Synthesis and Crystal Structure Analysis of C_{60} Fulleride Dianions in Solvates of $[A([2.2.2]crypt)]_2[C_{60}]$ (A = K, Rb, Cs)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Reduction of C_{60} with the alkali metals A = K, Rb and Cs in tetrahydrofuran as a solvent and addition of [2.2.2]crypt [1], dimethylformamide and cyclohexane lead to the formation of crystalline samples of $[A([2.2.2]crypt)]_2[C_{60}](C_6H_{12})_2(C_3H_7NO)_2(C_4H_8O)_2$ (A = K, Rb, Cs) **1a**, **1b** and **1c** as major fractions. As a by-product of compound **1a**, a second minor fraction containing $[K([2.2.2]crypt)]_2[C_{60}](C_3H_7NO)_4$ **2** was obtained. The structures of the four compounds have been determined by single-crystal X-ray analyses. The $[C_{60}]^{2-}$ dianions are predominantly ordered. As the main structural motif the structures of compounds **1a**, **1b** and **1c** contain pseudo-hexagonal layers of $[C_{60}]^{2-}$ dianions. Compound **1c** contains a rare example of a Cs^+ sequestering [2.2.2]crypt molecule. The packing of the ionic units in compound **2** also shows layers of distorted hexagons formed by $[C_{60}]^{2-}$ dianions which arranged in pairs with short contacts of 10.3 Å between their centers of gravity.

Key words: Fullerides, Crystal Structure, Dianion, Hexagonal Packing

Introduction

The discovery of superconductivity in alkali metal fullerides such as K_3C_{60} with relatively high transition temperatures lead to the examination of the electronic structures of fulleride anions [2]. Due to the triply degenerate LUMO of the C_{60} molecule, anions C_{60}^{1-} to C_{60}^{6-} are stable and distortions of the I_h-symmetric C_{60} polyhedron is expected for various anions on the basis of the Jahn-Teller theorem [3]. Beside these distortions, the packing of the fullerides and inter-fulleride distances also have a crucial influence on T_c. In intercalated fcc compounds of the type $A_{3-x}A'_xC_{60}$ (A, A′ = K, Rb, Cs) T_c varies from 19.3 K for K_3C_{60} (lattice parameter $a_0 = 14.253$ Å) to 31.3 K for Rb_2CsC_{60} ($a_0 = 14.493$ Å) [4]. Since the exact composition of many bulk metal fulleride phases is not well defined and structural changes within the fulleride cage are expected to be small, structure determinations of fulleride containing compounds by X-ray single diffraction is an important issue. An overview of the structural properties of $[C_{60}]^{n-}$ polyanions and their electronic and magnetic behaviour is given in reference [5].

A number of crystal structures with ordered $[C_{60}]^{2-}$ dianions of compositions $[M(NH_3)_x]C_{60} \cdot yNH_3$ (M = Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Ba^{2+}, $[Bis(benzyltrimethylammonium)]_2^{2+}$; $x = 0, 6, 7$; $y = 1, 3, 6$) have been determined by Jansen *et al.* [6–9], but the strong ellipsoidal distortion of the C_{60} cage which has been found in the first crystal structure determination of an ordered $[C_{60}]^{2-}$ dianion, $[PPN]_2C_{60}$ (PPN^+ = bis(triphenylphosphanyl)iminium cation) [10], could not be confirmed.

It has been shown that the synthetic procedures originally developed for the preparation and crystallization of systems with larger homoatomic anions $E_n^{3/4-}$ (E = Ge, Sn, Pb) [11, 12] can also be successfully applied for the synthesis of compounds containing C_{60}^{2-} [13] and C_{60}^{3-} [14] anions. By using different combinations of polar solvents we have been able to prepare and to crystallize a series of $[C_{60}]^{2-}$ containing salts and to determine their structures. We report here on the synthesis and structural properties of the complexes $[A([2.2.2]crypt)]_2[C_{60}](C_6H_{12})_2(C_3H_7NO)_2(C_4H_8O)_2$ **1a** (A = K), **1b** (A = Rb), **1c** (A = Cs) and $[K([2.2.2]crypt)]_2[C_{60}](C_3H_7NO)_4$ **2**.

