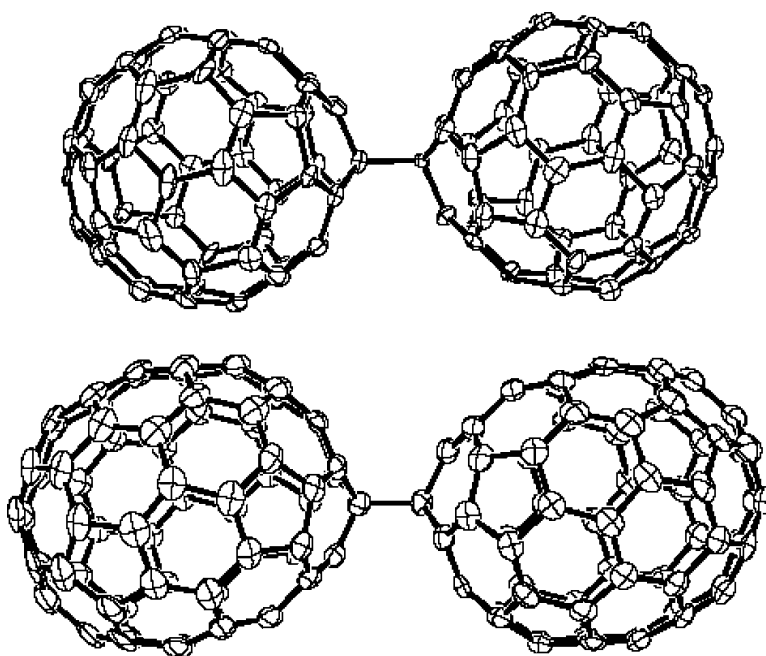


Formation of Single-Bonded (C) and (C) Dimers in Crystalline Ionic Complexes of Fullerenes

Dmitri V. Konarev, Salavat S. Khasanov, Gunzi Saito, Akihiro Otsuka, Yukihiro Yoshida, and Rimma N. Lyubovskaya

J. Am. Chem. Soc., **2003**, 125 (33), 10074-10083 • DOI: 10.1021/ja035546a • Publication Date (Web): 29 July 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Formation of Single-Bonded (C_{60}^-)₂ and (C_{70}^-)₂ Dimers in Crystalline Ionic Complexes of Fullerenes

Dmitri V. Konarev,^{*,†,‡} Salavat S. Khasanov,^{†,§} Gunzi Saito,^{*,†} Akihiro Otsuka,^{†,||}
Yukihiko Yoshida,[†] and Rimma N. Lyubovskaya[‡]

Contribution from the Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow region 142432 Russia, Institute of Solid-State Physics RAS, Chernogolovka, Moscow region, 142432, Russia, and Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Received April 9, 2003; E-mail: konarev@icp.ac.ru; saito@kuchem.kyoto-u.ac.jp

Abstract: New ionic complexes of fullerenes C_{60} and C_{70} with decamethylchromocene $Cp^*_2Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ (**1**), $Cp^*_2Cr \cdot C_{60} \cdot (C_6H_6)_2$ (**2**); the multicomponent complex of $(Cs^+)(C_{70}^-)$ with cyclotrimeratylene $CTV \cdot (Cs)_2 \cdot (C_{70})_2 \cdot (DMF)_7 \cdot (C_6H_6)_{0.75}$ (**3**); bis(benzene)chromium $Cr(C_6H_6)_2 \cdot C_{60} \cdot (C_6H_4Cl_2)_{0.7}$ (**4**), $Cr(C_6H_6)_2 \cdot C_{60} \cdot C_6H_5CN$ (**5**), $Cr(C_6H_6)_2 \cdot C_{70} \cdot C_6H_4Cl_2$ (**6**), $Cr(C_6H_6)_2 \cdot C_{60}$ (**7**); cobaltocene $Cp_2Co \cdot C_{60} \cdot C_6H_4Cl_2$ (**8**), $Cp_2Co \cdot C_{70} \cdot (C_6H_4Cl_2)_{0.5}$ (**9**); and cesium $Cs \cdot C_{70} \cdot (DMF)_5$ (**10**) have been obtained. The complexes have been characterized by the elemental analysis, IR-, UV-vis-NIR spectroscopy, EPR and SQUID measurements. It is shown that C_{60}^- exists as a single-bonded diamagnetic $(C_{60}^-)_2$ dimer in **1**, **2**, **4**, **5**, and **8** at low temperatures (1.9–250 K). The dimers dissociate above 160–250 K depending on donor and solvent molecules involved in the complex. C_{60}^- dimerizes reversibly and shows a small hysteresis (<2 K) at slow cooling and heating rates. The single-bonded diamagnetic $(C_{70}^-)_2$ dimers are also formed in **6**, **9**, and **10** and begin to dissociate only above 250–360 K. The IR and UV-vis-NIR spectra of σ -bonded negatively charged fullerenes are presented.

Introduction

Ionic compounds of fullerenes are interesting both by their unusual physical properties (superconductivity and ferromagnetism)¹ and a large variety of dimeric and polymeric structures of negatively charged fullerenes.² Most of ionic charge transfer (CT) complexes of fullerenes: TDAE $\cdot C_{60}$,³ $Cp_2Co \cdot C_{60} \cdot CS_2$,⁴ $Cp_2Co \cdot C_{60} \cdot C_6H_5CN$,⁵ $Cp^*_2Ni \cdot C_{60} \cdot CS_2$,⁶ $Cr^{III}TPP \cdot C_{60} \cdot (THF)_3$,⁷ various salts of C_{60}^{n-} ($n = 1, 2$ and 3) with PPN^+ , Ph_4P^+ and others⁸ contain monomeric fullerene radical anions.

The linear C_{60}^- polymer bonded by two single bonds (cyclobutane ring) is formed in metallic $M \cdot C_{60}$ phases ($M =$

K, Rb, and Cs).⁹ The linear C_{70}^{2-} and C_{60}^{3-} polymers bonded by one single bond were observed in $M \cdot C_{70} \cdot nNH_3$ salts ($M =$ Ca, Sr, and Ba),¹⁰ and in Na_2RbC_{60} and Li_3CsC_{60} phases.¹¹ A single-bonded linear C_{60}^- polymer was also found in ionic $Cr(C_6H_5Me)_2 \cdot C_{60} \cdot CS_2$. The C_{60} anions form linear chains with a 9.6 Å distance between the centers and the shortest $C(C_{60}) \cdots C(C_{60})$ distance of 2.12 Å. However, the disorder in the fullerene part does not allow satisfactory characterization of this polymer.¹² C_{60}^{4-} forms a two-dimensional polymer bonded by four single bonds in Na_4C_{60} .¹³

The first single-bonded $(C_{60}^-)_2$ dimer was found in metastable $M \cdot C_{60}$ phases ($M =$ K, Rb, and Cs).¹⁴ Azafullerene forms a neutral single-bonded $(C_{59}N)_2$ dimer, which is isoelectronic to $(C_{60}^-)_2$ and has similar properties.¹⁵ A reversible phase transition

[†] Division of Chemistry, Graduate School of Science, Kyoto University.

[‡] Institute of Problems of Chemical Physics RAS.

[§] Institute of Solid-State Physics RAS.

^{||} Research Center for Low Temperature and Materials Sciences, Kyoto University.

- (1) (a) Rosseinsky, M. J. *J. Mater. Chem.* **1995**, *5*, 1497–1513. (b) Gotschy, B. *Fullerene Sci. and Technol.* **1996**, *4*, 677–698. (c) Konarev, D. V.; Lyubovskaya, R. N. *Russ. Chem. Rev.* **1999**, *68*, 19–38.
- (2) Prassides, K. In *The Physics of Fullerenes-Based and Fullerene-Related Materials*; Andreoni, W., Ed.; Kluwer Academic Publishers: Netherlands, 2000, pp 175–202.
- (3) Allemand, P.-M.; Khemani, K. C.; Koch, A.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301–303.
- (4) Balch, A. L.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Eds. Kadish, K. M.; Ruoff, R. S. **1994**, *24*, 1231–1243.
- (5) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212–5217.
- (6) Wan, W. C.; Liu, X.; Sweeney, G. M.; Broderick, W. E., *J. Am. Chem. Soc.* **1995**, *117*, 9580–9581.
- (7) Pénicaud, A.; Hsu, J.; Reed, C. A.; Koch, A.; Khemani, K.; Allemand, P.-M.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 6698–6670.

- (8) (a) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075–1119. (b) Bilow, U.; Jansen, M. *J. Chem. Soc., Chem. Commun.* **1994**, 403–404.
- (9) (a) Stephens, P. W.; Bortel, G.; Faigel, G.; Tegze, M.; Jánossy, A.; Pekker, S.; Oszlányi, G.; Forró, L. *Nature* **1994**, *370*, 636–639. (b) Winter, J.; Kuzmany, H.; Soldatov, A.; Persson, P.; Jacobsson, P.; Sundqvist, B. *Phys. Rev. B* **1996**, *54*, 17 486–17 492.
- (10) (a) Brumm, H.; Peters, E.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2069–2071. (b) Wedig, U.; Brumm, H.; Jansen, M. *Chem. Eur. J.* **2002**, *8*, 2769–2774.
- (11) (a) Bendele, G.; Stephens, P.; Prassides, K.; Vavekis, K.; Kortados, K.; Tanigaki, K. *Phys. Rev. Lett.* **1998**, *80*, 736–739. (b) Margadonna, S.; Prassides, K.; Knudsen, K.; Hanfland, M.; Kosaka, M.; Tanigaki, K. *Chem. Mater.* **1999**, *11*, 2960–2965.
- (12) Broderick, W. E.; Choi, K. W.; Wan, W. C. *Electrochemical Soc. Proc.* **1997**, *14*, 1102–1113.
- (13) Oszlányi, G.; Baumgarther, G.; Faigel, G.; Forró, L. *Phys. Rev. Lett.* **1997**, *78*, 4438–4441.

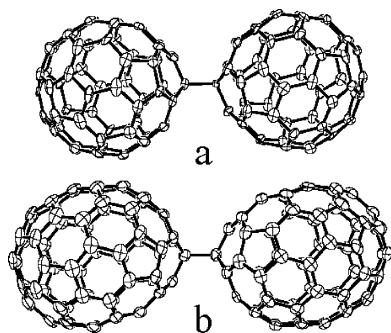


Figure 1. Molecular structure of the (C₆₀⁻)₂ dimer in Cp*₂Cr·C₆₀⁻ (C₆H₄Cl₂)₂ (**1**)¹⁸(a); and the (C₇₀⁻)₂ dimer in CTV·(Cs)₂(C₇₀)₂(DMF)₇·(C₆H₆)_{0.75} (**3**)¹⁹ (b).

