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Ionic complex of fullerene C_{60}^{2-} dianions with $(MDABCO^+)_2$·Mn^{II}TPP coordination assemblies: synthesis, crystal structure and magnetic properties

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ABSTRACT: The crystals of the ionic complex containing fullerene C_{60}^{2-} dianions and positively charged $(MDABCO^+)_2$·Mn^{II}TPP assemblies: $\{(MDABCO^+)_2 \cdot Mn^{II}TPP\} \cdot (C_{60}^{2-}) \cdot (C_6H_4Cl_2)_4 \cdot (CH_3CN)_2$ (**1**) were obtained for the first time ($MDABCO^+$: the cation of *N*-methyldiazabicyclooctane; TPP: tetraphenylporphyrin). The C_{60}^{2-} dianions are isolated in the complex with the shortest center-to-center distance of 13.228 Å. The Mn^{II} atoms are six-coordinated in the $(MDABCO^+)_2$·Mn^{II}TPP units. The length of the Mn-N(TPP) equatorial bonds of 2.093-2.098(1) Å corresponds to the high-spin state of the Mn^{II} atoms (S = 5/2) which was confirmed by the magnetic measurements ($\mu_{eff} = 5.61$ μ_B at 300 K). The Mn^{II} atoms are located exactly in the porphyrin plane and this results in the radial expansion of the porphyrin core. The long (2.537(1)-2.545(1) Å) Mn-N($MDABCO^+$) axial bonds indicate essential destabilization of the six-coordinated $(MDABCO^+)_2$·Mn^{II}TPP units due to the population of the d(z^2) orbital in high-spin state. The contribution from the C_{60}^{2-} dianions was not found in magnetic measurements on the basis of the contribution from high-spin Mn^{II}TPP and most probably they are diamagnetic in the 2-300 K range. Copyright © 2008 Society of Porphyrins & Phthalocyanines.

KEYWORDS: fullerene C_{60}, manganese(II) tetraphenylporphyrin, donor-acceptor complexes, coordination assemblies, crystal engineering, crystal structure.

INTRODUCTION

Fullerenes form a large variety of compounds with metalloporphyrins ranging from covalently and coordinatively linked dyad and triad molecules [1-3] to molecular and ionic donor-acceptor complexes [4-9]. The ionicity of the complex is an important factor for the manifestation of conductivity and magnetism [10]. However, due to relatively weak acceptor properties, fullerenes generally form molecular complexes with metalloporphyrins [4-7]. Only strong donors such as Cr^{II}TPP and Sn^{II}TpTP (TpTP: tetra(*p*-tolyl)porphyrin) can can ionize fullerenes in solid state in the presence of strongly coordinating ligands [8, 9].

We have been developing a multi-component approach, which allows the preparation of ionic fullerene complexes as single crystals. In this approach, neutral porphyrin molecules are involved in the ionic fullerene complex $(C^+) \cdot (C_{60}^{\bullet -})$ by using relatively weak coordination bonds between cations or $C_{60}^{\bullet -}$ with metalloporphyrins (the N-M or M-C bonds, respectively) to form (C^+)·(Porphyrin)·$(C_{60}^{\bullet -})$ complexes [11-16]. For these purposes, only a limited number of cations which have a free nitrogen atom like $MDABCO^+$ (the cation of *N*-methyldiazabicyclooctane) can be used. At such a coordination, positively charged coordi-

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*Correspondence to: Dmitri V. Konarev, email: konarev@icp.ac.ru, fax: +7 49652-21852 nation assemblies are formed which can even be co-crystallized with negatively charged fullerenes. The M^{II} atoms in these assemblies are six-coordinated as in $(MDABCO^+)_2$•M^{II}TPP (M = Zn, Co, Mn and Fe) [11] or five-coordinated as in $(MDABCO^+)$•Co^{II}TMPP (TMPP: tetra(*p*-methoxyphenyl)porphyrin) [12] and $(MDABCO^+)$•Co^{II}OEP (OEP: octaethylporphyrin) [13]. In these complexes, we observed the reversible formation of the Co-C(C_{60}^-) coordination bonds with the transition of the complex from paramagnetic to diamagnetic state [13], the unusual $(C_{60}^-)_2$ dimers bonded by two C-C bonds [12], and the diamagnetic $(C_{70}^-)_2$ dimers or antiferromagnetically interacting chains from $C_{60}^{\bullet-}$ [11]. Among different metalloporphyrins, only cobalt(II) porphyrinates are able to bind to $C_{60}^{\bullet-}$ forming stable Co-C(C_{60}^-) coordination bonds of 2.25-2.31 Å length. In this case, non-coordinated cations (C^+) such as TMP^+ (tetramethylphosphonium) [13], MPy^+ (*N*-methylpyridinium) [14], $(C_6H_6)_2Cr^{\bullet+}$ (bis(benzene)chromium) [15] and $TDAE^{\bullet+}$ (tetrakis(dimethylamino)ethylene) [16] were used in the synthesis. The resulting {Co^{II}porphyrin•(C_{60}^-)} anions are diamagnetic [13-15].

