The formation of diamagnetic singly bonded $(C_{70}^-)_2$ dimers in ionic complexes of fullerene C_{70} with tetrakis(dimethylaminoethylene)†

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Two complexes containing C_{70} anions and tetrakis(dimethylamino)ethylene radical cations $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)\cdot(C_6H_{14})_{0.5}$ (**1**) and $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)$ (**2**) were obtained as single crystals. Both complexes contain singly bonded $(C_{70}^-)_2$ dimers and have close composition. However, their crystal structures are different. Complex **1** has a layered structure in which layers from the $(C_{70}^-)_2$ dimers alternate with the $TDAE^{\bullet+}$-$C_6H_4Cl_2$ layers. Ionic fullerene layers contain large hexagonal vacancies which are occupied by completely ordered hexane molecules. Complex **2** has a three-dimensional packing of the $(C_{70}^-)_2$ dimers with large vacancies passing along the *c* axis and containing $TDAE^{\bullet+}$ and $C_6H_4Cl_2$ moieties. IR spectra of the $(C_{70}^-)_2$ dimers in both complexes show similar features with more than 40 absorption bands additionally to the absorption bands of parent C_{70}. According to the IR spectra the $(C_{70}^-)_2$ dimers are stable in **1** and **2** up to room temperature. Both complexes show narrow EPR signals characteristic of $TDAE^{\bullet+}$ ($g = 2.0032$, the linewidth of 0.3–0.4 mT at 77 K).

The complex of fullerene C_{60} with strong organic donor tetrakis(dimethylamino)ethylene attracts much attention due to the discovery of ferromagnetism with highest transition temperature for pure organic magnets (T_c = 16.1 K).[1] It was shown that $TDAE\cdot C_{60}$ is an ionic complex and contains closely packed one-dimensional chains of the $C_{60}^{\bullet-}$ radical anions which are separated by $TDAE^{\bullet+}$.[2,3] Some discrepancies in the estimation of magnetic properties of $TDAE\cdot C_{60}$ were understood when it was revealed that only annealed samples manifest ferromagnetism but non-annealed phase show only antiferromagnetic behaviour.[4] The structures of both phases were solved[3,5] to show that ferro- or antiferromagnetic behaviour of the compound is defined by mutual orientation of $C_{60}^{\bullet-}$ in the chains.

The study of ionic complexes of TDAE with C_{70} and higher fullerenes (C_{84}, C_{90} and C_{96}) shows that they are paramagnets with Weiss temperatures close to zero.[6–8] Magnetic susceptibility measurements for TDAE-C_{70} show the presence of about one spin per formula unit. TDAE-C_{70} manifests an EPR signal with $g = 2.0023$ and $\Delta H = 0.8$ mT, which is strongly different form that of $TDAE\cdot C_{60}$ ($g = 2.0003$ and $\Delta H = 2$ mT).[6] The TDAE-C_{70} complexes were obtained as powders and their crystal structures were not determined. Therefore, the reasons for the absence of ferromagnetism in TDAE-C_{70} complexes were not understood.

Now different ionic complexes of C_{70} were obtained as single crystals including one C_{70} complex with TDAE which contains also toluene molecule. The study of the crystal structures of these complexes[9–15] showed that the $C_{70}^{\bullet-}$ radical anions have strong tendency to dimerize forming diamagnetic singly bonded $(C_{70}^-)_2$ dimers (Fig. 1). Only in one ionic $(Ph_4P^+)_2\cdot(C_{70}^{\bullet-})\cdot(I^-)$ compound, the monomeric $C_{70}^{\bullet-}$ radical anions remain unchanged down to low temperatures due to the separation of $C_{70}^{\bullet-}$ by bulky Ph_4P^+ cations.[16] Moreover, recently it has been shown that the $C_{70}^{\bullet+}$ radical cations are also dimerized in the complex with $Ti_3Cl_{13}^-$ to form the singly bonded $(C_{70}^+)_2$ dimers.[17] Thus, dimerization is an important factor which should taken in account when studying ionic C_{70} complexes.