Table 1. UV–vis–NIR Spectra of **1–10**

donor	solution		solid state in KBr pellets			
	bands, nm	attribution ^a	N	state at RT	UV	NIR range
Cp* ₂ Cr	840, 941, 1313 (CH ₃ CN)	C ₆₀ ²⁻	1	C ₆₀ ⁻	–, 340	935, 1080
			2	C ₆₀ ⁻	–, 340	932, 1082
Cr(C ₆ H ₆) ₂	941, 1073 (CH ₃ CN)	C ₆₀ ⁻ +C ₆₀ ²⁻	3	(C ₇₀ ⁻) ₂ dimer	–	910, 1240
			4	C ₆₀ ⁻	265, 341	936, 1078
			5	C ₆₀ ⁻	267, 345	935, 1073
			6	(C ₇₀ ⁻) ₂ dimer	–	910, 1240
			7	(C ₆₀ ⁻) ₂ dimer or polymer	261, 335	906, 1060, 1240
Cp ₂ Co	827, 940 (CH ₃ CN)	C ₆₀ ²⁻	8	C ₆₀ ⁻	266, 342	935, 1080
			9	(C ₇₀ ⁻) ₂ dimer	–	910, 1240
Cp ₂ Cr	933, 1077 (C ₆ H ₅ CN)	C ₆₀ ⁻	10	(C ₇₀ ⁻) ₂ dimer	–	910, 1240

^a The characteristic absorption bands of C₆₀⁻ in C₆H₅CN are at 936–940 and 1080–1081 nm and those of C₆₀²⁻ in C₆H₅CN are at 840–844, 955–957, and 1321–1332 nm.²⁴

attributed to the C₆₀⁻ dimerization was observed in Cr(C₆H₅Me)₂·C₆₀ at 250 K, whose crystal structure was investigated by X-ray powder diffraction.^{16,17} Recently, single crystals of ionic C₆₀ complex: Cp*₂Cr·C₆₀⁻(C₆H₄Cl₂)₂ have been prepared and the molecular structure of the (C₆₀⁻)₂ dimer has been determined (Figure 1a).¹⁸ The phase transition associated with the C₆₀⁻ dimerization was observed at 220–200 K. Single-bonded (C₇₀⁻)₂ dimers (Figure 1b) were found in CTV·(Cs)₂·(C₇₀)₂·(DMF)₇·(C₆H₆)_{0.75},¹⁹ Cr(C₆H₆)₂·C₇₀⁻·C₆H₅Me,²⁰ and TDAE·C₇₀⁻·C₆H₅Me.²¹ The formation of the (C₇₀⁻)₂ dimers in the first

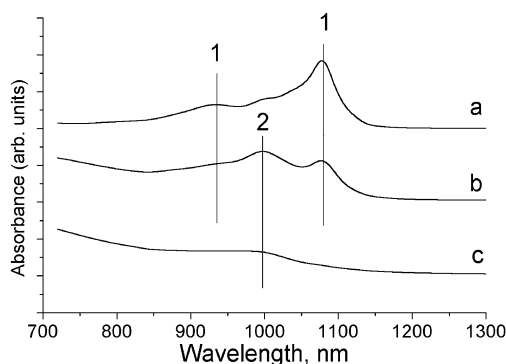


Figure 2. Vis–NIR spectra of the benzonitrile solution containing C₆₀ and Cp₂Cr at a 1:10 molar ratio: (a) 2 minutes after the preparation; (b) 1.5 hours after the preparation; (c) 3 hours after the preparation. Lines show the bands ascribable to C₆₀⁻ (1) and zwitter-ion (Cp₂Cr⁺–C₆₀⁻) (2).

and the latter complexes was justified by the X-ray diffraction on a single crystal.^{19,21} The study of these complexes seems promising due to that variation of donor and solvent molecules involved in the complex can lead to different dimers and polymers, whereas the possibility of the preparation of single crystals provides their structural characterization.

We systematically studied new ionic C₆₀ and C₇₀ complexes with strong donors, namely, decamethylchromocene (Cp*₂Cr, E⁺⁰/_{1/2} = –1.04 V²²), bis(benzene)chromium (Cr(C₆H₆)₂, E⁺⁰/_{1/2} = –0.72 V²³), cobaltocene (Cp₂Co, E⁺⁰/_{1/2} = –0.91 V²²), chromocene (Cp₂Cr, E⁺⁰/_{1/2} = –0.55 V²²) (all E⁺⁰/_{1/2} vs. SCE), and cesium both in solution and solid state. The complexes were characterized by the elemental analysis, IR, UV–vis–NIR spectra, EPR, and SQUID measurements. The phase transitions attributed to the C₆₀⁻ dimerization were found and the dimeric (C₆₀⁻)₂ and (C₇₀⁻)₂ phases were characterized. The IR and UV–vis–NIR spectra of σ -bonded negatively charged fullerenes have been presented. The reversibility of dimerization and the effect of the donor and solvent molecules involved in the complex on dimerization temperatures were studied.

Results and Discussion

Formation of Ionic Complexes. The interaction of C₆₀ with donors was studied in solution. C₆₀ and a 10-fold molar excess of the donors were dissolved in benzonitrile (C₆H₅CN) or acetonitrile (CH₃CN) in anaerobic conditions. According to the NIR spectra, C₆₀ was reduced by Cp₂Cr to C₆₀⁻, Cr⁰(C₆H₆)₂ to form the mixture of C₆₀⁻ and C₆₀²⁻, and Cp*₂Cr and Cp₂Co to C₆₀²⁻ (Table 1).^{8a,24} The spectra of solutions remain unchanged during several hours (excepting Cp₂Cr) indicating the formation of stable ions.

Dissolution of Cp₂Cr and C₆₀ produces initially violet solution in C₆H₅CN, which turns red-brown in 1.5 h and green-brown in 3 h. The NIR spectra (Figure 2) show the decay of characteristic absorption of C₆₀⁻ at 933 and 1077 nm and the evolution of a new broad peak with the maximum at 1000 nm. The total intensity of absorption in the NIR range also decreases with time. Such a change is similar to that in the interaction of C₆₀ with unsaturated amines 1,8-diazabicyclo-[5,4,0]-undec-7-

- (14) (a) Zhu, Q.; Cox, D. E.; Fischer, J. E. *Phys. Rev. B* **1995**, *51*, 3966–3969. (b) Oszlányi, G.; Bortel, G.; Faigel, G.; Tegze, M.; Grárásy, L.; Pekker, S.; Stephens, P. W.; Bendele, G.; Dinnebie, R.; Mihály, G.; Jánosy, A.; Chauvet, O.; Forró, L. *Phys. Rev. B* **1995**, *51*, 12 228–12 232. (c) Oszlányi, G.; Bortel, G.; Faigel, G.; Grárásy, L.; Bendele, G.; Stephens, P. W.; Forró, L. *Phys. Rev. B* **1996**, *54*, 11 849–11 852; (d) Kosaka, M.; Tanigaki, K.; Tanaka, T.; Atake, T.; Lappas, A.; Prassides, T. *Phys. Rev. B* **1995**, *51*, 12 018–12 021.
- (15) (a) Hummelen, J. C.; Kight, B.; Pavlovich, J.; Gonzales, R.; Wudl, F. *Science* **1995**, *269*, 1554–1556. (b) Simon, F.; D. Aréon, D.; Tagmatarchis, N.; Garaj, S.; Forro, L.; Prassides, K.; *J. Phys. Chem. A* **1999**, *103*, 6969–6971. (c) Hasharoni, K.; Bellavia-Lund, C.; Keshavarz-K. M.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 11 128–11 129.
- (16) Hönnerscheid, A.; Wüllen, L.; Jansen, M.; Rahmer, J.; Mehring, M. *J. Chem. Phys.* **2001**, *115*, 7161–7165.
- (17) Hönnerscheid, A.; Dinnebie, R.; Jansen, M.; *Acta Crystallogr. Sect. B* **2002**, *58*, 482–488.
- (18) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Saito, G. *J. Am. Chem. Soc.* **2002**, *124*, 8520–8521.
- (19) Konarev, D. V.; Khasanov, S. S.; Vorontsov, I. I.; Saito, G.; Antipin, Yu. M.; Otsuka, A.; Lyubovskaya, R. N. *Chem. Commun.* **2002**, 2548–2549.
- (20) Yoshida, Y.; Otsuka, A.; Konarev, D. V.; Saito, G. *Synth. Met.* **2003**, *133–134*, 703–705.
- (21) Oshima, K.; Kambe, T.; Fujiwara, M.; Nogami, Y. *Synth. Met.* **2003**, *133–134*, 609–701.

- (22) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882–1893.
- (23) Treichel, P. M.; Essenschmayer, G. P.; Efner, H. F.; Klabunde, K. J. *Inorg. Chim. Acta* **1981**, *48*, 41–44.
- (24) Konarev, D. V.; Driehko, N. V.; Graja, A. *J. Chim. Phys.* **1998**, *95*, 2143–2156.

Table 2. Data for the Crystals of 1–10

N	complex	elemental analysis			found/calcd.			color and shape
		C, %	H, %	N, %	Cl, %	O, %	M, %	
1	Cp* ₂ Cr·C ₆₀ ·(C ₆ H ₄ Cl ₂) ₂	according to X-ray diffraction data ¹⁸						black parallelepipeds
2	Cp* ₂ Cr·C ₆₀ ·(C ₆ H ₆) ₂	88.19 /89.77	3.25 /3.41	0.0 /0.0		8.56 ^a /2.60	4.22 /4.22	black parallelepipeds
3	CTV·(Cs) ₂ ·(C ₇₀) ₂ ·(DMF) ₇ ·(C ₆ H ₆) _{0.75}	according to X-ray diffraction data ¹⁹						black hexagonal plates
4	Cr(C ₆ H ₆) ₂ ·C ₆₀ ·(C ₆ H ₄ Cl ₂) _{0.7}	85.14 /86.04	1.37 /1.39		4.67 /4.67	8.82 ^a /3.01	4.89 /4.89	black-brown polycrystals
5	Cr(C ₆ H ₆) ₂ ·C ₆₀ ·C ₆ H ₅ CN	88.25 /89.19	1.91 /1.60	1.42 /1.31	0.0 /0.0	8.42 ^a /3.01	4.89 /4.89	black parallelepipeds
6	Cr(C ₆ H ₆) ₂ ·C ₇₀ ·C ₆ H ₄ Cl ₂	85.88 /86.08	1.49 /1.30		4.76 /5.78	7.87 ^a /2.60	4.24 /4.24	black-brown polycrystals
7	Cr(C ₆ H ₆) ₂ ·C ₆₀	89.65 /90.16	1.85 /1.73			8.5 ^a /3.10	5.01 /5.01	black-brown powder
8	Cp ₂ Co·C ₆₀ ·C ₆ H ₄ Cl ₂	84.21 /83.84	2.27 /1.28		5.70 /6.52	7.82 ^a /2.94	5.42 /5.42	black polycrystals
9	Cp ₂ Co·C ₇₀ ·(C ₆ H ₄ Cl ₂) _{0.5}	86.48 /87.79	1.65 /1.06	0.0 /0.0	2.86 /3.13	9.01 ^a /2.82	5.20 /5.20	black polycrystals
10	C ₈ ·C ₇₀ ·(DMF) ₅	74.62 /75.21	2.12 /2.55	4.23 /4.37		19.09 ^a /8.17	9.70 /9.70	elongated plates

^a Calculated by the difference (100%) – ((C, H, Cl, N), %)

ene and 1,1',3,3'-tetramethyl-Δ^{2,2'}-bi(imidazoline) in C₆H₅CN.²⁵ In both cases, this interaction can be described by a two-step model. On the first fast step C₆₀ is reduced by chromocene to form individual Cp₂Cr⁺ and C₆₀^{•-} ions. The second slow step is the addition of Cp₂Cr⁺ to C₆₀^{•-} accompanied by the formation of covalently linked (probably by η²-type) zwitter-ionic compound (Cp₂Cr⁺–C₆₀^{•-}) followed by radical recombination in this compound (Cp₂Cr–C₆₀). The reaction of C₆₀ with vanadocene,²⁶ titanocene,²⁷ and nickelocene²⁸ also yields the (η²-Cp₂M)_xC₆₀ compounds.

