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The Synthesis and Properties of *o*-Semiquinolate Copper Complexes

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*New neutral bis-*o*-semiquinolate copper(II) complexes with benzosemiquinone-1,2; 3,5- and 3,6-di-tert-butylbenzosemiquinone-1,2 and perchloroxanthrensemiquinone-1,2 were synthesised. The results of physical measurements showed that these complexes were the copper(II) ones with two paramagnetic ligands. Besides chemical properties of these complexes, we also studied, in particular, redox reactions, thermal decomposition, interaction with n- and π-donor compounds, etc. A useful method of synthesis of spin-marked copper(I) complexes by reaction of bis-3,5-di-tert-butylbenzosemiquinolate copper(II) complexes with n- and π-donor ligands is proposed. This method is illustrated by the preparation of new bis-(tert-butylisocyanide)-3,5-di-tert-butylbenzosemiquinolate-1,2 complexes.*

Introduction

In the previous publications [1, 2] we reported the synthesis of new tris-ligand complexes of transition metals of III, V, VI groups with the paramagnetic anion-radical of *o*-semiquinone as a ligand.

The paramagnetic state of ligands which we first supposed from the results of physical measurements and chemical investigations of complexes obtained has been lately confirmed by other authors in their works on the molecular structure of some similar complexes [3, 4].

Neutral bis-ligand Co(II) and Ni(II) complexes being the derivatives of 9,10-phenanthrenquinone [5] and 3,5-di-tert-butylbenzoquinone-1,2 [6, 7] also contain paramagnetic *o*-semiquinolate ligands. This fact was confirmed by physical measurements and chemical investigations of these complexes [7] and by the results of X-ray structure analysis of the Co(II) complex with 3,5-di-tert-butylbenzoquinone-1,2 [8].

Similar copper(II) complexes were unknown until recently. Balch and co-workers who were the first to prepare the neutral bis-*o*-semiquinolate nickel(II) complex described [9] bis-catecholate copper(II) complexes which could be obtained by oxidation of the corresponding bis-catecholate. Mono-ligand *o*-semiquinolate copper(I) complexes with n- or π-donor ligands were described in our ref. [10, 12].

In this paper we report the preparation and properties of neutral bis-*o*-semiquinolate copper(II) complexes.

Results and Discussion

Neutral bis-*o*-semiquinolate complexes were obtained by the interaction of copper(II) salts with the corresponding *o*-semiquinolate of alkaline metals (or thallium) in THF as well as by the reaction of copper(II) halogens or carboxylates with equal amounts of *o*-quinone and the corresponding catechol in alcoholic alkali.

$$CuX_2 + 2Na(Tl)SQ \xrightarrow{THF} Cu(SQ)_2 + 2Na(Tl)X \quad (1)$$

$$CuX_2 + Q + QH_2 + 2LiOH \rightarrow Cu(SQ)_2 + 2LiX + 2H_2O \quad (2)$$

where Q is *o*-quinone and QH_2 is the corresponding catechol.

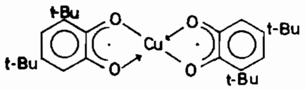
The second reaction is more preferable for the preparation of such complexes in a pure crystalline state without any further purification by recrystallization methods.

These reactions can be used for the synthesis of bis-*o*-semiquinolate complexes of benzoquinone-1,2; 3,5- and 3,6-di-tert-butylbenzoquinone-1,2; perchloroxanthrenquinone-1,2 and 9,10-phenanthrenquinone. We carried out a more detailed investigation of bis(3,5-di-tert-butylbenzosemiquinolate-1,2) copper(II) complex. This complex, being a dark-blue crystaline solid, is moderately soluble in most organic solvents, but insoluble in water. In the crystalline state it is stable to atmospheric oxygen for several months, but decomposes in solutions. According to the DAT data the decomposition temperature of the compound is 120 °C.

The measured magnetic moment, μ_{eff}, is 2.98 MB at 198 K and is 2.65 MB at 77 K. The experimental value of the magnetic moment, μ_{eff}, agrees well with the theoretical value 3 MB for the three unpaired weakly interacting electrones, one of them being localized on the copper atom (d^9 electron configuration) and each of the other two is on its *o*-semiquinolate ligand. Small decrease of μ_{eff} with temperature is due to the weak antiferromagnetic interaction in the complex.

