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Synthesis and Single-Crystal Structure Analysis of $[Ba(NH_3)_7]C_{60}\cdot NH_3$

Klaus Himmel and Martin Jansen*

Institut für Anorganische Chemie der Rheinischen
Friedrich-Wilhelms-Universität Bonn,
Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany

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Introduction

Since the discovery of the fullerenes[1] the electronic properties of C_{60} have attracted considerable interest. Due to the extraordinarily high symmetry of this molecule its HOMO (h_u) and LUMO (t_{1u}) are degenerate. Oxidation or reduction leads to electronic states whose exact energies are often difficult to specify. This is in particular valid for the dianion C_{60}^{2-}. While C_{60}^{-} and C_{60}^{3-} show the expected paramagnetism, the ground state of C_{60}^{2-} is still subject to controversial discussion.[2−5] Molecular orbital calculations predict multiple low-lying excited states for the dianion.[6−12] Since most of these calculations assume that I_h symmetry is retained, the small energy gaps between the predicted ground state and the excited states could possibly be modified substantially by Jahn−Teller distortions.[13,14] To decide whether such distortions are static or dynamic in nature, precise X-ray crystal structure data are desirable. However, up to now only a few crystal structure determinations of the required quality have been reported. This is largely due to the fact that in most cases only microcrystalline powders have become available.

As we have shown in our earlier work,[15] fulleride ions can be stabilized orientationally by introducing bulky organic cations into the structure. Other groups have used different organic or metal-organic cations, or cryptates of alkali metals.[16−21] Nevertheless, these structures quite often exhibit disorder in the anionic or cationic parts of the structure, thereby reducing the accuracy of the information gained from structure determinations. In this note, we present the synthesis and X-ray single-crystal structure analysis of $[Ba(NH_3)_7]C_{60}\cdot NH_3$, containing fully ordered C_{60} dianions in a high-symmetry environment.

Table 1. Crystallographic Data for $[Ba(NH_3)_7]C_{60}\cdot NH_3$

$C_{60}H_{24}N_8Ba$	$M = 994.21$ g/mol
$a = 1222.3(2)$ pm	space group $R3m$ (No.160)
$c = 2146.1(6)$ pm	$T = 113(2)$ K
$V = 2.777(1)$ nm^3	$\lambda = 71.069$ pm (Mo Kα)
$Z = 3$	$\mu = 1.136$ mm^{-1}
$D_c = 1.784$ g/cm^3	$R(F_o) = 0.023$
	$wR_2(F_o^2) = 0.055$

Experimental Section

Synthesis. $[Ba(NH_3)_7]C_{60}\cdot NH_3$ was synthesized by reaction of barium and C_{60} in liquid ammonia. All reactions were carried out under dry argon, either in all-glass reaction and handling vessels that were dried in vacuo, or in a glovebox. Liquid ammonia (Bayer AG, purity 2.8) was first distilled from sodium, then from potassium, and was stored as a potassium−ammonia solution at 195 K. Buckminsterfullerene C_{60} (Hoechst AG, gold grade) was dried before use for 12 h at 300 °C in vacuo. Barium (Alfa, 99.9%) was used as received.

A 16.5 mg amount of Ba (1.2×10^{-4} mol) and 85 mg of C_{60} (1.18×10^{-4} mol, finely ground powder) were placed in a modified Schlenk apparatus, and the vessel was cooled by a dry ice/ethanol slush. Approximately 6 mL of liquid ammonia was condensed into the apparatus through a vacuum line. The reaction mixture was allowed to warm slowly to 238 K. After 2 h, the initially blue color of the solution changed to pale red, indicating the presence of fulleride anions in the solution. The black precipitate at the bottom of the vessel was visually indistinguishable from the C_{60} placed there at the beginning. To ensure complete reaction, the mixture was left at 238 K for additional 8 weeks, leading to larger crystals of improved quality. The crystalline product (shiny black platelets) evolves ammonia when subjected to vacuum, leaving a dull, finely divided residue.