The crystals of C₆₀ and C₇₀ complexes (Table 2) with Cp*₂Cr, Cr⁰(C₆H₆)₂, and Cp₂Co were obtained by dissolution of fullerene and corresponding donor in C₆H₄Cl₂ (**1**, **4**, **6**, and **8**), C₆H₆/C₆H₅CN (**2**, and **5**), C₆H₄Cl₂/C₆H₅CN (**9**), and C₆H₆/DMF (**3**, **10**) mixtures and their crystallization during slow diffusion of hexane. Mixing C₆₀ and Cr⁰(C₆H₆)₂ in C₆H₆ or C₆H₅Me results in solid polycrystalline **7**.

C₆₀ Complexes with Decamethylchromocene (Cp*₂Cr). C₆₀ forms Cp*₂Cr·C₆₀·(C₆H₄Cl₂)₂ (**1**), and Cp*₂Cr·C₆₀·(C₆H₆)₂ (**2**) depending on solvent used.

The IR and vis–NIR spectra of **1** and **2** are similar at room temperature (RT = 285 K) and show the ionic ground state of the complexes with monomeric C₆₀^{•-}. It was justified by the shift of F_{1u}(4) mode of C₆₀ in the complexes to 1392–1393 cm⁻¹ relative to C₆₀ (1429 cm⁻¹) and the essential increase of the integral intensities of F_{1u}(2) (575 cm⁻¹) and F_{1u}(4) modes relative to that of F_{1u}(1) mode (526 (**1**) and 523 (**2**) cm⁻¹) as in C₆₀^{•-} radical anion salts (Rb⁺)·(C₆₀^{•-})²⁹ and (Ph₄X⁺)₂·(C₆₀^{•-})·(Y⁻) (X = P, As; Y = Cl, I).³⁰ The intense bands in the solid-state vis–NIR spectra of **1** and **2** (Table 1) also indicate the formation

of C₆₀^{•-}.^{8a,24} The band of neutral Cp*₂Cr at 418 cm⁻¹ is shifted to 437 cm⁻¹ in **1**, to 438 cm⁻¹ in **2** and to 437 cm⁻¹ in ionic (Cp*₂Cr⁺)·(PF₆⁻),²² indicating the formation of Cp*₂Cr⁺ in **1** and **2**. The absence of additional bands in the IR spectra, excepting solvent ones, which must appear at dimerization or polymerization of C₆₀^{•-}³¹ corresponds to the monomeric state of C₆₀^{•-}.

The fragment of the RT crystal structure of **1**¹⁸ is shown in Figure 3a. The complex contains orientationally disordered monomeric C₆₀^{•-} and ordered Cp*₂Cr⁺ (not depicted in Figure 3a). The C₆H₄Cl₂ molecules are disordered between two orientations linked to each other by rotation about the mass center in the molecular plane. Monomeric C₆₀^{•-} forms the zigzag chains along the diagonal to the *ac*-plane with the equal center-to-center distance of 10.10 Å (10.02 Å for pristine C₆₀ at RT³²).

A reversible structural transformation accompanied by the unit cell multiplication takes place upon cooling **1** below 220–200 K. The zigzag chain arrangement of C₆₀^{•-} is observed in a low-temperature (100 K) dimeric structure as well (Figure 3b). However, the distances between the centers of C₆₀^{•-} are not equal: one short distance of 9.28 Å indicates the formation of a σ-bonded (C₆₀^{•-})₂ dimer and the second distance of 9.91 Å is close to that in the RT structure of **1** and pristine C₆₀ at 153 K (9.94 Å³³).

The (C₆₀^{•-})₂ dimers are statistically disordered between two orientations linked to each other by rotation of (C₆₀^{•-})₂ about the intercage C–C bond by an angle of 142°. The occupancy factors are 0.75 and 0.25. The length of intercage C–C bond in the (C₆₀^{•-})₂ dimer is 1.597(7) Å. The estimated intercage C–C bond dissociation energy is 63 ± 4¹⁸ and 35 ± 5 kJ·mol⁻¹ for **1** and **2**, respectively.

Magnetic susceptibilities of **1** and **2** were measured in the 300–1.9 K range (Table 3). The temperature dependencies of their magnetic moments (μ_{eff}) are presented in Figure 4. The

- (25) (a) Skiebe, A.; Hirsch, A.; Klos, H.; Gotschy, B. *Chem. Phys. Lett.* **1994**, *220*, 138–140. (b) Schilder, A.; Gotschy, B.; Seidl, A.; Gompper, R. *Chem. Phys.* **1995**, *193*, 321–326.
 (26) Cherkasov, V. K.; Rad'kov, Yu. F.; Lopatin, M. A.; Bochkarev, M. N. *Russ. Chem. Bull.* **1994**, *43*, 1834–1836.
 (27) Burlakov, V. V.; Usatov, A. V.; Lyssenko, K. A.; Antipin, M. Yu.; Novikov, Yu. N.; Shur, V. B. *Eur. J. Inorg. Chem.* **1999**, 1855–1857.
 (28) Konarev, D. V.; Lyubovskaya, R. N.; Drichko, N. V.; Yudanova, E. I.; Shul'ga, Yu. M.; Litvinov, A. L.; Semkin, V. N.; Tarasov, B. P. *J. Mater. Chem.* **2000**, 803–818.
 (29) Picher, T.; Winkler, R.; Kuzmany, H. *Phys. Rev. B, Solid State* **1994**, *49*, 15 879–15 889.
 (30) Semkin, V. N.; Spitsina, N. G.; Krol, S.; Graja, A. *Chem. Phys. Lett.* **1996**, *256*, 616–622.

- (31) Dresselhaus, M. S.; Dresselhaus, G. In *Fullerene Polymers and Fullerene Polymer Composites*; Eklund, P. C., Rao, A. M., Eds.; Springer-Verlag: Berlin, 1999, p 1–57.
 (32) Heiney, P. A.; Fischer, J. E.; McGhie, A. R.; Romanov, W. J.; Denenstien, A. M.; McCauley, J. P., Jr.; Smith, A. B., III; Cox, D. E. *Phys. Rev. Lett.* **1991**, *67*, 1468–1468.
 (33) Burgi, H.-B.; Blanc, E.; Schwarzenbach, D.; Liu, S.; Lu, Y.-J.; Kappers, M. M.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 640–643.

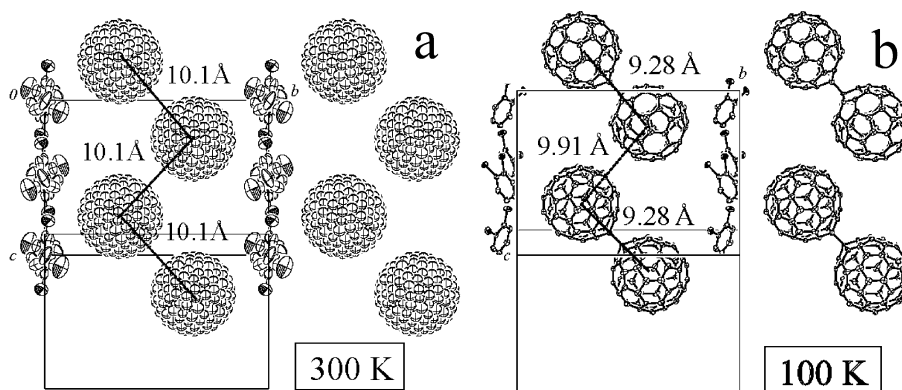


Figure 3. Packing of C_{60}^- and $C_6H_4Cl_2$ in $Cp^*_2CrC_{60}(C_6H_4Cl_2)_2$ (**1**) at 300 (a) and 100 K (b). $Cp^*_2Cr^+$ cations are omitted for clarity. The view along the diagonal to the ac -plane is shown. Zigzag chains from C_{60}^- are shown by dashed lines. Only the major orientation of the $(C_{60}^-)_2$ dimers is shown for low temperature structure (b).