All multi-component ionic complexes between metalloporphyrins and fullerenes obtained thus far contain only fullerenes in the -1 charged state. In this work, for the first time, we have obtained the complex of metalloporphyrin with -2 charged C_{60}. The synthetic route for the preparation of the crystals of {$(MDABCO^+)_2$•Mn^{II}TPP}•(C_{60}^{2-})•$(C_6H_4Cl_2)_4$•$(CH_3CN)_2$ (**1**) was developed. The crystal structure of **1** was solved. The complex was characterized by the IR- and UV-visible-NIR spectra. Its magnetic properties were studied by the SQUID technique, which allowed us to determine the spin state of $(MDABCO^+)_2$•Mn^{II}TPP and C_{60}^{2-}. The geometry of the $(MDABCO^+)_2$•Mn^{II}TPP units in **1** and in other fullerene complexes was discussed.

EXPERIMENTAL

Materials

Manganese(III) tetraphenylporphyrin chloride (Mn^{III}TPPCl), $NaBH_4$, diazabicyclooctane (DABCO), sodium ethanethiolate (CH_3CH_2SNa), methyl iodide (CH_3I) were purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. Solvents were purified in an argon atmosphere. *o*-dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure, acetonitrile (CH_3CN) was distilled over CaH_2, P_2O_5 and K_2CO_3 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** 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 and sealed in anaerobic conditions in 2 mm quartz tubes for SQUID measurements under 10^{-5} Torr. The KBr pellets for IR and UV-visible-NIR measurements were prepared in a glove box.

Synthesis

N-methyldiazabicyclooctane iodide (MDABCO•I) and Mn^{II}TPP were obtained as described in the literature [13, 11]. The crystals of **1** were obtained by the following procedure: C_{60} (25 mg, 0.035 mmol), a 10-fold molar excess of CH_3CH_2SNa (30 mg, 0.36 mmol) and a 5-fold molar excess of MDABCO•I (44.5 mg, 0.175 mmol) were stirred in CH_3CN (4 mL) for 2 h at 60 °C. During stirring, the color of the solution changed from violet to red. The NIR spectrum was measured to indicate the selective reduction of fullerene to the -2 charged state. *o*-$C_6H_4Cl_2$ (10 mL) was added and Mn^{II}TPP (~24 mg, 0.035 mmol) was dissolved in the obtained solution. The mixture was cooled, filtered in a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and hexane (26 mL) was layered over the solution. The diffusion was carried out for 2 months to give crystals of **1** on the wall of the tube. The solvent was decanted from the crystals, which were washed with hexane to give black prisms with a characteristic blue luster (up to 1 × 1 × 0.5 mm^3 in size) with 50% yield. The composition of the complex was determined by the X-ray diffraction on a single crystal: {$(MDABCO^+)_2$•Mn^{II}TPP}•(C_{60}^{2-})•$(C_6H_4Cl_2)_4$•$(CH_3CN)_2$ (**1**). Several single crystals selected from the synthesis have the same unit cell parameters. Due to high air-sensitivity of **1**, reasonable elemental analysis was not possible (even for one sample, the determined content of carbon differs by 1-2% due to oxidation).

General

UV-visible-NIR spectra were measured in KBr pellets on a Shimadzu-3100 spectrometer in the 240-2600 nm range. FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrophotometer (400-7800 cm^{-1}). A Quantum Design MPMS-XL SQUID magnetometer was used to measure static susceptibilities of polycrystalline **1** between 300 and 1.9 K at 100 mT static magnetic field. A sample holder contribution and core-temperature-independent diamagnetic susceptibility (χ_0) were subtracted from the experimental values. The values of Θ and χ_0 were calculated in a high-temperature range using the appropriate formula: $\chi_M = C/(T-\Theta) + \chi_0$ and the experimental data in the 10-300 K range.

X-ray crystal structure determination

Crystal data of **1**: $C_{292}H_{160}Cl_{16}Mn_2N_{20}$, $M_r = 4625.48$ g.mol^{-1}, black prisms, triclinic, $P\overline{1}$, $a = 13.2880(10)$, $b = 18.8610(10)$, $c = 21.9240(10)$ Å, $\alpha = 89.640(10)$, $\beta = 81.270(10)$, $\gamma = 72.390(10)^o$, $V = 5172.0(5)$ Å^3, $Z = 2$, $d_{calc} = 1.488$ g.cm^{-3}, $\mu = 0.402$ mm^{-1}, $F(000) = 2378$, $T = 100$ (2) K, max. $2\theta_{max} = 54.34^o$, reflections measured 73645, unique reflections 20868, $R_{int} = 0.0285$, reflections with $I > 2\sigma(I) = 15490$, parameters refined 2081, restrains 4632, $R_1 = 0.0553$, $wR_2 = 0.1703$, G.O.F. = 1.056.

The intensity data for the structural analysis were collected on a MAC Science DIP-2020K oscillator type X-ray imaging plate diffractometer with graphite monochromated MoK_α radiation at low temperatures using an Oxford Cryostream cooling system. Raw data reduction to F^2 was carried out using the DENZO program [35]. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97 [36]. Non-hydrogen atoms were refined in the anisotropic approximation. The 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 $U_{iso} = 1.5U_{eq}$.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center under number 682288. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336033; email: deposit@ccdc.cam.ac.uk or *www.ccdc.cam.ac.uk*).