Structure Determination. Crystals of the title compound were transferred directly from liquid ammonia into a 3:1 mixture of perfluoroether oils (Fomblin Y Hvac 140/13, Aldrich; RS 216, Riedel de Haën) which was cooled to 220 K by a stream of cold nitrogen. A crystal ($0.2 \times 0.15 \times 0.1$ mm) suitable for X-ray structure analysis was selected under a microscope and picked up with the tip of a glass capillary mounted on a goniometer head. The crystal was then immediately submerged in liquid nitrogen and transferred to the diffractometer.[22]

The crystal data are given in Table 1. Lattice parameters were determined by a CAD4 indexing program and refined by a least-squares routine with the angular settings of 25 reflections ($7.91 < \theta < 27.39°$). Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation to $\theta_{max} = 27°$ by using ω/θ BPB scans (no. of measd reflcns, 7256; no. of indep reflcns, 1279 ($R_{int} = 0.0331$); no. of obsd reflcns with $I > 2\sigma(I)$, 1267). Three intensity control reflections were measured every hour, showing no decay. Intensity data were corrected for Lorentz and polarization effects.[23] Absorption correction was not applied since the linear absorption coefficient μ and the internal R value for the collected data

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* Corresponding author. Phone: +49 228 73 3114, 2708. FAX: +49 228 73 5660. E-mail: mjansen@snchemie2.chemie.uni-bonn.de.

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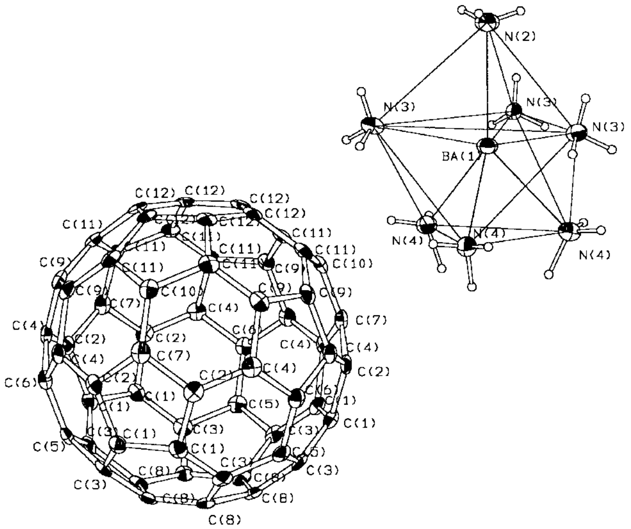

Figure 1. ORTEP[32] plot of the fulleride dianion together with the cationic $[Ba(NH_3)_7]^{2+}$ complex (50% probability ellipsoids; hydrogen atoms are assigned circles with an arbitrary radius).

are relatively low. The structure was solved by Patterson methods[24] and refined on F^2 using all 1279 independent reflections[25] (no. of parameters, 133; one restraint (floating cell origin)). All hydrogen atoms were located by difference Fourier synthesis and refined isotropically coupled to the thermal parameters of the nitrogen atoms. The structure could be refined in space group $R3m$ (No. 160) to a final wR_2 value of 0.066 [corresponding to a conventional R value of 0.026 by using only reflections with $I > 2\sigma(I)$]. However, the refinement of a Flack absolute structure parameter x[26] suggested the presence of racemic twinning. Consequently, the structure was refined using a twinned model. This approach led to a final wR_2 value of 0.056 [corresponding to a conventional R value of 0.023 by using only reflections with $I > 2\sigma(I)$]. Fractional contributions of the components were determined as 0.38(2) (= x) and 0.62 (= $1 - x$). The most prominent maximum and minimum in the final difference Fourier map were 0.86 e/Å^3 (in the vicinity of Ba) and −0.34 e/Å^3, respectively.

Results and Discussion

The crystal structure of $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ can be described as distorted NaCl-like; the fulleride molecule ions form an approximate fcc substructure, where barium heptaammine complexes occupy the octahedral sites. The structure incorporates one additional molecule of NH_3 of solvation per formula unit.

