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Spectral and Electrochemical Characterization of Dibenzotetraaza[14]annulenes

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The UV/Vis absorption spectra and cyclic voltammograms (CV) of the Cu(II) and Ni(II) complexes of γ,γ′-alkoxycarbonyl derivatives of α,α′- diphenyldibenzotetraaza[14]annulene are analyzed and compared. The observed ratio of absorption intensities at the peaks of π-π* transitions is linearly correlated with the difference of HOMO and LUMO energy levels of the substituents. Moreover, the measured values of the mid-peak potential of metal redox reactions on a Pt electrode in DMF are linearly correlated with the ionization potential values of the appropriate substituents.

Keywords: Dibenzotetraaza[14]annulenes; Absorption spectra; Cyclic voltammetry; Inductive effect; Ionization potential; Copper complexes

INTRODUCTION

Dibenzotetraaza[14]annulenes are interesting macromolecules both for theoretical and practical reasons. Because of their similarity to porphyrins and corrins dibenzotetraaza[14]annulenes may be attractive models of many important enzymes (cytochromes, peroxidases, catalase, and oxygenases), oxygen transferring proteins (hemoglobin, myoglobin), and chlorophylls. Dibenzotetraaza[14]annulenes, like porphyrins, have co-planar nitrogen donor atoms and substantial bond unsaturation and delocalization in the macrocylic framework. Contrary to porphyrins these complexes are Hückel anti-aromatic (4n) systems and adopt nearly planar, or saddle-shaped conformations, depending upon the ring substitution. It has been shown that the substituents in the β and γ positions of the macrocycle considerably modify the spatial structure of the system, as indicated by the XRD studies in the solid phase and NMR studies in solutions [1,2].

Metal complexes of dibenzotetraaza[14]annulenes are efficient catalysts of redox reactions [3–5]. Ni (II) and Cu(II) complexes of dibenzotetraaza[14]annulenes and tetramethyldibenzotetraaza[14]annulenes electropolymerise in acetonitrile solutions. The process is inhibited in DMF, and has not been observed for tetraphenyldibenzotetraaza[14]annulene [6].

The effect of various substituents on the electrochemical characteristics of porphyrins and their complexes was a subject of numerous studies [7]. The effect of the substituents on the relative spectral intensities and the potentials of redox transformations was described using the Hammett constant σ, at the definite solvent, temperature and supporting electrolyte. For the ring- and peripherally substituted metal tetraphenylporphyrins the slopes of the lines relating the CV half-wave potential values over σ, for cation radical and anion radical formation reactions were in the order of 0.08, to 0.3 V/σ unit, while for the metal oxidations and metal reductions they were in the order of 0.03 to 0.04 V/σ unit. Using a different set of σ parameters Hochgesang and coworkers [8] obtained the slopes in the order 0.15 to 0.25 V/σ, for Ni and Cu complexes of tetraphenyldibenzotetraaza[14]annulenes.

The aim of this work was to study the effect of various substituents on the absorption electronic spectra and CV wave positions of Cu(II) and Ni(II) complexes of dibenzotetraaza[14]annulene derivatives.

EXPERIMENTAL

Materials

Sodium perchlorate (Merck) was dried at 60° in vacuum. N,N-dimethylformamide (DMF) (Spectranal, Riedel-de Haën) with the maximum water

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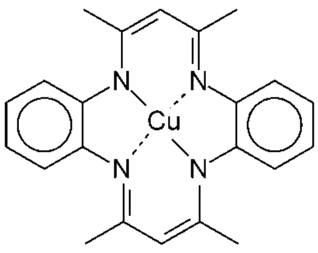
content of 0.05% v/v was additionally dehydrated over molecular sieves.

The investigated complexes were synthesized according to the procedures described earlier [1,2]. The Ni(II) complexes (**3Ni**, **11Ni**) and one free ligand (**10L**) were studied too.