Table 3. Data of Magnetic Measurements

N	Θ , K (temp range, K)	observed μ_{eff}, μ_B (temp. range, K)	calculated μ_{eff}, μ_B per formula unit
1	-1.12 (50–190)	3.85 (50–190)	3.87 ($S = 3/2$)
		4.20 (240–300)	4.27 ($S = 3/2, 1/2$)
2	-0.85 (10–160)	3.80 (10–160)	3.87 ($S = 3/2$)
		4.14 (190–300)	4.27 ($S = 3/2, 1/2$)
3	-0.51 (2–350)		Complex is diamagnetic ($\chi_0 = -0.0017 \text{ emu} \cdot \text{mol}^{-1}$). The Curie tail corresponds to 2.4% of total C_{70}
4	-0.06 (10–140)	1.73 (10–160)	1.73 ($S = 1/2$)
		2.40–2.45 (240–300)	2.45 ($S = 1/2, 1/2$)
5	-0.18 (10–220)	1.74 (10–220)	1.73 ($S = 1/2$)
		2.12 (300)	2.12 (intermediate value between $S = 1/2$ and $S = 1/2, 1/2$)
6	-0.06 (10–250)	1.64 (10–250)	1.73 ($S = 1/2$)
		1.78 (300)	
7	-3.5 (70–300)	1.80 (70–300)	1.73 ($S = 1/2$)
8	-0.72 (2–250)	0.04–0.08 (1.9–250)	Complex is diamagnetic. The Curie tail corresponds to 3.3% of total C_{60}
			1.73 ($S = 1/2$)
10	-0.46 (2–350)	1.52 (350–380)	Complex is diamagnetic ($\chi_0 = -0.0025 \text{ emu} \cdot \text{mol}^{-1}$). The Curie tail corresponds to 0.7% of total C_{70}

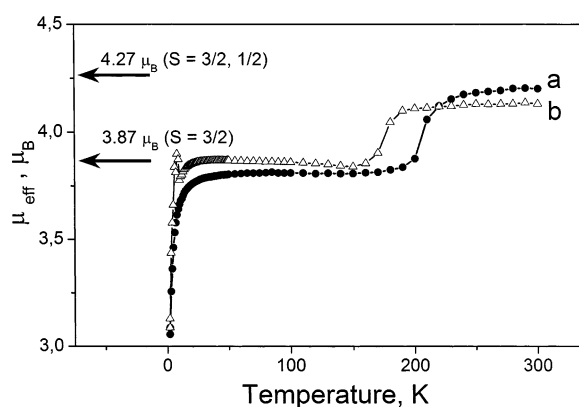


Figure 4. Dependencies of the magnetic moment (μ_{eff}) vs temperature for polycrystalline (a) $Cp^*_2CrC_{60}(C_6H_4Cl_2)_2$ (**1**), and (b) $Cp^*_2Cr(C_{60})(C_6H_6)_2$ (**2**) between 300 and 1.9 K. The behavior is reversible.

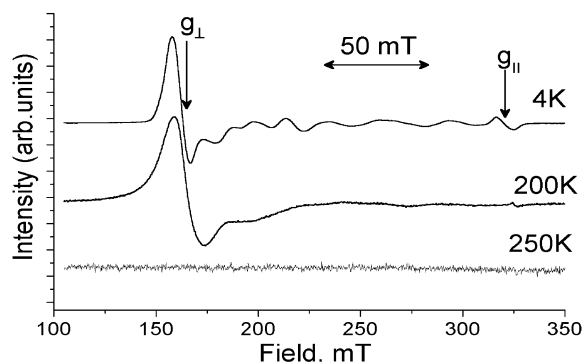
magnetic moments are equal to 4.14–4.20 μ_B at 300 K (the μ_{eff} for the noninteracting $S = 3/2, 1/2$ system is 4.27 μ_B). Therefore, both spins from $Cp^*_2Cr^+$ ($S = 3/2$) and $C_{60}^{\bullet-}$ ($S = 1/2$) contribute to magnetic susceptibility. A close value of 4.20 μ_B was observed in $(Cr^{III}TPP^+)(C_{60}^{\bullet-})(THF)_3$ with the same spin state ($S = 3/2, 1/2$). A stepwise reversible decrease in the magnetic moment of **1** and **2** from 4.14 to 4.20 down to 3.81–3.88 μ_B was detected in the 230–200 K and 190–160 K ranges for **1** and **2**, respectively (Figure 4). Below these temperatures

the magnetic moments are defined by the spins localized on $Cp^*_2Cr^+$ (the μ_{eff} for the $S = 3/2$ system is 3.87 μ_B). The decrease in the magnetic moment of **1** and **2** clearly indicates the disappearance of the contribution of $C_{60}^{\bullet-}$ spins ($S = 1/2$) consistent with the reversible formation of the diamagnetic $(C_{60}^-)_2$ dimers. The reversible decrease of the magnetic moment from 2.5 μ_B down to 1.72 μ_B was also observed in $Cr(C_6H_5Me)_2 \cdot C_{60}$ at 250 K as a result of $C_{60}^{\bullet-}$ dimerization.¹⁶ The decrease in the magnetic moments of **1** and **2** below 30 K (Figure 4) indicates a weak antiferromagnetic interaction between the $Cp^*_2Cr^+$ spins. However, the spin ordering was not observed down to 1.9 K.

The EPR signals for **1** and **2** were not observed at RT (Figure 5 shows the EPR spectrum of **1** at 250 K). Similarly, ionic $Cr^{III}TPP \cdot C_{60} \cdot (THF)_3$ is EPR silent in the 300–4 K range.⁷ It can be assumed that monomeric $C_{60}^{\bullet-}$ and $Cp^*_2Cr^+$ can give one very broad resonating signal via a strong exchange coupling between these ions. Upon cooling **1** below 220–200 K (Figure 5, 200 and 4 K) and **2** below 180–160 K, new signals appear in the EPR spectra. The signal in **1** is asymmetric and is characterized by resonances near $g_{\perp} = 3.974$ with the line half-width (ΔH) of 7 mT and $g_{\parallel} = 2.013$ with $\Delta H = 5.5$ mT at 4 K. This signal can be ascribed to $Cp^*_2Cr^+$ with $S = 3/2$ ground state. Solid $(Cp^*_2Cr^+)(PF_6^-)^{22}$ produces a similar EPR signal with $g_{\perp} = 4.02(1)$ and $g_{\parallel} = 2.001(1)$. The g-factor and ΔH of

Table 4. EPR Parameters (*g*-factor and the line half-width (ΔH)) for **1–10** at RT (285 K) and 4 K

N	RT		attribution of the signal	4 K		attribution of the signal
	<i>g</i> -factor	ΔH , mT		<i>g</i> -factor	ΔH , mT	
1	not observed			3.974	7.0	Cp* ₂ Cr ⁺ (<i>S</i> =3/2), <i>g</i> _⊥
				3.728	12.3	
				3.467	14.0	
				2.013	5.5	
2	not observed			3.937	7.7	<i>g</i> _∥ Cp* ₂ Cr ⁺ (<i>S</i> =3/2), ⊥
				3.784	17.0	
				3.417	18.8	
3	2.0042	0.8	impurity (<0.4% of total C ₇₀)			
	2.0024	0.2				
	1.9923	2.0				
4	1.9913	3.30	Cr ^I (C ₆ H ₆) ₂ ^{•+} + C ₆₀ ^{•-}	1.9858	2.21	Cr ^I (C ₆ H ₆) ₂ ^{•+}
5	1.9910	2.94	Cr ^I (C ₆ H ₆) ₂ ^{•+} + C ₆₀ ^{•-}	1.9949	2.78	Cr ^I (C ₆ H ₆) ₂ ^{•+} , <i>g</i> _∥
				1.9835	2.46	
6	1.9857	3.10	Cr ^I (C ₆ H ₆) ₂ ^{•+}	1.9859	2.75	Cr ^I (C ₆ H ₆) ₂ ^{•+}
7	1.9977	1.71	Cr ^I (C ₆ H ₆) ₂ ^{•+} , <i>g</i> _∥	1.9957	2.02	Cr ^I (C ₆ H ₆) ₂ ^{•+} , <i>g</i> _∥
8	1.9901	1.74	<i>g</i> _⊥	1.9858	1.74	<i>g</i> _⊥
8	1.9988	3.97	C ₆₀ ^{•-}	1.9979	0.5	C ₆₀ ^{•-} (calc. 2–3% of total C ₆₀)
9	2.0025	0.26	impurities (<0.1% of total C ₇₀)	1.9998	0.3	trace of C ₇₀ ^{•-}
9	2.0013	0.15	C ₇₀	2.0047	0.76	impurity
10	2.0025	0.22	impurity (<1% of total C ₇₀)	2.0027	0.36	impurity

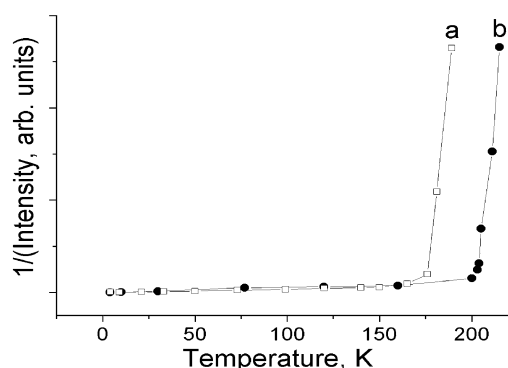
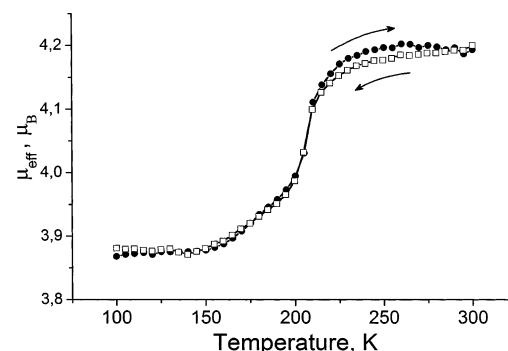
**Figure 5.** EPR spectrum of polycrystalline Cp*₂CrC₆₀(C₆H₄Cl)₂ (**1**) at 4200 and 250 K.

the EPR signal from Cp*₂Cr⁺ in **1** and **2** only weakly depend on temperature down to 4 K. The *g*_⊥-component of the EPR signal of polycrystalline **1** is strongly asymmetric and consists of at least 9 components. The most intense component has *g*₁ = 3.974 and ΔH = 7 mT and each next component shifts to smaller *g*-factor and becomes wider (Table 4). For **2** the spectrum is similar. The asymmetric EPR signals in **1** and **2** are probably a result of polycrystallinity of the samples.

The temperatures of the appearance of the EPR signals from Cp*₂Cr⁺ in **1** and **2** (Figure 6) correlate with those of the disappearance of the contribution of the C₆₀^{•-} spins to magnetic susceptibility (Figure 4). The formation of the diamagnetic (C₆₀⁻)₂ dimer breaks down the exchange coupling between Cp*₂Cr⁺ and monomeric C₆₀^{•-} at RT and leads to EPR active species containing paramagnetic Cp*₂Cr⁺ and the diamagnetic (C₆₀⁻)₂ dimers at low temperatures.

The temperature dependency of magnetic susceptibility of polycrystalline **1** in the cooling and heating processes was studied in the 100–300 K range (Figure 7). At a slow rate (5 K per minute, the waiting time is 3 h at 100 and 300 K) the temperature dependency of magnetic moment of **1** is nearly the same for both processes with the hysteresis smaller than 2 K.