Molecule disorder in 1

The crystallographically independent part contains two halves of the $(MDABCO^+)_2$•Mn^{II}TPP, two halves of C_{60}^{2-}, four $C_6H_4Cl_2$ molecules and two CH_3CN molecules. One of two phenyl substituents of both crystallographically independent $(MDABCO^+)_2$•Mn^{II}TPP units are disordered between two orientations with the 0.73/0.27 occupancies due to a slightly different position and rotation angle. One C_{60}^{2-} dianion is disordered between two orientations with the 0.84/0.16 occupancies. These orientations are linked by the rotation of C_{60}^{2-} around the six-fold axis passing through the two oppositely located hexagons by 60°. The second C_{60}^{2-} dianion is disordered between three orientations with the 0.49/0.0.34/0.17 occupancies. All four $C_6H_4Cl_2$ molecules are disordered. Two molecules are disordered between two orientations (the 0.82/0.18 and 0.60/0.40 occupancies), one molecule is disordered between four orientations (the 0.60/0.17/0.13/0.10 occupancies), and one molecule is disordered between six orientations (the 0.59/0.29/0.05/0.05/0.04/0.04 occupancies).

RESULTS AND DISCUSSION

Selective reduction of C_{60} by propanethiol in the presence of potassium carbonate was carried out in polar DMSO and a DMSO/benzene mixture up to the -2 and -1 charged states [17]. Later, commercially available CH_3CH_2SNa was used for selective preparation of C_{60}^{2-} in acetonitrile [18]. We modified this reaction to prepare ionic C_{60}^{2-} complexes with different organic cations. An excess of CH_3CH_2SNa and the salt of organic cation (we used MDABCO•I) and C_{60} were stirred in acetonitrile (CH_3CN). The reduction occurred up to the -2 charged state (according to the NIR spectra) and was accompanied by the cationic metathesis reaction. The addition of *o*-dichlorobenzene ($C_6H_4Cl_2$) and Mn^{II}TPP with further diffusion of hexane into the obtained solution yielded the crystals of $\{(MDABCO^+)_2$•$Mn^{II}TPP\}$•(C_{60}^{2-})•$(C_6H_4Cl_2)_4$•$(CH_3CN)_2$ (**1**). The composition of the complex was determined by X-ray diffraction on a single crystal. Several single crystals selected from the synthesis had the same unit cell parameters.

There are two $MDABCO^+$ cations per one C_{60}. Therefore, fullerene should have -2 charged state. The IR- and UV-visible-NIR spectra of **1** justify this fact. The IR-spectrum contains the absorption bands of C_{60} at 517, 572, and 1367 cm^{-1}. $F_{1u}(4)$ mode of C_{60} (positioned at 1429 cm^{-1} in neutral fullerene) is most sensitive to charge transfer [19]. The C_{60} radical anion salts with -1 charged fullerenes have the positions of this mode at 1388-1395 cm^{-1} [19-22]. The position of $F_{1u}(4)$ mode in the spectrum of **1** shifts essentially stronger to smaller wave numbers (1367 cm^{-1}) indicating the formation of C_{60}^{2-}. The close position of $F_{1u}(4)$ mode at 1369 cm^{-1} was found in the spectrum of $(Cp^*_2Co^+)_2$•(C_{60}^{2-})•$(C_6H_4Cl_2, C_6H_5CN)_2$, which involves C_{60} in -2 charged state [23]. The NIR spectrum of **1** unambiguously indicates the formation of C_{60}^{2-} due to the presence of characteristic absorption bands at 834, 945 and 1320 nm (Fig. 1, arrows) [20, 21].

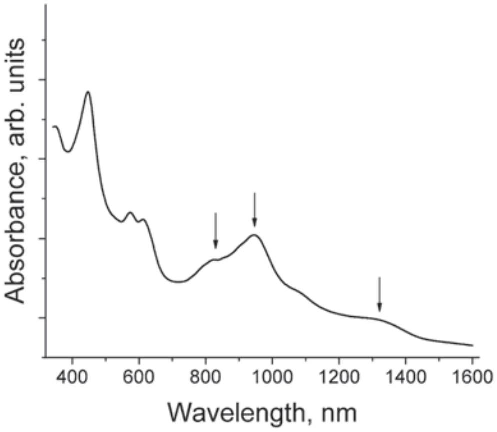

Fig. 1. UV-visible-NIR spectrum of **1** in KBr pellet in the 340-1600 nm range

$Mn^{II}TPP$ manifests absorption bands in the spectrum of **1** at 446 (the Soret band), 572 and 614 nm (the Q-bands). The starting porphyrin has the position of these bands at 443, 572 and 611 nm (starting $Mn^{II}TPP$ can contain coordinated EtOH used in the synthesis [24] and, correspondingly, the Soret band can even be shifted relative to pure $Mn^{II}TPP$). It is seen that the coordination of two $MDABCO^+$ cations to $Mn^{II}TPP$ shifts the Soret band by 3 nm to the red side. Similar shifts of the Soret band (by 6-10 nm) were found previously in the spectra of the complexes containing similar $(MDABCO^+)_2 \cdot Mn^{II}TPP$ assemblies and -1 charged fullerenes C_{60} and C_{70} [11].

