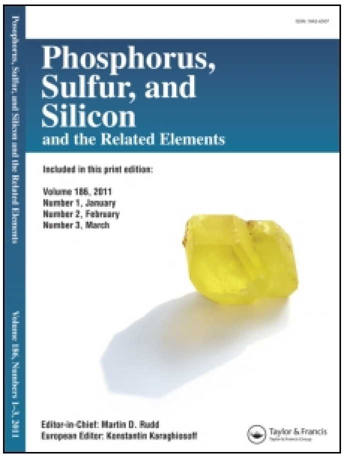

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Theoretical and Quantitative Structural Relationship Studies of Electrochemical Properties of the Nanostructures of *Cis*-Unsaturated Thiocrown Ethers and Their Supramolecular Complexes [X-UT-Y][M@C_{82}] (M=Ce, Gd)

Avat (Arman) Taherpour[a]
[a] Chemistry Department, Faculty of Science, Islamic Azad University, Arak, Iran

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THEORETICAL AND QUANTITATIVE STRUCTURAL RELATIONSHIP STUDIES OF ELECTROCHEMICAL PROPERTIES OF THE NANOSTRUCTURES OF *CIS*-UNSATURATED THIOCROWN ETHERS AND THEIR SUPRAMOLECULAR COMPLEXES [X-UT-Y][M@C_{82}] (M = Ce, Gd)

Avat (Arman) Taherpour
Chemistry Department, Faculty of Science, Islamic Azad University, Arak, Iran

The endohedral lanthanidofullerenes, an important type of organolanthanides, are stabilized by the delocalization of the negative charges on the cages of fullerenes. Since the discovery of these classes of carbon compounds and their unusual structures and properties of these molecules, many potential applications have been suggested. Unsaturated thiocrown ethers with* cis*-geometry are a group of crown ethers that, in light of the size of their cavities and their conformational restriction compared to a corresponding saturated system (1–9), demonstrate interesting properties for physicochemical studies. Endohedral lanthanidofullerenes M@C_x ($x = 82$ and M = Ce, Gd) were introduced as a new class of the spherical fullerene group with unique properties. Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atom(s) to the surrounding fullerene cage. Two of these molecules are the Ce@C_{82} (10) and Gd@C_{82} (11). The supramolecular complexes of 1–9 with Ce@C_{82} (10) and Gd@C_{82} (11) have been shown to possess a host–guest interaction for electron transfer processes, and these behaviors have previously been reported. Topological indices have been successfully used to construct effective and useful mathematical methods for finding good relationships between structural data and the various chemical and physical properties. To establish a good structural relationship between the structures of 1–9 and M@C_x that were introduced here, an index that is represented as μ_{cs} was utilized. This index is the ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers for 1–9. In this study, the relationship between this index and oxidation potential ($^{ox}E_1$) of 1–9, as well as the free energy of electron transfer (ΔG_{et}, by the Rehm-Weller equation) between 1–9 and 10 and 11 as [X-UT-Y][Ce@C_{82}] (12) and [X-UT-Y][Gd@C_{82}] (13) complexes, is presented.

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Keywords Endohedral metallofullerenes; molecular topology; oxidation potential; Rehm–Weller equation; unsaturated thiocrown ethers

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Address correspondence to Avat (Arman) Taherpour, Chemistry Department, Faculty of Science, Islamic Azad University, P.O. Box 38135-567, Arak, Iran. E-mail: avat_1@Yahoo.co.uk; avatarman.taherpour@gmail.com

