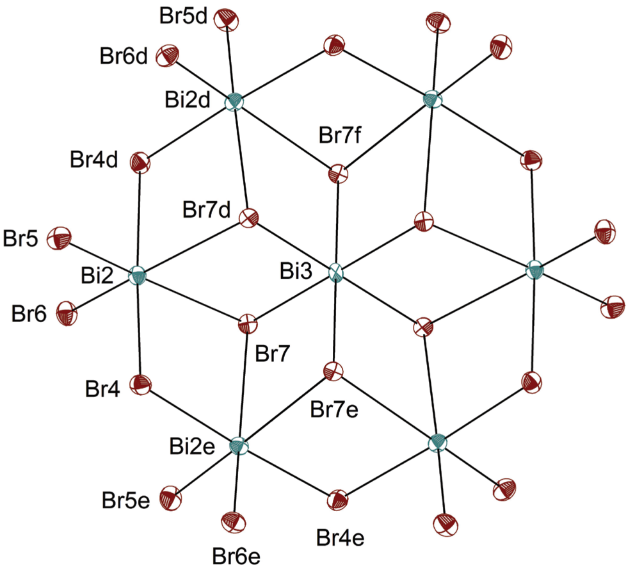

Figure 2 Thermal ellipsoid plot of the structure of the anionic part of **1**, $[Bi_7Br_{24}]^{3-}$ (**1b**).
Thermal ellipsoids are set at 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry equivalent atoms are given by *d*=y, 1-x+y, -z; *e*=1+x-y, x, -z; *f*=1-x+y, 2-x, z.

The environment of Bi3 in the $[Bi_7Br_{24}]^{3-}$ anion consists of six μ_3-bridging bromine atoms (Br7), while Br4 is coordinated to two bismuth atoms, and Bi5 and Bi6 are bonded terminal. The Bi-Br distances are similar to those found in $[Bi_4Br_{16}]^{4-}$ as reported by Rheingold et al. [2.663(4)–2.689(4) Å for terminal and 2.844(4)–3.156(4) Å for bridging bromides] (Rheingold et al., 1983). In the crystal lattice of $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (**1**), no close contacts between the anions and cations are noticed.

Conclusions

The reaction of $[FeCp^*(CO)_2]_2$ with $BiBr_3$ was expected to provide $[Bi\{FeCp^*(CO)_2\}Br_2]$ (**C**). However, unexpectedly the pentamethylcyclopentadienyl substituted bismuth bromido compound $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (**1**) was isolated. As it was described by Üffing et al., transfer of the Cp* ligand from aluminium to bismuth is possible (Üffing et al., 1999). A similar behavior within our studies was observed, a transfer of the Cp* ligand from iron to bismuth. The crystal structure determination revealed the formation of a cationic cluster $[Bi_6Cp^*_6Br_9]^{3+}$ and an anionic cluster $[Bi_7Br_{24}]^{3-}$, which do not show significant intermolecular bonding other than electrostatic interaction.