We synthesize new ionic complexes of C_{70} with TDAE as single crystals: $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)\cdot(C_6H_{14})_{0.5}$ (**1**) and $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)$ (**2**). The structures of the complexes are solved. The $C_{70}^{\bullet-}$ radical anions are dimerized in both complexes to form singly bonded $(C_{70}^-)_2$ dimers. Namely the formation of these dimers most probably defines the paramagnetic behaviour of the TDAE-C_{70} complexes. In this paper we discuss also the EPR and IR spectra of the complexes.

Results and discussion

Synthesis

Complex **1** was obtained by diffusion technique developed for the preparation of ionic fullerene complexes with strong organometallic donors.[18–21] Ionic C_{60} complexes with

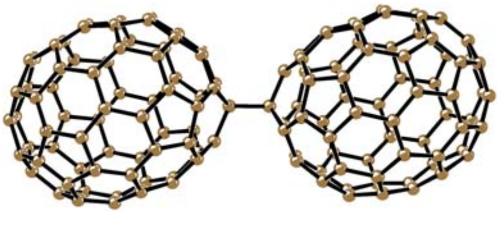

Fig. 1 Molecular structure of the singly bonded $(C_{70}^-)_2$ dimer.[10]

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bis(benzene)chromium,[20] decamethylchromocene[18,21] and decamethylcobaltocene[19,21] were obtained by this technique. Fullerene C_{60} did not form crystals of the complex with TDAE in *o*-dichlorobenzene ($C_6H_4Cl_2$), whereas the crystals of $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)\cdot(C_6H_{14})_{0.5}$ (**1**) were obtained in a small yield. Complex **1** contains two solvent molecules in the structure. Generally all phases obtained by this technique contain solvents.[18–20] However, the insertion of hexane into ionic fullerene structure was observed for the first time.

Previously we observed that in some cases neutral organometallic compounds can strongly affect the complex formation with fullerenes. For example, $Cu^{II}TPP$ and $Co^{II}TMPP$ (TPP: tetraphenylporphyrin: TMPP: tetrakis(4-methoxyphenyl)-porphyrin) form solvent containing phases with C_{60}: $Cu^{II}TPP\cdot C_{60}\cdot C_6H_5Me$[22] and $Co^{II}TMPP\cdot(C_{60})_2\cdot(C_6H_5Me)_3$.[23] Addition of ferrocene into the synthesis allows the preparation of pure solvent free phases $(Cu^{II}TPP)_2\cdot C_{60}$[22] and $Co^{II}TMPP\cdot C_{60}$.[23] In this case we used $Ni(acac)_2\cdot 2H_2O$ to assist the crystallization of ionic fullerene complex with TDAE. Fullerene C_{60} does not formed complex with TDAE in $C_6H_4Cl_2$ even in the presence of $Ni(acac)_2\cdot 2H_2O$. However, when fullerene C_{70} is used $Ni(acac)_2\cdot 2H_2O$ assists the formation of good quality single crystals of ionic complex with nearly quantitative yield. The analysis of these crystals shows that $Ni(acac)_2$ was not introduced into the structure. Instead of that $(TDAE^{\bullet+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)$ (**2**) complex of different composition and structure from those of **1** is obtained.

Crystal structure

Complex **1** forms a monoclinic unit cell in which all of the components are well ordered. The $C_{70}^{\bullet-}$ radical anions are dimerized forming the singly bonded $(C_{70}^-)_2$ dimers. The length of the intercage C–C bond is 1.586(3) Å, the intermolecular distance between the center of mass of two C_{70}^- anions in a dimer is 10.509 Å. Correspondingly, the dimer has configuration close to the C_{2h} symmetry. The observed geometric parameters are close to those for the $(C_{70}^-)_2$ dimers studied earlier. The length of intercage C–C bond was 1.584(9) Å and the distance between the centers of mass of two fullerenes was 10.417 Å.[10] Geometry of TDAE in **1** is rather close to that calculated[24] and experimentally[3] determined for the $TDAE^{\bullet+}$ radical cations. Two symmetrically equivalent part of TDAE are twisted about the C = C double bond, the dihedral angle between the planes formed by the symmetrically equivalent N–C–N groups is equal to 44.42°, the central C = C bond length is 1.420(2) Å and the averaged length of the $C–N(N(CH_3)_2)$ bonds is 1.362(2) Å.

