Tracing the Jahn-Teller Distortion of $\text{C}_{60}^{n-}$ in Isostructural Fullerides $\text{[M(NH}_3)_7\text{]}\text{C}_{60} \cdot \text{NH}_3$, $\text{M} = \text{Ba, Sr, K}$

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Dedicated to Professor Wolfgang Kaim on the Occasion of his 70th Birthday

Single crystals of new $\text{[Sr(NH}_3)_7\text{]}\text{C}_{60} \cdot \text{NH}_3$ (compound 1) and $\text{[K(NH}_3)_7\text{]}\text{C}_{60} \cdot \text{NH}_3$ (compound 2) were prepared by extracting mixtures of potassium and $\text{C}_6\text{O}_2$ with liquid ammonia, where for the synthesis of 1 solid strontium chloride was added to the extraction mixture. The procedure applied relies on self-contained continuous evaporation and condensation of ammonia at subcritical conditions in a special, sealed glass vessel, at room temperature (RT). According to single crystal structure analyses on data collected at 123 K, both, 1 and 2, are isostructural with $\text{[Ba(NH}_3)_7\text{]}\text{C}_{60} \cdot \text{NH}_3$ (compound 3). The structure determinations suffer either from systematic twinning (3), or positional disorder for 1 and 2. Crystals of 3, grown and handled throughout at low temperature (123 K), developed large enough twin domains such that an inversion twin type refinement in space group $R3m$ converged properly. For 1 and 2, the crystals of which were grown at RT and subsequently cooled for data collection, refinements of the same structure model were only possible in $R3m$ while applying split atom positions. For 1 and 3 the accuracy achieved was sufficient to extract a particular bonding distortion pattern for $\text{[C}_6\text{O}_2]^{3-}$, which is lifting the degeneracy of the HOMO according to the Jahn-Teller theorem. Independent quantum chemical calculations are lending convincing support to the experimental findings.

Introduction

Homo-atomic bonding is an issue of relevance for various fields in chemistry. So-called cluster compounds constitute a subgroup of substances featuring such a bonding scheme, for which, however, it has proven impossible to provide a definition which would enable for an unambiguous categorization of the diverse assemblages encountered.[11] Such assignments would be desirable, not only for formal reasons. More importantly, for analyzing the chemical and physical properties of a cluster compound, it is indispensable to know if the entity under consideration is a self-contained ensemble of atoms, or if it requires some stabilizing interaction with its environment. Obviously, some Zintl anions[2] represent clusters that are capable of existence in solution,[2b,c,3] and thus come close to the condition of self-sustained stability. Fullerenes can be regarded species least compromised in the latter respect since they exist in full integrity as solids, in solution and in the gas phase. These molecular allotropes of carbon are structurally quite robust, and the respective individual connectivity is preserved by a set of $\sigma$-bonds, while localization and number of $\pi$-electrons modulate structural details and electronic properties. This class of carbon clusters and its anions has provided an extremely fertile ground for extensive synthetic, structural and physical properties studies.[4]

Chemistry and physics of most abundant $\text{C}_6\text{O}_2$ are dominated by its ability to accept up to twelve excess electrons. Of particular interest is the superconductivity of compounds formed with alkali metals, $\text{A}_x\text{C}_6\text{O}_2$ ($\text{A}=\text{Na, K, Rb, Cs}$),[4d,e] where the $\text{C}_6\text{O}_2$ ions are threefold negatively charged on the average, but metallic conductivity would imply intermediary, fluctuating charges of $-2$ and $-4$. In superconducting $\text{C}_6\text{O}_2^{3-}$ compounds the structural relaxations that cause superconductivity may be seen at $\text{C}_6\text{O}_2^{2-}$ as a quasi-frozen charge fluctuation. Here, the HOMO is triply degenerate and unequally occupied with two electrons. Such a scenario inevitably should result in a Jahn-Teller (JT) effect.[5] A number of theoretical analyses have become available, which all agree in that the JT distortion should be fairly small, leading to orbital splittings of less than 0.1 eV.[6] As a geometric response, most investigators assumed a global distortion of the $\text{C}_6\text{O}_2$ cage to an ellipsoidal body.[7] This latter view has been questioned by demonstrating that the JT distortion is rather reflected by local bond distortions.[8]