INTRODUCTION

Chemistry has played a major role in developing new materials with novel and technologically important properties.[1–3] Carbon materials are found in a variety of forms, such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. The shapes of these nanosized new carbon structures include perfect spheres, ellipsoids, tubes, fibers, polyhedral, and further variations, all of them still conforming to the same structural principle as C_{60}. Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, and the unusual structures and properties of these molecules, many potential applications and physicochemical properties have been discovered and introduced.[1–4] At the present time, various empty carbon fullerenes with a different magic number "n," such as C_{20}, C_{60}, C_{70}, C_{80}, C_{180}, C_{240}, and so on, have been studied.[4,5] The fullerenes C_{180} and C_{240} are theoretical structures.[4,5] Endohedral metallofullerenes were first introduced as a new spherical fullerene group with unique properties.[3,4] One of the common structural molecules is the $M@C_{82}$ complex. Metallofullerenes are often characterized by the "charge-per-metal" atom encapsulated. This description implies that the oxidation of the metal atom during metallofullerene formation drives the extent of charge transfer to the fullerene cage. Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atoms to the surrounding fullerene cage.[5–8] Significantly, C_{82} and C_{84} are known to form endohedral metallofullerenes. The possibility of a charge transfer reaction during metallofullerene formation is responsible, considering the relatively large electron affinities of the fullerene cages.[5–9] It also suggests that the electronic structure of the fullerene cage is an important parameter for the formation of metallofullerenes. The voltammetry of a series of C_{82} and C_{84} metallofullerenes was investigated by Anderson et al.[6] in an attempt to understand their behavior in terms of the electronic structure.

The square-wave voltammetry for a series of related fullerenes and metallofullerenes measured in pyridine solutions containing 0.10 M tetra-*n*-butylammonium perchlorate has been reported.[5] Several dimetallic metallofullerenes, $M@C_x$, are found to have similar voltammetric responses regardless of metal identity or carbon number. Assignment of formal charges to the fullerene cage suggests that these metallofullerenes are isoelectronic and have related molecular orbital structures.[6] A variety of metallofullerenes having a C_{82} cage have been identified where either the type or the number of metal atoms within the C_{82} cage is altered (like $La@C_{82}$ and $Y@C_{82}$).[6,7] The symmetry of these metallofullerenes has not been characterized, but the voltammetry suggests that these species may have related electronic structures.[6–14] It was unexpected, however, to find a C_{82} or C_{84} metallofullerene having the appearance of related electronic structures. The $(Sc_2)^{+4}@(C_{84})^{-4}$ formal charges are assigned to the metallofullerene, in agreement with recent chromatographic results from Dorn.[5–16] The formal charges for $Er_2@C_{82}$ were assigned as $(Er_2)^{+6}@C_{82}{}^{-6}$.[6,16,60] The voltammetery of $Sc_2@C_{84}$ is nearly identical to that of $Er_2@C_{82}$, suggesting that the identity of the encapsulated metal ion does not influence the electronic structure of dimetallic metallofullerenes (DMFs). This result corresponds with reports in the literature for the electrochemistry of monometallic C_{82} metallofullerenes (e.g., $La@C_{82}$ and $Y@C_{82}$).[17,18–20] Hoffman et al. show by emission measurements that Er exists as the "+3" cation in $Er_2@C_{82}$.[12] Relative concentrations of nine isomers of $Ca@C_{82}$ derived from the C_{82} isolated-pentagon-rule satisfying cages have been computed over a wide temperature interval.[15] The computations are based on the Gibbs energy constructed from partition functions supplied with molecular parameters from density functional theory calculations. Five structures show significant populations at higher temperatures: $C_{2v} > C_s > C_2 > C_{3v} > C_s$. The computed relative stabilities agree well with available observations. As for Er@C_{82}, it may be mentioned that minor isomers are likely analogous to Ca@C_{82}.[15] Determination of the charge-per-Sc atom for Sc_2@C_{84} **(10)** by chromatography, however, suggests that the Sc atoms have a "+2" charge.[6,21]

In 1991, Smalley and his collaborators demonstrated that fullerenolanthanides can be produced by laser vaporization of graphite and lanthanum oxide and extracted by toluene.[7,8,23] The physical measurements, such as EPR,[21,24–30] mass spectrometry,[21,31–34] extended X-ray absorption fine structure (EXAFS),[21,35,36] and X-ray photoelectron spectroscopy (XPS),[21,28] were performed on the extracts containing the mixture of fullerenolanthanides and empty fullerenes.

