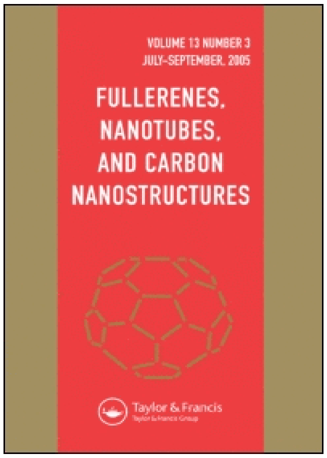

Fullerenes, Nanotubes and Carbon Nanostructures

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Ionic Multi-Component Complexes of Fullerenes: Structures and Magnetic Properties

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Ionic Multi-Component Complexes of Fullerenes: Structures and Magnetic Properties

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Abstract: New ionic multi-component complexes $(TBPDA)_2\cdot(C_{60}^{\bullet -})\cdot(D^+)$, where TBPDA is N,N,N′,N′-tetrabenzyl-*p*-phenylenediamine and D is decamethylchromocene ($Cp^*{}_2Cr$, **1**), decamethylcobaltocene ($Cp^*{}_2Co$, **2**), and tetrakis(dimethylamino)ethylene (TDAE, **3**). The presence of D^+, $C_{60}^{\bullet -}$ and neutral TBPDA in **1**–**3** was proved by the IR and UV-visible-NIR spectra. D^+ and $C_{60}^{\bullet -}$ form loose layers in **1** and **3** and are spatially separated by bulky TBPDA molecules. The EPR spectra of the complexes show single Lorentzian line with $g = 2.2526$ and $\Delta H = 215\,mT$ (**1**), $g = 1.9999$ and $\Delta H = 6.7\,mT$ (**2**), and $g = 2.0009$ and ΔH of $2.93\,mT$ (**3**) at RT. The EPR signal of **2** was attributed to $C_{60}^{\bullet -}$ ($Cp^*{}_2Co^+$ is diamagnetic), whereas those in **1** and **3** to resonating signal between $C_{60}^{\bullet -}$ ($g = 1.9996$–2.0000) and cations $Cp^*{}_2Cr^+$ (**1**) or $TDAE^{\bullet +}$ (**3**) due to indirect coupling. The EPR signals from **2** and **3**

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are split into two components below 50 and 60 K and the magnetic moments of **1–3** decrease below 50–100 K. Both effects are associated with the formation of field-induced short-range antiferromagnetically ordered clusters. It was shown that D^+ cations do not noticeably affect the antiferromagnetic interaction of spins in **1–3** probably due to their isolation by benzyl groups of TBPDA.

Keywords: Fullerene, metallocenes, crystal engineering, solid-state structures, IR and EPR spectroscopy, magnetic properties

INTRODUCTION

Fullerenes are acceptors and form molecular and ionic complexes with different donor molecules (1). However, a number of organic and organometallic donors able to ionize fullerenes in solid state is rather small. Those are various metallocenes, unsaturated amines, and some metalloporphyrins (1, 2). We developed a multi-component approach to modify ionic complexes of fullerenes, in which a neutral D_1 molecule was introduced into an ionic complex to produce a new compound with two donor counterparts: $(D_1)\cdot(D_2^{\bullet+})\cdot(\text{fullerene}^{\bullet-})$ (3, 4). In such a complex D_1 forms a supramolecular packing pattern, whereas D_2 is a strong donor with small size relatively to D_1 and is potentially able to ionize fullerene moiety. In this work we obtain a series of new multi-component complexes $(\text{TBPDA})_2\cdot(C_{60}^{\bullet-})\cdot(D^+)$, where TBPDA is N,N,N′,N′-tetrabenzyl-*p*-phenylenediamine and D is the cations with different shape and spin states: $Cp^*{}_2Cr^+$ has $S = 3/2$, $TDAE^{\bullet+}$ has $S = 1/2$ and $Cp^*{}_2Co^+$ is diamagnetic ($S = 0$).

