On the Geometry of the Fulleride Dianion $C_{60}{}^{2-}$ in Crystalline Fullerides – Syntheses and Crystal Structures of $[M(NH_3)_6]C_{60} \cdot 6\ NH_3$ ($M = Mn^{2+}, Cd^{2+}$)☆

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The fullerides $[M(NH_3)_6]C_{60}$ ($M = Mn^{2+}$, Cd^{2+}) have been synthesized by ion exchange in liquid ammonia and analyzed by X-ray single-crystal diffraction. With both complex cations the $C_{60}{}^{2-}$ units are in fixed orientations, and their geometries have been determined with good accuracy. An inspection of the fulleride dianions with respect to geometric deformations in the title compounds and three further independent determinations has led to the conclusion that no significant static Jahn-Teller distortion is present.

Introduction

Due to the high symmetry of icosahedral C_{60} its LUMO is triply degenerate (t_{1u}). In accordance with the Jahn-Teller theorem[1] partial filling of the LUMO with one to five electrons should remove this degeneracy and possibly cause a structural distortion in the carbon cage. The nature and the degree of this distortion, however, are difficult to determine experimentally since in most cases structure determinations suffer from orientational disorder of the almost spheric fullerides. Jahn-Teller distortion could reduce the symmetry to D_{5d}, D_{3d}, D_{2h}, C_{2h}, or C_i, all of which are subgroups of I_h. From linear approximation D_{5d} and D_{3d} structures have been derived as possible minima, and the D_{2h} structure as a saddle point of the associated potential energy surface[2]. For the monoanion $C_{60}{}^{-}$ the relative energies of these configurations have been calculated as roughly equal[3]. Thus, rearrangement among different Jahn-Teller distorted structures on the potential energy surface would be an easy process. Density functional calculations[4] have yielded D_{2h} symmetry for the singlet and D_{3d} symmetry for the triplet ground state of the dianion $C_{60}{}^{2-}$. All theoretical approaches end up with the result that structural changes due to a Jahn-Teller splitting of the formerly degenerate t_{1u} LUMO should be very small. Only modest static Jahn-Teller energy gains of approximately 0.1 eV are predicted which fall in the range of typical vibrational frequencies. Thus, $C_{60}{}^{2-}$ anions could well be subject to a dynamic exchange between several Jahn-Teller distorted structures[5][6][7]. In the superposition of, e.g., the six degenerate D_{5d} configurations the higher symmetry I_h would be restored. In order to be able to investigate the degree of distortion and to decide, whether those distortions are static or dynamic in nature, precise X-ray crystal structure data are desirable.

In our earlier work we have introduced bulky organic cations into the structure to stabilize fulleride anions in a fixed orientation[8][9]. Other groups have used different organic or organometallic cations, or cryptates of alkali metals[10][11][12][13][14]. Nevertheless, many of the structures still exhibit disorder in the anionic or cationic parts of the structure, thereby reducing the accuracy of the information gained from structure determinations. By the synthesis of $[Ba(NH_3)_7]C_{60} \cdot NH_3$[15] we have demonstrated that complex ammines are well suited to fix the orientation of the fulleride cages. More recently we have exemplified with the preparation of $[Ni(NH_3)_6]C_{60} \cdot 6\ NH_3$ that a broad variety of fulleride salts with different counterions is accessible by ion exchange in liquid ammonia[16]. Here we present the synthesis and characterization of two new fullerides, $[M(NH_3)_6]C_{60} \cdot 6\ NH_3$ ($M = Mn^{2+}$, Cd^{2+}). Both compounds are sufficiently well determined to allow for an inspection of geometrical distortions in the $C_{60}{}^{2-}$ cage. The results are discussed with respect to the Jahn-Teller effect and compared to those obtained in the crystal-structure investigations of $[Ba(NH_3)_7]C_{60} \cdot NH_3$, $[Ni(NH_3)_6]C_{60} \cdot 6\ NH_3$ and $(PPN)_2C_{60}$ [PPN^+ = bis(triphenylphosphanyl)iminium cation][12].

Results and Discussion

Like isostructural $[Ni(NH_3)_6]C_{60} \cdot 6\ NH_3$ the title compounds crystallize in a distorted rock salt type of structure (Figure 1). The fulleride dianions form a distorted *fcc* sublattice where hexaammine complexes of the metal ions occupy the octahedral sites.