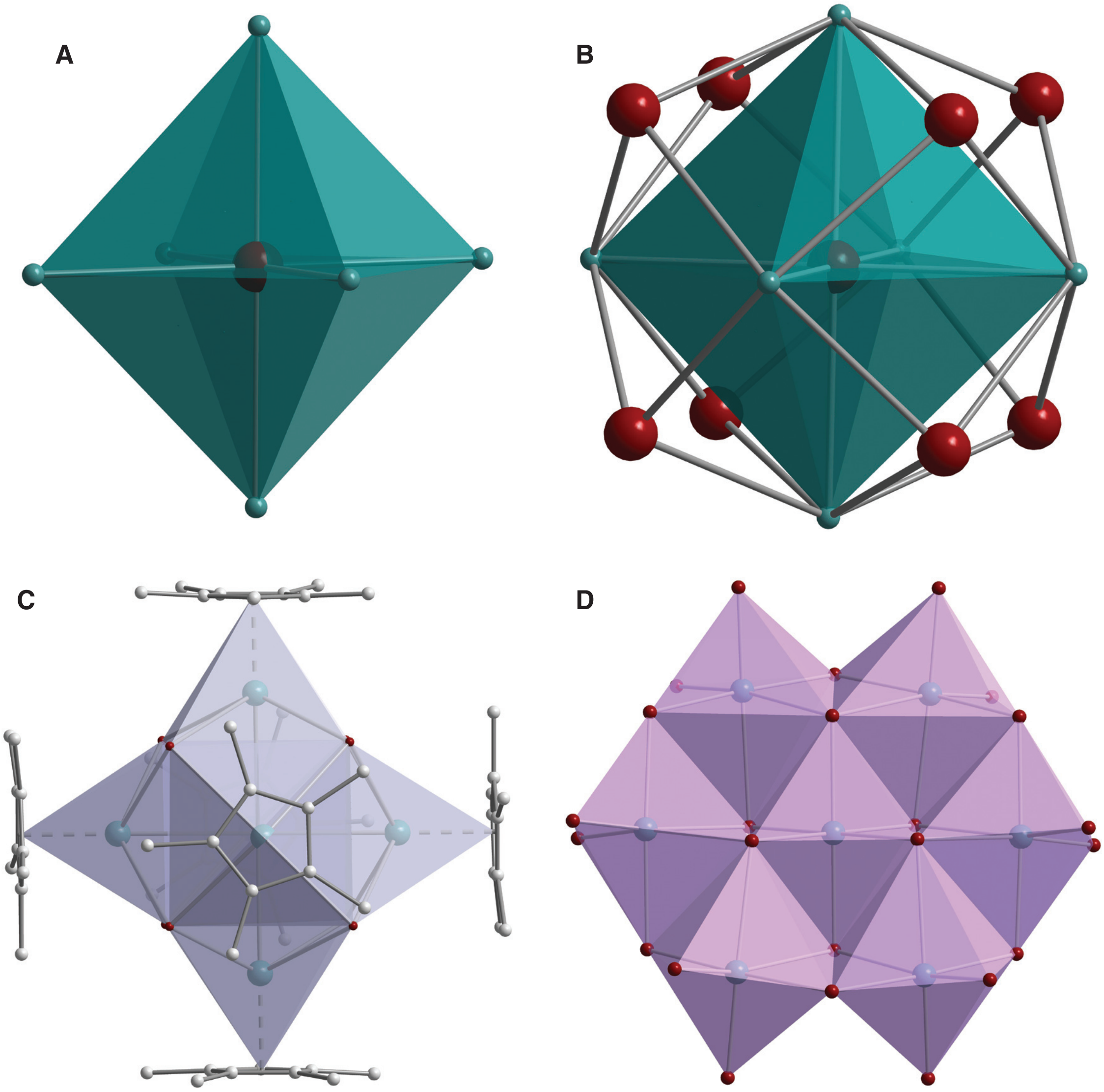

Figure 3 View of structural arrangements of the anion and the cation of $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (**1**).
(A) Bi octahedron containing an interstitial Br atom inside the $\{Bi_6\}$ cage; (B) an interstitial Br–containing Bi_6 octahedron capped by μ_3-coordinated Br^- ligands; (C) a Bi octahedron containing an interstitial Br atom and six η^5-coordinated Cp* ligands; (D) seven distorted edge-sharing $BiBr_6$-octahedra connected by μ_2- and μ_3-bridging bromides.

Experimental section

General procedures

All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying reagents immediately prior to use. The $BiBr_3$ (purchased from Aldrich) was used without further purifications, and the starting material $[FeCp^*(CO)_2]_2$ (Noyori et al., 1971) was synthesized according to a literature procedure (Barras et al., 1993). Infrared spectra with 4 cm^{-1} resolution were recorded on a Nicolet FTIR-200 spectrophotometer from Thermo Scientific (Thermo Fisher Scientific Inc., Waltham, MA, USA) as KBr pellet samples. ^1H NMR spectra were recorded with a Bruker Avance 500 (Typ Avance III 500, Bruker Corporation, Billerica, MA, USA) at room temperature. The ^1H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CDCl_3$: ^1H 7.26 ppm). The CHN-analyses were carried out with a CHN-Analyser Type FlashAE 1112 from Thermo Scientific (Thermo Fisher Scientific Inc., Waltham, MA, USA). Melting points of compounds were measured with a Melting Point B-540 apparatus (Büchi Labortechnik GmbH, Essen, Germany).

Crystallographic studies

Crystal data, data collection, and refinement parameters for **1** are given in Table 2. All data were collected on an Oxford Gemini S diffractometer (Agilent Technologies Sales & Services GmbH & Co. KG, Life Sciences & Chemical Analysis, Waldbronn, Germany) at 100 K (**1**) using Cu $K\alpha$ radiation (λ=0.71 Å). For protection against oxygen and moisture, the preparation of the single crystals was performed in perfluoro alkyl ether (ABCR GmbH&Co KG, Karlsruhe, Germany; viscosity 1600 cSt). The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-square procedures on F^2 using SHELXL-97 (Sheldrick, 1990). The drawings were created with the Diamond program (DIAMOND 2001). All non-hydrogen atoms were refined anisotropically. Cambridge Crystallographic Data Centre (CCDC) deposition number 1015598 (**1**) can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (1)

Solid $BiBr_3$ (0.200 g, 0.45 mmol) was added to a vigorously stirred solution of $[FeCp^*(CO)_2]_2$ (0.220 g, 0.45 mmol) in 30 mL of CH_2Cl_2. After 18 h, the amount of solvent was reduced to 20 mL, and hexane was added. After 4 months of crystallization at 4°C, a crop of violet crystals of $[Bi_6Cp^*_6Br_9][Bi_7Br_{24}]$ (**1**), suitable for single-crystal X-ray diffraction, was obtained. ^1H NMR (500 MHz, $CDCl_3$): δ 1.84 (s, 90H, $C_5(CH_3)_5$). IR/KBr [ν, cm^{-1}]: 1637(m); 1399 (w); 1260 (w); 1099 (w); 1026 (w); 801 (m); 614 (w). Anal. Calcd. for $C_{60}H_{90}Bi_{13}Br_{33}$ (6164.93 g/mol) C, 11.69; H, 1.47. Found: C, 11.04; H, 1.40.

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