$(\text{TBPDA})_2\cdot C_{60}\cdot Cp^*{}_2Cr$ (**1**), $(\text{TBPDA})_2\cdot C_{60}\cdot Cp^*{}_2Co$ (**2**), and $(\text{TBPDA})_2\cdot C_{60}\cdot \text{TDAE}$ (**3**) were obtained in anaerobic conditions by the diffusion method in which C_{60}, D and an excess of TBPDA dissolved in the C_6H_6/C_6H_5CN mixture were precipitated with hexane. The composition of **1** and **3** was determined by X-ray diffraction on a single crystal and **2** by elemental analysis (Found, %: C = 89.41, H = 4.86, N = 2.69; calc., %: C = 89.82, H = 4.74, N = 2.82; Co = 2.62).

The IR spectra of **1–3** in a KBr matrix were a superposition of the spectra of C_{60}, D, and TBPDA. $F_{1u}(4)$ mode, which is the most sensitive to charge transfer to the C_{60} molecule, is shifted to $1388\,\text{cm}^{-1}$ in the spectra of the complexes indicating the formation of $C_{60}^{\bullet-}$. The formation of $C_{60}^{\bullet-}$ is also justified by the NIR spectra of **1–3** with the bands at $10.75–10.77 \times 10^3$ and $9.20 \times 10^3\,\text{cm}^{-1}$.

Complexes **1** (5) and **3** (4) crystallize in a tetragonal system with $I\bar{4}$ and $I4/m$ space groups and have similar structures (Figure 1). $C_{60}^{\bullet-}$ and $Cp^*{}_2Cr^+$ (**1**) or $TDAE^{\bullet+}$ (**3**) occupy positions with $\bar{4}$ or $4/m$ symmetry and are statistically disordered between two orientations in **3** and four orientations in **1** due to that they lie on a higher symmetry position than their own symmetry. The ordered TBPDA molecules occupy positions with $2/m$ symmetry.

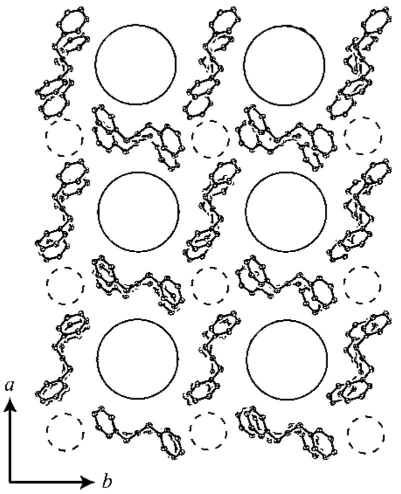

Figure 1. General view of the crystal structures of **1** and **3** on the *ab*-plane. The positions of disordered $C_{60}^{\bullet -}$ radical anions are shown by large circles and those of the cations ($Cp^*_2Cr^+$ and $TDAE^{\bullet +}$) are shown by smaller dashed circles.

$C_{60}^{\bullet -}$, $Cp^*_2Cr^+$ ($TDAE^{\bullet +}$) and TBPDA form square loose layers in **1** and **3** parallel to the *ab* plane (Figure 1). $C_{60}^{\bullet -}$ radical anions alternate in these layers with the central phenylene (-C_6H_4-) groups of TBPDA along the *a* and *b* directions (Figure 2) forming π-π stacking with them. Each $Cp^*_2Cr^+$ is located within the layer in the cavities formed by eight benzyl groups of TBPDA and are completely separated from each other. The interlayer space is filled with the benzyl groups of TBPDA. Thus, **1** and **3** are dilute systems, in which the $C_{60}^{\bullet -}$ and D^+ ions are spatially separated in all three directions by the TBPDA molecules. Nevertheless, the $C_{60}^{\bullet -}$ radical anions alternate and have the π-π interaction with phenylene groups of TBPDA, which can mediate weak magnetic coupling between $C_{60}^{\bullet -}$ spins within the layer.