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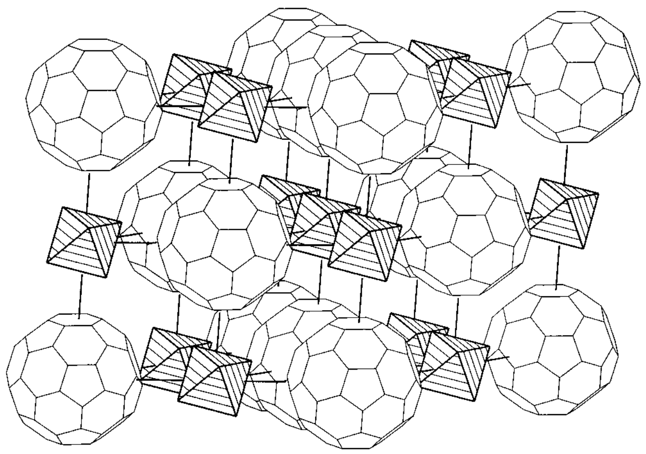
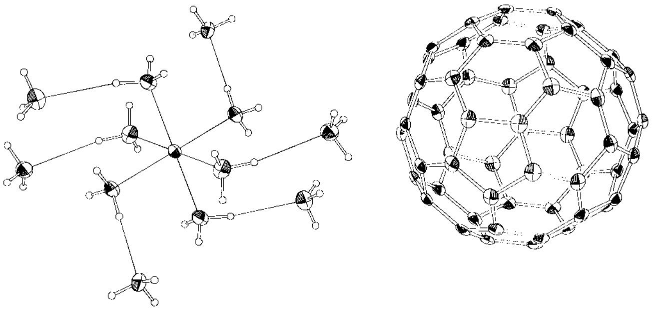
Figure 1. Rock salt type arrangement of fulleride anions and transition metal ammine complexes



Each molecule of ammonia of solvation is coordinated via a hydrogen bond to one of the ammonia molecules in the ligand sphere of the ammine complex. This extended coordination sphere (Figure 2) can change its shape flexibly to meet the needs of the octahedral site of the $C_{60}{}^{2-}$ sublattice, at the same time absorbing differences in the size of the cations [$r(Ni^{2+}) = 69$ pm, $r(Mn^{2+}) = 83$ pm (high spin), $r(Cd^{2+}) = 95$ pm[17]] and fixing the orientation of the fulleride anion.

Figure 2. ORTEP plot[24] of the fulleride dianion in $[Mn(NH_3)_6]C_{60}\cdot 6\ NH_3$ (50% probability ellipsoids)



The obvious relationship between the structures presented here and the NaCl-type structure implies Coulomb interactions mainly to determine the crystal structure. However, the deviation from cubic symmetry indicates the presence of other forces which affect the structure at the same time. Short distances of hydrogen atoms to the fulleride carbon atoms suggest interactions between the $N^{\delta-}{-}H^{\delta+}$ dipoles and electron density on the surface of the dianion. The hydrogen atoms are located above the centres of the 6:6 and 6:5 ring junctures where the majority of π-electron density is located. Similar interactions between $C^{\delta-}{-}H^{\delta+}$ dipoles and fullerides have been reported previously and are assumed to be responsible for the stabilization of the dianion in a fixed orientation[12].

In all fullerides of complex ammoniates thermal displacement parameters of the carbon atoms are physically reasonable and do not indicate any static or rotational disorder. Thus, the structures seem to be of sufficient accuracy to allow for an inspection of geometric distortions of $C_{60}{}^{2-}$, e.g. of Jahn-Teller type. In an earlier investigation of $(PPN)_2C_{60}$ [PPN^+ = bis(triphenylphosphanyl)iminium cation][12] such distortions have been reported to be present. 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.

For an evaluation of the degree of ellipsoidal distortion from the ideal sphere we have considered the longest and shortest carbon-to-carbon diameters. In Table 1 such diameters of the title compounds, of $[Ni(NH_3)_6]C_{60}\cdot 6\ NH_3$, $[Ba(NH_3)_7]C_{60}\cdot NH_3$, $(PPN)_2C_{60}$, and of neutral C_{60} as determined in two different investigations[18][19] are given. The variation in diameters is largest for $(PPN)_2C_{60}$ and very small for $[Ba(NH_3)_7]C_{60}\cdot NH_3$, while all other compounds fall in between. Remarkably, even in the most reliable determinations neutral C_{60} exhibits a small deviation from the ideal shape of a sphere.

In order to reveal any particular pattern in the arrangement of atoms with an elongated or shortened radial distance to the centre of the fullerene cage, the distances between the carbon atoms and the centre of the fulleride dianion have been calculated with the program package PARST97[20]. The calculations were based on the lattice parameters, the atom coordinates and their respective standard deviations as determined in the different crystal-structure analyses.