The crystal structure of **1** was solved at 100(2) K. It contains two crystallographically independent C_{60}^{2-} and $(MDABCO^+)_2 \cdot Mn^{II}TPP$ species. There is a large free space in the packing of porphyrins, fullerenes and cations, which allows the insertion of four $C_6H_4Cl_2$ and two CH_3CN molecules per formula unit. The $C_6H_4Cl_2$ molecules are disordered, whereas both CH_3CN molecules are ordered. The C_{60}^{2-} dianions are disordered. One dianion is disordered between two orientations with the 0.82/0.18 occupancies and the second dianion is disordered between three orientations with the 0.49/0.34/0.17 occupancies. The environment of two crystallographically independent C_{60}^{2-} is very similar. Each C_{60}^{2-} is surrounded by four $MDABCO^+$ cations (Fig. 2). There are also two $Mn^{II}TPP$ and several solvent molecules, which form van der Waals C…C and C… Cl contacts with C_{60}^{2-} (not shown in Fig. 2). The C_{60}^{2-} dianions are completely separated from each other. The shortest center-to-center distance is 13.228 Å. The distance between two crystallographically independent C_{60}^{2-} is 15.367 Å (this pair is shown in Fig. 2). This is not the case in the complexes containing $(MDABCO^+)_2 \cdot Mn^{II}TPP$ units and -1 charged fullerenes as more dense packing is realized as one-dimensional chains from $C_{60}^{\bullet -}$ or layers from the $(C_{70}^-)_2$ dimers [11].

Two $MDABCO^+$ cations coordinate to $Mn^{II}TPP$. Therefore, the Mn^{II} atoms are six-coordinated with distorted octahedral surroundings (Fig. 3). This is a quite rare coordination mode for $Mn^{II}TPP$ since previously it was shown that even in a large excess of li-

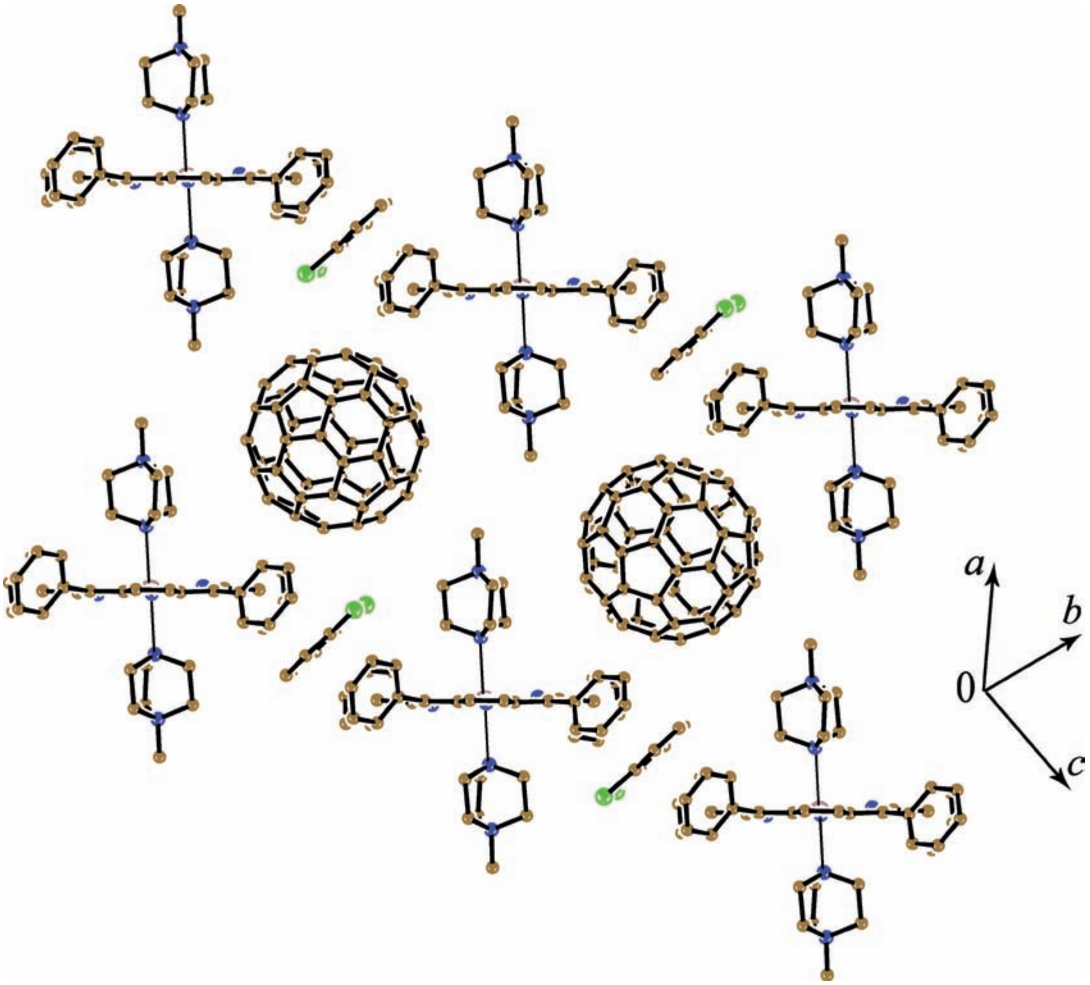

Fig. 2. Fragment of the crystal structure of **1** showing the surroundings of two crystallographically independent C_{60}^{2-} dianions. Only one major occupied orientation is shown for both C_{60}^{2-}. Solvent molecules (except one $C_6H_4Cl_2$ molecule in major occupied orientation) are omitted for clarity

gands, only five-coordinated high-spin $Mn^{II}TPP\cdot L$ species (L = Py, 1-MeIm, 2-MeIm) are formed [24]. The $(MDABCO^+)_2\cdot Mn^{II}TPP$ units in **1** are most probably stabilized in the solid state due to the interaction with the fullerene anions. We showed that such coordination units are also formed in the complexes with -1 charged fullerenes [11].

