A reassignment of the EPR spectra previously attributed to Cu@C_{60}

Bevan Elliott,[a] Keqin Yang,[b] Apparao M. Rao,[b] Hadi D. Arman,[a] William T. Pennington[a] and Luis Echegoyen*[a]

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EPR spectra attributed to the endohedral metallofullerene Cu@C_{60} are better explained by the previously characterized Cu(II) dithiocarbamate family of compounds.

Though many endohedral mono-metallofullerenes having relatively large carbon cages have been isolated, characterized, and chemically functionalized, M@C_{60} and M@C_{70} species have so far remained largely elusive due to their low solubility in common organic solvents and their general instability in air. Recently, a report of the synthesis, isolation, and characterization of a new endohedral fullerene, Cu@C_{60}, was published by Huang *et al* in this journal.[1] In their synthesis, copper ions sputtered into a nitrogen rf-plasma collided with sublimated C_{60}, and the resulting deposit was solubilized in CS_2 and subsequently examined by EPR spectroscopy. The two observed overlapping patterns of four completely resolved hyperfine lines having slightly different hyperfine splittings and the correct isotopic intensities gave unequivocal proof of paramagnetism arising from unpaired electron density on ^{63,65}Cu nuclei. On the basis of a TOF-MS spectrum with a main peak at *m*/*z* 783, the *g*-value of the EPR hyperfine pattern, and its m_I-dependent line widths, the assignment to a carbon-60 cage containing an off-center Cu^{2+} ion was made. In 2005, Dinse and co-workers published both room-temperature and liquid nitrogen-frozen CS_2 solution EPR spectra of a radical which was produced in a standard Krätschmer–Huffman (K–H) arcing apparatus by unintentional addition of copper from the graphite electrode mounts.[2] Since their room-temperature solution spectrum was identical to that in the previous study, Dinse and co-workers also assigned it to Cu@C_{60}, though they did not report a mass spectrum of the compound. The m_I-dependent spectral line widths and the temperature behavior, as well as DFT structure optimizations of the radical, were believed to be indications that the off-center Cu^{2+} endohedral ion was 'internally docking' to the inner carbon cage on the EPR timescale. Also in 2005, a theoretical paper motivated by the first report of Cu@C_{60} was published.[3] In it, energy optimization calculations using the Hartree–Fock method yielded a model of Cu@C_{60} with an off-center copper ion inside a deformed carbon cage and a small but positive binding energy. In this paper, we report attempts to synthesize Cu@C_{60} by K–H arc in large enough quantities for complete characterization, and the surprising finding that the isolated radical corresponds to a dithiocarbamate copper complex, not Cu@C_{60}. However, the radical's EPR spectrum is identical to that assigned to Cu@C_{60}.

In an effort to duplicate the published results, a modified K–H apparatus was utilized.[4] In a 300 Torr helium atmosphere, an 80 A dc arc was struck between a graphite anode and a core-drilled cathode into which a piece of copper metal had been inserted. The soluble portion of the soot produced from this synthesis was extracted in CS_2, and EPR spectra showed the presence of the copper radical previously reported, but in very small amounts. To increase the yield (monitored by the intensity of the EPR signal), variations in the elemental composition and configuration of the rods, helium pressure, arc current, and extraction solvents were explored. Cathode composition included pure graphite, core-drilled graphite with an inserted copper slug, and pure copper. Anodes were either pure graphite or composite carbon/copper powder annealed molded rods. Extraction solvents consisted of CS_2, pyridine, or mixtures of the two, since M@C_{60} species have been shown to be preferentially extractable in pyridine and aniline.[5] Yields of the copper-centered radical remained low until both yttrium and nickel were added in catalytic amounts to the anode. Milligram quantities of the radical compound were then collected when a 1 : 1 mixture of CS_2–pyridine was used to extract soot produced by arcing a carbon/Y/Ni composite anode against a pure copper cathode.

The compound was purified by column chromatography in a 1 : 1 eluent ratio of toluene : CS_2 after first evaporating the CS_2–pyridine mixture and redissolving and filtering in CS_2. Two yellow bands having similar R_f values by TLC were eluted separately, and the band containing the paramagnetic species was collected, dried, and redissolved in CS_2 for EPR studies. Fig. 1 shows the X-band first-derivative EPR absorption spectrum of the radical in solution at room temperature. With *g*-values of 2.0483 and 2.0477 and hyperfine coupling constants of 77.4 and 82.7 G for ^{63}Cu and ^{65}Cu nuclei, respectively, in an isotopic ratio of 2.25, this spectrum is identical to those reported by Huang *et al*,[1] and Dinse and co-workers.[2]