Magnetic properties of polycrystalline **1**, **2** and **3** were studied by EPR (Table 1, Figure 2) and SQUID (Figure 3) techniqies from RT down to liquid helium temperatures. **2** shows broad Lorentzian line with g-factor of 1.9999 and line halfwidth of $\Delta H = 6.7$ mT (Figure 2). This signal is characteristic of $C_{60}^{\bullet -}$, which has g-factor in the 1.9996–2.0000 range and ΔH of 3–5 mT at RT (1). Diamagnetic and EPR silent $Cp^*_2Co^+$ gives no contribution to the EPR spectrum of **2**. The EPR signal of **3** with g-factor of 2.0009 and $\Delta H = 2.93$ mT is similar to that of $TDAE \cdot C_{60}$ ($g = 2.0003$ and $\Delta H = 2.2$ mT at RT (6)). Intermediate g-factors of 2.0009 and 2.0003 between those of $C_{60}^{\bullet -}$ and $TDAE^{\bullet +}$ ($g = 2.0035$ (7)) indicate that these signals are resonating ones between these ion-radicals. However, if in $TDAE \cdot C_{60}$ this signal appear due to direct exchange coupling between $C_{60}^{\bullet -}$ and $TDAE^{\bullet +}$ (8), in **3** only indirect coupling between these ion-radicals can be supposed (for example, through the neutral TBPDA

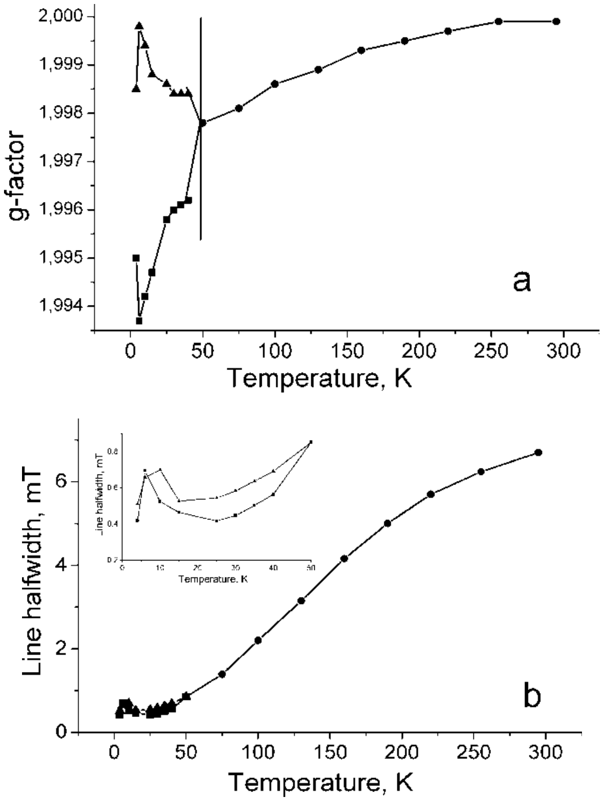

Figure 2. Temperature dependence of g-factor (a) and line halfwidth (b) for $(TBPDA)_2 \cdot C_{60} \cdot Cp^*Co$ (**2**) in the 4–295 K range.

molecules). The EPR spectrum of **1** contains single very broad Lorentzian line with g = 2.2526 and ΔH of 215.6 mT at RT. Similar EPR signal was previously observed for a high-temperature monomeric phase of $Cp^*_2Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ (g = 2.2210 and ΔH of about 100 mT at 320 K (9)). The observed

Table 1. EPR parameters of **1**–**3**

	290 K		4 K	
Compound	g-factor	ΔH, mT	g-factor	ΔH, mT
1	2.2526	215.6	2.7563	168
	1.9999	6.7	1.9985	0.42
2			1.9950	0.51
	2.2526	215.6	2.7563	168
3	2.0009	2.93	2.0063	0.76
			1.9966	0.205