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		1a[a]	**1b**[a]	**1c**[a]	**2**[a]	**3**[b]
Crystal system		triclinic	triclinic	triclinic	triclinic	monoclinic
Space group		$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	Cc (No. 9)
Cell constants	a [Å]	13.1086(1)	13.2064(3)	13.1543(2)	13.3193(1)	22.696(4)
	b [Å]	14.3329(1)	14.2010(3)	14.3851(2)	18.6182(2)	15.580(2)
	c [Å]	15.0993(1)	15.0171(4)	15.0256(2)	18.9229(2)	27.523(4)
	α [°]	106.954(1)	106.884(1)	106.996(1)	79.278(1)	
	β [°]	104.920(1)	105.949(1)	104.679(1)	71.877(1)	106.20(2)
	γ [°]	106.274(1)	105.478(1)	106.463(1)	89.376(1)	
Volume [Å^3]		2420.67(3)	2400.20(1)	2426.00(6)	4376.33(7)	9345(54)
Z		2	2	2	2	4

Table 1. Unit cell parameters of **1a**, **1b**, **1c**, **2** and **3**.

[a] This work; [b] Lit. [13].

Results and Discussion

In general, the $[C_{60}]^{2-}$ dianions are formed upon dissolving the corresponding alkali metal together with C_{60} in a polar solvent. Crystallization of species with defined reduction states is promoted by the complexation of the alkali metal ion by a cryptand, followed by the addition of a mixture of ether and hydrocarbons. In the case of the potassium salt a second minor fraction **2** was obtained. Since its structure differs with respect to the packing of the fulleride units it will be discussed separately. All structures contain two $[A([2.2.2]crypt)]^+$ units per fullerene and thus the resulting charge of the C_{60} unit is -2.

Crystal structure of $[A([2.2.2]crypt)]_2[C_{60}](C_6H_{12})_2(C_3H_7NO)_2(C_4H_8O)_2$ (A = K, Rb, Cs)

The results of the single crystal structure analysis of **1b** and **1c** are shown in Figures 1 to 4 and Tables 1 and 2. The unit cells contain one formula unit of **1b** and **1c**, respectively, and due to the centrosymmetricity of the crystals, there are only 30 independent atomic positions for the carbon atoms of the fulleride. All of these atoms in **1b** and **1c** could be located from fourier maps, however, free refinement of all parameters was unstable. Additional maxima in the electron density found close to the atomic positions of the C atoms indicate a small rotational disorder, which could not be resolved by lowering the symmetry to $P1$. Thus, some restraints between parameters were chosen for the refinement of the structure models. According to the results of the crystal structure determinations of salts with ordered $[C_{60}]^{2-}$ dianions [6 – 10], the bonds shared by two six-membered rings of the fuller cage (6:6) were fixed to 1.40 Å and those shared by a five- and a six-membered ring (5:6) to 1.45 Å. The distances were then independently refined within a deviation of 0.02 Å and refinements were carried out without disorder models. The atomic displacement vectors are larger and more