The geometry of $Mn^{II}TPP$ is defined to a great extent by the spin state of the Mn^{II} atoms. We analyzed the geometric parameters of the $(MDABCO^+)_2\cdot Mn^{II}TPP$ units in **1** (Fig. 3a) and other fullerene complexes [11] (Table 1). The Mn-N(TPP) bonds are long (2.081-2.110 (2) Å) and characteristic of high-spin $Mn^{II}TPP$ (S = 5/2). High-spin four-coordinated $Mn^{II}TPP\cdot(C_6H_5CH_3)_2$ units have similar bond lengths (2.082-2.085(2) Å [25]). The elongation of the Mn-N(TPP) bonds is associated with the singly occupied $d(x^2-y^2)$ orbital in the high-spin state of $Mn^{II}TPP$, which is antibonding relative to the Mn-N(TPP) bonds. This orbital is unoccupied in high-spin $Mn^{III}TPP$ [26], low-spin (NO)·MnTPP·(MPip) [27] and intermediate spin state (S = 3/2) $Mn^{II}Pc$ (Pc: phthalocyanine) [28] that provides shorter equatorial Mn-N bonds (1.94-2.03 Å, Table 1).

The M^{II} atoms in the high-spin state are large. They can displace out of the mean porphyrin plane oscillating between two positions or can be located in the porphyrin plane. For both positions of the M^{II} atoms, radial expansion of the porphyrin core should occur. For example, the radial expansion of the porphyrin core was found in the high-spin $Fe^{II}TPP\cdot(THF)_2$ when the iron(II) atoms are positioned in the porphyrin plane [29] (Table 1). In high-spin $Mn^{II}TPP\cdot(C_6H_5CH_3)_2$, the radial expansion of the porphyrin core is accompanied by the displacement of the Mn^{II} atoms by ±0.177 Å out of the mean porphyrin plane [25].

The degree of radial distortion of the porphyrin core can be estimated from the difference in the length of two Mn…C distances, and the perpendicular displacements of the atoms from the 24-atom porphyrin plane (Fig. 3b). The largest displacements were found for the nitrogen atoms of pyrrole rings (these values are listed in Table 1). The Mn^{II} atoms are positioned exactly in the porphyrin plane in $(MDABCO^+)_2\cdot Mn^{II}TPP$ when it forms a complex with the $(C_{70}^-)_2$ dimers [11]. This results in the largest radial expansion of the porphyrin core (Table 1). For the $(MDABCO^+)_2\cdot Mn^{II}TPP$ units in the previously described complex with $C_{60}^{\bullet-}$, the thermal parameter of the Mn^{II} atom, for the vibration perpendicular to the porphyrin plane is essentially higher than that of the N atoms, and the disorder model in which the Mn^{II} atom was distributed between two symmetry-equivalent, out-of-plane positions with isotropic temperature factors can be applied. However, the accuracy of the crystal structure determination does not allow the position of the Mn^{II} atoms with anisotropic temperature factors, to be simultaneously refined because they show large correlations [11]. The out-of-plane displacement of the Mn^{II} atoms from the mean porphyrin plane estimated using this model, was ±0.127 Å. In this case, moderate radial expansion of the porphyrin core is realized (Table 1). Both crystallographically independent $(MDABCO^+)_2\cdot Mn^{II}TPP$ units in **1** have the Mn^{II} atoms exactly in the porphyrin plane since they are located in the centers of symmetry, whereas the radial expansion of the porphyrin core has moderate values (Table 1). Thus, all $(MDABCO^+)_2\cdot Mn^{II}TPP$ units manifest radial expansion of the porphyrin core