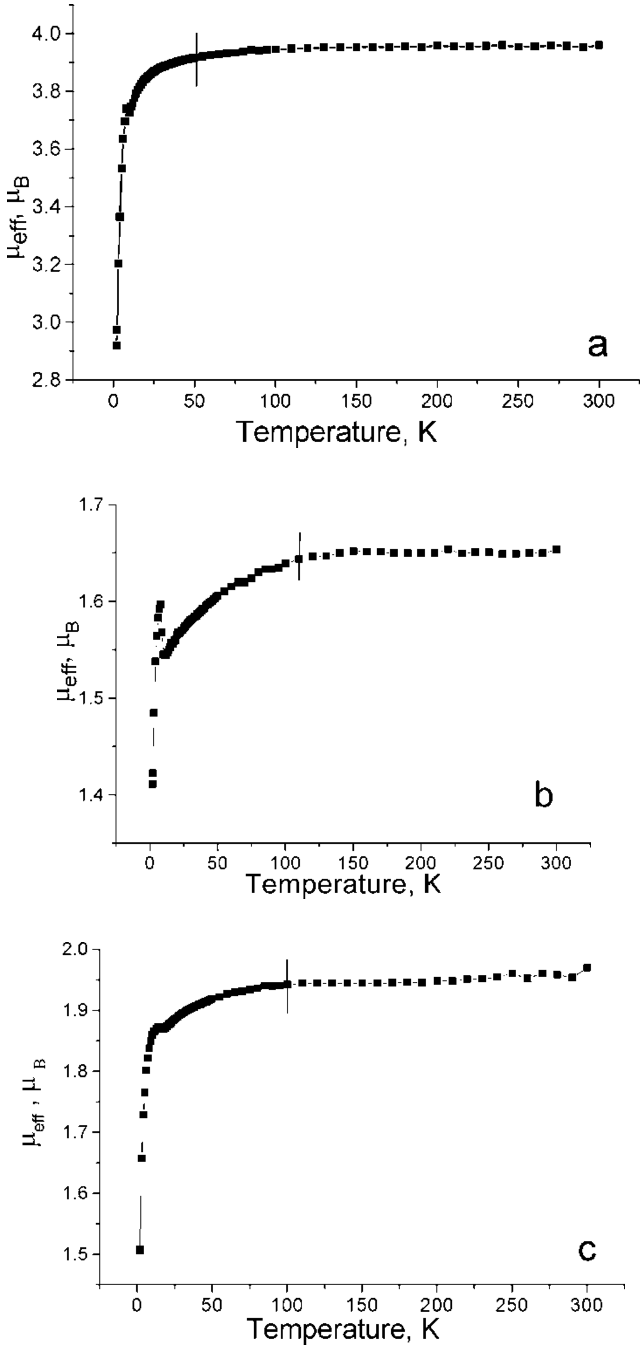

Figure 3. Temperature dependence of magnetic moments of **1** (a), **2** (b) and **3** (c) in the 1.9–300 K range.

EPR signals in both complexes are resonating ones between $C_{60}^{\bullet -}$ and $Cp^*{}_2Cr$ due to mean g-factor values between those for $C_{60}^{\bullet -}$ (1.9996–2.0000) and $Cp^*{}_2Cr$ (an asymmetric EPR signal with $g_{\perp} = 4.02(1)$ and $g_{//} = 2.001(\mathbf{1})$ (10)). The reason for that can be direct strong exchange coupling between $Cp^*{}_2Cr^+$ and $C_{60}^{\bullet -}$ ions in $Cp^*{}_2Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ and their indirect coupling in **1**.