The complex has a layered structure. Layers of the $(C_{70}^-)_2$ dimers arranged parallel to the *bc* plane are separated by the $TDAE^{\bullet+}$-$C_6H_4Cl_2$ layers (Fig. 2a) to prevent the formation of Van der Waals (VdW) C···C contacts between fullerenes from the neighbouring layers. The structure of the fullerene layer is shown in Fig. 2b. Each $(C_{70}^-)_2$ dimer forms shortened VdW C···C contacts with four neighbouring dimers (shown by green dashed lines in Fig. 2b). The length of these contacts varies from 3.310 to 3.376 Å. The distance between the centers of mass of the neighbouring C_{70}^- anions is equal to 10.958 Å for all four neighbouring dimers. Fullerene layers contain large vacancies which accommodate hexane molecules. They are frozen in one completely ordered conformation in spite of the absence of shortened VdW C···C and C···H contacts between hexane and C_{70}^- (Fig. 2b). The presence of completely ordered neutral hexane molecules in ionic structure is quite unusual. Both $TDAE^{\bullet+}$and $C_6H_4Cl_2$ moieties also partially enter the vacancies in the fullerene layers (Fig. 2c). Each $(C_{70}^-)_2$ dimer is surrounded by eight $TDAE^{\bullet+}$ radical cations (Fig. 3a) with shortened VdW C···C and H···C contacts in the 3.337–3.397 and 2.660–2.892 Å range.

Four of eight surrounding $TDAE^{\bullet+}$ radical cations are located close to the intercage C–C bond of $(C_{70}^-)_2$. Such arrangement of $TDAE^{\bullet+}$ can maximize electrostatic interaction between $(C_{70}^-)_2$

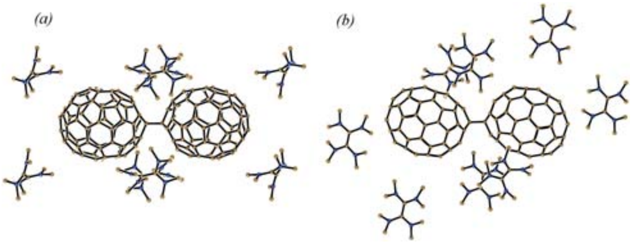

Fig. 3 Surrounding of the $(C_{70}^-)_2$ dimer from the $TDAE^{\bullet+}$ radical cations in **1** (a) and **2** (b).

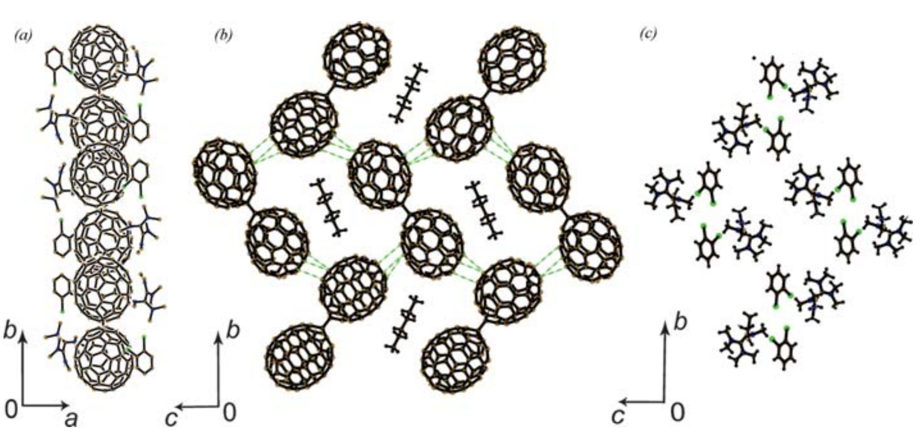

Fig. 2 Views on the crystal structure of **1**: (a) view along the *c* axis and fullerene layers; (b) view along the *a* axis on the layer containing $(C_{70}^-)_2$ dimers and hexane; (c) view along the *a* axis on the $TDAE^{\bullet+}$-$C_6H_4Cl_2$ layer. Shortened VdW C···C contacts are shown by green dashed lines.

