

Expanding the coordination chemistry of buckminsterfullerene: synthesis and characterization of (*N,N'*-dimethylethylenediamine-[60]-fullerene)copper(II) bromide

N.R. Conley, J.J. Lagowski *

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, A5300, Austin, TX 78712-0165, USA

Received 15 November 2003; accepted 16 May 2004

Available online 26 June 2004

Abstract

The chelate (*N,N'*-dimethylethylenediamine-[60]-fullerene)copper(II) bromide was synthesized in 79% yield by the dropwise addition of a solution of *N,N'*-dimethylethylenediamine-[60]-fullerene in tetrahydrofuran (THF) to a solution of excess copper(II) bromide in THF. The resulting brown precipitate was characterized by electron spin resonance (ESR) spectroscopy and elemental analysis.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Fullerene; *N,N'*-Dimethylethylenediamine; Copper complex; Copper chelate; ESR spectroscopy

1. Introduction

Since their discovery in 1985 [1], fullerenes have been found to undergo a large number of chemical transformations [2]. One such transformation is the addition of a diamine, namely piperazine, homopiperazine, or *N,N'*-dimethylethylenediamine, to the fullerene cage at a site where there are two adjacent six-membered rings [3,4]. We recognized that these diamine addition products might serve as unique ligands and chose to investigate the *N,N'*-dimethylethylenediamine adduct because (1) its coordination site is the least sterically hindered and (2) preparation of the copper chelate of its non-fullerenated counterpart **1**, which may serve as a useful model compound in the spectroscopic analysis, has already been described [5]. Here, we report the synthesis and characterization of (*N,N'*-dimethylethylenediamine-[60]-fullerene)copper(II) bromide **2**, the first chelate of a substituted ethylenediamine-derivatized fullerene (see Fig. 1).

* Corresponding author. Tel.: +1-512-471-1403/3288; fax: +1-512-471-3288.

E-mail addresses: lagarto2@aol.com (N.R. Conley), jjl@mail.utexas.edu (J.J. Lagowski).

2. Experimental

N,N'-Dimethylethylenediamine (99%), anhydrous copper(II) bromide (99.5%), and [60]-fullerene (99.5+%) were purchased from Aldrich Chemicals, Mallinckrodt Chemical Works, and MER Corp., respectively. Toluene (ACS reagent grade), *N,N*-dimethylformamide (ACS reagent grade), and tetrahydrofuran (HPLC grade) were purchased from Fisher Chemicals. All reagents were used as received without further purification. *N,N'*-Dimethylethylenediamine-[60]-fullerene [4]

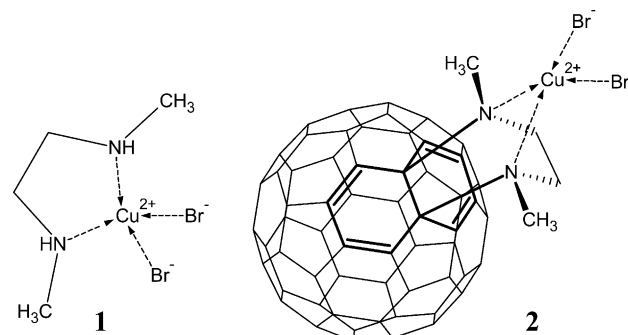


Fig. 1. Structures of chelates **1** and **2**.

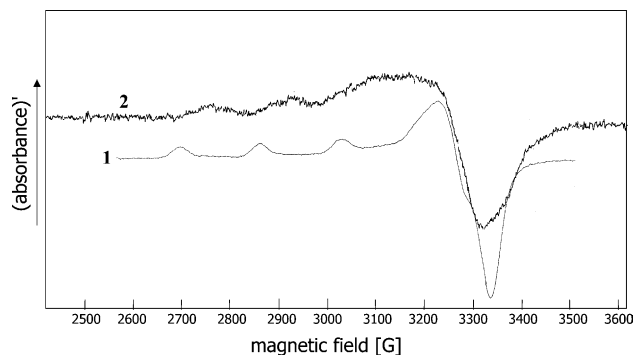


Fig. 2. ESR spectra of chelates **1** and **2** in frozen DMF at 120 K.

and **1** [5] were prepared as previously reported. Electron spin resonance (ESR) spectra were collected on an IBM-Bruker ER 300 Spectrometer at X-band with a 100-kHz modulation frequency using dilute frozen solutions in *N,N*-dimethylformamide at 120 K. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN, USA).

2.1. Synthesis of **2**

A deoxygenated solution of *N,N'*-dimethylethylenediamine-[60]-fullerene (0.0359 g, 0.0445 mmol) in THF (90 ml) was added dropwise to a deoxygenated solution of copper(II) bromide (0.0515 g, 0.231 mmol, 5.2 eq) in THF (20 ml). Upon complete addition, the solution was heated to 60 °C for 5 min under nitrogen and cooled to room temperature. The cloudy reaction mixture was transferred to test tubes, which were stoppered and allowed to sit for 24 h. The resulting brown precipitate was collected by centrifugation, combined, washed with THF (2 × 5 ml), and dried under vacuum to give **2** (0.0362 g, 0.0351 mmol) in 79% yield.

3. Results and discussion

3.1. ESR spectroscopy

The ESR spectra of **1**¹ and **2** are shown in Fig. 2 and contain the characteristic copper hyperfine structure due to electron–nuclear interaction. The location of the g_{\perp} component prevents resolution of all four g_{\parallel} hyperfine lines in either spectrum, however. No nitrogen super-hyperfine structure is observed.