The EPR signal of **2** essensially narrows with the temperature decreases and g-factor monotonically shifts to 1.9978 at 50 K (Figure 2). Below 50 K EPR signal becomes asymmetric and splits into two components. These components shift in the opposite directions to higher and lower magnetic fields with the temperature decrease (g = 1.9985 and 1.9950 at 4 K, Figure 2a). The shifts are accompanied by small broadening of both components (Figure 2b). The magnetic moment of **2** ($\mu_{eff} = 1.65\ \mu_B$ at 300 K) is nearly temperature independent down to ~100 K and begins to decrease below this temperature (Figure 3b). Both effects in SQUID and EPR originate from the antiferromagnetic interaction of spins due to the formation of a field-induced short-range ordered cluster (11). We observed very similar behavior for **3** with temperatures for the splitting of EPR signal and the decrease of the magnetic moment below 60 and ~100 K, respectively (Figure 3c).

The EPR signal of **1** strongly shifts to larger values with the temperature decrease (g = 2.7563 at 4 K), whereas ΔH remains very broad in the whole temperature range (~160–230 mT). The magnetic moment of **1** ($\mu_{eff} = 3.96\ \mu_B$ at 300 K) indicates a contribution from $Cp^*{}_2Cr^+$ (S = 3/2) and $C_{60}^{\bullet -}$ (S = 1/2) (μ_{eff} is 4.27 μ_B for a system non-interacting S = 3/2, 1/2 spins). Magnetic moment of **1** is temperature independent down to 50 K and decreases below this temperature due to the antiferromagnetic interaction of spins.

The antiferromagnetic character of interaction of spins in **1**–**3** was justified by SQUID measurements. All three complexes show small negative Weiss constants of −0.7 K for **1**, −1.8 K for **2** and −2.3 K for **3**.

Thus, new ionic multi-component complexes $(TBPDA)_2 \cdot (C_{60}^{\bullet -}) \cdot (D^+)$, containing $Cp^*{}_2Cr^+$ (**1**), $Cp^*{}_2Co^+$ (**2**) and $TDAE^{\bullet +}$ (**3**) were obtained. In the crystal structures of **1** and **3** the D^+ and $C_{60}^{\bullet -}$ ions form loose layers, in which they are spatially separated by the bulky TBPDA molecules. As this takes place, the $C_{60}^{\bullet -}$ radical anions alternate with the phenylene groups of TBPDA to form π-π stacking with them, whereas D^+ cations are isolated in the voids formed by eight benzyl groups of TBPDA. Complexes show single Lorentzian EPR lines with g = 1.9999 and ΔH of 6.7 mT (**2**), g = 2.0009 and ΔH of 2.93 mT (**3**), and g = 2.2526 and ΔH of 215 mT (**1**) at RT. Two-component ionic complexes of C_{60}: $TDAE{\cdot}C_{60}$ (6), and $Cp^*{}_2Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ (9) have similar EPR signals. In two-component complexes this is a result of direct exchange coupling between two ion-radicals, whereas **1** and **3** they are spatially separated and only indirect coupling can be supposed. Below 60 K (**3**) and 50 K (**2**) the EPR signals are split into two components and shift in the opposite directions to lower and higher fields. The magnetic moments of **1**–**3** also decrease below 50–100 K. This is explained by the formation of field-induced short-range antiferromagnetically ordered clusters (11). The substitution of paramagnetic $Cp^{*}{}_2Cr^{+}$ and $TDAE^{\bullet +}$ by diamagnetic $Cp^{*}{}_2Co^{+}$ do not affect noticeably the antiferromagnetic interaction of spins in **1**–**3**. In accordance with X-ray diffraction data, this interaction is most probably realized between $C_{60}^{\bullet -}$ spins in the layer through the phenylene groups of TBPDA. D^{+} cations are excluded from this interaction due to their complete spatial and magnetic isolation by benzyl groups of TBPDA. Large distances between $C_{60}^{\bullet -}$ in the layers and the mediation of magnetic coupling through the diamagnetic phenylene groups is a reason for relatively weak antiferromagnetic interaction between $C_{60}^{\bullet -}$ spins in **1**–**3** (Weiss constants are only -0.7–-2.3 K).