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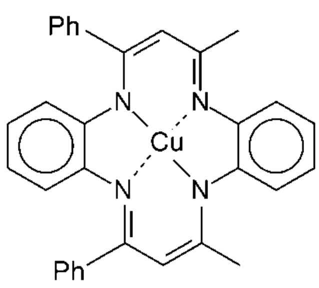

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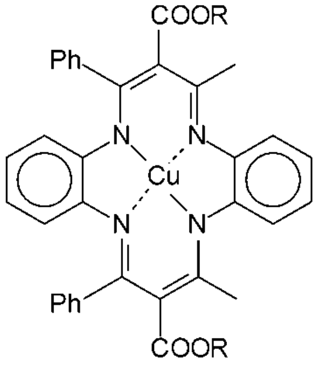

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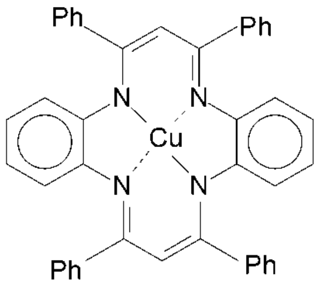

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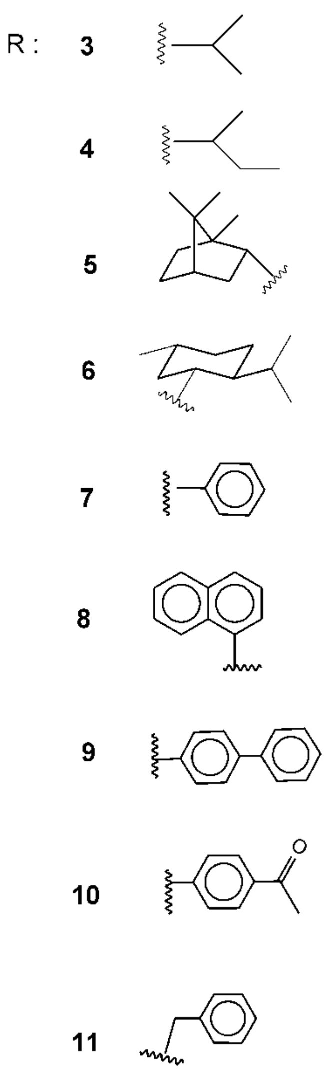
Measurements

The ultraviolet and visible spectra covering the 250–700 nm wavelength range were measured using a Shimadzu PC 2101 spectrophotometer, in DMF solutions, at room temperature.

The CV experiments were carried out using the digital potentiostat ECI1286 (SOLARTRON-SCHLUMBERGER) in a typical electrochemical cell in three-electrode configuration. 0.1 M $NaClO_4$ or 0.1 M TBAP were used as base electrolytes. The Pt working electrode had an exposed area of about 0.2 cm^2. Another Pt wire electrode was used as a counter-electrode and an aqueous saturated calomel electrode (SCE) served as the reference electrode. The SCE was separated from the working solution by a salt bridge filled with the solution of the base electrolyte in DMF. All potentials were reported with respect to the SCE. Oxygen-free argon was used to remove oxygen from the solution. All electrochemical experiments were carried out at 25.0 ± 0.1°C.



If both cathodic and anodic peaks for a given process were observed in CV experiments the formal redox potential was approximated by the mid-peak potential. In some cases irreversible anodic processes were observed (no corresponding cathodic peak). In such cases the potential of a peak is given.

COMPUTATIONS

In computations of the electronic structures of the investigated molecules the density functional theory (DFT) with the StoBe computer code [9] was applied. A full geometry optimization was performed within the Vosko-Wilk-Nusair LDA functional [10]. The electronic parameters of the systems were calculated within GGA-RPBE approximation [11,12]. The Kohn-Sham orbitals were represented by linear combinations of atomic orbitals which themselves are described by extended all-electron sets of the contracted Gaussian type orbitals [13,14].