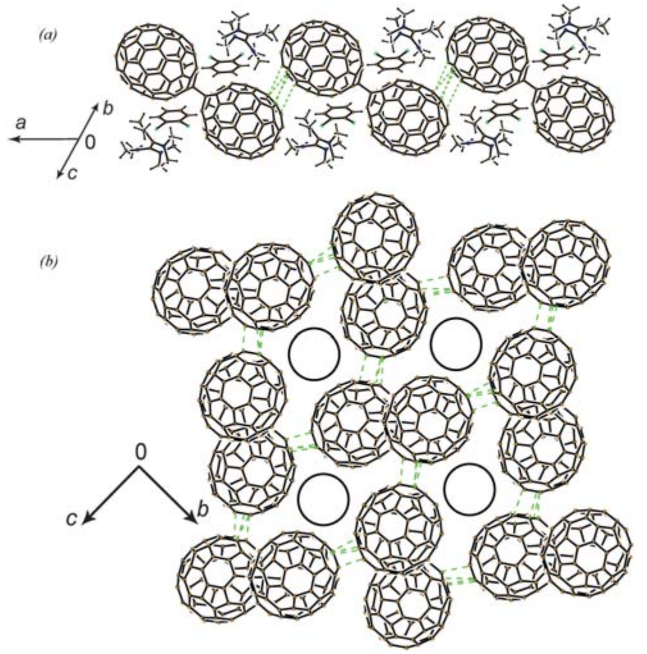

Fig. 4 Views on the crystal structure of **2**. (a) Zigzag chains of the $(C_{70}^-)_2$ dimers arranged along the *a* axis and accommodating $TDAE^{\bullet+}$ and $C_6H_4Cl_2$ moieties; (b) view along the fullerene zigzag chains and the *a* axis. Shortened Van der Waals C···C contacts are shown by green dashed lines.

and $TDAE^{\bullet+}$. Actually it was shown[25] that in similar $(C_{60}^-)_2$ dimer negative charge is localized near intercage C–C bond of $(C_{60}^-)_2$.

Complex **2** has monoclinic unit cell and contains ordered singly bonded $(C_{70}^-)_2$ dimers, $TDAE^{\bullet+}$ and solvent $C_6H_4Cl_2$ molecules disordered between three orientation (Fig. 4 shows only one orientation of $C_6H_4Cl_2$ occupied by 73.2%). The length of the intercage C–C bond for the $(C_{70}^-)_2$ dimer of 1.583(2) Å and the intermolecular distance between the center of mass of two C_{70}^- anions of 10.472 Å are close to those distances for the $(C_{70}^-)_2$ dimer in **1**. The bond length and angles for the TDAE molecule indicate the formation of the $TDAE^{\bullet+}$ radical cation. Two symmetrically equivalent part of TDAE are twisted about the C═C double bond with the dihedral angle of 33.95°. The central C═C bond length is 1.412(2) Å and the averaged length of the $C–N(N(CH_3)_2)$ bonds is 1.362(2) Å.

Zigzag chains consisting of the $(C_{70}^-)_2$ dimers can be outlined in **2** along the *a* axis (Fig. 4a). Each dimer has two neighbours in the chain and form multiple VdW C···C contacts in the 3.312–3.396 Å range. Zigzag fullerene chains are located close to each other and form also VdW C···C contacts in the *bc* plane in the 3.061–3.384 Å range (Fig. 4b). Therefore, this complex has three-dimentinal (3D) packing of the $(C_{70}^-)_2$ dimers. In this packing, vacancies occupied by the $TDAE^{\bullet+}$ and $C_6H_4Cl_2$ moieties are formed along the *a* axis (are shown by circles in Fig. 4b). Each $(C_{70}^-)_2$ dimer forms VdW contacts with eight $TDAE^{\bullet+}$ (Fig. 3b). Four of them locate close to the intercage C–C bonds of the dimer. The $TDAE^{\bullet+}$-$(C_{70}^-)_2$ distances in **2** are longer than those in **1**. As a result, no short VdW C···C or N···C contacts are formed between $TDAE^{\bullet+}$ and $(C_{70}^-)_2$, whereas there are several H···C contacts between $TDAE^{\bullet+}$ and $(C_{70}^-)_2$ in the 2.710–2.870 Å range.