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REFERENCES

1. Konarev, D.V. and Lyubovskaya, R.N. (1999) Donor-acceptor complexes and ion-radical salts based on fullerenes. *Russ. Chem. Rev.*, 68: 19–38.
2. Balch, A.L. and Olmstead, M.M. (1998) Reactions of transition metal complexes with fullerenes (C_{60}, C_{70}, etc) and related materials. *Chem. Rev.*, 98: 2123–2165.
3. Konarev, D.V., Khasanov, S.S., Otsuka, A., Yoshida, Y., Lyubovskaya, R.N., and Saito, G. (2003) The interaction of fullerenes C_{60}, C_{70}, and $C_{60}(CN)_2$ radical anions with cobalt(II) tetraphenylporphyrin in solid multicomponent complexes. *Chem. Eur. J.*, 9: 3837–3848.
4. Konarev, D.V., Neretin, I.S., Saito, G., Slovokhotov, Yu.L. , Otsuka, A., and Lyubovskaya, R.N. (2003) Ionic multi-component complexes containing $TDAE^{\bullet +}$ and $C_{60}^{\bullet -}$ radical ions and neutral D_1 molecules: $D_1 \cdot TDAE \cdot C_{60}$. *Dalton Trans.*, 3886–3891.
5. Crystallographic data of **1**: $C_{148}H_{94}CrN_4$, $M_r = 1980.27$, black square plates, tetragonal, $I\bar{4}$, $a = b = 13.9732(3)$, $c = 24.3682(11)$ Å, V = 4757.9(3) Å^3, Z = 2, $\rho_{calc} = 1.382\,g \cdot cm^{-3}$, $\mu = 0.186\,mm^{-1}$, F(000) = 2068, $T = 90(1)$ K, max $2\Theta = 59.98^{\circ}$, $N_{tot} = 42648$ reflections 6879 of which were independent, R_1 [$I > 2\sigma(I)\bullet$] = 0.0885 for 5626 reflections [$I > 2\sigma(I)\bullet$] with 482 parameters and 7956 restrains, wR_2= 0.2358, final G.O.F = 1.078.
6. Tanaka, K., Zakhidov, A.A., Yoshizawa, K., Okahara, K., Yamabe, T., Yakushi, K., Kikuchi, K., Suzuku, S., Ikemoto, L., and Achiba, Y. (1993) Magnetic properties of TDAE-C_{60} and TDAE-C_{70}, where TDAE is tetrakis(dimethylamino)ethylene. *Phys. Rev. B*, 47: 7554–7559.

7. Kuwata, K. and Geske, D.H. (1964) The cation radical of tetrakis(dimethylamino)ethylene. *J. Am. Chem. Soc.*, 86: 2101–2105.
8. Gotschy, B. (1996) Magnetism in C_{60} charge transfer complexes. *Full. Sci. Technol.*, 4: 677–698.
9. Konarev, D.V., Khasanov, S.S., Saito, G., and Lyubovskaya, R.N. (2004) The formation of σ-bonded $(\text{fullerene}^-)_2$ dimers and $(\text{Co}^{\text{II}}\text{TPP} \cdot \text{fullerene}^-)$ anions in ionic complexes of C_{60}, C_{70}, and $C_{60}(CN)_2$. *Recent Res. Devel. Chem.* (Research Signpost, Trivandrum, Kerala, India), 2: 105–140.
10. Robbins, J.L., Edelstein, N., Spencer, B., and Smart, J.C. (1982) Synthesis and electronic structures of decamethylmetallocenes. *J. Am. Chem. Soc.*, 104: 1882–1893.
11. Maneiro, A.L., Pasimeni, L., Brunel, L.C., Pardi, L.A., Cao, G., and Guertin, R.P. (1998) High field ESR study of TDAE-C_{60} powder at different larmor frequencies. *Solid State Commun.*, 106: 727–732.