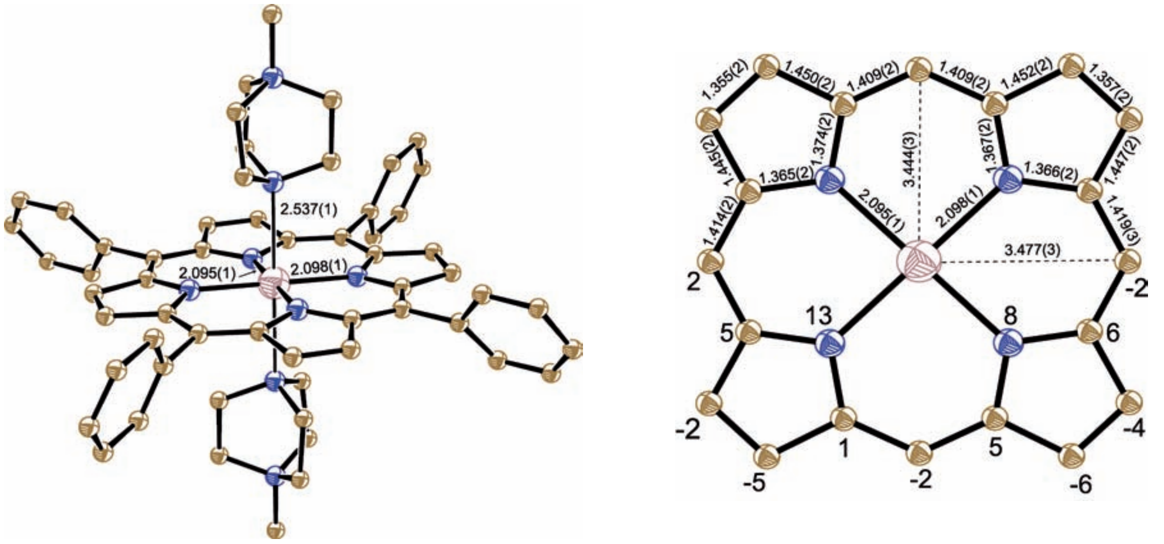

Fig. 3. Molecular structure of one of two $(MDABCO^+)_2\cdot Mn^{II}TPP$ units in **1** (with the larger radial expansion) (a); the structure of the porphyrin core (b). Upper half shows the structurally independent bond lengths and lower half shows perpendicular displacements of the atoms (in 0.01 Å units) from the mean 24-atom porphyrin plane

Table 1. Geometric parameters of the six-coordinated M^{II}TPP units in high- and low-spin states

Complex	M-N(TPP), Å	M-N(L), Å	M…C distances, difference, Å	Displacement of N atoms from the porphyrin plane, Å
{(MDABCO$^+$)$_2$•Mn^{II}TPP}•(C$_{60}^{\bullet -}$)$_2$•solvent [high-spin, 11]	2.081(2), 2.110 (2) Mn^{II} displaces out of plane by ± 0.127 Å	2.531(2)	3.456(2), 3.479(2) 0.023	0.063, 0.122
{(MDABCO$^+$)$_2$•Mn^{II}TPP}•(C$_{70}^{-}$)$_4$ •(MDABCO$^+$)$_2$•solvent [high-spin, 11]	2.097(2), 2.098(2) Mn^{II} in plane	2.515(2)	3.446(2), 3.486(2) 0.040	0.117, 0.125
{(MDABCO$^+$)$_2$•Mn^{II}TPP}•(C$_{60}^{2-}$)•solvent[a] [this work]	2.093(1), 2.094(1) Mn^{II} in plane	2.545(1)	3.449(3), 3.469(3) 0.020	0.104, 0.118
{(MDABCO$^+$)$_2$•Mn^{II}TPP}•(C$_{60}^{2-}$)•solvent[a] [this work]	2.095(1), 2.098(1) Mn^{II} in plane	2.537(1)	3.444(3), 3.477(3) 0.033	0.076, 0.133
Mn^{II}TPP•(C$_6$H$_5$CH$_3$)$_2$ [high-spin, 25]	2.082(2), 2.085(2) Mn^{II} displaces out of plane by ± 0.177 Å	-	3.466(3)	0.030, -0.140
(NO)•MnTPP•(Mpip) [low-spin (S = 1/2), 27]	aver. 2.028(4) Mn^{II} displaces out of plane to NO by ~0.1 Å	2.206(5) Mpip 1.644(5) NO	-	-
{(MDABCO$^+$)$_2$•Co^{II}TPP}•(C$_{60}^{\bullet -}$)$_2$•solvent [low-spin, 11]	1.980(2), 1.997(2) Co^{II} in plane	2.478(2)	3.432(2), 3.443(2) 0.012	0.012, 0.062
Fe^{II}TPP•(THF)$_2$ [high-spin (S = 2), 29]	2.054(2), 2.060(2) Fe^{II} in plane	2.351(3)	3.435(3), 3.466(3) 0.031	0.100, 0.120
Fe^{II}TPP•(Pip)$_2$ [low-spin (S = 0), 30]	2.000(3), 2.008(3) Fe^{II} in plane	2.127(3)	3.434(4), 3.449(4) 0.015	0.007, 0.008

[a] Data for two crystallographically independent units in **1**.

whereas the Mn^{II} atoms can locate in the porphyrin plane or displace out of this plane. The transition of metalloporphyrin to the low-spin state decreases the length of the M-N(TPP) bonds (1.980-1.997(2) Å) and the radial expansion of the porphyrin core as in (MDABCO$^+$)$_2$•Co^{II}TPP, Table 1).

The Mn-N(MDABCO$^+$) distances are long in the (MDABCO)$_2$•Mn^{II}TPP units (2.515-2.545(1) Å) showing their essential destabilization. That is the reason why high-spin Mn^{II}TPP with two coordinated ligands was not observed previously. Mn^{II}TPP in the high-spin state occupied the d(z^2) orbital and namely an unpaired electron from this orbital is involved in the bonding with the ligands. The length of the M-N(L) bonds for low-spin Fe^{II}TPP•(Pip)$_2$ [30] and (NO)•MnTPP•(MPip) [27] is essentially smaller (Table 1). The exception is low-spin (MDABCO$^+$)$_2$•Co^{II}TPP, which has an occupied d(z^2) orbital (the Co…N(L) distance is 2.478(2) Å) [11]. It was shown that the removal of one electron from the d(z^2) orbital in Co^{III}TPP$^+$ leads to a noticeable shortening of the Co-N(L) bonds in (Co^{III}TPP$^+$)•(piperidine)$_2$ (2.060(3) Å) [31], compared with the Co-N(L) bonds in Co^{II}TPP•(piperidine)$_2$ (2.436(2) Å) [32]. The additional contribution to the destabilization of the (MDABCO$^+$)$_2$•Mn^{II}TPP units can provide the repulsion between positively charged MDABCO$^+$ cations (the distance between charges is 10.18 Å).