Complex of C₇₀ Fulleride with Cyclotrimeratrylene (CTV). According to the X-ray diffraction on a single crystal the multi-component complex CTV·(C₅)₂·(C₇₀)₂·(DMF)₇·(C₆H₆)_{0.75} (**3**)

**Figure 6.** Temperature dependencies of reversible intensity of the EPR signal from Cp*₂Cr⁺ (*S* = 3/2) in polycrystalline (a) Cp*₂Cr(C₆₀)(C₆H₆)₂ (**2**) and (b) Cp*₂CrC₆₀(C₆H₄Cl)₂ (**1**).**Figure 7.** Temperature dependency of magnetic moment (μ_{eff}) for polycrystalline Cp*₂CrC₆₀(C₆H₄Cl)₂ (**1**) upon the heating (full circles) and cooling (open squares) processes.

contains single-bonded (C₇₀⁻)₂ dimers, which begin to dissociate above 300 K, and the abrupt increase in the magnetic moment is observed only above 360 K. The length of the inter cage C–C bond in the (C₇₀⁻)₂ dimer was found to be 1.584(9) Å.¹⁹

The IR and UV–vis–NIR spectra of **3** indicate an essential spectral difference between the (C₇₀⁻)₂ dimers and the monomeric C₇₀^{•-} radical anions (Figure 8). The solid NIR spectrum of (C₇₀⁻)₂ is specified by the presence of two bands at 910 and 1240 nm (Figure 8b) instead of one band at 1373 nm in the

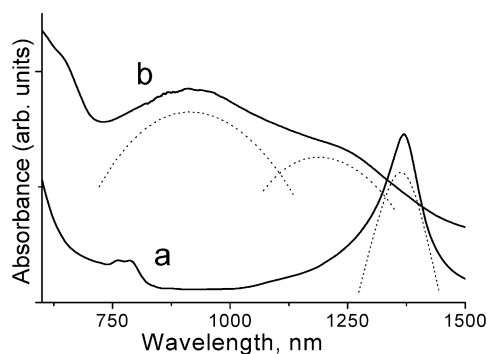


Figure 8. Vis–NIR spectra of (a) monomeric C_{70}^- generated in the $C_6H_4Cl_2$ solution by the reduction of C_{70} with an equimolar amount of $Cr(C_6H_6)_2$; and (b) the $(C_{70}^-)_2$ dimer in polycrystalline $CTV(Cs)_2(C_{70}^-)_2(DMF)_7(C_6H_6)_{0.75}$ (**3**) in KBr pellet.

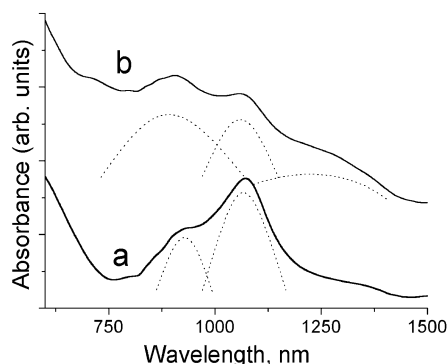


Figure 9. Vis–NIR spectra of (a) monomeric C_{60}^- in polycrystalline $Cr(C_6H_6)_2C_{60}(C_6H_4Cl_2)_{0.7}$ (**4**); and (b) the $(C_{60}^-)_2$ dimer or polymer in polycrystalline $Cr(C_6H_6)_2C_{60}$ (**7**) in KBr pellets.

solution spectrum of C_{70}^- (Figure 8a). The IR spectrum of $(C_{70}^-)_2$ consists of more than 20 bands,¹⁹ whereas only 10 bands are pronounced in the spectrum of parent C_{70} . The appearance of additional “silent” modes is attributed to C_{70}^- symmetry breaking in the dimer. These modes can be used to identify the $(C_{70}^-)_2$ dimers in the complexes.

C_{60} and C_{70} Complexes with Bis(benzene)chromium ($Cr(C_6H_6)_2$). Bis(benzene)chromium complexes of C_{60} and C_{70} : $Cr(C_6H_6)_2 \cdot C_{60} \cdot (C_6H_4Cl_2)_{0.7}$ (**4**), $Cr(C_6H_6)_2 \cdot C_{60} \cdot C_6H_5CN$ (**5**), $Cr(C_6H_6)_2 \cdot C_{70} \cdot C_6H_4Cl_2$ (**6**), and $Cr(C_6H_6)_2 \cdot C_{60}$ (**7**) have been obtained. According to the IR spectra, **4** and **5** also have the ionic ground state with monomeric C_{60}^- . $F_{1u}(4)$ C_{60} mode shifts in the complexes to 1388 – 1390 cm^{-1} whereas the bands of neutral $Cr^0(C_6H_6)_2$ at 459 and 490 cm^{-1} shift to 418 – 419 and 460 cm^{-1} in **4** and **5** as in $Cr^I(C_6H_6)_2^{+}(I^-)$.³⁴ The solid NIR spectra of **4** and **5** contain the bands attributable to C_{60}^- (Table 1, Figure 9 a).

The SQUID and EPR data for **4** and **5** are listed in Tables 3 and 4. The magnetic moment of **4** at RT ($2.45 \mu_B$) is close to calculated one for the $S = 1/2, 1/2$ system. These spins are localized on $Cr^I(C_6H_6)_2^{+}$ and C_{60}^- . The magnetic moment stepwise and reversibly decreases below 240 K down to $1.73 \mu_B$ at 160 K (Figure 10, **4**) (μ_{eff} for $S = 1/2$ system is $1.73 \mu_B$). This decrease is accompanied by the changes in the EPR spectrum. The EPR signal of **4** has $g = 1.9913$ at RT (Figure 11, **4**). This value is intermediate between those for $Cr^I(C_6H_6)_2^{+}$ ($g = 1.986^{35}$) and C_{60}^- ($g = 1.998^{8a}$) indicating strong exchange

coupling between these ions. On cooling **4** in the 240 – 150 K range the g -factor shifts to 1.986 , that is characteristic of $Cr^I(C_6H_6)_2^{+}$ ³⁵ (Figure 11, **4**).

The magnetic moment of **5** is $1.74 \mu_B$ below 230 K and remains unchanged down to 10 K. Above 230 K the magnetic moment increases with temperature up to $2.12 \mu_B$ at 300 K (the μ_{eff} intermediate between $1.73 \mu_B$ ($S = 1/2$) and $2.45 \mu_B$ ($S = 1/2, 1/2$)) (Figure 10, **5**). Probably, the magnetic moment can further increase with temperature up to $\sim 2.45 \mu_B$ above 350 K.

The EPR behavior of **5** is more complicated than that of **4** (Table 4, Figure 11, **5**). The EPR signal is a Lorentzian line with $g = 1.9910$ and $\Delta H = 3$ mT at RT. The g -factor shifts to 1.988 and the signal becomes narrower as in **4** with the temperature decrease down to 230 K. However, below 230 K, the signal broadens and splits into two components below 150 K ($g_{||} = 1.9949$ and $g_{\perp} = 1.9835$ at 4 K). Such asymmetric signal with $g_{||} = 2.0026$ and $g_{\perp} = 1.9757$ was observed for $Cr^I(C_6H_6)_2^{+}$ in rigid solution.³⁵ The reason for the different symmetric and asymmetric EPR signals from $Cr^I(C_6H_6)_2^{+}$ in **4** and **5** is not clear. However, both SQUID and EPR measurements indicate a reversible disappearance of the contribution of the C_{60}^- spins on cooling **4** and **5** in the 240 – 160 and 300 – 230 K ranges as a result of C_{60}^- dimerization. The interstage C–C bond dissociation energy was estimated from the data of magnetic measurements to be 25 ± 2 and 41 ± 3 $kJ \cdot mol^{-1}$ for **4** and **5**, respectively.

It was shown that in the spectrum of $Cr(C_6H_6)_2 \cdot C_{70} \cdot C_6H_4Cl_2$ (**6**) the IR bands of C_{70} appeared at same position^{36a} as those in the spectrum of **3**¹⁹ containing the $(C_{70}^-)_2$ dimers, whereas the IR bands at 418 and 459 cm^{-1} indicated the presence of $Cr^I(C_6H_6)_2^{+}$. The two characteristic bands at 910 and 1240 nm in the NIR spectrum of **6** (as in Figure 8b) also justify the formation of $(C_{70}^-)_2$.

The magnetic moment of **6** is equal to $1.64 \mu_B$ at 250 K and only slightly increases with temperature up to $1.78 \mu_B$ at 300 K (Figure 10, **6**). The EPR signal of **6** with $g = 1.9857$ (Table 4) at RT is characteristic of $Cr^I(C_6H_6)_2^{+}$ ³⁵ and does not shift with the temperature decrease down to 10 K (Figure 11, **6**). Such a behavior indicates the formation of the $(C_{70}^-)_2$ dimers and the contribution of only $Cr^I(C_6H_6)_2^{+}$ spins to magnetic and spin susceptibility. The increase of the magnetic moment of **6** above 250 K suggests the dissociation of the $(C_{70}^-)_2$ dimers to C_{70}^- (about 8% of total C_{70} at 300 K).

Fast precipitation of the complex in C_6H_6 or C_6H_5Me yields solvent-free $Cr(C_6H_6)_2 \cdot C_{60}$ (**7**).^{12,37} The IR spectrum of **7** is very rich at RT indicating the splitting of four C_{60} modes into three components and the appearance of new weak “silent” modes.^{36b} This spectrum differs from those of **4** and **5** and indicates broken symmetry of C_{60}^- due to the formation of a σ -bonded structure. The formation of linear polymers in $(Rb^+)(C_{60}^-)$ results in similar changes.³⁸ Instead of characteristic bands of C_{60}^- new

(35) Elschenbroich, C.; Bilger, E.; Koch, J. *J. Am. Chem. Soc.* **1984**, *106*, 4297–4299.

(36) (a) The absorption bands in IR-spectrum of **6** attributed to the $(C_{70}^-)_2$ dimer: $494w, 508w, 530s, 548m, 556m, 575m, 628w, 638w, 658w, 668w, 695w, 800s, 713w, 720m, 842m, 901w, 944w, 1110w, 1158m, 1176m, 1209w, 1258w, 1279m, 1307w, 1323m, 1353w, 1363w, 1392s, 1429m, 1415w, 1480w, 1508w, 1540w, 1558m$ cm^{-1} . (b) The absorption bands in IR-spectrum of **7** attributed to the $(C_{60}^-)_2$ dimer or polymer: $499w, 520w, 528w, 540s, 554w, 572s, 607s, 724m, 752w, 774s, 920w, 1010w, 1031w, 1121w, 1172w, 1194m, 1250w, 1322w, 1339w, 1383s, 1406m$ cm^{-1} .

(37) (a) Kaplunov, M. G.; Golubev, E. V.; Kulikov, A. V.; Spitsina, N. G. *Izv. Acad. Nauk, Ser. Khim.* **1999**, 785–787. (b) Yoshida, Y.; Otsuka, A.; Drozdova, O. O.; Saito, G. *J. Mater. Chem.* **2003**, *13*, 252–257.

(34) Fritz, H. P.; Lüttke, W.; Stammreich, H.; Forneris, R. *Chem. Ber.* **1959**, *92*, 3246–3250.