We report on analysis of structural data from three isostructural fullerides of composition $\text{[A(NH}_3)_7\text{]}\text{C}_{60} \cdot \text{NH}_3$, $\text{A} = \text{Sr, K}$ and $\text{Ba}$, (compounds 1, 2, 3), which on one hand would offer the opportunity to assess the influence of inter-fulleride separations for equally charged $\text{C}_6\text{O}_2^{2-}$ species on the local...
distortions, on the other to trace the effect of the lower number of electrons in the HOMO in less charged C$_{60}$- . Although the structural changes with respect to pristine C$_{60}$ are close to the limits of experimental error, the systematic trends seen in different structures are lending support to the view that the JT effect in fullerides C$_{60}$- and of C$_{60}$ causes local intramolecular distortions of bond-lengths, reducing the point group symmetries from I$_h$ of C$_{60}$ to D$_{3d}$ or D$_{3h}$ respectively, for the $-2$ and $-1$ anions. The present experimental findings have been substantially corroborated by unconditional DFT based structure optimizations.

Results

Synthesis. New [K(NH$_3$)$_2$]C$_{60}$·NH$_3$ (compound 2) was obtained by extracting mixtures of potassium and fullerene (C$_{60}$) with (sub-critical) liquid ammonia at room temperature for about one month in a special glass extraction vessel, see Figure 1, which was designed in analogy to a setup reported earlier. For [Sr(NH$_3$)$_2$]C$_{60}$·NH$_3$ (1) the same procedure was applied, however, solid strontium dichloride was added to the starting mixture. In case of 1, after a few days, tiny black crystals had formed in the receiver, which grew to a size of about 0.2 mm within four weeks. In case of 2, crystals were noticeable after two weeks, and grew to black crystals with a dimension of about 0.1 mm. The ammoniates 1 and 2 are stable at RT under the autogeneous pressure of liquid ammonia. The obtained crystals are sensitive to air, moisture and elevated temperatures.

Complications in crystal structure refinements. Both, the new compounds, are isostructural to previously reported [Ba(NH$_3$)$_2$]C$_{60}$·NH$_3$[11] the crystal structure of which was successfully refined as an inversion twin in space group R-3m (No 166). Unexpectedly, attempts to refine the crystal structures of the Sr and K compounds along the same procedure failed. Instead, the refinements of 1 and 2 only converged when assuming a split atom model in space group R-3m (No 166). However, although the twin refinement failed, it is possible to represent the refined split atom structure in real space as superposition of two (inversion) twin domains. Thus, the basic crystal structures of [A(NH$_3$)$_2$]C$_{60}$·NH$_3$, A=Sr, K and Ba, if unaffected by twinning or disorder, are correctly described in the acentric space group $R3m$ (No 160). Interestingly, the split atom model does not apply to the Ba compound. Without providing further evidence, we relate this marked dissimilarity to the different temperature protocols applied during synthesis. Fullerides are notorious for formation of rotator phases. We assume that crystals of 1 and 2 grow as rotator phases at RT, with the dynamic disorder freezing at mounting the crystals for data collection at low temperature. This quench was obviously too fast for forming extended domains of the different orientations. Crystals of the Ba compound, however, where grown below the boiling point of liquid ammonia, in a temperature regime where the ordered phases are apparently stable, enabling this phase to develop domains larger than the coherence length of the radiation used, while the frozen disorder of 1 and 2 occurs in domains which are smaller than the coherence length.