IR spectra

The IR spectra of **1** and **2** are similar (ESI).† They contain more than 60 absorption bands. Most of them can be attributed to the $(C_{70}^-)_2$ dimer. The appearance of additional absorption bands is due to the breaking of symmetry of the C_{70} molecule at dimerization. Parent C_{70} has only 10 IR-active bands.[26] The spectrum of the $(C_{70}^-)_2$ dimer is well reproducible. A similar set of the absorption bands can be found in the spectra of other ionic complexes containing the $(C_{70}^-)_2$ dimers.[10,11] It is seen from the IR spectra of **1** and **2** that even at room temperature dimers are still present in both complexes. That is in agreement with high thermal stability of the $(C_{70}^-)_2$ dimers, which begin to dissociate only above 360 K.[10] The positions of the absorption bands of TDAE in the spectra of **1** and **2** indicate the formation of $TDAE^{\bullet+}$ radical cations as in $TDAE\cdot C_{60}$.[24]

EPR spectra

A narrow line with $g = 2.0031$ and $\Delta H = 0.39$ mT is observed in the spectrum of **1** at room temperature ($RT = 295$ K). Temperature decrease down to 77 K results in a slight narrowing of the signal to 0.32 mT at the same *g*-factor value (Fig. 5a). The spectrum of **2** shows a single Lorentzian line with $g = 2.0032$ and the linewidth of $(\Delta H) = 0.46$ mT at RT. Temperature decrease only slightly changes this signal ($g = 2.0031$ and $\Delta H = 0.34$ mT at 77 K, Fig. 5b). Previously it was shown[27] that the $TDAE^{\bullet+}$ radical cations have EPR signal in solution with $g = 2.0035$, therefore the observed signals in **1** and **2** can be attributed to $TDAE^{\bullet+}$. The

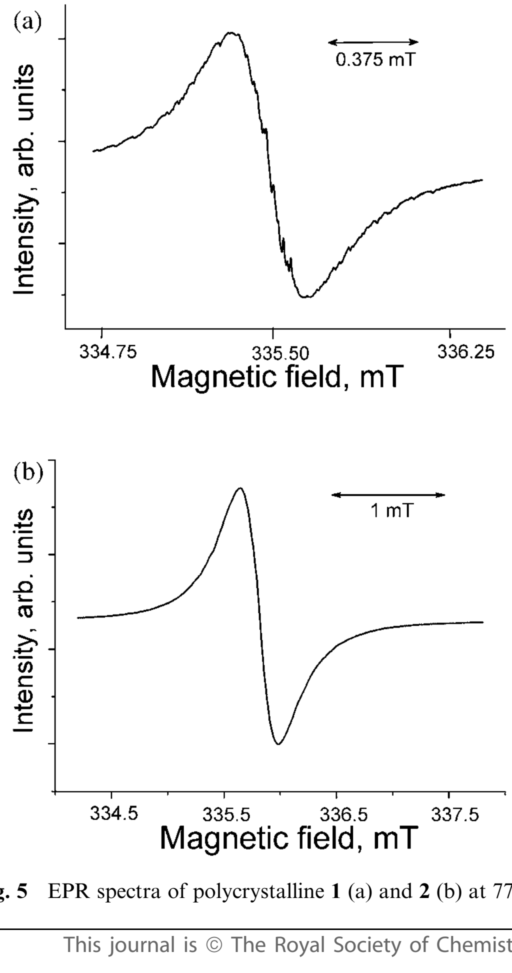

Fig. 5 EPR spectra of polycrystalline **1** (a) and **2** (b) at 77 K.

spectrum of **1** at 77 K (Fig. 5a) manifests complicated hyperfine structure with the splitting of 0.01–0.02 mT. Such splitting is also characteristic of $TDAE^{•+}$ in solution and is realized due to interaction of spin with four nitrogen atoms of TDAE.[27] The observation of this splitting in solid state is possible due to the $TDAE^{•+}$ radical cations are separated by the diamagnetic $(C_{70}^-)_2$ dimers. The estimation of the number of spins from the integral intensity of the signals indicates the presence of about one $S = 1/2$ spin per a formula unit. Thus in both complexes only EPR signals from $TDAE^{•+}$ are observed whereas the diamagnetic $(C_{70}^-)_2$ dimers do not show the EPR signals.