RESULTS

Ultraviolet and Visible Spectra

The yellowish free ligand (**10L**) showed intense $\pi \rightarrow \pi^*$ transitions at 270 (I) and 342 nm (II), and additional, not well separated transition at 301 nm. The positions and energies of the first two peaks were theoretically predicted for dichlorotetramethyldibenzotetraaza[14]annulene, and observed in acetonitrile [15]. These peaks were shifted to about 280 and 386 nm in the Cu(II) and Ni(II) complexes. Moreover, the d → d ligand to metal charge transfer peaks at about 640 nm for Cu(II) and about 587 nm for Ni (II) were observed. Finally, the peaks at about 420 nm, most probably corresponding to the metal ion – ligand charge transfer were common for both metal ions (Table I). For Ni(II) and Cu(II) complexes of tetraphenyldibenzotetraaza[14]annulene in methylene chloride the following peaks were obtained respectively: 275(3.03), 406 (2.81), 461 (1.34), 672 (0.040), and 266(3.34), 356 (0.764), 406 (2.00), 462 (1.30), 622 (0.444) [8]. The observed peaks did not change significantly with the HOMO and LUMO energies of the substituents, but the ratio of absorption intensities of the $\pi \rightarrow \pi^*$ transitions was almost linearly correlated with the difference between E_{HOMO} and E_{LUMO} (Fig. 1).

Cyclic Voltammetry

DMF used as a solvent showed the measuring window between −1.4 and 1.0 V. **10L** showed no peaks between −1.4 and about 0.9 V. At the potentials higher than about 0.9 V irreversible oxidation of the ligand started. Within the same range of scan potentials all Cu(II) and Ni(II) dibenzotetraaza[14]annulene complexes showed one quasi-reversible oxidation process with the anodic peak current i_{la} and one quasi-reversible reduction process with the cathodic peak current i_{mc}. The peaks current ratio i_{la}/i_{mc} was close to one. The separation of the peaks in the forward and reverse scans in the reduction process was within the range of 62 to 89 mV, and that of the oxidation process was within the range of 59 to 91 mV. The redox process in the cathodic part of the voltammogram was unequivocally the Me^{2+}/Me^{1+} redox transformation, whereas that in the anodic part of the voltammogram may be the metal oxidation (Me^{2+}/Me^{3+}), as proposed by Taraszewska for a similar class of compounds [18]. Cu (II) complexes,

TABLE I Absorption maxima observed for the investigated complexes in DMF

R Complex	λ [nm] ε [$10^4 M^{-1} cm^{-1}$]					
	Peak				Metal	
	I		II	III	Cu(II)	Ni(II)
1	287		382	417	637	
	2.96		4.75	1.92	0.17	
1 [9]	288		388	417	641	
	2.45		4.88	1.92	0.20	
2	283		395	439	658	
	2.59		2.58	1.24	0.14	
4	288		390	429	649	
	2.675		2.58	1.28	0.16	
5	283		392	432	640	
	3.33		3.24	1.37	0.12	
6	284		390	430	620	
	2.55		2.23	1.00	0.12	
7	284		386	422	636	
	1.39		2.23	1.06	0.15	
8	285		386	420	621	
	2.78		2.23	1.09	0.12	
9	285		386	420	621	
	2.779		1.880	1.092	0.115	
10	276		380		632	
	3.82		3.15		0.16	
10L	270	301	342			
	4.08	3.595	3.30			
3Ni	273		392	434.5		590.5
	3.075		2.373	1.407		0.615
11Ni	275		391	430		587
	2.98		2.21	1.26		0.56