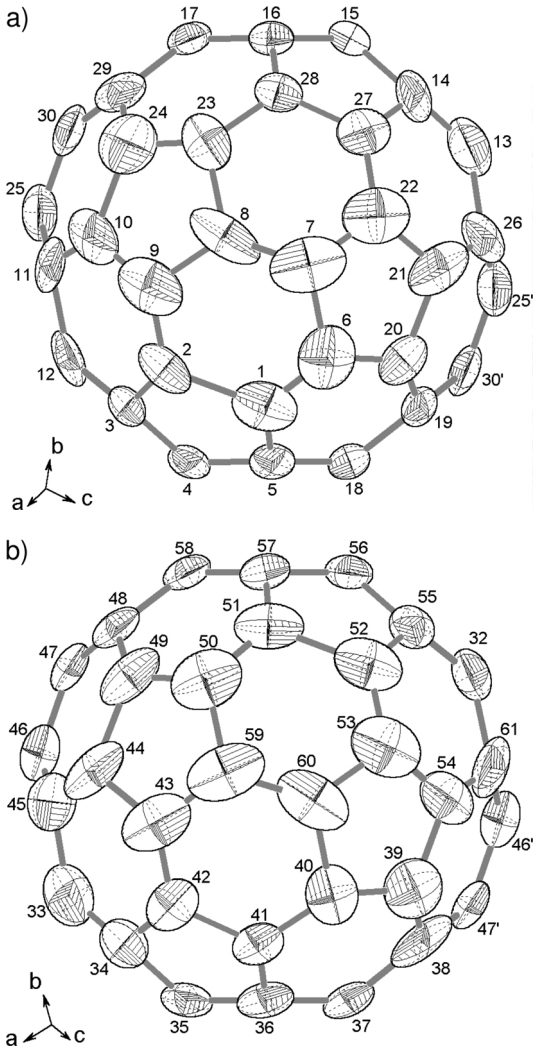

Fig. 1. Structures of the fulleride dianions in a) compound **1b** and b) compound **1c**. Displacement ellipsoids are shown at 50% probability level.

anisotropic at the atoms of the 'equator' of the fuller cage, indicating a very small rotational disorder par-

	1b	**1c**	**2**
Empirical formula	$C_{54}H_{48}N_2O_6Rb$	$C_{61}H_{63}CsN_3O_8$	$C_{108}H_{100}K_2N_8O_{16}$
Formula weight [g/mol]	906.42	1099.05	1844.16
Temperature [K]	100(2)	120(2)	120(2)
ρ_{calcd} [g/cm^3]	1.254	1.505	1.399
Absorption coefficient [mm^{-1}]	1.082	0.828	0.187
$F(000)$	942	1138	1940
Crystal size [mm^3]	$0.30 \times 0.25 \times 0.10$	$0.50 \times 0.40 \times 0.30$	$0.30 \times 0.20 \times 0.10$
$2\theta_{max}$ [°]	50.62	50.68	46.62
Reflections collected	33549	56531	80337
Independent reflections	8614 ($R_{int} = 0.043$)	8823 ($R_{int} = 0.045$)	12531 ($R_{int} = 0.053$)
Data/restraints/parameters	8614/160/604	8823/176/690	12531 / 900 / 1755
Goodness of fit on F^2	1.094	1.041	1.023
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.071$	$R_1 = 0.063$	$R_1 = 0.064$
	$wR_2 = 0.187$	$wR_2 = 0.159$	$wR_2 = 0.156$
R Indices (all data)	$R_1 = 0.084$	$R_1 = 0.072$	$R_1 = 0.084$
	$wR_2 = 0.195$	$wR_2 = 0.166$	$wR_2 = 0.170$
Largest diff. peak / hole [e Å^{-3}]	2.006 / −0.567	2.244 / −1.039	0.725 / −0.755

Table 2. Results of the crystal structure determination of **1b**, **1c**, **2** and experimental details.