The observed signals in **1** and **2** are similar to that in $(TDAE^{•+})\cdot(Co^{II}TPP\cdot C_{60}^-)$. In this compound diamagnetic σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions are formed and only paramagnetic $TDAE^{•+}$ is EPR active below 195 K. Correspondingly this compound manifests a narrow signal with $g = 2.003–2.005$.[28] In contrast to **1** and **2**, ferromagnetic $TDAE\cdot C_{60}$ has an essentially broader signal with smaller *g*-factor ($g = 2.0003$ and $\Delta H = 2$ mT at RT).[6] This signal can appear due to strong exchange interaction between $C_{60}^{•-}$ and $TDAE^{•+}$. As a result, *g*-factor and ΔH have intermediate value between those characteristic of individual paramagnetic species. Similarly the presence of both paramagnetic $C_{60}^{•-}$ and $TDAE^{•+}$ in $(TBPDA)_2\cdot(C_{60}^{•-})\cdot(TDAE^{•+})$ produces only one signal with $g = 2.0009$ and $\Delta H = 2.9$ mT at RT.[21]

Comparison of TDAE-C_{70} and TDAE·C_{60} complexes

The donor–acceptor complexes of C_{70} with TDAE have an ionic ground state similarly to $TDAE\cdot C_{60}$. Short VdW C···C contacts are present between fullerenes in both complexes. However, since the $C_{70}^{•-}$ radical anions have stronger tendency to dimerize, they easily form diamagnetic singly bonded $(C_{70}^-)_2$ dimers. That is the main difference between paramagnetic TDAE-C_{70} complexes in which only spins from the isolated $TDAE^{•+}$ radical cations are observed, and ferromagnetic $TDAE\cdot C_{60}$ complex in which both paramagnetic $C_{60}^{•-}$ and $TDAE^{•+}$ species are manifested.

$TDAE\cdot C_{60}$ is a rare example of ionic fullerene complex in which dimerization is not realized in spite of the presence of short contacts between fullerenes. It was shown[29,30] that fullerene anions are polymerized in $TDAE\cdot C_{60}$ only under 7 kbar pressure. Stability of the dimers from the negatively charged fullerenes is to a great extent defined by electron repulsion. The distances between the charges in dimers increase with fullerene cage size. Therefore, the anions of higher fullerenes should have essentially higher stability of negatively charged dimers than smaller fullerenes. For example, the $(C_{70}^-)_2$ dimers are more stable (beginning of dissociation above 360 K[10]) than the $(C_{60}^-)_2$ dimers (beginning of dissociation in the 120–250 K range[11,18,31–33]). The dimeric state for the C_{84}, C_{90} and C_{96} anions can be even more stable than that for C_{70}. We suppose that paramagnetism of the complexes of TDAE with higher fullerenes ($C_{84–96}$)[7] is also due to the formation of the diamagnetic single bonded $(\text{fullerene}^-)_2$ dimers.

Conclusion

Two complexes of C_{70} with tetrakis(dimethylamino)ethylene were obtained: $(TDAE^{•+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)\cdot(C_6H_{14})_{0.5}$ (**1**) and $(TDAE^{•+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)$ (**2**). In spite of close composition, **1** has a layered and **2** has a three-dimensional packing of the $(C_{70}^-)_2$ dimers. Both complexes contain singly bonded $(C_{70}^-)_2$ dimers which are diamagnetic and EPR silent. The formation of these dimers can be the main reason for the paramagnetic behaviour of TDAE-C_{70} complexes studied previously and in this work.

Experimental

Materials

Tetrakis(dimethylamino)ethylene (TDAE) was purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. $Ni(acac)_2\cdot 2H_2O$ was obtained from $Ni(ClO_4)_2\cdot 6H_2O$, acetylacetone and KOH in water. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure and hexane was distilled over Na/benzophenone. The solvents were degassed and stored in a glove box. All manipulations for the synthesis of air sensitive **1** and **2** were carried out in a MBraun 150B-G glove box with controlled atmosphere and the content of H_2O and O_2 less than 1 ppm. The crystals were stored in a glove box. EPR measurements were carried out for the samples in argon atmosphere at 77 K and room temperature. KBr pellets for IR measurements were prepared in a glove box.