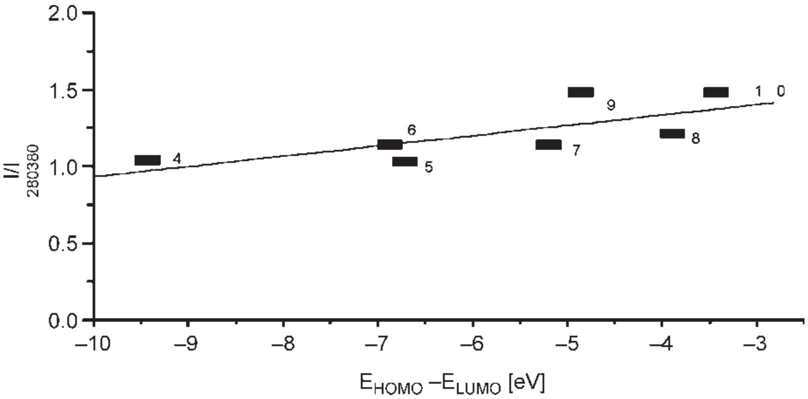


FIGURE 1 Effect of the substituents on the ratio of absorption intensities at the first and second absorption peaks.

which are not substituted in the positions γ, γ′ showed a similar behavior in the cathodic part of the voltammogram to the substituted ones, whereas the process in the anodic part of the voltamperogram was completely irreversible (no peak in the reverse scan was visible). The presence of phenyl substituents in the position β and alkoxycarbonyl substituents in the position γ shifted the metal redox mid-peak potentials of dibenzotetraaza[14]annulenes to more anodic values. The effect is more pronounced for substitution in the position β as well as for the aromatic than aliphatic substituents in the position γ. The presented results may be compared also with that of the tetraphenyl Cu(II) and Ni(II) complexes and their ligand [8]. Table II collects $E_{1/2}$ values for the **1**, **2**, as well as Cu(II) and Ni(II) complexes of tetraphenyldibenzotetraaza[14]annulene (**12Cu** and **12Ni**).

Table III collects the values of the mid-peak potentials of the oxidation and reduction peaks, as well as E_{HOMO} and E_{LUMO} for the studied substituents in the γ position.

The degree and mode of transmission of electron density from various points on the ligand through the σ and π orbitals to the central atom/ion affects the visible absorption spectra, potentials of redox reactions and ligation of the free bases and their respective metal complexes. Values of E_{redox} of the redox reactions of many complexes depend linearly on the Hammett constant, σ [7,16–18]. According to the Janak's theorem E_{HOMO} values show the ionization potential. We have checked that the proportionality of the Hammett constants used by Kadish in description of the induction effect of simple peripheral substituents on the half-wave redox potentials of porphyrins [17] to the respective E_{HOMO} values of these substituents is very good. Hence here the observed values of the mid-peak potentials were correlated with E_{HOMO} values.

The values of E_{redox} observed for Cu^{+2}/Cu^{+1} transformations vary with the slope of 0.038 ± 0.009 V/eV with σ, while for Cu^{+2}/Cu^{+3} transformations the slope is 0.048 ± 0.006 V/eV (or 0.038 ± 0.003 V/eV, without **4**) (Fig. 2). It indicates that the effect of the substituents in the position γ studied is rather weak. It is even lower for the two studied nickel complexes. The substituent induction effect on Cu^{+2}/Cu^{+1} redox potential of dibenzotetraaza[14]annulene may be compared with the effects observed for Cu^{+2}/Cu^{+1} redox potential in peripherally substituted tetraphenylporphyrins (0.048 V/eV) and Co^{+2}/Co^{+3} redox potential in tetraphenylporphyrins (0.054 V/eV) and in phtalocyanins (0.030 V/eV), calculated based on the data from ref. [16], [17], and [19], respectively.

TABLE II Effect of phenyl substituents in β position on the mid-peak potential values

Complex	**1**	**2**	12 − Cu	12 − Ni
$E_{1/2}^{red}$	0.46 V_{irr}	0.53 V_{irr}	0.68 V^a[8]	0.76 V^a[8]
$E_{1/2}^{ox}$	− 1.30 V	− 1.15V	− 0.96 V [8]	− 1.28 V[8]

[a] in 0.1 M TEAP in methylene chloride solutions

CONCLUSIONS

UV/Vis absorption spectra and cyclic voltammograms of the Cu(II)γ,γ′-alkoxycarbonyl derivatives (3–11) were studied. Variation in the γ substituent did not