Unsaturated thiocrown ethers with *cis*-geometry (**1–9**) demonstrate interesting properties for physicochemical studies due to their conformational restriction compared to a corresponding saturated system and to the size their cavities. The presence of sulfur atoms in the structure of crown ethers accounts for the different properties of thiocrown ethers. The *cis*-unsaturated thiocrown ethers **1–9** were synthesized, and their structures were confirmed.[5,37–47] 1,4-Dithiin is the smallest member of compounds **1–9** to have been widely studied.[6–17] In 2001, the structures of [X-UT-Y] (X = 6, 9, 12, 15, 18, 21, 24 and 27; Y = 2–9) **1–9** were reported by Tsuchiya et al.[37] In that report, ^{1}H and ^{13}C NMR signals, X-ray crystallography and ORTEP drawings, cavity size, and UV spectral data of [X-UT-Y] **1–9** were considered carefully.[37] In 2006, the oxidation potential ($^{ox}E_1$), cyclic voltammetry (Fc/Fc^+), and the free energy of electron transfer (ΔG_{et}) of the supramolecular complex of [X-UT-Y][C_{60}] and [X-UT-Y][La@C_{82}] of *cis*-unsaturated thiocrown ethers **1–9** were considered by Tsuchiya et al.[38] The endohedral metallofullerenes and complexes with the thiocrown ethers have shown interesting properties for applications and studies. In 2006, the oxidation potential ($^{redox.}E_1$) of Sc_2@C_{84} **(10)** and Er_2@C_{82} **(11)** were reported by Anderson et al.[6]

Graph theory has been found to be a useful tool in QSAR (quantitative structure activity relationship) and QSPR (quantitative structure property relationship).[48–54] Numerous studies have been performed related to the abovementioned fields by using the so-called topological indices (TI).[54–57,60] In 1993 and 1997, a related complex of applications of the Wiener and Harary indices in fullerene science was reported.[55,56]

The use of effective mathematical methods to suitably correlate between several data properties of chemicals is important. The ratio of the summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) was a useful numerical and structural value of the unsaturated thiocrown ethers **1–9** that were utilized here.

In this article, the electrochemical behaviors of a series of M@C_x (where M = Sc or Er, and x = 82 or 84) were determined by studying the relationship between the index μ_{cs} and oxidation potential ($^{ox}E_1$) of **1–9**, as well as the free energy of electron transfer (ΔG_{et}) between **1–9** and **10** and **11**, as well as [X-UT-Y][Sc_2@C_{84}] **(12)** and [X-UT-Y][Er_2@C_{82}] **(13)** complexes were investigated.[59] The QSAR studies of this index relative to some of the structural data of thiocrown ethers **1–9**, their maximum wavelength (λ_{max}), cavity size, and oxidation potential ($^{ox}E_1$), as well as the free energy of electron transfer (ΔG_{et}) between **1–9** and C_{60} and La@C_{82}, Sc_2@C_{84}, and Er_2@C_{82}, were reported previously.[57,59,60]

GRAPHS AND MATHEMATICAL METHOD

All graphing operations were performed using the Microsoft Office Excel 2003 program. The ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) seems to be a useful numerical and structural value for the unsaturated thiocrown ethers **1–9** that were utilized here. See Equation (1).

$$\mu_{cs} = (n_s + n_c)/(n_s \cdot n_c) \tag{1}$$

where $n_c = 2n_s$, thus making the coefficient of μ_{cs} equal to

$$\mu_{cs} = 3/(2n_s) \tag{2}$$

For modeling, both linear (MLR) and nonlinear (ANN) models were used in this study. To calculate the values that were not reported previously, equations 1–6 of this study were utilized.[58–60] Some of the other indices were examined, and the best results and equations for extending the physicochemical data were chosen.[58–60]