Description of crystal structures. The general structural organization of the three isostructural fullerides corresponds to the rock salt pattern, whereby the fullerides form an approximate fcc substructure, with the respective cationic species filling the octahedral voids, see Figure 2. These voids are lined by eight solvate ammonia molecules that are pointing with the hydrogen atoms towards the fulleride anions. The resulting ensembles of eight ligands represent a coordination polyhedron corresponding to a double minimum potential. The

**Figure 1.** Liquid ammonia special glass extraction vessel: a inert-gas and NH$_3$(g) supply, b access path for reagents, c glass filter, d storage of reactant, e receiver – collecting vessel, f cooling water supply.

**Figure 2.** Rock salt analogous arrangement of Sr$^{2+}$ and C$_{60}^{2-}$ in [Sr(NH$_3$)$_2$]C$_{60}$·NH$_3$. Ammonia molecules are omitted. All atoms are presented with thermal ellipsoids, carbon atoms with 75% probability and Sr$^{2+}$ with 95% probability.
cations Sr$^{2+}$, K$^+$ and Ba$^{2+}$ may switch in a diffusionless process between the two sites, while part of the ammonia molecules follow and shift slightly, the positions of the fullerides, however, stay virtually unchanged. This phenomenon constitutes the main reason for the order-disorder transitions encountered. In Figure 3 the situation is visualized by showing a superposition of the two orientations. Accordingly, the coordination number of the cations is best described as $7(+1)$, and the first sphere coordination polyhedron as a monocapped trigonal prism.

The C$_{60}^{2-}$ and C$_{60}^-$ anions preserve the connectivity of the pristine fullerene, corresponding to a truncated icosahedron. Further, the bond alternating pattern where the 30 so-called [6,6] double bonds, which connect two hexagons, are shorter (139.1 pm) than the 60 [5,6] bonds (145.5 pm) connecting a hexagon and a pentagon, is essentially maintained. As a response to the additional electrons hosted by the anionic species, these intramolecular separations are systematically modulated, which is the main subject of the Discussion paragraph. Unfortunately, different from our previous studies, the structure determinations now performed for 1 and 2 suffer from local disorder. For 2 the reliability of intra-fulleride distances is moreover limited since the completeness of intensity data is below standard due to experimental implications. In spite of these limitations in precision, for all compounds 1, 2 and 3, there are no doubts as to the correctness of their general structural organisation. Still, we compare the intra-fulleride bondlengths of 1 and the respective data from fully ordered 3$^{[11]}$ with values obtained by DFT based calculations.

Discussion

Upon reduction of C$_{60}$ its 3-fold degenerate, anti-bonding LUMO of symmetry $t_{1u}$ accepts the additional electrons. In case of the doubly charged anion, a single carbon atom (2$p$) represents a symmetry equivalent configuration, where Hund’s rule applies and the ground state is a triplet. Still, no magnetic state has been found for any of the known C$_{60}^{2-}$ compounds. The underlying diamagnetic ground state can only be achieved by a JT distortion. Inspired by earlier calculations$^{[12]}$ searches for experimental evidence of ellipsoidal distortions of the original sphere failed$^{[11,13]}$. Meanwhile, several reports have appeared, providing evidence for local bond lengths modulations rather than global distortions to reflect the Jahn-Teller distortion$^{[8,14]}$. Paths of symmetry descent lifting the degeneracy of the frontier orbitals$^{[8]}$ of C$_{60}^{2-}$ are visualized in Figure 4.

First we calculated$^{[15]}$ the possible electronic ground states at DFT level employing the TPSS functional$^{[16]}$ together with def2-TZVP basis sets$^{[17]}$ and using the conductor-like screening model (COSMO).$^{[18]}$ Starting from the neutral species, optimizations of the structure parameters were carried out for the singlet state, where the $a_{1u}$ representation (see Figure 5) is occupied with two electrons of opposite spin, as well as for the triplet state, where the $e_u$ representation (see Figure 5) is occupied with two electrons of the same spin. For both cases one gets slight changes in the bond distances (compared to C$_{60}$) of $+0.7$ pm on average, which are listed in Table 1. The

Figure 3. Cation coordination polyhedron, coordination number 7 $+1$, ammonia: blue ellipsoids (50% probability), second orientation shown in pale colors.