An interesting peculiarity of the crystal structure is represented by the coordination of Ba^{2+}. To date, only two homoleptic barium ammine complexes have been characterized by X-ray crystal structure analysis: in $[Ba(NH_3)_9]^{2+}$ [27] Ba is coordinated by nine NH_3 which form a distorted tricapped trigonal prism; in $[Ba(NH_3)_8]^{2+}$ [28] Ba is bonded to eight molecules of NH_3 forming a distorted square antiprism. The unique crystallochemical properties of fullerides as unusually large, rigid, noncoordinating anions force the barium to adapt its coordination sphere to the size and shape of the interstitial sites in the fulleride substructure. The result is a barium heptaammine complex $[Ba(NH_3)_7]^{2+}$ (Figure 1), best described as a monocapped trigonal antiprism. While the Ba−N distances range from 2.854(4) to 2.941(7) Å, the distance between Ba and the isolated molecule of NH_3 is fairly large, 4.934 Å, and has to be classified as noncoordinatory.

Table 2. Bond Distances (Å) in C_{60}^{2-} [a]

		6:6 Ring Bonds			
C(1)−C(3)	1.397(4)	(6×)	C(8)−C(8)#3	1.397(6)	(3×)
C(2)−C(4)	1.388(4)	(6×)	C(9)−C(11)	1.397(4)	(6×)
C(5)−C(6)	1.415(5)	(3×)	C(12)−C(12)#4	1.396(6)	(3×)
C(7)−C(10)	1.412(6)	(3×)			
			mean (6:6)	1.398(5)	(30×)
		5:6 Ring Bonds			
C(1)−C(1)#3	1.442(5)	(3×)	C(4)−C(9)	1.456(4)	(6×)
C(1)−C(2)	1.455(4)	(6×)	C(8)−C(8)#4	1.443(5)	(3×)
C(2)−C(7)	1.443(4)	(6×)	C(9)−C(9)#4	1.442(6)	(3×)
C(3)−C(5)	1.441(4)	(6×)	C(10)−C(11)	1.444(4)	(6×)
C(3)−C(8)	1.450(4)	(6×)	C(11)−C(12)	1.447(4)	(6×)
C(4)−C(6)	1.447(4)	(6×)	C(12)−C(12)#3	1.454(6)	(3×)
			mean (5:6)	1.447(4)	(60×)

[a] Symmetry operations: #3, $-y, -x, z$; #4, $x, x - y, z$.

However, the more important component in this structure is the fulleride dianion C_{60}^{2-}. Its thermal parameters (Figure 1) are physically meaningful and indicate the absence of static orientational disorder of the dianion. Thus, the structure is of sufficient accuracy to allow for an inspection of possible distortions, e.g. of Jahn−Teller type.

So far, the best X-ray crystal structure analysis of a compound containing dianions of C_{60}, $(PPN)_2C_{60}$ (PPN^+ = bis(triphenylphosphine)iminium ion),[18] was published by Reed et al. The authors have observed a change in point symmetry of the fullerene moiety from I_h to C_i and have interpreted this distortion as due principally to the Jahn−Teller effect. In the same paper interactions between $C^{\delta-}{-}H^{\delta+}$ bonds of complex cations and the faces of the fullerene anion have been discussed as being possibly responsible for the fixed position of the fullerene. It should be noted, however, that this interaction could lead in itself to a slight shift in the electron distribution on the fullerene surface and thereby to a slight shift of the atom positions from the ideal geometry. Thus, it cannot be excluded that the distortions observed are induced by intermolecular interactions in a triclinic environment.