MALDI-TOF-MS of this compound did not yield the expected peak corresponding to Cu@C_{60} despite repeated attempts. Instead, shown in Fig. 2, the most intense feature of the spectrum was a double peak at *m*/*z* 383 and 385 with an isotopic ratio indicative of a copper-containing species. Cyclic voltammetry in *o*-dichlorobenzene (Fig. 3) showed only two reversible waves at 0.11 and −1.04 V *vs.* Fc/Fc^+ within the entire solvent window, a behaviour that is not typical of fullerenes. At this point, it was discovered that the compound was highly soluble in many organic solvents ranging in polarity from CS_2 to methanol. Again, no known pristine fullerenes behave this way. The compound was then dissolved in THF, and UV-Vis spectra collected. The spectrum in Fig. 4 shows an intense absorption at 272 nm with a shoulder at 287 nm which dominates the spectrum, and a broad band with

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[a] *Department of Chemistry, Clemson University, Clemson, SC, USA. E-mail: luis@clemson.edu; Fax: +1 (864) 656 6613; Tel: +1 (864) 656 0778*
[b] *Department of Physics, Clemson University, Clemson, SC, USA*

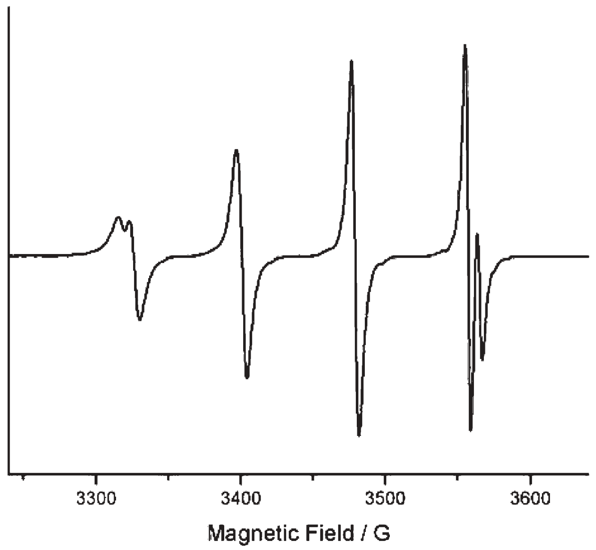

Fig. 1 X-Band EPR spectra in CS_2 of the purified Cu^{2+} radical compound.

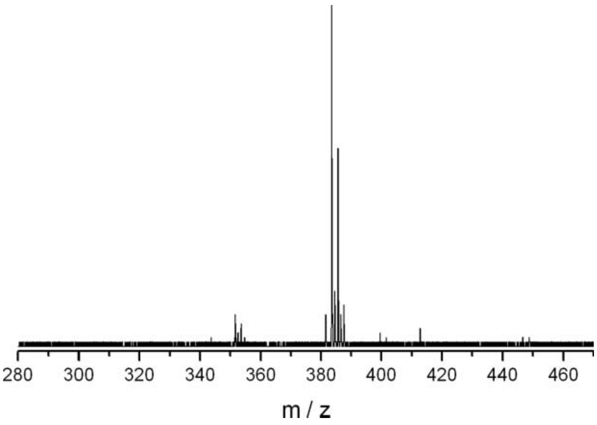

Fig. 2 MALDI-TOF-MS spectrum of the purified Cu^{2+} radical compound.

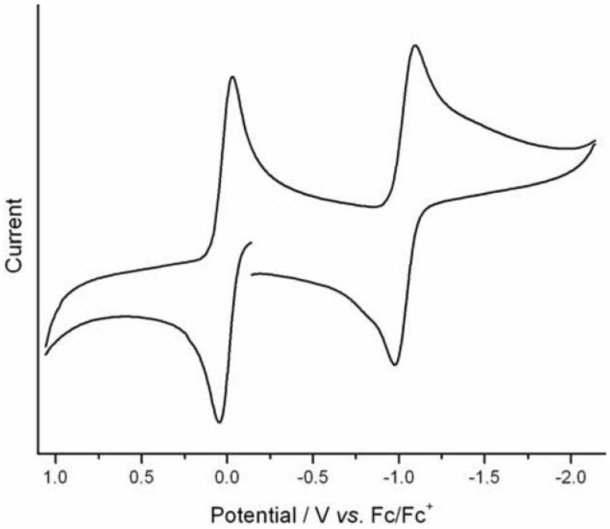

Fig. 3 Cyclic voltammogram in oxygen-free THF with $TBAPF_6$ as the supporting electrolyte. Pt working and auxiliary electrodes with a Ag/Ag^+ pseudo-reference electrode were utilized in a one-compartment cell.