Figure 4. The minimal symmetry reduction paths for lifting the degeneracy of the originally triply degenerate HOMO ($t_{1u}$) of C$_{60}^{2-}$ by a JT distortion (top). Positions of the symmetry inequivalent (6,6)-bonds in C$_{60}^{2-}$ for the D$_{5d}$ representation. The four different types are represented by different colours, c.f. reference [8b].
Figure 5. Top: Plot of the electron density of the threefold degenerate LUMO in C$_{60}^–$ contours are drawn at 0.002 a.u. Bottom: Plot of the amplitudes of the three columns of the LUMO, the first (left) transforming in D$_{3h}$ symmetry like $d_{xy}$, the second and the third (middle, right) like $e_{g}$ contours are drawn at 0.025 a.u.

Table 1. Experimental values for [M(NH$_3$)$_2$]C$_{60}^–$·NH$_3$ (M=Ba, Sr, K) (first two columns), as well as calculated numbers (TPSS functional, def2-TZVP bases, COSMO) of symmetry-distinct C–C distances (in D$_{3h}$ symmetry) for the singlet and the triplet state of C$_{60}^–$. The numbers in parentheses indicate the changes with respect to C$_{60}$. The energies of frontier orbitals for HF and DFT(TPSS) in Tables S2 and S4 of the supplementary material.

| M       | C$_{60}^–$, singlet | C$_{60}^–$, triplet |
|---------|---------------------|---------------------|
| Ba(6x)  | 1.411(8)/1.401(4)   | 1.423               | 1.399               |
|         | (+ 0.026)           | (+ 0.002)           |                     |
| Sr(12x) | 1.396(6)/1.390(2)   | 1.407               | 1.407               |
|         | (+ 0.010)           | (+ 0.010)           |                     |
| K(6x)   | 1.395(6)/1.398(4)   | 1.397               | 1.413               |
|         | (+ 0.000)           | (+ 0.016)           |                     |
| C(6x)   | 1.389(5)/1.400(3)   | 1.401               | 1.411               |
|         | (+ 0.004)           | (+ 0.014)           |                     |

The assumption of a global distortion of the dianion,$^{[20]}$ was discarded by earlier experimental studies.$^{[11,13]}$ These latter findings are corroborated by the theoretical results obtained in this work. We calculated the inertia tensor (divided by the mass of C) according to

$$\Theta = \sum_{i=1}^{60} \begin{pmatrix} y_i^2 & -x_i y_i & -x_i z_i \\ -x_i y_i & x_i^2 + z_i^2 & -y_i z_i \\ -x_i z_i & -y_i z_i & x_i^2 + y_i^2 \end{pmatrix}$$

The diagonal elements amount to (503.62, 503.62, 503.62) (in Å$^2$) for the icosahedral neutral cluster, to (506.53, 506.53, 502.81) for the dianion in the singlet state and to (504.67, 504.67, 506.50) for the dianion in the triplet state, the off-diagonal elements are zero throughout. These diagonal elements can be translated to ratios of the axes of the ellipsoids of inertia, yielding a slight prolate deformation for the singlet state (z-axis longer than x or y axis by 0.74%) and an even slighter oblate deformation for the triplet state (z axis shorter than x or y axis by 0.36%). This is somewhat less than the deformation shown in ref. 14a, and one to two orders of magnitude smaller than distortions usually discussed for the jellium model.$^{[20]}$

In Table 1 we compile the respective experimental (6,6) bonds for 1 and 3 along with the calculated ones. Total energies for all employed methods are listed in Table S1, energies of frontier orbitals for HF and DFT(TPSS) in Tables S2 (singlet) and S3 (triplet), and Cartesian coordinates for DFT (TPSS) in Table S4 of the supplementary material.