The Rehm–Weller equation[57] estimates the free energy change between a donor (D) and an acceptor (A) as:

$$\Delta G^\circ = e[E_D{}^\circ - E_A{}^\circ] - \Delta E^* + \omega_1 \tag{3}$$

where e is the unit electrical charge, $E_D{}^\circ$ and $E_A{}^\circ$ are the reduction potentials of the electron donor and acceptor, respectively, ΔE^* is the energy of the singlet or triplet excited state, and w is the work required to bring the donor and acceptor to within the ET distance. The work term in this expression can be considered to be zero, inasmuch as there exists an electrostatic complex before the electron transfer.[57]

DISCUSSION

It was reported that each of the metallofullerenes has a remarkably small potential difference between the first oxidation and the first reduction.[20] This may suggest that the HOMO of M@C_{82}, originally the LUMO$^+$ of the C_{82}, is singly occupied (i.e., SOMO) as purposed for La@C_{82}.[20] The ionization potential, electron affinity, oxidation, and reduction potentials of Ce@C_{82} and Gd@C_{82} (E in volts vs. Fc/Fc$^+$ and radii of lanthanides) were reported previously. It was found that the ionic radii of Ln^{3+} show good linear relationships with the first redox potentials.[20] The ionization potentials and electron affinities of M@C_{82} (M = lanthanides) were reported as obtained by ab initio calculations.[20,62] The first oxidation and reduction processes occur on the SOMO whose electron density is higher on the cage close to the M^{3+} (M = lanthanides).[20,62,63] The electrons on the SOMO are bound to the cage with a higher energy when the metal–carbon distance decreases because the electrostatic interactions between electrons and the metal intensify.[20] Several important metallofullerenes, M@C_{82} (where M = Ce and Gd), were found to have similar voltammetric responses regardless of metal identity or carbon number. Assignment of formal charges to the fullerene cage (that they are characterized by the "charge-per-metal" atom encapsulated) suggests that these metallofullerenes are isoelectronic and have related molecular orbital structures.[6] The predicted complex structures of unsaturated thiocrown ethers (**1–9**) with **10** and **11** were introduced here as [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][Gd@C_{82}] **(13)** complexes. The potential difference between the oxidation and reduction in these structures is related to the band gap of HOMO-LUMO orbitals. The electronic properties of Ce@C_{82} and Gd@C_{82} are very similar to that of La@C_{82}, although both Ce and Gd have 4*f* level electrons. It was suggested that these 4*f* electrons do not play an important role in fullerenolanthanide chemistry as seen in organic and inorganic lanthanide chemistry.[20,64,65]

The values of the relative data of **1–9** are shown in Table I. The values shown in Table I demonstrate that μ_{cs} decreases with increasing molecular size of the compounds **1–9**. In Table I, the related values for the supramolecular complexes of [X-UT-Y] **1–9** with Ce@C_{84} **(10)** and Gd@C_{82} **(11)** are also shown. Table I shows the calculated values of oxidation potential ($^{ox}E_1$), as well as the free energy of electron transfer (ΔG_{et}) between some of the [X-UT-Y] and their complexes with **10** and **11**.

The X-ray crystal structures and ORTEP drawings for some of the structures of **1**–**9** [X-UT-Y] (X = 15, 18, 21, 24 and 27; Y = 5–9) were determined. These show there are cavities in these molecules, and also that the sulfur atoms are nearly coplanar.[37] The average radii of the cavity sizes for **4–8** are 1.76, 2.34, 3.48, 4.43, and 5.36 Å, respectively.[11,37,38] The ^{13}C and ^{1}H NMR results (in $CDCl_3$) were reported previously. These results show that compound **4** has the highest chemical shifts in both ^{1}H and ^{13}C NMR. The electron density of the C=C increases with the size of the rings from **4**→**9** and diminishes from **4**→**1** with decreasing ring size of [X-UT-Y].[37,38] The first and second reduction potentials ($^{red}E_1$) of Ce@C_{82} **(10)** are −0.41 and −1.41 volts, and for Gd@C_{82} **(11)**, they are to −0.39 and −1.38 volts, respectively.[20] The oxidation potentials ($^{ox}E_1$) of **4–7** were measured to be 0.82, 0.79, 0.73, and 0.69 V, respectively.[6,37,38] The free energies of electron transfer (ΔG_{et}) between **1–9** with **10** and/or **11** to produce [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][(Gd@C_{82}] **(13)** complexes were calculated by the Rehm–Weller equation6,[7,36,57,59,60] (see Figure 1).