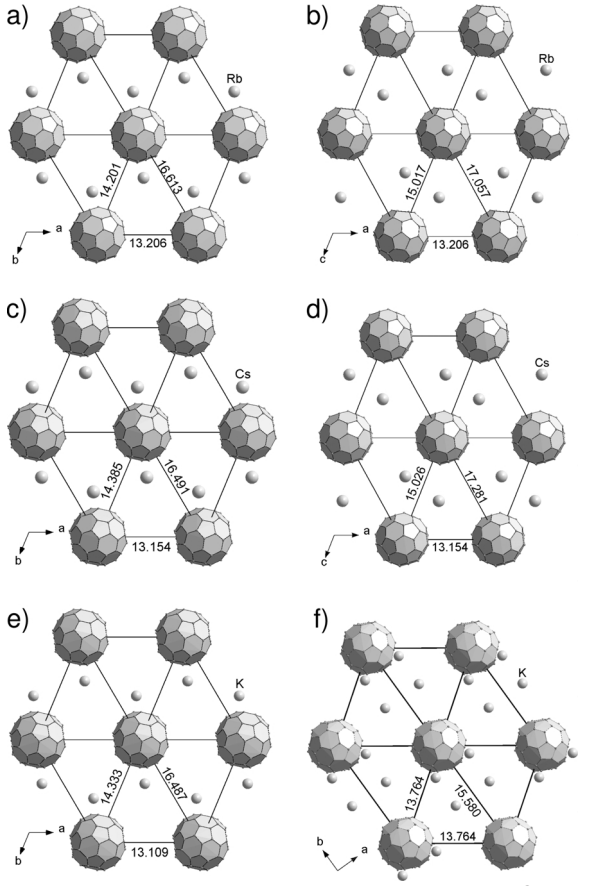

Fig. 2. Distorted pseudohexagonal layers of the $[C_{60}]^{2-}$ dianions. a) **1b** and c) **1c** in the *ab* plane, b) **1b** and d) **1c** in the *ac* plane. e) Distorted pseudohexagonal layers of the $[C_{60}]^{2-}$ dianions in **1a** and f) in **3** [13] in the *ab* planes. All distances refer to the centers of gravity of the $[C_{60}]^{2-}$ and are in Å. Alkali metal cations of $[A([2.2.2]crypt)]^+$ units are represented as grey atoms.

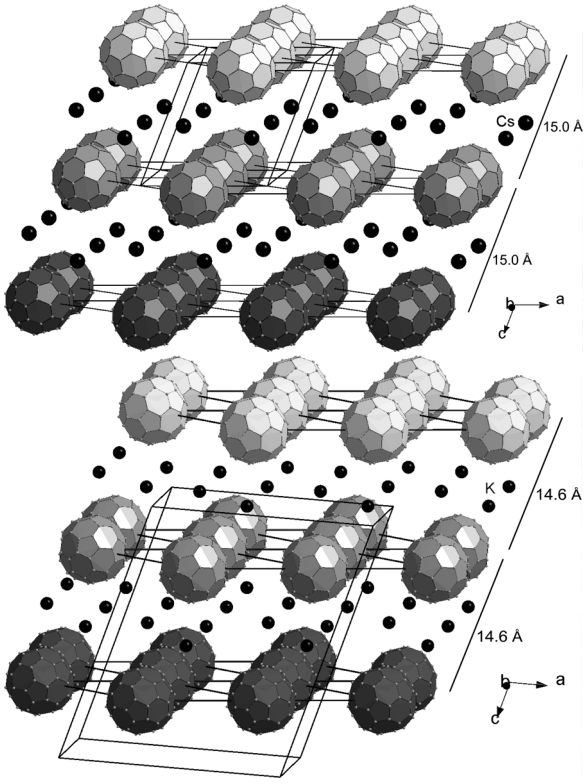

Fig. 3. Pseudohexagonal layers of the $[C_{60}]^{2-}$ dianions and intercalating cesium cations in **1c** (top) and $[C_{60}]^{2-}$ dianions and intercalating potassium cations in **3** [13] (bottom) viewed along the pseudohexagonal layers ([2.2.2]crypt and solvent molecules omitted for clarity).

allel to the S_{12} axis of the fulleride unit (Fig. 1). A small rotational disorder along this axis leaves the positional parameters of the atoms of the upper and lower

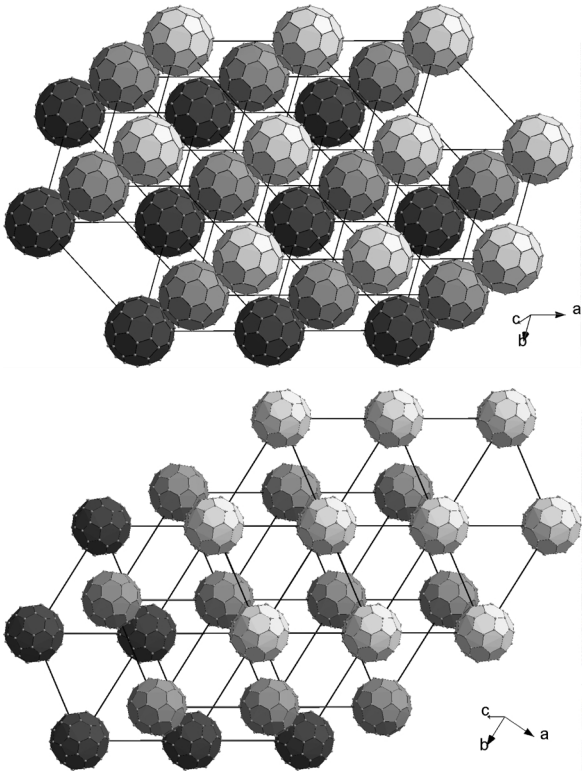

Fig. 4. Stacking order of the distorted hexagonal layers of the $[C_{60}]^{2-}$ dianions in **1c** (top) and in **3** [13] (bottom), viewed perpendicular to the hexagonal layers (A atoms, [2.2.2]crypt and solvent molecules are omitted for clarity). Fullerenes shown in black, dark grey, and light grey color indicate three layers of each structure.