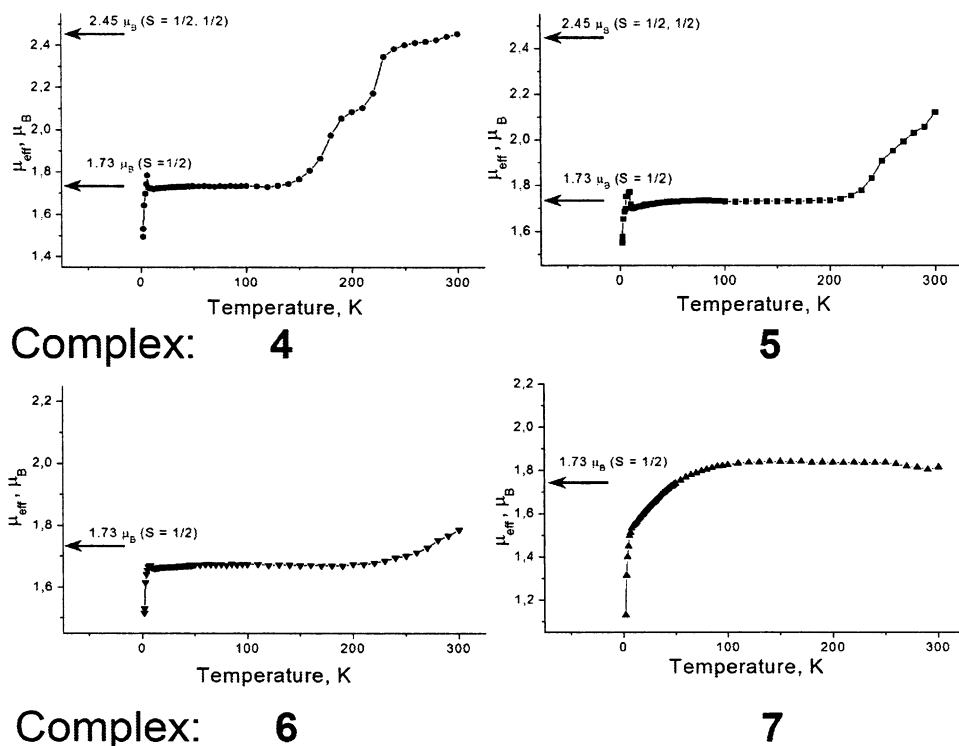


Figure 10. Dependencies of the magnetic moment (μ_{eff}) vs temperature for polycrystalline $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}(\text{C}_6\text{H}_4\text{Cl}_2)_{0.7}$ (**4**); $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_5\text{CN}$ (**5**); $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{70}\cdot\text{C}_6\text{H}_4\text{Cl}_2$ (**6**); and $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}$ (**7**) between 300 and 1.9 K.

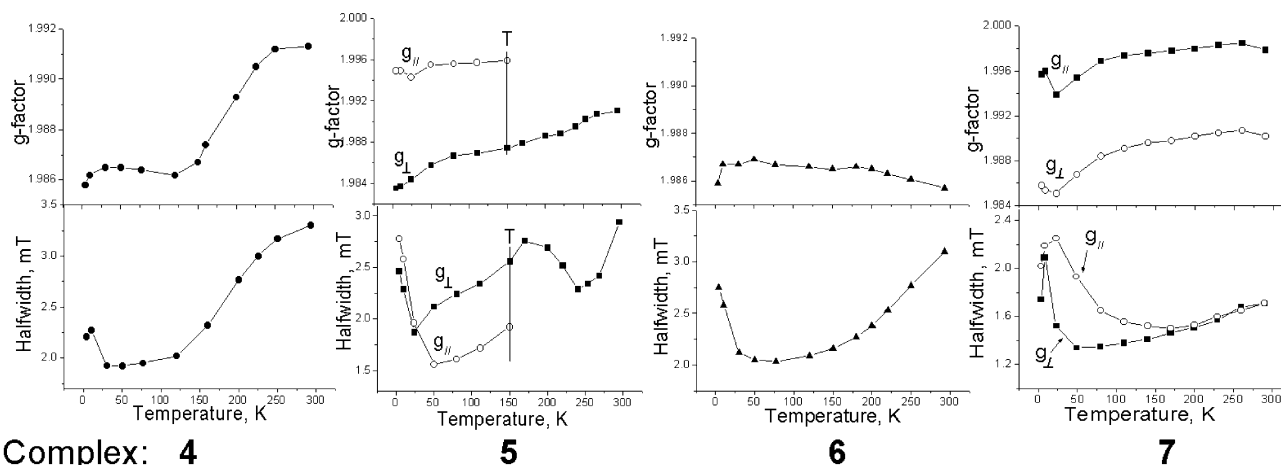


Figure 11. Temperature dependencies of g-factor and the line half-width (ΔH , mT) of the EPR signals from polycrystalline: $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}(\text{C}_6\text{H}_4\text{Cl}_2)_{0.7}$ (**4**); $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_5\text{CN}$ (**5**); $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{70}\cdot\text{C}_6\text{H}_4\text{Cl}_2$ (**6**); and $\text{Cr}(\text{C}_6\text{H}_6)_2\cdot\text{C}_{60}$ (**7**).

bands appear in the NIR spectrum of **7** at 906, 1060, and 1240 nm (Figure 9b). These bands have not been found in the NIR spectra of **4** and **5** containing the same ions and can be attributed to the σ -bonded structure from C_{60}^- .

The magnetic moment of **7** is equal to $1.84 \mu_{\text{B}}$ at 300 K and remains unchanged down to 70 K (Figure 10, **7**) indicating the contribution of one $S = 1/2$ spin. The EPR signal from **7** is asymmetric at RT and has two Lorentzian lines with $g_1 = 1.9979$ and $g_2 = 1.9902$ (Figure 11, **7**) similarly to the data of Broderick et al.¹² These lines can be attributed to the parallel and perpendicular components of the asymmetric signal from $\text{Cr}(\text{C}_6\text{H}_6)_2^{*+}$ (Table 4). The splitting of the EPR signal in **7** is similar to that in **4** below 150 K. The EPR signal of C_{60}^- has

not been found and, hence, the spins are localized mainly on $\text{Cr}(\text{C}_6\text{H}_6)_2^{*+}$. That is evidence of the formation of the $(\text{C}_{60}^-)_2$ dimers. However, the dimer in **7** is stable up to 300 K in contrast to dimers in other complexes studied. Therefore, another σ -bonded nondimeric structure composed of C_{60}^- is also possibly formed. X-ray diffraction data are necessary for the precise determination of this structure.

The magnetic moments of the complexes decrease below 10 K for **4–6** and 70 K for **7** (Figure 10). The EPR signals from **4–7** noticeably broaden below these temperatures (Figure 11) indicating an antiferromagnetic interaction of the $\text{Cr}(\text{C}_6\text{H}_6)_2^{*+}$ spins. The spin ordering is not observed down to 1.9 K.

C₆₀ and C₇₀ Complexes with Cobaltocene (Cp₂Co). Ionic C_{60} complexes: $\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{CS}_2$,⁴ $\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_5\text{CN}$,⁵ and C_{70} complex: $\text{Cp}_2\text{Co}\cdot\text{C}_{70}$ ³⁹ with cobaltocene were characterized,

(38) Kuzmany, H.; Winkler, R.; Pichler, T. *J. Phys. Condens. Matter* **1995**, *7*, 6601–6624.

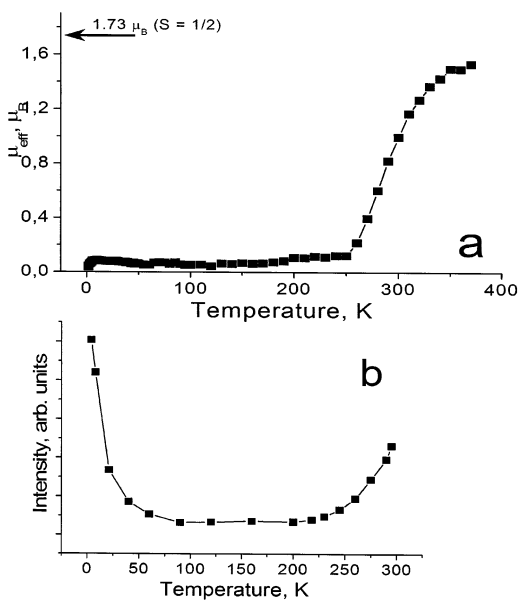


Figure 12. Temperature dependencies of (a) the magnetic moment (μ_{eff}) of $\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_4\text{Cl}_2$ (**8**) in the 1.9–380 K range; and (b) the intensity of the EPR signal from $\text{C}_{60}^{\bullet-}$ in **8** in the 4–285 K range.

and it is shown that they contain monomeric $\text{C}_{60}^{\bullet-}$ (at 123 K)⁴ and $\text{C}_{70}^{\bullet-}$ (at 4–300 K).³⁹ We prepared new C_{60} and C_{70} complexes with cobaltocene $\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_4\text{Cl}_2$ (**8**), and $\text{Cp}_2\text{Co}\cdot\text{C}_{70}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{0.5}$ (**9**), whose electronic states are different from those of the above-mentioned complexes.

The ionic ground state of **8** with monomeric $\text{C}_{60}^{\bullet-}$ at RT is justified by the characteristic bands in IR- and vis-NIR spectra (Table 1). However, the complex is a diamagnetic one in the 1.9–250 K range according to SQUID measurements and contains the diamagnetic Cp_2Co^+ cations and the $(\text{C}_{60}^-)_2$ dimers. The Curie tail in this temperature range corresponds to the contribution of only 3.3% of $S = 1/2$ spins. On heating **8** in the 250–350 K range, the reversible increase in the magnetic moment up to $1.52 \mu_{\text{B}}$ (at 350 K) is observed (Figure 12 a) as a result of the dissociation of the $(\text{C}_{60}^-)_2$ dimers to $\text{C}_{60}^{\bullet-}$. Above 350 K, C_{60}^- exists mainly in a monomeric form. The estimated intercage C–C bond dissociation energy is $52 \pm 3 \text{ kJ mol}^{-1}$.

Two low-temperature signals were observed in the EPR spectrum of **8**. The main signal with $g = 1.9979$ and $\Delta H = 0.5$ (4 K) mT can be ascribed to $\text{C}_{60}^{\bullet-}$. The signal has weak intensity (calc. only 2–3% from the total amount of C_{60}) and the major part of the complex is EPR silent. The paramagnetic contribution (the Curie tail) to magnetic and spin susceptibility of **8** in the 1.9–250 K range is given by only 2–3% of spins localized on $\text{C}_{60}^{\bullet-}$. These spins are preserved in the sample probably due to incomplete $\text{C}_{60}^{\bullet-}$ dimerization at high enough cooling rate. Above 250 K, the intensity of the EPR signal of $\text{C}_{60}^{\bullet-}$ increases (Figure 12, b) in accordance with the magnetic measurements. A narrow weak signal with $g = 1.9998$ and ΔH of 0.3 mT (4 K) attributed to reduced impurities⁴⁰ has an almost temperature independent g-factor and ΔH in the 4–285 K range.