The IR- and UV-spectroscopy data confirm *o*-semiquinolate nature of the ligands in the investigated complex. The IR spectra of complex (I) show a series of strong absorption bands at 1465 cm^{-1}, 1475 cm^{-1} and at 1530 cm^{-1} that are characteristic of a chelated *o*-semiquinolate ligand. Its UV spectra show absorption bands at 305 nm (4.15), 385 nm (3.52) and at 720 nm (2.7). They are similar to those of the previously investigated complex of $La(SQ)_3$ which shows the absorption bands at 305 nm (3.98), 360 nm (3.45) and 760 nm (2.65) [2].

Consequently, the results of physical measurements and chemical properties indicate that this complex is the copper(II) one with two paramagnetic *o*-semiquinolate ligands.



I

Such structure of the complex agrees well with its chemical properties. In the reaction of $Cu(SQ)_2$ with metallic sodium the two electron reduction of the complex (which very likely proceeds stepwise) takes place,

$$Cu(SQ)_2 + 2Na \rightarrow Na_2Cu(Cat)_2 \qquad (3)$$

leading to the formation of bis-catecholate copper(II) complex similar to that described by Balch and coworkers [9]. The observed ESR spectrum typical for copper(II) complexes ($g_i = 2.113$, $A_{Cu} = 80$ G) shows clearly that only the *o*-semiquinolate ligands were reduced, but the valent state of the central atom was unchanged.

The valency state of the *o*-semiquinolate copper(II) complexes is also unchanged in the reactions of the complex with, for example, $AgOCOCF_3$;

$$Cu(SQ)_2 + 2AgOCOCF_3 \rightarrow$$
$$2Ag + Cu(OCOCF_3)_2 + 2Q \qquad (4)$$

In this case similarly to the reduction, the redox process occurs only in *o*-semiquinolate ligands to give *o*-quinone. The valent state of copper is unchanged too and this is confirmed by the observed copper(II) ESR spectrum of $Cu(OCOCF_3)_2$ ($g_\perp = 2.078$, $A_{Cu\perp} = 18$ G; $g_\parallel = 2.360$, $A_{Cu\parallel} = 144$ G).

The ability of *o*-semiquinolate ligand to redox transformations causes also the formation of metallic copper and *o*-quinone due to the intramolecular redox reaction.

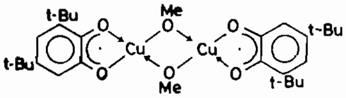
$$Cu(SQ)_2 \rightarrow Cu + 2Q \qquad (5)$$

Bis-*o*-semiquinolate copper(II) complexes react easily with inorganic acids and organic proton containing compounds, *e.g.*, with acetylacetone to give the corresponding derivative of copper(II), *i.e.*, *o*-quinone and catechol.

$$Cu(SQ)_2 + 2HCl \rightarrow CuCl_2 + Q + QH_2 \qquad (6)$$

$$Cu(SQ)_2 + 2AcAcH \rightarrow Cu(AcAc)_2 + Q + QH_2 \qquad (7)$$

$Cu(SQ)_2$ reacts also with alcohols. However, there is no complete replacement of the SQ-ligand in this case. More drastic conditions are necessary to complete these reactions. So interaction with methanol leads to substitution of only one *o*-semiquinolate ligand and to the formation of a dark-blue crystalline product which element composition and properties correspond to a dimeric copper(II) complex with bridge methoxy groups.



II

Complexes of the type $Cu(SQ)_2$ can enter into the reactions of redox substitution with other *o*-quinones which have a higher redox potential.

$$Cu(SQ)_2 + 2Q' \rightarrow Cu(SQ')_2 + 2Q \qquad (8)$$

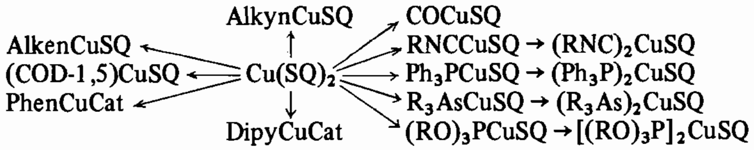
The reactions of bis-*o*-semiquinolate copper(II) complexes with neutral n- and π-ligands leading to the formation of copper(I) complexes with spin-marked SQ-ligand are of speical interest from the point of view of *o*-semiquinolate ligand usage as spin marks in the chemistry of coordination compounds [10, 12].

$$Cu(SQ)_2 + nL \rightarrow L_nCuSQ + Q \qquad (9)$$

This reaction is also a redox one and it is similar to the reaction of reduction of copper(II) halides and haludo-halides by donor ligands described by Gazo and co-workers [11].