six-membered rings almost unchanged (*e.g.* in Fig. 1 visible atoms 56 to 58 and 35 to 37), whereas it has a stronger influence on the 'equator-atoms' (atoms 45, 46, 44, 43, 59, 60, 53, 54, 61, 46). In **1c** the tetrahydrofuran molecule was refined with split positions, whereas for **1b** the disorder of the tetrahydrofuran and dimethylformamide solvent molecules could not be resolved and has been taken care of by the PLATON SQUEEZE procedure [15, 16]. The structure of **1a** could not be refined properly due to a larger amount of disorder of both the fullerene and solvent molecules, but the location of the $[K([2.2.2]crypt)]^+$ units and the centers of gravity of the C_{60} molecules could be determined unequivocally.

In the crystal structures of **1a**, **1b** and **1c** the fulleride dianions are arranged in distorted hexagonal layers (Figs. 2a – 2e). The layers are chosen in a way that the shortest distances between the fullerene centers are represented. In the *ab* plane the distances between the centers of gravity of the fulleride anions range from 13.11 to 16.61 Å and in the *ac* plane they lie between 13.15 and 17.28 Å. In all three structures the shortest distance between two $[C_{60}]^{2-}$ units is 13.2 Å, and this value corresponds to the shortest cell axes in **1a**, **1b** and **1c**. For comparison, the shortest distance in the crystal structure of $[K([2.2.2]crypt)]_2[C_{60}](C_6H_5CH_3)_4$ **3** [13] is 13.8 Å (Fig. 2f). Since the resulting interatomic contacts between neighbouring fulleride units are longer than 6 Å, reciprocal magnetic interactions between possibly paramagnetic spin states cannot be expected.

The principle of 'close packing of spheres' seems to be the main structural motif in the structures of compounds containing $[C_{60}]^{2-}$ anions. The distorted hexagonal layers in the *ab* plane are separated by bulky $[A([2.2.2]crypt)]^+$ ions (Fig. 3), and the distances between the fulleride centers of neighbouring layers are 15.0 Å for **1a**, **1b** and **1c**, and thus somewhat longer than the distance between the corresponding layers in compound **3** (14.6 Å). They are close to the distances within the layer because – as mentioned above – the hexagonal layers of the *ac* plane are also separated by the $[A([2.2.2]crypt)]^+$ ions.

Differences in the packing with respect to the stacking sequence in compounds **1b**, **1c** and **3** become obvious from the view perpendicular to the layers. In **1b** and **1c** the hexagonal layers are observed in all three directions, leading to a distorted cubic packing (Fig. 4). In **3** two layers pile up in a hexagonal-type variant, whereas the third layer is neither in a position leading to a three-dimensional hexagonal nor to a cubic packing. However, in both packing variants the cations occupy tetrahedral vacancies formed by the $[C_{60}]^{2-}$ units. The four shortest distances between the alkali cations and the centers of gravity of the fulleride cages range from 8.72 to 10.16 Å in **1c** and from 8.49 to 10.58 Å in **3**, while the remaining longer distances range from 14.21 to 14.77 Å in **1c** and from 12.54 to 14.74 Å in **3**.

In **1c** a rare example of a sequestered Cs^+ cation is realized. Interestingly, only two other crystal structures with a $[Cs([2.2.2]crypt)]^+$ ion have been reported so far, namely a thiocyanate hydrate $[Cs([2.2.2]crypt)]SCN{\cdot}H_2O$ **4** [17] and a ceside $[Cs([2.2.2]crypt)]Cs$ **5** [18]. The capability of incorporating K as well as Cs cations proves the high flexibility of the cryptand towards the size of the alkali metal cations (K^+ 1.51 Å, Rb^+ 1.61 Å, Cs^+ 1.74 Å, CN 8). In these cations $[A([2.2.2]crypt)]^+$ the N-N distances

Table 3. Average N-N distance, A-N and A-O bond lengths in the $[A([2.2.2]crypt)]^+$ ions in Å.