TABLE III Mid-peak potentials of the complexes and computed energy level values for the substituents

Complex	E_{red} [V]	E_{ox} [V]	$-E_{HOMO}$ [eV]	E_{LUMO} [eV]
3	− 1.030	0.635	7.56	2.02
4	− 1.088	0.595	7.60	1.82
5	− 1.007	–	5.70	1.01
6	− 0.997	0.691	5.77	1.10
7	− 0.985	0.686	6.18	− 0.99
8	− 0.970	0.719	5.33	− 1.90
9	− 0.985	0.700	6.12	− 1.27
10	− 0.962	0.711	5.62	− 1.73
11	− 1.011	0.708	5.86	− 0.90
3Ni	− 1.364	0.848	7.56	2.02
11Ni	− 1.377	0.851	5.86	− 0.9

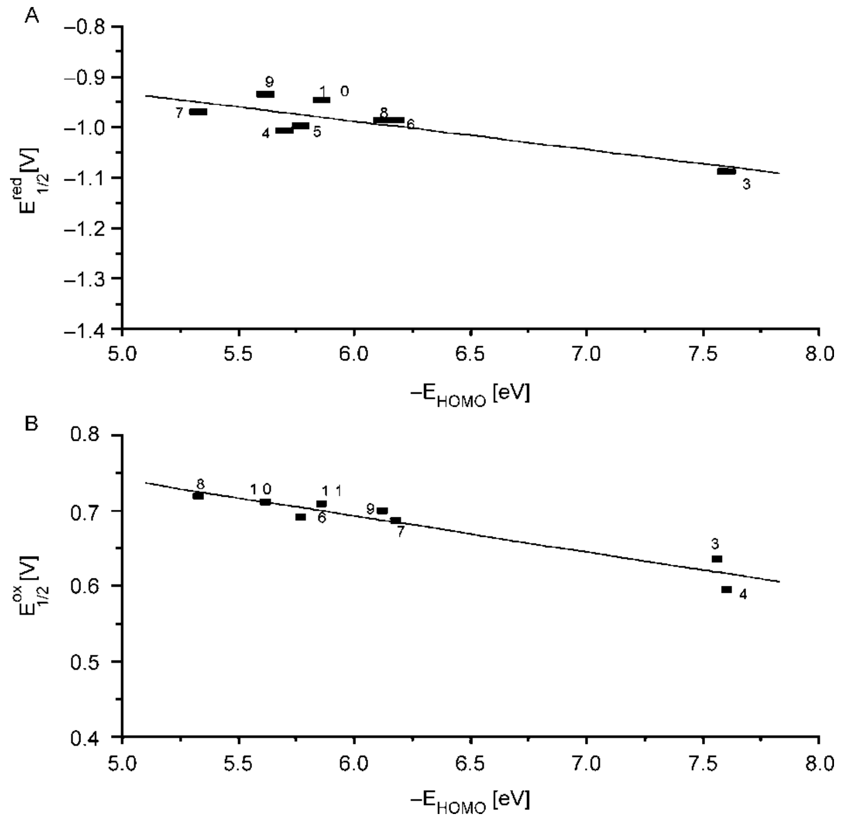


FIGURE 2 The induction effect of the substituents on: a) - the Cu^{+2} reduction and b) - the Cu^{+2} oxidation formal potentials.

change the position of absorption peaks much. The observed ratio of absorption intensities at the peaks of π-π^* transitions was linearly correlated with the difference of the HOMO and LUMO energy levels of the substituents. Moreover, the measured values of the mid-peak potential of metal redox reactions and of the organic ligand quasi-reversible oxidation reactions on Pt electrode in DMF were linearly correlated with the HOMO energy levels of substituents. For metal reduction mid-peak potential the effect of γ substituents seems to have an intermediate value between those observed for simple peripheral substitution of tetraphenyl-porphyrin and phtalocyanin. Aromatic substituents exerted a greater induction effect than the aliphatic ones.

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