The synthesis and investigation of some complexes of the type L_nCuSQ by the ESR method have already been described in Ref. [10]. The reaction (9) offers new ways for the synthesis of complexes shown in the Scheme.

Some of the above reactions (Scheme) are reversible, for example reactions with CO, alkens. Other reactions in which phospines, phosphites, isocyanides and arsines are used as ligands are almost completely

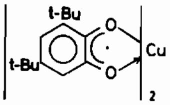
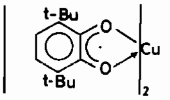
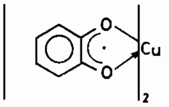
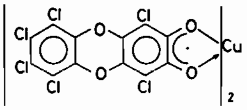
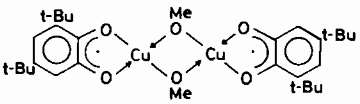
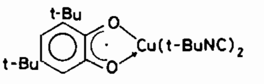


Scheme.

shifted to the formation of L_nCuSQ complexes and they can be used for the preparation of such complexes. Thus we have obtained bis–(tert-butylisocyanide)-3,5-di-tert-butylbenzosemiquinolate of copper(I) by the reaction of bis-3,5-di-tert-butylbenzosemiquinolate of copper(II) with tert-butylisocyanide. It is a dark brown crystalline compound well soluble in organic solvents, stable in air and paramagnetic. The value of μ_{eff} = 1.72 MB corresponds to one unpaired electron. The ESR spectrum parameters, *i.e.*, g_i = 2.0037, A_{Cu} = 9.3 G, A_H = 3.2 G are similar to those of semiquinolate derivatives of copper(I) [10, 12] and indicate that the unpaired electron is essentially localized on the *o*-semiquinolate ligand. The IR and UV spectroscopy data confirm this structure.

One more application of reaction (9) should be pointed out. This reaction in combination with high sensitivity of modern ESR spectrometers makes it possible to develop an analytical method for determination (both quantitative and qualitative) of n- and π-donor compounds in solutions. It is very important

TABLE I. Elemental analysis.

Compound	Element	% Found	% Calcd.	Colour, Decomposition temp. (°C)
1	2	3	4	5
	C	66.75	66.66	Dark blue crystals
	H	7.83	7.93	119–121
	Cu	12.30	12.69	
	C	66.23	66.66	Dark blue crystals
	H	7.17	7.93	119–121
	Cu	12.25	12.69	
	C	49.36	50.80	Dark blue crystals
	H	3.06	2.85	114–116
	Cu	23.86	22.40	
	C	30.94	31.82	Violet crystals
	Cl	46.35	46.98	134–136
	Cu	7.00	7.06	
	C	56.95	57.20	Dark blue crystals
	H	7.23	7.30	107–109
	Cu	20.76	20.30	
	C	63.79	64.04	Dark brown crystals
	H	8.35	8.51	69–71
	N	6.05	6.22	
	Cu	14.80	14.12	

to note that the form of the ESR spectrum of L_nCuSQ depends upon the nature of L ligand [10], thus allowing identification of L ligand.

Experimental

Preparation of $Cu(DB_{3,5}SQ)_2$ *I*

To a solution of 0.01 mole of 3,5-di-tert-butylbenzosemiquinone-1,2 and 0.01 mole of copper(II) halide in 40 ml of methanol was gradually added a solution of 0.01 mole of the corresponding catechol and 0.02 mole of LiOH in 70 ml of methanol under nitrogen. The reaction mixture became blue-green and a dark blue crystalline product precipitated for several hours. Then the precipitate was filtered, washed with cold methanol and dried *in vacuo* at room temperature for six hours.

The complex was obtained in 90% yield. Derivatives of other *o*-quinones were prepared in essentially the same way.

Preparation of $Cu_2DB_{3,5}SQ)_2(OMe)_2$ *II*

This complex was prepared by boiling complex I in methanol for a long time under nitrogen. The yield was 35–40%.

Preparation of $DB_{3,5}SQCu(tBuNC)_2$ *III*

To a solution of 0.025 mole of tert-butylisocyanide in 20 ml of toluene was gradually added in portions the suspension of 0.01 ml of complex I in 30 ml of toluene. The reaction mixture became dark brown and then a dark brown crystalline product precipitated. The resulting precipitate was filtered and dried *in vacuo* at room temperature for six hours. The yield of the product was 75–80%. Analytical results are given in Table I.

The ESR spectra were determined using a PE-1301 spectrometer.

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