The magnetic parameters obtained from these spectra are listed in Table 1; g_{\perp} values were approximated by the method of Yokoi and Isobe [6] and were used to calculate the isotropic g values according to Eq. (1).

$$g_{\text{iso}} = (1/3)(g_{\parallel} + 2g_{\perp}) \quad (1)$$

The work of Peisach and Blumberg demonstrated that an empirical plot of A_{\parallel} vs. g_{\parallel} could be used to group copper proteins according to the identity of the coordinating atoms [7]. Using literature values of A_{\parallel} and g_{\parallel} for several 2N-[8] and 4N-coordinate [6,8–11] copper chelates as well as the values for **1** and **2** determined in this study, we have prepared a modified Peisach–Blumberg plot, shown in Fig. 3.

From Fig. 3 it is apparent that the A_{\parallel} and g_{\parallel} parameters can be used to distinguish between copper chelates with four coordinating nitrogen atoms and copper chelates with only two coordinating nitrogen atoms. The scarcity of published magnetic parameters for the latter [8], however, results in a smaller data set that precludes the precise determination of an empirically defined border, and therefore, none is shown. Nevertheless, it is evident that **1** and **2** are located within close proximity of the 2N-coordinate chelates, as expected for mono-*N,N'*-dimethylethylenediamine chelates.

3.2. Elemental analysis

The results of the elemental analysis of **2** are shown in Table 2.

The nitrogen, copper, and bromide analyses are in good agreement with theory. Although the percent carbon is somewhat low, this is likely the result of

Table 1
Magnetic parameters for chelates **1** and **2**

Chelate	g_{\parallel}	g_{\perp}	g_{iso}	$A_{\parallel} (\times 10^{-4} \text{ cm}^{-1})$
1	2.281	2.058	2.133	176
2	2.251	2.060	2.124	163

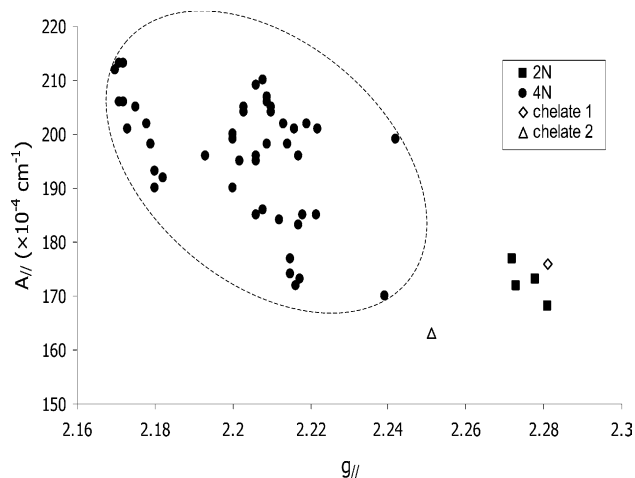


Fig. 3. Modified Peisach–Blumberg plot.

¹ Although the preparation of **1** has been previously reported [5], the compound was not studied by ESR spectroscopy.

Table 2
Elemental analysis results for **2**

Element	Experimental (%)	Theory (%)	Difference (%)
C	71.90	74.62	-2.72
H	1.91	0.98	0.93
N	2.61	2.72	-0.11
Cu	6.15	6.17	-0.02
Br	15.20	15.51	-0.31

incomplete combustion; carbon values that are 1–4% below the calculated values are typical for fullerene derivatives [12]. We attribute the discrepancy in the hydrogen analysis to solvent molecules that were trapped during the precipitation, although it is possible that ligand displacement of bromide for THF occurs to a small extent.

4. Conclusions

Precipitation of **2** was effected in good yield by the dropwise addition of a solution of *N,N'*-dimethylethylenediamine-[60]-fullerene in THF to an excess of cop-

per(II) bromide in THF. The structural assignment of **2** is consistent with the ESR spectrum and elemental analysis. Preliminary work suggests that this method is generally applicable to the synthesis of other transition metal chelates of *N,N'*-dimethylethylenediamine-[60]-fullerene.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] R. Taylor, D.R.M. Walton, *Nature* 363 (1993) 685.
- [3] N.-X. Wang, *Tetrahedron* 58 (2002) 2377.
- [4] K.-D. Kampe, N. Egger, M. Vogel, *Angew. Chem., Int. Ed. Engl.* 32 (1993) 1174.
- [5] D.W. Meek, S.A. Ehrhardt, *Inorg. Chem.* 4 (1965) 584.
- [6] H. Yokoi, T. Isobe, *Bull. Chem. Soc. Jpn.* 41 (1968) 2835.
- [7] J. Peisach, W.E. Blumberg, *Arch. Biochem. Biophys.* 165 (1974) 691.
- [8] R. Barbucci, M.J.M. Campbell, *Inorg. Chim. Acta* 16 (1976) 113.
- [9] H. Yokoi, T. Isobe, *Bull. Chem. Soc. Jpn.* 42 (1969) 2187.
- [10] H. Yokoi, M. Sai, T. Isobe, *Bull. Chem. Soc. Jpn.* 42 (1969) 2232.
- [11] V.G.K.M. Pisipati, G. Satyanandam, N.V.S. Rao, *Org. Magn. Res.* 17 (1981) 235.
- [12] J.C. Hummelen, B. Knight, J. Pavlovich, R. González, F. Wudl, *Science* 269 (1995) 1554.