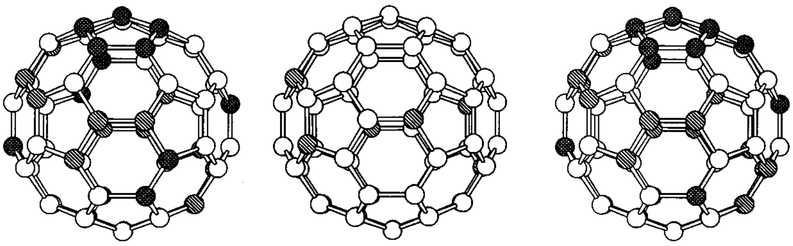
For each fulleride the individual distances (d_i) of the carbon atoms from the centre have been compared to the mean radius r. All differences $d_i - r$ that are larger than three times the standard deviation of the individual radial distances have been treated as significant.

The results of the calculations are visualized in Figure 3. For the fulleride moieties in the different crystal structure analyses those atoms with a significantly elongated radial distance to the centre are plotted with a crossed hatching, those with a shortened radial distance are plotted with a simple hatching.

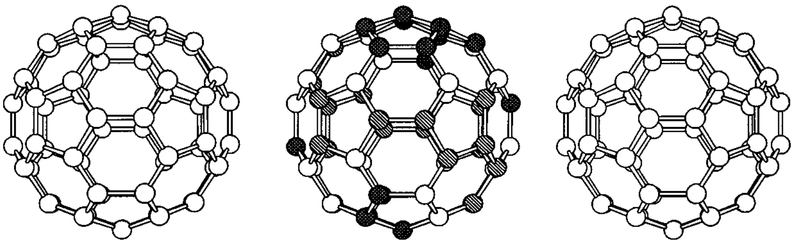
Three of the triclinic structures {$[Mn(NH_3)_6]C_{60}\cdot 6\ NH_3$, $[Ni(NH_3)_6]C_{60}\cdot 6\ NH_3$, and $(PPN)_2C_{60}$} seem to exhibit similarities in the pattern. Elongated atoms form a closed pentagon, suggesting a symmetry reduction to D_{5d} which has been discussed previously[7] as the most probable distortion caused by the Jahn-Teller effect. However, the elongations discussed here are as small as 0.01 A and in addition to experimental error might be caused by crystal packing effects. As some of the dianions, e.g. in $[Ba(NH_3)_7]C_{60}\cdot NH_3$, are not significantly distorted at all, the present experimental data give no conclusive evidence for an intrinsic distortion of $C_{60}{}^{2-}$ due to a static Jahn Teller effect.

In order to check our approach, the deviation from ideal I_h symmetry was determined using a procedure which has been described previously[4]: 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 a C_{60} cage of I_h symmetry

Figure 3. Geometry of fulleride anions as determined in different crystal structure analyses; atoms with an elongated distance to the centre are plotted with a cross-hatched pattern, those with a shortened distance relative to the mean radius are plotted as hatched spheres



$[Mn(NH_3)_6]C_{60}\cdot 6NH_3$ $[Cd(NH_3)_6]C_{60}\cdot 6NH_3$ $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$



$[Ba(NH_3)_7]C_{60}\cdot NH_3$ $(PPN)_2C_{60}$ C_{60}[19]

with the same average single and double bond lengths as found for the anion) were calculated and the root mean squares (r.m.s.) value for the distances between corresponding atoms was determined. To put these values into an appropriate context we have applied the same formalism to neutral C_{60} and have included the results in Table 1.

Table 1. Geometry of the fullerides: largest and shortest carbon-to-carbon distances (Ø$_{max.}$, Ø$_{min.}$) and their difference ΔØ are given; r.m.s values were calculated as described in the text

Compound	Ø$_{max.}$ [Å]	Ø$_{min.}$ [Å]	ΔØ [Å]	r.m.s. value [Å]
$[Ni(NH_3)_6]C_{60}\cdot 6\ NH_3$ (triclinic)	7.1106 (C13−C13′)	7.0408 (C16−C16′)	0.0698	0.0118
$[Mn(NH_3)_6]C_{60}\cdot 6\ NH_3$ (triclinic)	7.1132 (C4−C4′)	7.0484 (C9−C9′)	0.0648	0.0110
$[Cd(NH_3)_6]C_{60}\cdot 6\ NH_3$ (triclinic)	7.1034 (C14−C14′)	7.0286 (C13−C13′)	0.0748	0.0144
$[Ba(NH_3)_7]C_{60}\cdot NH_3$ (trigonal)	7.0923 (C5−C10)	7.0781 (C3−C11)	0.0142	0.0075
$[PPN]_2C_{60}$ (triclinic)	7.1264 (C15−C15′)	7.0394 (C9−C9′)	0.087	0.0155
C_{60} (cubic)[19]	7.0926 (C8−C8′)	7.0678 (C2−C2′)	0.0248	0.031
C_{60} (cubic)[18]	7.112 (C8−C8′)	7.0824 (C4−C4′)	0.0296	0.0171

Again the dianion in $[Ba(NH_3)_7]C_{60}\cdot NH_3$ shows the smallest variation from ideal atom positions, while this time the deviation from I_h is strongest for neutral C_{60}. Even for $(PPN)_2C_{60}$, which has shown the greatest ellipsoidal distortion, the deviation from icosahedral atom positions is modest. Neutral C_{60} clearly can not be subject to a Jahn-Teller distortion. Thus, the observed deviations can only reflect experimental error and perhaps effects of crystal packing. Since in a crystalline environment not all symmetry elements of point group I_h can agree with a given site symmetry, small deviations from the ideal have to be expected as a result of experimental error, even at very favourable experimental conditions.