	1a (K)	**2** (K)	**3**[13] (K)	**1b** (Rb)	**1c** (Cs)	**4**[17] (Cs)	**5**[18] (Cs)
N-N	6.02	6.05	6.02	6.04	6.10	6.07	6.14
A-N	3.01	3.02	3.01	3.02	3.05	3.03	3.07
A-O	2.84	2.82	2.83	2.89	2.97	2.97	2.96

and average A-N bond lengths vary only slightly, and the increasing size of the metal cation is more reflected by differences in the average A-O bond lengths (Table 3).

Crystal structure of $[K([2.2.2]crypt)]_2[C_{60}]\cdot(C_3H_7NO)_4$

The results of the single crystal structure analysis of **2** are shown in Figs. 5a – 5c. The unit cell contains two formula units of **2**, and the 60 crystallographically independent carbon atoms of the $[C_{60}]^{2-}$ unit are found directly from Fourier calculations. Refinement procedures were carried out as described for **1b** and **1c**. The difference fourier density map showed electron density around some centers of the 5- and 6-membered rings, indicating a partial disorder of the fulleride units. Using a split model for the $[C_{60}]^{2-}$ dianion led to an occupancy of 0.75 *versus* 0.25.

In the crystal structure of **2** the fulleride dianions form slightly corrugated layers of distorted hexagons (Fig. 5a), with a remarkably short distance of 10.3 Å between two fulleride centers. This distance is short as compared to the structures discussed above and also with respect to the corresponding contacts in the metallic binary phases A_3C_{60}. It is close to the one observed in the intercalated superconducting fcc-Rb_2CsC_{60} phases, where the centers of gravity of the fulleride cages are separated by 10.25 Å. The surface-to-surface contacts of the fullerides in **2** occur *via* the 6-membered rings, with a C-C distance of about 3.9 Å (Fig. 5b). Therefore, magnetic interactions between possibly paramagnetic spin states are expected. However, since compound **2** is only a minor by-product of the reaction and thus is obtained only in low yields and since the crystals of 2 decompose within minutes after removal of the solvent, no magnetic or EPR data could be obtained until now.

The layers of distorted hexagons are stacked primitively and form channels occupied by the $[K([2.2.2]crypt)]^+$ ions (Fig. 5c). The distance of the fulleride centers between the layers is 13.3 Å corresponding to the shortest unit cell axis.