Coordinated nitrogen atoms of the two ligands and the metal(II) atom of porphyrin lie along a straight line in the six-coordinated units. The angles between the perpendicular to the mean porphyrin plane and this line is only 1° in Co^{II}TPP•(piperidine)$_2$ [32], and 2° in (MDABCO$^+$)$_2$•Co^{II}TPP and (MDABCO$^+$)$_2$•Mn^{II}TPP in the complex with C$_{60}^{\bullet -}$ [11]. The large expansion of the porphyrin core is observed in (MDABCO$^+$)$_2$•Mn^{II}TPP in the complex with the (C$_{70}^{-}$)$_2$ dimers [11] and in Fe^{II}TPP•(THF)$_2$ [29]. In this case, the angles are 5° and 8.3°, respectively. For the (MDABCO$^+$)$_2$•Mn^{II}TPP units in **1** the intermediate values of these angles were found (2.7°).

Magnetic properties of **1** were studied by SQUID and EPR techniques in the 1.9-300 K range. The magnetic moment of the complex is equal to 5.61 μ_B at 300 K indicating the high-spin state of the (MDABCO$^+$)$_2$•Mn^{II}TPP units (S = 5/2, μ_{eff} = 5.91 μ_B). Previously, it was shown that these coordination units also have a high-spin state (S = 5/2) in the complexes with -1 charged fullerenes [11]. The contribution of the C$_{60}^{2-}$ dianions to magnetic susceptibility of **1** should be small. The C$_{60}^{2-}$ dianions are either diamagnetic from 4 K up to room temperature (rt = 295 K)

[33] or they can be diamagnetic at low temperatures but manifest the population of the excited triplet state at higher temperatures [23, 34]. Nevertheless, even at rt the population of the excited triplet state is small and does not exceed 6% [23]. Such a small contribution cannot be revealed on the basis of high-spin Mn^{II}TPP. The Weiss temperature of -0.8 K (10-300 K) shows only weak magnetic interaction of spins. This can be explained by the large distances between paramagnetic $(MDABCO^+)_2 \cdot Mn^{II}$TPP units separated by the diamagnetic C_{60}^{2-} dianions, which cannot effectively transfer magnetic interaction. Previously, similar magnetic behavior was observed in the complex containing the high-spin $(MDABCO^+)_2 \cdot Mn^{II}$TPP units and the diamagnetic $(C_{70}^-)_2$ dimers (the Weiss temperature is close to zero) [11].

CONCLUSION

For the first time the multi-component ionic complex **1** containing C_{60}^{2-} dianions and positively charged $(MDABCO^+)_2 \cdot Mn^{II}$TPP assemblies was obtained as single crystals. The Mn^{II} atoms are six-coordinated in **1** and have high-spin state (S = 5/2). The long Mn-N(TPP) (2.095-2.098(1) Å) and Mn-N($MDABCO^+$) bonds (2.537-2.545(1) Å) can be attributed to the population of the $d(x^2-y^2)$ and $d(z^2)$ orbitals in the high-spin Mn^{II}TPP. The Mn^{II} atoms position in the porphyrin plane and that results in the radial expansion of the porphyrin core since they have large size in the high-spin state. The displacement of the Mn^{II} atoms from the 24-atom porphyrin plane was also found at the moderate radial expansion of the porphyrin core (as in the complex of $(MDABCO^+)_2 \cdot Mn^{II}$TPP with $C_{60}^{\bullet -}$) [11]. Thus, for the $(MDABCO^+)_2 \cdot Mn^{II}$TPP units, both in-plane and out-of-plane positions of the Mn^{II} atoms are possible. The contribution from the C_{60}^{2-} dianions can not be revealed in SQUID measurements on the basis of high-spin Mn^{II}TPP. Therefore, they are most probably diamagnetic in the 2-300 K range. Diamagnetism of the C_{60}^{2-} dianions defines the absence of noticeable magnetic interactions in **1** since high-spin $(MDABCO^+)_2 \cdot Mn^{II}$TPP units are magnetically isolated by diamagnetic C_{60}^{2-} dianions.

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Supporting information

IR spectra and crystallographic data in CIF format for complex **1** are given in the supplementary material. This material is available at http://www.u-bourgogne.fr/jpp/.