The considerations presented here have led us to the conclusion that at the present state of knowledge there is no experimental evidence for a static deviation from icosahedral symmetry of the dianion C_{60}^{2-}. As an alternative a dynamic Jahn-Teller effect could be discussed. The related "breathing" movement of the fullerene cage should lead to enlarged thermal parameters of the carbon atoms in radial direction with respect to the centre of the fulleride. However, the thermal displacement parameters as determined reflect the rigid body librational motion of the fulleride rather well and do not show any significant enlargement in radial direction (Figure 2). Thus, the amplitudes of vibrations caused by a dynamic Jahn-Teller effect must be smaller than or equal to the thermal displacement parameters in radial direction, as determined by X-ray crystallography. Based on theoretical calculations only very small deviations from an ideal icosahedron have been predicted upon filling the formerly degenerate LUMO of neutral C_{60}. In this paper we present experimental evidence that in a crystalline environment I_h symmetry of anionic $C_{60}{}^{2-}$ units can be retained. Any deviation found is in the range of or smaller than the experimental error.

We are grateful to *Hoechst AG*, Frankfurt, for providing C_{60}.

Experimental Section

$[M(NH_3)_6]C_{60} \cdot 6\ NH_3$ ($M = Mn^{2+}$, Cd^{2+}) has been synthesized by ion exchange 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 glove box. 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. A thoroughly dried exchange resin (Amberlyst 15, Fluka) was loaded with M^{2+} ($M = Mn^{2+}$, Cd^{2+}) and placed on one side of an H-type glass vessel equipped with a glass sieve (porosity 3). K_2C_{60} was placed on the other side of the sieve. After cooling (ethanol/dry-ice slush) ammonia was condensed into the vessel until the glass sieve was completely covered. The reaction mixture was stored at 230 K for about 3 weeks. During this period K_2C_{60} slowly diffused onto the ion-exchange resin where $[M(NH_3)_6]C_{60} \cdot 6\ NH_3$ precipitated as shiny black platelets that are sensitive to air, moisture and elevated temperatures. Crystals were transferred from liquid ammonia into a mixture of inert oils (1:1 Perfluorpolyether 216, Riedel-de Haen/Perfluorpolyether Fomblin Y HVAC 40/11, Aldrich) which was cooled with a nitrogen stream to 230 K, and picked up on the tip of a glass capillary mounted on a goniometer head[21].

Table 2. Crystallographic data

	$[Mn(NH_3)_6]C_{60} \cdot 6\ NH_3$	$[Cd(NH_3)_6]C_{60} \cdot 6\ NH_3$
Formula	$C_{60}H_{36}N_{12}Mn$	$C_{60}H_{36}N_{12}Cd$
M_r [g/mol]	938.72	1037.41
Crystal system	triclinic	triclinic
Space group	$P1$	$P1$
a[pm]	996.7(1)	999.2(3)
b [pm]	1023.0(1)	1024.4(3)
c [pm]	1055.4(1)	1055.5(2)
α [°]	77.60(1)	77.49(2)
β [°]	79.56(1)	79.34(3)
γ [°]	79.13(1)	78.96(3)
V [nm^3]	1.0210(2)	1.0235(5)
Z	1	1
$\rho_{calcd.}$ [g cm^{-3}]	1.619	1.683
μ(Mo-K_α) [mm^{-1}]	0.55	0.599
Measured reflns.	6495	4715
Independent reflns.	3993	3598
Observed reflns. [$I > 2\sigma(I)$]	3201	2904
θ_{max} [°]	26	25
Parameters	385	361
$R1$ [$F > 4\sigma(F)$]	0.035	0.047
$wR2$ [F^2, all data]	0.102	0.118

Structure Determination: Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 71.069$ pm) at 113(2) K. The structures were solved by the Patterson method[22] and refined on F^2 using all independent reflections[23]. Hydrogen atoms of the ammonia molecules were located by difference Fourier synthesis. Details of the crystal structure determinations for $[M(NH_3)_6]C_{60} \cdot 6\ NH_3$ ($M = Mn$, Cd) are given in Table 2.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-408601 (Mn) and -408602 (Cd).

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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