The IR and solid-state NIR (Table 1) spectra of $\text{Cp}_2\text{Co}\cdot\text{C}_{70}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{0.5}$ (**9**) contain bands characteristic of the $(\text{C}_{70}^-)_2$ dimer. Two bands of the $(\text{C}_{70}^-)_2$ dimer at 910 and 1240 nm are

clearly distinguished from single band at 1373 nm in the solid-state spectrum of related $\text{Cp}_2\text{Co}\cdot\text{C}_{70}$ ³⁹ with monomeric $\text{C}_{70}^{\bullet-}$. **9** is EPR silent and shows only a weak EPR signal (<0.1% of total C_{70}) in the 4–285 K range attributable to impurities.⁴⁰ Thus, **9** is formulated as $(\text{Cp}_2\text{Co}^+)_2\cdot[(\text{C}_{70}^-)_2]\cdot(\text{C}_6\text{H}_4\text{Cl}_2)$ below 285 K.

C_{70} Complex with Cs. The complex crystallizes from DMF as $\text{Cs}\cdot\text{C}_{70}\cdot(\text{DMF})_5$ (**10**). The IR and NIR (Table 1) spectra of **10** indicate the formation of the $(\text{C}_{70}^-)_2$ dimers. SQUID measurements show diamagnetism in **10** in the 1.9–350 K range with the contribution of the Curie impurities < 0.7%. Above 350 K the magnetic moment of the complex increases due to dissociation of dimers. **10** is EPR silent in the 4–285 K range and only <1% of spins from total C_{70} contribute to spin susceptibility (Table 4).

Peculiarities of the Formation of the $(\text{C}_{60}^-)_2$ and $(\text{C}_{70}^-)_2$ Dimers in Ionic Complexes. New complexes of fullerenes C_{60} and C_{70} (**1–10**) have an ionic ground state in accordance with redox potentials of donors ($E^{+/0}_{1/2} < -0.55 \text{ V}$), which are more negative than those of fullerenes C_{60} and C_{70} ($E^{0/-}_{1/2} = -0.40$ – -0.44 V).⁴¹ Fullerene radical anions in **1–10** tend to dimerize to form the single-bonded $(\text{C}_{60}^-)_2$ and $(\text{C}_{70}^-)_2$ dimers in contrast to some previously studied ionic complexes ($\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{CS}_2$,⁴ $\text{Cp}_2\text{Co}\cdot\text{C}_{60}\cdot\text{C}_6\text{H}_5\text{CN}$,⁵ $\text{Cp}_2\text{Co}\cdot\text{C}_{70}$,³⁹ and $\text{Cp}^*\text{Ni}\cdot\text{C}_{60}\cdot\text{CS}_2$ ⁶). The possible difference between the complexes **1–10** and previously studied ones is the use of $\text{C}_6\text{H}_4\text{Cl}_2$ as a solvent instead of CS_2 or other solvents. The latter molecules can be inserted between the fullerene spheres^{42,43} thus preventing dimerization. As it is shown in Figure 3, $\text{C}_6\text{H}_4\text{Cl}_2$ tends to form columns^{18,44} allowing a close approach of the fullerene spheres to each other.

Dimerization of $\text{C}_{60}^{\bullet-}$ is reversible with a small hysteresis and affects magnetic properties of the complexes. The single-bonded $(\text{C}_{60}^-)_2$ and $(\text{C}_{70}^-)_2$ dimers are diamagnetic. It is possible that electron on LUMO of fullerene radical anions participates in the formation of the intercage C–C σ -bond. The formation of diamagnetic anions was observed previously on the σ -bonding between the $\text{Co}^{\text{III}}\text{TPP}$ and $\text{C}_{60}(\text{CN})_2^{\bullet-}$ radical anions (in this case electrons from LUMO of fullerene and d_{z^2} of $\text{Co}^{\text{III}}\text{TPP}$ participate in the σ -bonding).⁴⁵ Dimerization results in the decrease of the magnetic moments of the complexes and magnetic dilution of the paramagnetic centers ($\text{D}^{\bullet+}$) by bulky diamagnetic dimers. As a result, the complexes containing fullerene dimers are either diamagnetic or show a paramagnetic behavior with weak antiferromagnetic interactions of spins at low temperatures. The other consequences of dimerization are a break of exchange coupling between cations and fullerene radical anions observed in a high-temperature monomeric phase, and the appearance of the EPR signals from isolated cations in the low-temperature dimeric phase.

The complexes show a semiconductive behavior with RT conductivity of $\sim 10^{-5}$ – $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ (Table 5). These values

(39) Mrzel, A.; Umek, P.; Cevk, P.; Omerzu, A.; Mihailovic, D. *Carbon* **1998**, *36*, 603–606.

(40) Paul, P.; Bolskar, R. D.; Clark, A. M.; Reed, C. A. *Chem. Commun.* **2000**, 1229–1230.

(41) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364–4366.

(42) Konarev, D. V.; Valeev, E. F.; Slovokhotov, Yu. L.; Shul'ga, Yu. M.; Roschupkina, O. S.; Lyubovskaya, R. N. *Synth. Met.* **1997**, *88*, 285–287.

(43) Kveder, V. V.; Steinman, E. A.; Narimbetov, B. Zh.; Khasanov, S. S.; Rozenberg, L. P.; Shibaeva, R. P.; Bazhenov, A. V.; Gorbunov, A. V.; Maksimuk, M. Yu.; Konarev, D. V.; Lyubovskaya, R. N.; Ossipyan, Yu. A. *Chem. Phys.* **1997**, *216*, 407–415.

(44) Konarev, D. V.; Khasanov, S. S.; Saito, G.; Vorontsov, I. I.; Otsuka, A.; Lyubovskaya, R. N.; Antipin, Yu. M. *Inorg. Chem.* **2003**, *42*, 3706–3708.

(45) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Yoshida, Y.; Saito, G. *J. Am. Chem. Soc.* **2002**, *124*, 7648–7649.

Table 5. RT Conductivity of the Complexes

N	conductivity, S·cm ⁻¹
1	6 × 10 ⁻⁵
4	8 × 10 ⁻⁴
6	2 × 10 ⁻⁵
7	2 × 10 ⁻²
8	2 × 10 ⁻²

Table 6. Temperatures of the Existence of Monomeric and Dimeric Phases in **1–10**

$$(D^{+})_2[(C_{60(70)} - C_{60(70)})_2] \cdot (Sol)_{2x} (T < T_1) \rightleftharpoons 2[(D^{+}) \cdot (C_{60(70)}^{\bullet-}) \cdot (Sol)_x] (T > T_2)$$

dimeric phase			monomeric phase			
N	D	C ₆₀₍₇₀₎	sol.	x	T ₁ , K	T ₂ , K
1	Cp* ₂ Cr	C ₆₀	C ₆ H ₄ Cl ₂	2	200	230
2	Cp* ₂ Cr	C ₆₀	C ₆ H ₆	2	160	190
3	Cs	C ₇₀	CTV	1	360	390
			DMF	7		
			C ₆ H ₆	0.75		
4	Cr(C ₆ H ₆) ₂	C ₆₀	C ₆ H ₄ Cl ₂	0.7	160	240
5	Cr(C ₆ H ₆) ₂	C ₆₀	C ₆ H ₅ CN	1	240	>300
6	Cr(C ₆ H ₆) ₂	C ₇₀	C ₆ H ₄ Cl ₂	1	250	>300
7^a	Cr(C ₆ H ₆) ₂	C ₆₀	-	-	>300	
8	Cp ₂ Co	C ₆₀	C ₆ H ₄ Cl ₂	1	250	350
			C ₇₀	C ₆ H ₄ Cl ₂	0.5	>300
10	Cs	C ₇₀	DMF	5	350	>380

^a The formation of another σ -bonded structure is possible.

are typical for ionic complexes and salts containing fullerene radical anions.^{1c}

Temperature ranges of the existence of monomeric and dimeric phases in **1–10** are summarized in Table 6. The dissociation temperatures for the (C₆₀⁻)₂ dimers vary in the 160–250 K range, whereas those for the (C₇₀⁻)₂ dimers are in the 250–360 K range. The stability of the (C₆₀⁻)₂ dimers in the solid state depends on donor and solvent molecules involved in the complex. Probably the size of these molecules affects the distances between the fullerene anions in the crystal structure. Indeed, the increase in the distance between the centers of the C₆₀⁻ spheres from 9.986 Å in Cr(C₆H₅Me)₂·C₆₀ (RT)^{16,17} up to 10.10 Å in **1** (RT)¹⁸ decreases the dissociation temperature for the (C₆₀⁻)₂ dimer from 250 down to 200–220 K. Even small variation of the size of solvent molecules (C₆H₄Cl₂ and C₆H₆ in **1** and **2**, C₆H₄Cl₂ and C₆H₅CN in **4** and **5**) with the same donor molecule (Cp*₂Cr and Cr(C₆H₆)₂) shifts the dissociation temperatures by 40–70 K.

The inter cage C–C σ -bond dissociation energies fall into the range of 25–63 kJ·mol⁻¹ for the (C₆₀⁻)₂ dimer in **1**, **2**, **4**, **5**, and **8**. These energies indicate the weakness of these bonds in comparison with the single C–C bond, for example, in CH₃–CH₃ (the dissociation energy is 368 kJ·mol⁻¹).⁴⁶ The inter cage C–C bonds in the (C₆₀⁻)₂ and (C₇₀⁻)₂ dimers of 1.597(7)¹⁸ and 1.584(9) Å¹⁹ are also noticeably longer than the single C–C bond between sp³ carbons (1.541(3) Å).⁴⁷

The (C₇₀⁻)₂ dimer is more stable than the (C₆₀⁻)₂ one. This is manifested in the shorter inter cage C–C bond according to the X-ray diffraction data (1.584(9) Å in **3**¹⁹ vs 1.597(7) Å in **1**¹⁸) and higher temperature of the beginning of dissociation

(250–360 K vs 160–250 K, respectively (Table 6)). Dimer stability is defined mainly by the on-site Coulomb repulsive energy between fullerene anions. Because of this, the extended π -system of C₇₀⁻ stabilizes the C₇₀⁻ dimeric state relative to that of C₆₀⁻. The presence of two negative charges on the (C₆₀⁻)₂ dimer also substantially destabilized this dimer relative to isoelectronic neutral single-bonded (C₅₉N)₂ dimer formed by azofullerene. According to the data of Prassides et al.,^{15b} the (C₅₉N)₂ dimer begins to dissociate above 500 K and even at 740 K only 1 of every ~6000 dimers is cleaved into monomeric fragments.