REFERENCES

1. Sun Y, Drovetskaya T, Bolskar RD, Bau R, Boyd PDW and Reed CA. *J. Org. Chem.* 1997; **62**: 3642-3649.
2. Guldi DM. *Chem. Soc. Rev.*, 2002; **31**: 22-36.
3. El-Khouly ME, Ito O, Smith PM and D`Souza F. *J. Photochem. Photobiol. C: Photochem. Rev.* 2004; **5**: 79-104.
4. Olmstead MM, Costa DA, Maitra K, Noll BC, Phillips SL, Van Calcar PM and Balch AL. *J. Am. Chem. Soc.* 1999; **121**: 7090-7097.
5. Boyd PDW, Hodgson MC, Rickard CEF, Oliver AG, Chaker L, Brothers PJ, Bolskar RD, Tham FS and Reed CA. *J. Am. Chem. Soc.* 1999; **121**: 10487-10495.
6. Konarev DV, Neretin IS, Slovokhotov YL, Yudanova EI, Drichko NV, Shul`ga YM, Tarasov BP, Gumanov LL, Batsanov AS, Howard JAK and Lyubovskaya RN. *Chem. Eur. J.* 2001; **7**: 2605-2616.
7. Konarev DV, Kovalevsky AY, Li X, Neretin IS, Litvinov AL, Drichko NV, Slovokhotov YL, Coppens P and Lyubovskaya RN. *Inorg. Chem.* 2002; **41**: 3638-3646.
8. Pénicaud A, Hsu J, Reed CA., Koch A, Khemani KC, Allemand PM and Wudl F. *J. Am. Chem. Soc.* 1991; **113**: 6698-6670.
9. Stinchcombe J, Pénicaud A, Bhyrappa P, Boyd PDW and Reed CA. *J. Am. Chem. Soc.* 1993; **115**: 5212-5217.
10. Saito G, Teramoto T, Otsuka A, Sugita Y, Ban T, Kusunoki M and Sakaguchi KI. *Synth. Met.* 1994; **64**: 359-368.
11. Konarev DV, Khasanov SS, Otsuka A, Saito G and Lyubovskaya RN. *Inorg. Chem.* 2007; **46**: 2261-2271.
12. Konarev DV, Khasanov SS, Otsuka A, Saito G and Lyubovskaya RN. *J. Am. Chem. Soc.* 2006; **128**: 9292-9293.
13. Konarev DV, Khasanov SS, Otsuka A, Saito G and Lyubovskaya RN. *Chem. Eur. J.* 2006; **12**: 5225-5230.
14. Konarev DV, Neretin IS, Saito G, Slovokhotov YL, Otsuka A and Lyubovskaya RN. *Eur. J. Inorg. Chem.* 2004; 1794-1798.
15. Konarev DV, Khasanov SS, Otsuka A, Yoshida Y, Lyubovskaya RN and Saito G. *Chem. Eur. J.* 2003; **9**: 3837-3848.
16. Konarev DV, Neretin IS, Saito G, Slovokhotov YL, Otsuka A and Lyubovskaya RN. *Dalton Trans.* 2003; 3886-3891.
17. Subramanian R, Boulas P, Vijayashree MN,

D`Souza F, Jones MT and Kadish KM. *J. Chem. Soc. Chem. Commun*. 1994; 1847-1848.

18. Allard E, Rivière L, Delaunay J, Dubois D and Cousseau J. *Tetrahedron Lett*. 1999; **40**: 7223-7226.
19. Picher T, Winkler R and Kuzmany H. *Phys. Rev. B* 1994; **49**: 15879-15889.
20. Reed CA and Bolskar RD. *Chem. Rev*. 2000; **100**: 1075-1120.
21. Konarev DV, Drichko NV and Graja A. *J. Chim. Phys*. 1998; **95**: 2143-2156.
22. Konarev DV, Khasanov SS, Saito G, Otsuka A, Yoshida Y and Lyubovskaya RN. *J. Am. Chem. Soc*. 2003; **125**: 10074 -10083.
23. Konarev DV, Khasanov SS, Saito G, Vorontsov II, Otsuka A, Lyubovskaya RN and Antipin YM. *Inorg. Chem*. 2003; **42**: 3706-3708.
24. Reed CA, Kouba JK, Grimes CJ and Cheung SK. *Inorg. Chem*. 1978; **17**: 2666-2670.
25. Kirner JF, Reed CA and Scheidt WR. *J. Am. Chem. Soc*. 1977; **99**: 1093-1101.
26. Day VW, Stults BR, Tasset EL, Day RO and Marianelli RS. *J. Am. Chem. Soc*. 1974; **96**: 2650-2652.
27. Piciulo PL, Rupprecht G and Scheidt WR. *J. Am. Chem. Soc*. 1974; **96**: 5293-9395.
28. Kirner JF, Dow W and Scheidt WR. *Inorg. Chem*. 1976; **15**: 1685-1690.
29. Reed CA, Mashiko T, Scheidt WR, Spartalian K and Lang G. *J. Am. Chem. Soc*. 1980; **102**: 2302-2306.
30. Radonovich LJ, Bloom AB and Hoard JL. *J. Am. Chem. Soc*. 1972; **94**: 2073-2378.
31. Scheidt WR, Cunningham JA and Hoard JL. *J. Am. Chem. Soc*. 1973; **95**: 8289-8294.
32. Scheidt WR. *J. Am. Chem. Soc*. 1974; **96**: 84-89.
33. Paul P, Kim KC, Sun D, Boyd PDW and Reed CA. *J. Am. Chem. Soc*. 2002; **124**: 4394-4401.
34. Konarev DV, Saito G and Lyubovskaya RN. *Fullerenes, Nanotubes Carbon Nanostruct*. 2004; **12**: 147-154.
35. Otwinowski Z and Minor W. *Processing of X-ray diffraction data collection in oscillation mode* In *Methods in Enzymology* Carter CW and Sweet RM. (Eds.) Academic Press: 1997; p 276.
36. Sheldrick GM. SHELX97 University of Göttingen, Germany, 1997.