Synthesis

The crystals of $(TDAE^{•+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)\cdot(C_6H_{14})_{0.5}$ (**1**) were obtained by diffusion. Fullerene C_{70} (25 mg, 0.03 mmol) and an excess of TDAE (0.5 mL) were dissolved in $C_6H_4Cl_2$ solution (14 mL) by stirring at 60 °C during 4 h. Cooled solution was filtered into the diffusion tube and 25 mL of hexane was layered over. After 1 month the crystals formed on the walls of the tube. Solvent was decanted and crystals were washed with hexane to give black prisms (up to 1 × 0.3 × 0.3 mm in size) with 30% yield.

The crystals of $(TDAE^{•+})\cdot(C_{70}^-)\cdot(C_6H_4Cl_2)$ (**2**) were obtained by diffusion. Fullerene C_{70} (25 mg, 0.03 mmol), an excess of TDAE (0.5 mL) and 60 mg of $Ni(acac)_2\cdot 2H_2O$ were dissolved in $C_6H_4Cl_2$ solution (14 mL) by stirring at 60 °C during 4 h. The cooled solution was filtered into the diffusion tube and 25 mL of hexane was layered over. After 1 month the crystals formed on the walls of the tube. Solvent was decanted and crystals washed with hexane to give black plates (up to 2 × 0.5 × 0.5 mm in size) with 90% yield.

The composition of **1** and **2** was determined from X-ray diffraction data for a single crystal. Several single crystals tested from the same synthesis shows similar unit cell parameters. Complexes **1** and **2** have different shape of crystals. Crystal testing under microscope confirms the presence of only one phase in each synthesis.

General

FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrometer (400–7800 cm^{-1}). EPR spectra of **1** and **2** were recorded at room temperature and 77 K with a Radiopan SE/X-2547 spectrometer at RT and 77 K.

X-Ray crystal structure determination

Crystal data of **1** at 120(2) K: $C_{178}H_{70}Cl_4N_8$, M_r = 2462.22 g mol^{-1}, black prism, monoclinic, $P2_1/c$, $a = 10.3429(5)$, $b = 27.917(1)$, $c = 18.849(1)$ Å, $\beta = 101.261(5)$, $V = 5337.7(4)$ Å^3, $Z = 2$, $d_c = 1.532$ g cm^{-3}, $\mu = 0.186$ mm^{-1}, $F(000) = 2524$, max. $2\theta_{max} = 59.4°$. In total, 50 972 reflections were measured, 13 220 of which were independent. The least-squares refinement on F^2 was done to R_1 [$F > 2\sigma(F)$] = 0.0475 for 13220 observed reflections, wR_2 = 0.0660 for all 13 220 observed reflections with 865 parameters and 0 restraints; final GOF = 1.070.

Crystal data of **2** at 100(2) K: $C_{172}H_{56}Cl_4N_8$, M_r = 2376.05 g mol^{-1}, black plate, monoclinic, $P2_1/c$, $a = 16.919(1)$, $b = 17.141(1)$, $c = 18.257(2)$ Å, $\beta = 110.19(1)$, $V = 4969.3(7)$ Å^3, $Z = 2$, $d_c = 1.588$ g cm^{-3}, $\mu = 0.196$ mm^{-1}, $F(000) = 2424$, $2\theta_{max} = 57.4°$. In total, 35 140 reflections were measured, 12 473 of which were independent. The least-squares refinement on F^2 was done to R_1 [$F > 2\sigma(F)$] = 0.0458 for 10 105 observed reflections, wR_2 = 0.0586 for all 12 473 observed reflections with 879 parameters and 440 restraints; final GOF = 1.084.

The intensity data for the structural analysis were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated MoKα radiation using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97.[34] Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the "riding" model with $U_{iso} = 1.2U_{eq}$ of the connected non-hydrogen atom or as ideal CH_3 groups with $U_{iso} = 1.5U_{eq}$.

Disorder in the crystal structures

All components are well ordered in **1**. Only $C_6H_4Cl_2$ molecules are disordered in the crystal structure of **2** between three orientations with the 0.750(2)/0.125(1)/0.125(1) occupancies.

Acknowledgements

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