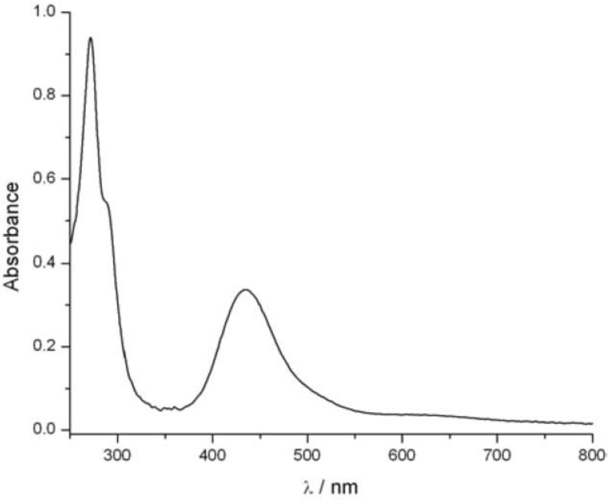

Fig. 4 UV-Vis spectrum in THF of the purified copper compound.

λ_{max} at 435 nm followed by a very broad, weaker, tailing band that extends past 700 nm.

As no clear evidence indicating the presence of $Cu@C_{60}$ was yet present except for the EPR spectrum in our characterization of this compound, crystallization and X-ray diffraction were attempted. Slow evaporation of a concentrated solution in CS_2 yielded flat reddish-black parallelpipeds which were examined by single-crystal X-ray diffraction at room temperature. The resulting structure, a copper ion coordinated to two thiocarbamate ligands with terminal piperidine groups, shown in Fig. 5, was quite unexpected.† A search of single-crystal structures yielded a result identical to ours,[6] namely, bis(piperidine-1-dithiocarbamato) copper(II), the divalency of the copper causing the paramagnetism of the compound. The complexation of CS_2 ligands by Cu^{2+} is easily explained, but the origin of our piperidine N-terminal ligands is not as clear. One possible source is the pyridine used in the extraction.

More information about the Cu(II) dithiocarbamate family of compounds was obtained from an extensive literature search. Those reports mentioned herein are merely representative, not exhaustive, since the literature abounds with such examples. The first report of electron spin resonance of a divalent copper dithiocarbamate compound was published in 1959 in *Nature*.[7] The reported X-band benzene solution spectrum of the Cu(II) diisopropyl dithiocarbamate complex is in all respects identical

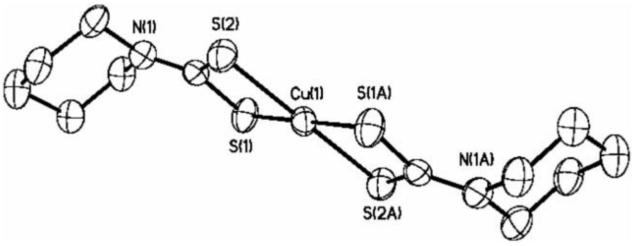

Fig. 5 Single-crystal X-ray structure of bis(piperidine-1-dithiocarbamato)copper(II). Thermal ellipsoids are shown at 50% probability and solvent molecules are omitted for clarity. The central metal atom lies on an inversion center and the atoms generated by the inversion are labelled with suffix (A).

to that published by Huang *et al.*, and Dinse and co-workers, and as shown in this report. According to this early article, exchanging the terminal groups on the dithiocarbamate ligand (ethyl, isopropyl and methyl phenyl) had little or no effect on the solution EPR spectrum. Also interesting in this article was the authors' explanation of the m_I-dependent line widths, which were attributed to insufficient averaging of anisotropy in the resonance structure. Another solution EPR study of a series of Cu(II) dithiocarbamate complexes offered a different interpretation: that the variation in linewidths is due to the orientation of the copper nuclear spin with respect to the applied magnetic field.[8]

EPR spectra of solid-phase cupric dithiocarbamate complexes have also been reported in the literature. Room-temperature EPR spectra of thin films of PVC doped with 0.5% Cu(II) diethyldithiocarbamate[9] are identical to the low-temperature spectra reported by Dinse and co-workers, as are liquid-nitrogen solid-solution spectra of the same molecule in another article.[10] Previously reported voltammetry and UV-Vis spectra of cupric dithiocarbamate complexes with a series of different N-terminal ligands showed qualitative similarity with our results, with the *N*,*N*-dipiperidine species quantitatively identical to our data.[11]

Though theoretically the endohedral mono-metallofullerene Cu@C_{60} is a stable molecule,[3] the only evidence to date of the existence of Cu@C_{60} is the mass spectrum reported by Huang *et al.*[1] However, the EPR spectra assigned to Cu@C_{60} can be accounted for by the compounds formed by the complexation of CS_2 in solution by Cu^{2+} ions. Despite repeated attempts under a wide variety of conditions, we failed to detect the presence of Cu@C_{60}. More research, both experimental and theoretical, is needed to ascertain the stability and existence of divalent d-block metals encapsulated by small fullerenes.

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Notes and references

† The unit cell parameters for $[Cu(C_6H_{10}NS_2)_2]$ synthesized in this study are as follows: space group = $P2_1/c$, a = 6.1726(16), b = 5767(2), c = 15.266(4) Å, β = 95.442(10)°, V = 804.5589 $Å^3$.

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