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Magnetic properties of [70]fulleride compounds

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Abstract

New ionic DA-type charge transfer solids of C_{70}^- were prepared with bis(benzene)chromium (Bz_2Cr) and decamethylmetallocenes (Cp_2^*M) (M = Ni, Cr). In the solid-state EPR spectra, no signals confirming C_{70}^- spins were detected below room temperature (RT), probably due to either an electronic or chemical dimerization. Above RT, a signal characteristic of a strong exchange coupling between donor cation and C_{70}^- spins gradually emerged for Bz_2Cr complex, owing to the decoupling of the dimers. In dimethyl sulfoxide at RT, a signal characteristic of C_{70}^- spins was observed at $g = 2.0012$–2.0014 with a narrow linewidth.
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1. Introduction

[70]Fullerene molecule has only one isomer with D_{5h} symmetry, and has thus been the most extensively studied higher fullerene [1]. Experimentally, C_{70} is capable of accepting at least six electrons in appropriate solvent [2], and the difference between the first and second redox potentials is closely similar to that of C_{60} [3], implying the comparable bare on-site Coulomb repulsion. Therefore C_{70}^{n-} fullerides can be expected to offer a narrow-band system as established in C_{70}^{n-} fullerides. However, experimental work on C_{70}^{n-} fulleride remains sparse because early transport studies of K_xC_{70} thin films showed the absence of superconductivity [4]. As for charge transfer (CT) complexes with organic donor/cation, there appears to be only two C_{70}^- solids that have been electronically characterized, one being $(TDAE^+)(C_{70}^-)$ [5] and the other being $(Ph_4P^+)_2(C_{70}^-)(I^-)$ [6]. In both compounds, C_{70}^- spins are paramagnetically localized down to low temperature without showing any magnetic ordering. In this paper, we report three ionic donor (D)–acceptor (A) C_{70}^- CT solids with bis(benzene)chromium $(Bz_2Cr^+)(C_{70}^-)(PhMe)$ (**1**), and decamethylmetallocenes $(Cp_2^*Ni^+)(C_{70}^-)(PhMe)$ (**2**) and $(Cp_2^*Cr^+)(C_{70}^-)(PhMe)$ (**3**), mainly concerning the magnetic properties.

2. Experiment

Complexes **1**–**3** were prepared by stoichiometric mixing of respective component molecules in toluene under an inert atmosphere of helium gas in a glovebox [Found (Calcd.) for **1**: C 91.58 (93.68), H 1.62 (1.77); **2**: C 89.68 (92.31), H 2.81 (3.03); **3**: C 86.53 (92.81), H 2.84 (3.05)]. All measurements were carried out with particular attention to prevent the exposure of the samples to air.

3. Results and discussion

Table 1 summarizes NIR and EPR data of complexes **1**–**3**. Neutral C_{70} molecule shows a dominant visible band at 469 nm, while upon reduction an additional band characteristic of C_{70}^- was found at 1369–1370 nm [7] for **1**–**3** in dimethyl sulfoxide (DMSO) solution. Also the spectra suggest the negligible counter ion effects on intramolecular transition of C_{70}^-.

There have been fewer reports on the well-characterized EPR spectra of each C_{70}^{n-} species [1]. As displayed in Fig. 1, the room temperature (RT) EPR spectrum of **3** in DMSO are characterized by a Lorentzian-shaped signal at $g = 2.0014$ with $\Delta H_{pp} = 1.1$ G. Similar EPR feature was observed for **2** ($\Delta H_{pp} = 1.0$ G at $g = 2.0014$). Also complex **1** exhibits a similar resonance ($\Delta H_{pp} = 1.7$ G at $g = 2.0012$) together with a distinct broad signal accompanied with hyperfine structure. The broad signal gives $g = 1.9862$ and hyperfine splitting (A) of ca. 3.5 G. According to the EPR studies on

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Table 1
NIR and EPR data of complexes **1–3**[a]

Complex	NIR[b] (nm)	EPR in the solid-state		EPR in solution[b]	
		ΔH_{pp} (G)	g factor	ΔH_{pp} (G)	g factor
1	1369	36.6	1.9862	11.6	1.9862[c]
				1.7	2.0012
2	1370	Silent	Silent	1.0	2.0014
3	1370	Silent	Silent	1.1	2.0014

[a] At RT.
[b] In DMSO.
[c] With hyperfine structure.