In Figures 2–5 (Figures 4 and 5 are available online in the Supplementary Materials), two-dimensional diagrams show the relationships between the main values that were

n	0	1	2	3	4	5	6	7	8
No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

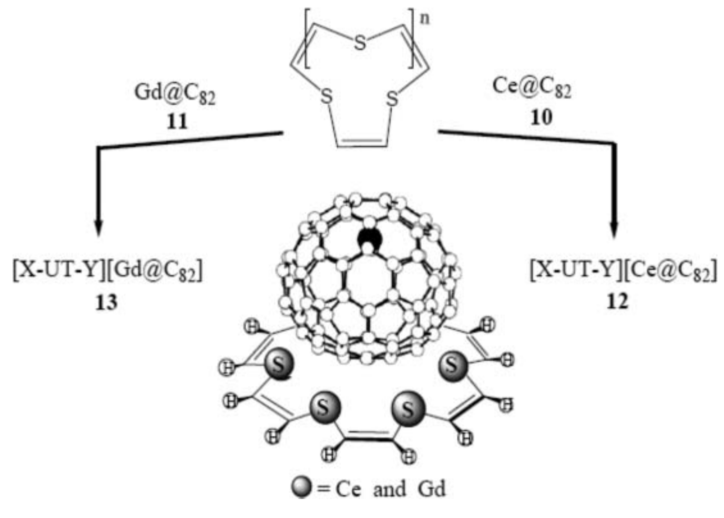

Figure 1 The total structures of unsaturated thiocrown ethers **1–9**, their supramolecular complexes of [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][Gd@C_{82}] **(13)**. (The form of M@C82 was extracted from Ref. [20]).

Table I The values of data coefficients of unsaturated thiocrown ethers [X-UT-Y] **1–9** and the values of the free energy of electron transfer (ΔG_{et}) in kcal mol^{-1} between unsaturated thiocrown ethers **1–9** with [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][Gd@C_{82}] **(13)** complexes

No.	Formula of * [X-UT-Y]	n_s	n_c	μ_{cs}	$^{ox}E_1$ (Volt)	ΔG_{et} (kcal mol^{-1}) First redox. [X-UT-Y][Ce@C_{82}] **(12)** complexes	ΔG_{et} (kcal mol^{-1}) Second redox. [X-UT-Y][Ce@C_{82}] **(12)** complexes	ΔG_{et} (kcal mol^{-1}) First redox. [X-UT-Y][Gd@C_{82}] **(13)** complexes	ΔG_{et} (kcal mol^{-1}) Second redox. [X-UT-Y][Gd@C_{82}] **(13)** complexes
1	6-UT-2 (1,4-dithiin)	2	4	0.7500	1.02	32.28	55.34	31.82	54.65
2	9-UT-3	3	6	0.5000	0.97	31.13	54.19	30.67	53.50
3	12-UT-4	4	8	0.3750	0.89	29.28	52.35	28.83	51.65
4	15-UT-5	5	10	0.3000	0.82	27.62	50.73	27.21	50.04
5	18-UT-6	6	12	0.2500	0.79	26.98	50.04	26.52	49.35
6	21-UT-7	7	14	0.2143	0.73	25.60	48.66	25.13	47.96
7	24-UT-8	8	16	0.1875	0.69	24.67	47.27	24.21	47.04
8	27-UT-9	9	18	0.1667	0.66	23.98	47.04	23.52	46.35
9	30-UT-10	10	20	0.1500	0.63	23.29	46.35	22.83	45.66

The first and second reduction potentials ($^{red}E_1$) of Ce@C_{82} **(10)** are –0.41 and –1.41 volts, respectively, and of Gd@C_{82} **(11)** are –0.39 and –1.38 volts, respectively.