Conclusions

[K(NH$_3$)$_2$]C$_{60}^–$·NH$_3$ and [Sr(NH$_3$)$_2$]C$_{60}^–$·NH$_3$ were synthesized by extraction of feedstocks consisting of elemental potassium and the respective stoichiometric amount of C$_{60}$ while adding excess of SrCl$_2$ in the latter case, with liquid ammonia at RT. Both the new compounds are isostructural with the Ba analogue,$^{[21]}$ which was grown from liquid ammonia at $–70$ °C. The complex cations and anions adopt arrangements corresponding to the rock salt pattern in space group $R\bar{3}m$. All crystals display twinning, mimicking a centrosymmetric average structure in $R\bar{3}m$. Due to the different temperatures of crystal growth, the twin domains are of substantially different size, such that only the Ba compound (crystals grown at low temperature) could be refined as an inversion twin, while the K and Sr representatives (crystals grown at RT and cooled to 100 K for data collection) only allowed structure refinements assuming split atom positions. Nevertheless, the precision achieved has enabled to extract a specific distortion pattern of the 6,6 bonds in the fulleride cages, indicating a JT distortion lifting the degeneracy of the partly occupied HOMO of the anion. DFT based calculations confirm the diamagnetic ground state related and the distortions of individual bonds lowering the point group symmetry of the C$_{60}$$^{2–}$ to $D_{3h}$. The shifts in
bond lengths as discussed are only slightly exceeding the esd's of the experimentally determined bond lengths. However, if the distortions observed were caused by random error, they should be random as well and not follow a systematic pattern as corroborated by the fact that the same trends have been observed in several independent investigations, and have been backed here by state of the art DFT calculations. At the same time this appears to disprove earlier assumptions of a global spherical distortion of the cages to effect a JT distortion.

**Experimental Section**

**Synthesis.** All preparations were carried out under dry argon in glass vessels. In the first step, nominal \( K_2C_{60} \) was prepared by putting elemental potassium onto the glass filter of the special glass vessel (Figure 1, c). The amount of potassium was determined via difference weighing. Afterwards, the stoichiometric amount of \( C_{60} \) was added. For the synthesis of compound 1 approximately a tenfold excess of \( SrCl_2 \) was added to the laterally connected storage vessel (Figure 1, d). After all solid starting materials had been placed properly in the extraction vessel, approx. 40 ml of dried liquid ammonia was condensed into the receiver, and the glass vessel was separated from the vacuum line by sealing. In a first step “\( K_2C_{60} \)” was extracted for three days at room temperature yielding a dark red solution in the receiver (Figure 1, e). Afterwards, \( SrCl_2 \) was transferred onto the glass filter and was extracted for three additional three to four weeks. For 1 after a few more days, tiny black cuboid-like crystals had grown in the receiver. Finally, after four weeks, black crystals with a diameter of about 0.2 \( \times \) 0.2 \( \times \) 0.2 mm were obtained. For 2 it lasted two weeks, until the first crystals were formed in the receiver. Finally, after four weeks, black crystals with a diameter of about 0.1 \( \times \) 0.1 \( \times \) 0.1 mm had grown.

**Single crystal structure determination.** The crystal data are given in Table 2. The crystal structure of 3 was re-refined based on the originally collected and stored intensity data for 1 and 2, single crystal intensity data were collected on single crystals of rough dimensions 0.2 \( \times \) 0.2 \( \times \) 0.2 mm\(^3\) for 1 and 0.1 \( \times \) 0.1 \( \times \) 0.1 mm\(^3\) for 2, respectively. The diffraction data were collected with graphite monochromated Mo-K\(_\alpha\), \( \lambda = 0.71073 \) Å) radiation on an Enraf-Nonius-CAD4 at \(-150\) °C with \( \omega / 2\theta \)-scanning. The structures were solved by dual-space algorithm using SHELXT\(^{[24]}\) and the non-hydrogen atoms were refined by full-matrix least-squares methods using SHELXL-97.\(^{[25]}\) The hydrogen atoms were located by difference fourier synthesis and refined applying a “riding”-model with fixed isotropic displacement parameters to the adjacent nitrogen atoms. Reflection conditions for both compounds correspond to five possible spacegroups \( R\overline{3}m(166), R\overline{3}m(160), R\overline{3}2(155), R\overline{3}(148) \) and \( R\bar{3}(146) \).