The present structure contains fulleride units in a fixed orientation without any hint of disorder. The average bond lengths found for the 5:6 ring junctures and the 6:6 ring junctures (Table 2) agree within experimental error to those theoretically predicted[29] and reported for $(PPN)_2C_{60}$. The fixed orientation of the dianion is possibly a result of interactions with hydrogen atoms. Those showing closest contacts to the fulleride surface are situated above the 6:6 and 6:5 ring junctures where considerably high electron density should be located. The influence of the hydrogen atoms on the geometry of the fulleride dianion is difficult to assess. However, as in this case the high symmetry is maintained there is no evidence for a distorting influence. According to calculations for C_{60}^{-} [13] axial elongations along the 5-fold, 3-fold, and 2-fold axes of the icosahedron would lead to minima of the associated potential energy surface. Thus, Jahn−Teller distortions could possibly reduce the I_h symmetry of C_{60} to D_{5d}, D_{3d}, or D_{2h}. Density functional calculations[29] for the dianion have predicted two low-lying, essentially degenerate electronic states of D_{2h} and D_{3d} symmetry, respectively. The site symmetry (C_{3v}) observed in the present structure is consistent with both a distortion of D_{3d} character and the ideal icosahedral symmetry. In the present case the

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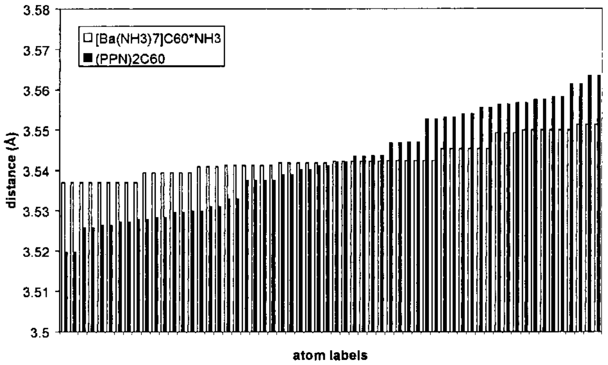

Figure 2. Distances from the center of the fullerene to the carbon atoms for $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ (white bars) and $(PPN)_2C_{60}$ (black bars).

latter seems to be true. As is shown in the diagram (Figure 2), the spread of distortions for the $C_{60}{}^{2-}$ anion in $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ (white bars) is much less pronounced than for the dianion in $(PPN)_2C_{60}$ (black bars).[18] The longest atom-to-atom diameter is 7.092(7) Å (C5−C10), and the shortest is 7.078(6) Å (C3−C11). This difference in diameter is significantly smaller than the one observed for $(PPN)_2C_{60}$ (0.086 Å) and even slightly smaller than the greatest variation in the diameter as determined for neutral C_{60} (0.025 Å).[30] To evaluate the degree of deviation from the ideal I_h symmetry we have used an approach similar to the one used by Green et al.[29] First, the dianion was oriented in a fixed Cartesian frame, with x, y, and z directions coinciding with C_2 symmetry axes. For each atom, the Cartesian displacements from the icosahedral position (i.e., from the position of that atom in an I_h C_{60} cage with the same average single and double bond lengths as the anion) were calculated and the root-mean-squares value for the distances between corresponding atoms was determined. For the present compound an rms value of 0.0075 was found as compared to 0.0155 for the dianion in $(PPN)_2C_{60}$. To put these values in the appropriate context we have applied the same formalism to neutral C_{60} as determined in two different investigations. The rms values obtained are 0.031[30] and 0.0171.[31] Obviously, in a crystalline environment the deviation of neutral fullerene, which is not subject to the Jahn−Teller effect, from ideal icosahedral symmetry is significantly larger than the distortion of the $C_{60}{}^{2-}$ dianion as observed in $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$.

These figures suggest that within the accuracy of our calculations and experimental data for $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ the ideal I_h symmetry of the dianion is retained. Although we have observed stronger distortions in another triclinic crystal structure,[21] we believe that the deformations of the fullerene cage are not intrinsic, i.e., a result of the asymmetric occupation of a degenerate MO as predicted by Jahn and Teller, but caused by the interaction with a local environment of low symmetry.

Conclusion. $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ has been obtained as well-crystallized material suitable for single-crystal structure analysis. The fulleride dianion is in a fixed orientation, and does not show any significant deviation from the ideal (I_h) point symmetry. Thus, distortions that are expected to occur due to the Jahn−Teller effect are either very small or of dynamic character.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determination of $[Ba(NH_3)_7]C_{60}{\cdot}NH_3$ are available on the Internet only. Access information is given on any current masthead page.

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