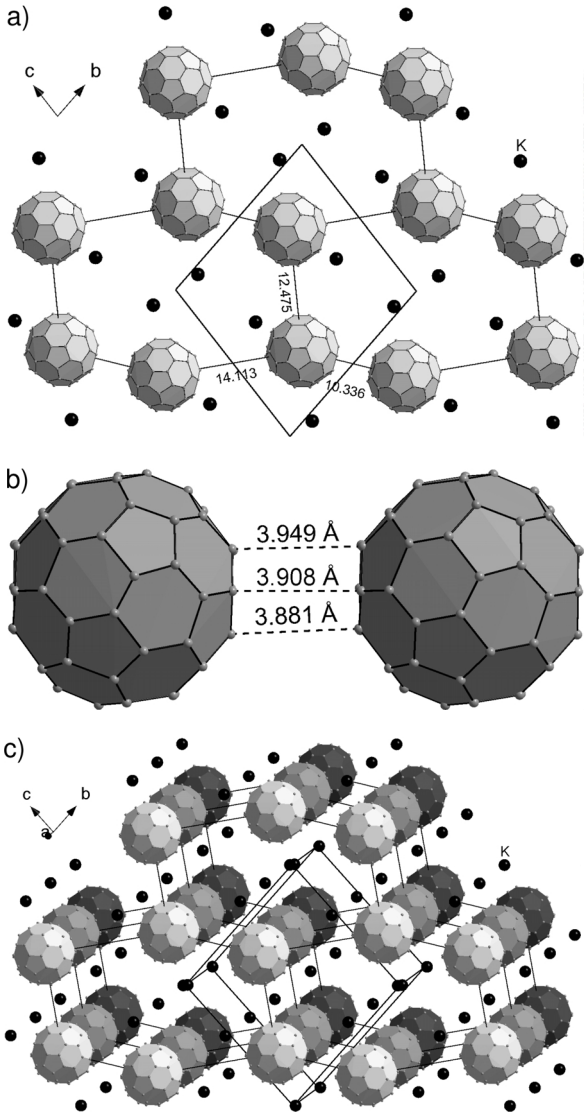

Fig. 5. a) Layer of distorted hexagons of the $[C_{60}]^{2-}$ dianions in **2** (distances between the centers of the $[C_{60}]^{2-}$ in Å); b) shortest carbon-carbon contacts between two $[C_{60}]^{2-}$ dianions in **2**; c) layers of distorted hexagons of the $[C_{60}]^{2-}$ dianions in **2** and intercalating potassium cations viewed along the channels ([2.2.2]crypt and solvent molecules omitted for clarity). Fulleride cages shown in black, dark grey, and light grey color indicate three layers of the structure.

Conclusion

The usage of polar solvents allows the synthesis of well-defined salts containing $[C_{60}]^{2-}$ dianions and $[A([2.2.2]crypt)]^+$ cations. In most of the compounds the $[C_{60}]^{2-}$ dianions form distorted hexagonal layers,

separated by the bulky cations, and the resulting three-dimensional packing can be described as a hexagonal close packing of spheres, with cations occupying all tetrahedral voids. A minor fraction of a compound $[K([2.2.2]crypt)]_2[C_{60}](C_3H_7NO)_4$ **2** was obtained. The packing of the ionic units shows slightly corrugated layers of distorted hexagons of $[C_{60}]^{2-}$ dianions and unusually short contacts between pairs of fulleride anions. The layers form a packing which can be derived from a primitive hexagonal arrangement of spheres.

Experimental Section

Syntheses

$[A([2.2.2]crypt)]_2[C_{60}](C_6H_{12})_2(C_3H_7NO)_2(C_4H_8O)_2$ **1a** (A = K), **1b** (A = Rb) and **1c** (A = Cs) and $[K([2.2.2]crypt)]_2[C_{60}](C_3H_7NO)_4$ **2**.

To perform the reduction, C_{60} (50 mg, 70 μmol), potassium (5 mg, 140 μmol, Merck, 99.9%) **1a** and **2**, rubidium (12 mg, 140 μmol, Aldrich, 99.6%) **1b** or cesium (18 mg, 140 μmol, Riedel-de Haën, 99.5 %) **1c** and [2.2.2]crypt (53 mg, 140 μmol, Merck) were weighed into a 20 ml Schlenck tube in a glove box with an argon atmosphere and oxygen/moisture levels below 0.1 ppm. Tetrahydrofuran (3 ml, Merck, water content below 75 ppm, stored in the above mentioned glove box) was added and the mixture stirred at room temperature for approximately 18 h. During this time the reaction mixture changed from a solution to a dispersion. Dimethylformamide (1 ml, freshly distilled over calcium hydride) was added to obtain a solution before filtration. The solution was sonicated for 15 min and layered with cyclohexane (5 ml, Merck, water content below 50 ppm, stored in the above mentioned glove box). The products crystallized nearly quantitative over the course of 1 week as dark red, rhombic plates of **1a**, **1b**, **1c** and **2**, respectively.

X-Ray analyses

The results of the crystal structure determination of **1a**, **1b**, **1c**, **2** and experimental details are summarized in Tables 1 and 2. The crystals were selected under perfluorinated polyether in a glove box with an argon atmosphere and oxygen/moisture levels below 0.1 ppm and mounted on a glass capillary. Data collection: Enraf-Nonius KappaCCD diffractometer with a rotating anode generator FR 591, Mo-K_α radiation. Structure solution with SHELXS, refinement with SHELXL [19, 20]. CCDC 249896 - 249898 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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