| Table 2. Crystal data and structure refinement data of \([M(NH_3)_4]C_{60}^\cdot NH_3\) (\( M = K, Sr, Ba \)) |
| --- |
| **Formula sum** | \( C_{60}H_{128}N_4K \) | \( C_{60}H_{128}N_4Sr \) | \( C_{60}H_{128}N_4Ba \) |
| **Form. sum. weight** | 895.97 | 944.49 | 994.21 |
| **Space group (no.)** | \( R\overline{3}m(No\text{ }166) \) | \( R\overline{3}m(No\text{ }166) \) | \( R\overline{3}m(No\text{ }160) \) |
| **Lattice constants** | \( a = 12.420 \) Å \( \beta = 90° \) \( \gamma = 120° \) | \( a = 12.225 \) Å \( \beta = 90° \) \( \gamma = 120° \) | \( a = 12.223 \) Å \( \beta = 90° \) \( \gamma = 120° \) |
| **Temperature (K)** | 123 (2) K | 123 (2) K | 113 (2) K |
| **\( R_{/wR} \)** | 0.0422/0.0882 | 0.0401/0.0955 | 0.0223/0.0542 |
| **Goodness of Fit** | 1.076 | 1.076 | 1.067 |
| **Largest diff. peak/hole** | 0.166/\( -0.152 \) e · Å\(^{-3}\) | 0.436/\( -0.409 \) e · Å\(^{-3}\) | 0.846/\( -0.312 \) e · Å\(^{-3}\) |

| Table 3. Structure solutions by dual-space algorithm using SHELXT\(^{[24]}\) |
| --- |
| \([Sr(NH_3)_4]C_{60}^\cdot NH_3\) (1): | | | |
| **R1** | **Rweak** | **Alpha** | **Space Group** |
| 0.255 | 0.048 | 0.044 | \( R\overline{3}m \) |
| 0.240 | 0.019 | 0.042 | \( R\overline{3}m \) |
| 0.255 | 0.035 | 0.047 | \( R3 \) |
| 0.253 | 0.048 | 0.049 | \( R3 \) |
| 0.255 | 0.022 | 0.050 | \( R3 \) |
| \([K(NH_3)_4]C_{60}^\cdot NH_3\) (2): | | | |
| **R1** | **Rweak** | **Alpha** | **Space Group** |
| 0.169 | 0.007 | 0.052 | \( R\overline{3}m \) |
| 0.178 | 0.008 | 0.043 | \( R3 \) |
| 0.165 | 0.004 | 0.046 | \( R3 \) |
| 0.162 | 0.005 | 0.051 | \( R3 \) |
| 0.155 | 0.003 | 0.034 | \( R3 \) |
| \([Ba(NH_3)_4]C_{60}^\cdot NH_3\) (3): | | | |
| **R1** | **Rweak** | **Alpha** | **Space Group** |
| 0.212 | 0.210 | 0.142 | \( R\overline{3}m \) |
| 0.058 | 0.168 | 0.041 | \( R3 \) |
| 0.185 | 0.281 | 0.152 | \( R3 \) |
| 0.184 | 0.296 | 0.156 | \( R3 \) |
| 0.058 | 0.173 | 0.043 | \( R3 \) |