$Bz_2Cr^{\bullet+}$ cation radical ($g = 1.9859$) [8], the broad signal is readily assigned to $Bz_2Cr^{\bullet+}$ with the hyperfine coupling between the unpaired electron spin and the nuclear spins of the twelve protons in the benzene rings ($A^H = 3.44$ G) [9]. Consequently, the sharp signal appeared at $g = 2.0012$–2.0014 for C_{70}^- complexes **1–3** is unambiguously assigned to isolated C_{70}^- spins.

In the solid-state, complex **1** exhibits only the $Bz_2Cr^{\bullet+}$ cation radical signal at $g = 1.9862$. For complexes **2** and **3**, on the other hand, the absence of respective donor cation signals in DMSO was also confirmed in the solid-state EPR spectra at RT, likely due to the short spin–lattice relaxation time. Moreover, no EPR signal confirming C_{70}^- spins was detected for solids **1–3** between 4 and 300 K. This would be indicative of either an electronic or chemical dimerization of C_{70}^- anions. In this regard, the formation of the covalently linked $(C_{70})_2^{2-}$ dimers was previously argued for $Rb^+C_{70}^-$ below 400 K [10]. Upon heating the solid **1** above RT, a new signal appears gradually at $g = 1.991$, which is close to the mean value (1.994) between those of Bz_2Cr^+ and C_{70}^-

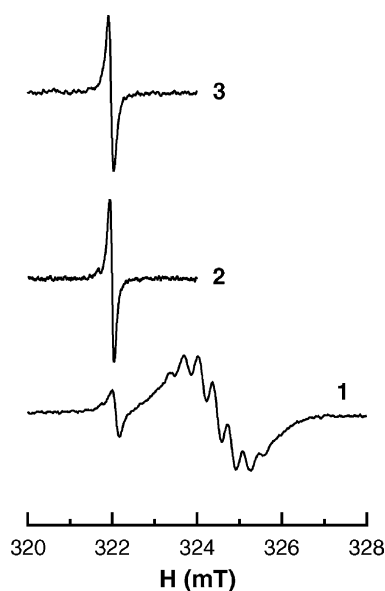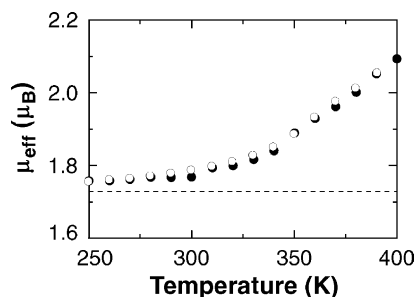Fig. 2. Temperature dependence of the effective moment (μ_{eff}) for $(Bz_2Cr^+)(C_{70}^-)(PhMe)$ (**1**). Closed and open circles are the data in the heating and cooling processes, respectively. A dotted line indicates the value for paramagnetic $S = 1/2$ state.

spins. Thus, the signal is characteristic of a strong exchange coupling between Bz_2Cr^+ and C_{70}^- spins. Regardless of the particular dimer that is actually formed, it appears that the dimers begin to decouple above RT.

Temperature dependence of the static susceptibility for **1** was measured between 2 and 400 K, and follows the Curie–Weiss law below 300 K. Effective moment (μ_{eff}) at 300 K is $1.77 \mu_B$, which is as expected for a paramagnetic $S = 1/2$ state (spin only value is $1.73 \mu_B$). Since the C_{70}^- anions would dimerize at the temperature and the Bz_2Cr^+ cations is anticipated to have an $S = 1/2$ ground state, it appears that only paramagnetic spins on the Bz_2Cr^+ cations are responsible for the magnetic moment. Upon heating above 300 K, the moment increases gradually and eventually attains to $2.09 \mu_B$ at 400 K as seen in Fig. 2, owing to the decoupling of the dimers. The transformation between dimer and monomer is thermally reversible. Magnetic investigations at high temperature for **2** and **3** are in progress.

4. Conclusion

Three C_{70}^- ionic solids with Bz_2Cr and Cp_2^*M (M = Ni, Cr) were newly prepared and characterized. In DMSO, an EPR signal characteristic of C_{70}^- spins was observed at $g = 2.0012$–2.0014 for **1–3**. In solid **1**, either an electronic or chemical C_{70}^- dimer is formed below RT, and the transformation between dimer and monomer occurs reversibly at around RT.

Fig. 1. EPR spectra for C_{70}^- complexes with Bz_2Cr (**1**), Cp_2^*Ni (**2**) and Cp_2^*Cr (**3**) in DMSO at RT.

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