*The data for the compounds and their complexes have not been previously reported. [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][Gd@C_{82}] **(13)** supramolecular complexes were neither synthesized nor reported.

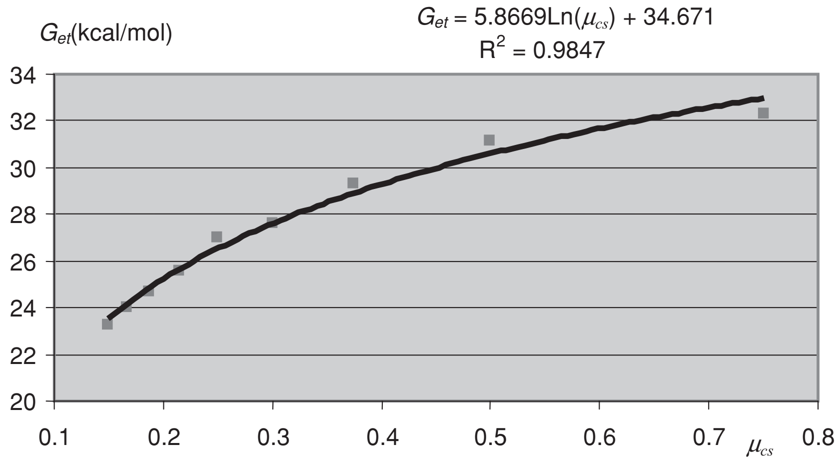

Figure 2 The relationship of μ_{cs} versus the free energy of electron transfer (ΔG_{et}) between **1–9** and the first reduction potential ($^{red}E_1$) of Ce@C_{82} **(10)** for [X-UT-Y][Ce@C_{82}] **(12)**.

demonstrated in Table I. In Table II, the correlation equations between μ_{cs} and ΔG_{et} for the supramolecular complexes [X-UT-Y][M@C_{82}] (M = Ce, Gd) **12** and **13** are shown.

Figure 2 shows the relationship between the values of μ_{cs} and the free energies of electron transfer (ΔG_{et}) between **1–9** and the first reduction potential ($^{red}E_1$) of Ce@C_{82} **(10)** for [X-UT-Y][Ce@C_{82}] complexes **(12)**. Equation 4 (Table II) describes Figure 2 and shows the *Nieperian* logarithmic behavior of the relationship between ΔG_{et} and μ_{cs}. See Table II. With this equation, it is possible to achieve a good approximation for extending the determination of ΔG_{et}. The R-squared value (R^2) for this graph is 0.9847. In light of this high correlation between μ_{cs} and the free energy of electron transfer (ΔG_{et}) between **1–9** and the first reduction potential ($^{red}E_1$) of Ce@C_{82} **(10)**, it is possible to use μ_{cs} to calculate the (ΔG_{et}) of [X-UT-Y][Ce@C_{82}] complexes. With increasing ring size of these compounds, the values of μ_{cs} decrease.

The curve in Figure 3 shows the relationship between the values of μ_{cs} and the free energy of electron transfer (ΔG_{et}) between **1–9** and the second reduction potential ($^{red}E_2$) of Ce@C_{82} **(10)** for [X-UT-Y][Ce@C_{82}] complexes **(12)**. In Figure 3, the line of best fit is curved. In accordance with Equation 5 (Table II), there is an effective equation between the μ_{cs} values and ΔG_{et}. By this equation, it is possible to achieve a good approximation for

Table II The Correlation Equations Between μ_{cs} and ΔG_{et} for the Supramolecular Complexes [X-UT-Y][M@C_{82}] (M = Ce, Gd)

	ΔG_{et} = a [Ln(μ_{cs})] + b	
Equation Number	a	b
4	5.8669	34.671
5	5.9499	57.792
6	5.8708	34.221
7	5.8695	57.048