| Table 4. Structure refinement results for \([Sr(NH_3)_4]C_{60}^\cdot NH_3\) (1) |
| --- |
| **R-3m (No \( 166 \))** | **R3m (No \( 160 \))** | **R3 (No \( 146 \))** |
| \( R_{/wR}^\prime \) | 0.0401/0.0955 | 0.0487/0.1184 | 0.0516/0.1100 |
| \( R(all \) data) \) | 0.0904/0.1118 | 0.1170/0.1438 | 0.1333/0.1285 |
| **GooF** | 1.076 | 0.999 | 1.000 |
| **Largest peak/hole** | 0.436/\( -0.409 \) e · Å\(^3\) | 0.622/\( -0.470 \) e · Å\(^3\) | 0.383/\( -0.386 \) e · Å\(^3\) |
While the structure solutions by dual-space algorithm\textsuperscript{24} for [Ba(NH\textsubscript{3})\textsubscript{5}]C\textsubscript{60}\cdot NH\textsubscript{3} (3) clearly indicate possible presence of the non-centrosymmetric space groups R3\textit{m} and R\textit{3}, respective comparative solutions for [Sr(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} (1) and [K(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} (2) are uncertain, the R values obtained for the possible space groups are quite similar (Table 3).

### Table 5. Atomic coordinates and equivalent displacement parameters of [Sr(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} from single crystal diffraction at 123 (2) K.

| Atom  | X     | Y     | Z     | Occ  | Ueq  |
|-------|-------|-------|-------|------|------|
| Sr1   | 3333  | 6667  | 6253(1)| 0.5  | 19(1) |
| N1    | 3333  | 6667  | 4902(2)| 1    | 35(1) |
| N2    | 4573(2)| 5427(2)| 5956(2)| 0.5  | 20(1) |
| N3    | 4253(3)| 5747(3)| 6183(2)| 0.5  | 23(1) |
| C1    | 4616(2)| 3469(2)| 7200(1)| 1    | 25(1) |
| C2    | 3766(2)| 2477(2)| 7578(1)| 1    | 24(1) |
| C3    | 3517(1)| 2718(2)| 8213(1)| 1    | 23(1) |
| C4    | 5254(1)| 4746(1)| 7446(1)| 1    | 24(1) |
| C5    | 5502(2)| 3323(2)| 6804(1)| 1    | 27(1) |
| C6    | 3369(2)| 1684(1)| 8604(1)| 1    | 23(1) |

### Table 6. Atomic coordinates and equivalent displacement parameters of [K(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} from single crystal diffraction at 123 (2) K.

| Atom  | X     | Y     | Z     | Occ  | Ueq  |
|-------|-------|-------|-------|------|------|
| K1    | 3333  | 6667  | 6287(3)| 0.5  | 66(2) |
| N1    | 3333  | 6667  | 4853(5)| 1    | 61(3) |
| N2    | 4619(5)| 5381(5)| 5905(6)| 0.5  | 36(3) |
| N3    | 4340(5)| 5660(5)| 6128(7)| 0.5  | 50(4) |
| C1    | 4650(2)| 3468(2)| 7200(2)| 1    | 31(1) |
| C2    | 3809(2)| 2489(2)| 7582(2)| 1    | 28(1) |
| C3    | 3567(2)| 2726(2)| 8213(2)| 1    | 29(1) |
| C4    | 5277(2)| 4723(2)| 7452(3)| 1    | 31(2) |
| C5    | 5513(2)| 3316(2)| 6809(2)| 1    | 28(1) |
| C6    | 3420(3)| 1710(2)| 8613(3)| 1    | 29(2) |

### Table 7. Selected bond-distances in [Sr(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} at 123 (2) K. Colourcode with ref. to Table 1.

| site 1 | site 2 | distance (Å) |
|--------|--------|--------------|
| Sr1    | N(2)   | 2.701(4)     |
| N(3)   | 2.723(1)|             |
| N(1)   | 2.866(5)|             |
| C1     | C(2)   | 1.390(2)     |
| C(4)   | 1.450(2)|             |
| C(5)   | 1.450(3)|             |
| C2     | C(3)   | 1.444(2)     |
| C(2)#1 | 1.451(3)|             |
| C3     | C(3)#2 | 1.400(3)     |
| C(6)   | 1.445(2)|             |
| C4     | C(6)#3 | 1.401(4)     |
| C5     | C(5)#1 | 1.398(4)     |
| C(5)#4 | 1.436(4)|             |