Both (C₆₀⁻)₂ and (C₇₀⁻)₂ dimers have characteristic IR and NIR spectra, which allow them to be identified in ionic complexes. Numerous additional bands observed in the IR spectra (see the Supporting Information) were attributed to the lowering of the symmetry of fullerenes in a dimer. Two or even three bands appear in the NIR spectra as a result of dimerization of fullerene radical anions (Figures 8b and 9b). The additional band can be associated with interfullerene electronic transitions within one dimer. Similarly, additional bands were observed in the spectrum of the σ -bonded (Co^{III}TPP·C₆₀(CN)₂⁻) anion, one of which was ascribed to the transition between Co^{III}TPP and C₆₀(CN)₂⁻ in the σ -bonded unit.⁴⁵

Conclusion

In summary, we have shown the formation of diamagnetic single bonded (C₆₀⁻)₂ and (C₇₀⁻)₂ dimers in ionic complexes of fullerenes C₆₀ and C₇₀. Dimerization is realized as reversible phase transitions and results in the changes in structural and magnetic properties of the complexes. Peculiarities of the (C₆₀⁻)₂ and (C₇₀⁻)₂ dimeric phases have been studied. It has been shown that the (C₇₀⁻)₂ dimers are more stable than the (C₆₀⁻)₂ ones and dimer stability depends on donor and solvent molecules involved in the complex. The IR and UV–vis–NIR spectra of the dimers are useful tools for their identification.

Experimental Section

Materials. Cp*₂Cr, Cp₂Co, and Cp₂Cr were purchased from Aldrich. Cr⁰(C₆H₆)₂ was purchased from Strem Chemicals. C₆₀ and C₇₀ of 99.98 and 99.0% purity, respectively were purchased from MTR Ltd.. Solvents were purified in argon atmosphere. *o*-Dichlorobenzene (C₆H₄Cl₂) was distilled over CaH₂. Toluene (C₆H₅Me), benzene (C₆H₆) and hexane were distilled over Na/benzophenone. Benzonitrile (C₆H₅CN) was distilled over Na/benzophenone. *N,N*-dimethylformamide (DMF) of HPLC grade (Aldrich) was distilled under reduced pressure. The solvents were degassed and stored in a glove box. All manipulations with **1–10** were carried out in a MBraun 150B–G glove box with controlled atmosphere and the content of H₂O and O₂ less than 1 ppm. The samples were stored in a glove box and were sealed in 2 mm quartz tubes for EPR and SQUID measurements under 10⁻⁵ Torr. KBr pellets for IR and UV–vis–NIR measurements were prepared in the glove box.

General. UV–vis–NIR spectra were measured on a Shimadzu UV-3100 spectrometer in the 240–2600 nm range. FT-IR spectra were measured in KBr pellets with a Perkin-Elmer Paragon 1000 FT-IR spectrometer (400–7800 cm⁻¹). A Quantum Design MPMS-XL SQUID magnetometer was used to measure static susceptibilities down to 1.9 K. A sample holder contribution and core temperature independent diamagnetic

(46) Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502–508.

(47) Kennard, O. In *CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, Florida, 1987; p F106.

susceptibility (χ_0) were subtracted from the experimental values. The values of χ_0 for **6**, **7**, **8** (in the 2–250 K range), and **10** were calculated from the high-temperature range with the appropriate formula: $\chi_M = C/(T - \Theta) + \chi_0$. The χ_0 values for **1**, **2**, **4**, and **5** were calculated using the Pascal constants: -2.3 , -1.41 , -0.83 , -0.54×10^{-4} emu mol⁻¹ for Cp*₂Cr,⁴⁸ Cr⁰(C₆H₆)₂,⁴⁹ C₆H₄Cl₂, and C₆H₆, respectively. The contribution of fullerenes to total susceptibility were ignored because of diamagnetic and paramagnetic components canceled out.⁵⁰ EPR spectra were recorded down to 4 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with JEOL ES-CT470 cryostat. Conductivity was measured by the two-probe technique in a glovebox. The intercase C–C σ bond dissociation energy was calculated from the slope of the dependency $\ln k$ vs $1/T$. The equilibrium constants ($k = [C_{60}^{\bullet-}]^2/[C_{60}-C_{60}]^{2-}$) of the reaction: $[C_{60}^{\bullet-}]^2 \rightleftharpoons 2[C_{60}^{\bullet-}]$ were estimated using data of magnetic measurements.

Synthesis. Diffusion was carried out in a glass tube of 1.5 cm in diameter and 40 mL volume with a ground glass plug during 1 month. The solvent was decanted and the crystals were washed with hexane and dried. The composition of the compounds was determined from the X-ray diffraction on a single crystal for **1** and **3**, and by the elemental analysis for **2**, **4–10** (Table 2). In **2**, and **4–10** the difference (100-%(C, H, Cl, N)) exceeds the calculated content of metals (Co and Cr) indicating the addition of oxygen to the complexes during the elemental analysis. Indeed, all complexes are air sensitive. Oxidation may be realized, for example, through the addition of oxygen to the fullerene radical anion: (fullerene)^{•-} + O₂ → (fullerene•O₂⁻). The addition of approximately one O₂ molecule per one formula unit of the complex is observed. Thus, the calculated C, H, N, and Cl (%) content was corrected for the following composition (Formula unit:O₂). We assume that oxygenation occurring during elemental analysis is extrinsic and omit oxygen through the manuscript. Previously, the addition of O₂ to C₆₀ ionic complexes during elemental analysis was also reported.^{3,51} The shape and color of the crystals of the compounds are given in Table 2.

The crystals of **2** were obtained by diffusion of hexane (20 mL) in the C₆H₅CN/C₆H₆ solution (1/4) (20 mL) containing C₆₀ (20 mg, 0.028 mmol) and Cp*₂Cr (9 mg, 0.028 mmol) (70% yield).

The crystals of **5** were obtained by diffusion of hexane (20 mL) in the C₆H₅CN/C₆H₆ solution (1/4) (20 mL) containing C₆₀ (20 mg, 0.028 mmol) and Cr(C₆H₆)₂ (12 mg, 0.056 mmol).

The crystals of two different shapes were formed and were separated under microscope giving **5** as well shaped black parallelepipeds (40% yield) together with black elongated plates (20% yield).

The crystals of **4** and **6** were prepared by diffusion of hexane (20 mL) in C₆H₄Cl₂ (20 mL) containing C₆₀ (20 mg, 0.028 mmol) (**4**) or C₇₀ (20 mg, 0.024 mmol) (**6**) and Cr(C₆H₆)₂ (12 mg, 0.056 mmol). After 1 month polycrystalline **4** and **6** (50–70% yield) were obtained.

Polycrystalline **7** was obtained by mixing filtered C₆H₆ (30 mL) or C₆H₅Me (25 mL) solution containing C₆₀ (20 mg, 0.028 mmol) with that (5 mL) containing Cr(C₆H₆)₂ (12 mg, 0.056 mmol). After 24 h, the colorless solution was filtered and the precipitate was washed with benzene and dried. The IR spectra and the elemental analyses of the products obtained from C₆H₆ and C₆H₅Me were identical and showed the absence of solvent molecules in the complex.

Polycrystalline **8** was obtained by mixing hot filtered C₆H₄Cl₂ solutions containing C₆₀ (20 mg, 0.028 mmol) in 20 mL and Cp₂Co (6.3 mg, 0.033 mmol) in 5 mL. 20 mL of hexane was layered over the obtained solution in a 50 mL flask. After 4 d, the solution was decolorized and black small crystals were crystallized (80% yield).

Polycrystalline **9** was obtained by diffusion of hexane in C₆H₅CN/C₆H₄Cl₂ solution (1/4) (20 mL) containing C₇₀ (20 mg, 0.024 mmol) and Cp₂Co (6.3 mg, 0.033 mmol) (70% yield).

The (Cs⁺)(C₇₀^{•-}) salt was generated in solution on dissolving C₇₀ (20 mg, 0.024 mmol) and cesium (3.5 mg, 0.0264 mmol) in 2 mL of DMF. **10** was crystallized during diffusion of hexane (20 mL) in the solution of (Cs⁺)(C₇₀^{•-}) in C₆H₆/DMF (9/1) the (50% yield).

Abbreviation in the Text. TDAE: tetrakis(dimethylamino-ethylene); Cp₂Co: bis(cyclopentadienyl)cobalt (II); Cp₂Cr: bis(cyclopentadienyl)chromium; Cr(C₆H₆)₂: bis(benzene)chromium (0); Cr(C₆H₅Me)₂: bis(toluenec)chromium (0); Cp*₂Ni: bis(pentamethylcyclopentadienyl)nickel (II); Cp*₂Cr: bis(pentamethylcyclopentadienyl)chromium; Cr^{III}TPP: 5, 10, 15, 20-tetraphenylporphyrin chromium (III); PPN⁺: bis(triphenylphosphorylidene)ammonium; Co^{II}TPP: 5, 10, 15, 20-tetraphenylporphyrinate cobalt (II); Ph₄P⁺: tetraphenylphosphonium; CTV: cyclotriveratrylene; THF: tetrahydrofuran; DMF: *N,N*-dimethylformamide; C₆H₆: benzene; C₆H₄Cl₂: *o*-dichlorobenzene; C₆H₅Me: toluene; C₆H₅CN: benzonitrile; CH₃CN: acetonitrile.

Acknowledgment. The work was supported by the COE Research on Elements Science No. 12CE2005, JSPS, and the RFBR Grant No. 03-03-32699a.

Supporting Information Available: Crystallographic data of **1** at 300 and 100 K (CIF files) and IR spectra of **1–10**. This materials is available free of charge via Internet at <http://pubs.acs.org>.

- (48) Gebert, E.; Reis, A. H.; Miller, J. S.; Rommelmann, H.; Epstein, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4403–4410.
 (49) Miller, J. S.; O'Hare, D. M.; Chakraborty, A.; Epstein, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 7853–7860.
 (50) (a) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbagh, G.; Kortan, A. R.; Muller, A. J.; Muijsce, A. M.; Rosseinsky, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature* **1991**, *350*, 46–47. (b) Luo, W.; Wang, H.; Ruoff, R.; Cioslowski, J.; Phelps, S. *Phys. Rev. Lett.* **1994**, *73*, 186–188.
 (51) Kitagawa, T.; Lee Y.; Takeuchi, K. *Chem. Commun.* **1999**, 1529–1530.

JA035546A