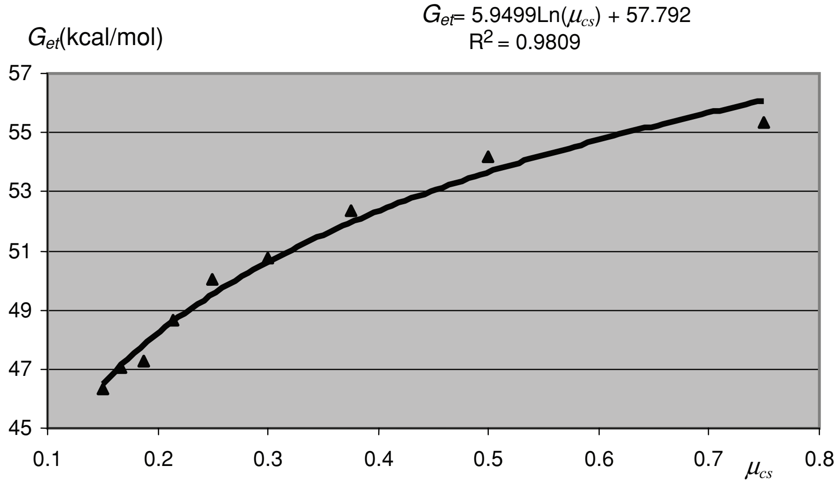

Figure 3 The relationship of μ_{cs} versus the free energy of electron transfer (ΔG_{et}) between **1–9** with the second reduction potential ($^{red}E_2$) of Ce@C$_{82}$ **(10)** for [X-UT-Y][Ce@C$_{82}$] **(12)**.

extending the determination of ΔG_{et} for these types of complexes. The R-squared value (R^2) for this graph is equal to 0.9809.

Similarly, Figures 4 and 5 show the same relationship for the analogous [X-UT-Y][Gd@C$_{82}$] complexes (see Supplemental Materials, Figures 4S and 5S).

The ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) shows a high correlation with the physicochemical and structural values of the unsaturated thiocrown ethers **1–9**. The results show the calculated values of free energy of electron transfer (ΔG_{et}) of the [X-UT-Y][Ce@C$_{82}$] **(12)** and [X-UT-Y][Gd@C$_{82}$] **(13)** supramolecular complexes on the basis of the first and second reduction potentials ($^{red}E_1$ and $^{red}E_2$) of Ce@C$_{82}$ **(10)** and Gd@C$_{82}$ **(11)**. The data for the compounds and their complexes were not previously reported. The compounds [X-UT-Y][Ce@C$_{82}$] **(12)** and [X-UT-Y][Gd@C$_{82}$] **(13)** supramolecular complexes were neither synthesized nor reported previously.

CONCLUSION

Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atom(s) to the surrounding fullerene cage. C$_{82}$ is known to readily form endohedral metallofullerenes. The *cis*-unsaturated thiocrown ethers **1–9** have important physicochemical properties. The electrochemical data of [X-UT-Y] **1–9** were reported in this article, including oxidation potential ($^{ox}E_1$) and the free energy of electron transfer (ΔG_{et}) on the basis of the first and second reduction potentials ($^{red}E_1$ and $^{red}E_2$) of Ce@C$_{82}$ **(10)** and Gd@C$_{82}$ **(11)** for the predicted supramolecular complexes of [X-UT-Y][Ce@C$_{82}$] **(12)** and [X-UT-Y][Gd@C$_{82}$] **(13)**. The predicted values of ΔG_{et} for **12** and **13** were calculated by using the Rehm–Weller equation. Using the ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}), the equations of the model can derive sound structural relationships between the aforementioned physicochemical data. By utilizing the equations of this model, one can calculate the values for the unsaturated thiocrown ethers [X-UT-Y]

(1–9) with Ce@C_{82} **(10)** and Gd@C_{82} **(11)**. The compounds [X-UT-Y][Ce@C_{82}] **(12)** and [X-UT-Y][Gd@C_{82}] **(13)** supramolecular complexes were previously neither synthesized nor reported.

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