Symmetry transformations used to generate equivalent atoms:
#1 x, x, y, z
#2 x+y+1/3, y-z+1/3, z
#3 x+y+2/3, y-z+2/3, z
#4 y+1, x-z+2/3, z

### Table 8. Selected bond-distances in [K(NH\textsubscript{3})\textsubscript{2}]C\textsubscript{60}\cdot NH\textsubscript{3} at 123 (2) K. Colourcode with ref. to Table 1.

| site 1 | site 2 | distance (Å) |
|--------|--------|--------------|
| K1     | N(2)   | 2.883(10)    |
| (N3)   | 2.911(10)|            |
| N(1)   | 3.042(13)|            |
| C1     | C(2)   | 1.389(4)     |
| C(5)   | 1.440(4)|             |
| C(4)   | 1.452(4)|             |
| C2     | C(3)   | 1.436(5)     |
| C(2)#1 | 1.451(5)|             |
| C3     | C(3)#2 | 1.402(5)     |
| C(6)   | 1.455(5)|             |
| C4     | C(6)#3 | 1.370(8)     |
| C5     | C(5)#1 | 1.389(5)     |
| C(5)#4 | 1.454(5)|             |

Symmetry transformations used to generate equivalent atoms:
#1 x, x, y, z
#2 x+y+1/3, y-z+1/3, z
#3 y+1/3, x+y+2/3, y-z+2/3, z
#4 y+1, x-z+2/3, z

### Table 9. Selected bond-distances in [Ba(NH\textsubscript{3})\textsubscript{5}]C\textsubscript{60}\cdot NH\textsubscript{3} at 113 (2) K. Colourcode with ref. to Table 1.

| site 1 | site 2 | distance (Å) |
|--------|--------|--------------|
| Ba1    | N(2)   | 2.855(5)     |
| N(4)   | 2.911(5)|            |
| N(3)   | 2.943(5)|            |
| C1     | C(1)#1 | 1.395(8)     |
| C(2)   | 1.448(5)|             |
| C(1)#2 | 1.454(7)|             |
| C2     | C(7)   | 1.396(6)     |
| C(3)   | 1.445(5)|             |
| C3     | C(4)   | 1.411(8)     |
| C(2)#2 | 1.445(5)|             |
| C4     | C(5)   | 1.442(5)     |
| C(5)#2 | 1.442(5)|             |
| C5     | C(6)   | 1.389(5)     |
| C(12)#1| 1.456(5)|             |
| C6     | C(8)   | 1.448(5)     |
| C(7)   | 1.455(5)|             |
| C7     | C(7)#1 | 1.442(8)     |
| C(9)   | 1.414(7)|             |
| C9     | C(10)  | 1.448(5)     |
| C10    | 1.444(5)|             |
| C11    | C(11)#3| 1.398(7)     |
| C12    | C(12)#3| 1.443(7)     |
| C12    | C(5)#1 | 1.456(5)     |

Symmetry transformations used to generate equivalent atoms:
#1 x, x, y, z
#2 x+y+2/3, y, z
#3 y+1, x-z+2/3, z

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Even if there is a slight preference for spacegroup R3m for 1 and R3 for 2, refinements in all suggested spacegroups were performed, considering several twinning possibilities. For both cases, the best refinements were achieved in space group R-3m, with a split atom model for the [Sr(NH₃)₂]⁺·NH₃ and [K(NH₃)₂]⁺·NH₃ parts. The best results for 1 are shown in Table 4. For 2, due to degradation of the crystal, the completeness of data achieved is very low (θmax = 25.098, completeness 65.5%), and the respective bonding data were not considered in the discussions on the bond lengths.

Positional parameters and relevant bondlengths for 1 and 2, respectively, are given in Tables 5–9. Crystallographic data for the structures determinations presented in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK (deposition numbers 1: 2007995; 2: 2061894; 3: 2061967). Copies of the data can be obtained free of charge on quoting the depository number CCDC-2007995 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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