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# Transition metal complexes, possessing redox-isomerism as a basis for new smart sensing materials

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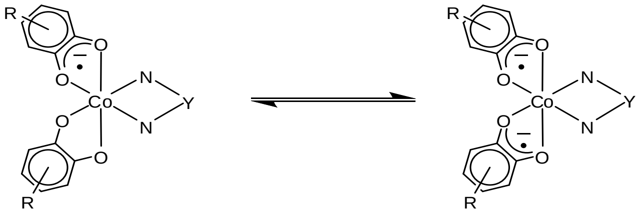
**Extensive studies on bistable molecules which can transform their physical properties with external stimuli, for developing molecule-based sensors have been performed [1-3]. It is known that some semiquinonato transition metal complexes undergo a redox-isomeric (valence-tautomeric) interconversion induced by temperature, light, pressure and magnetic field.**



| **Low-spin form** | **High-spin form** |
|---|---|
| **Co(III), d6, S = 0** | **Co(II), d7, S = 3/2** |
| **DBSQ, S = 1/2** | **DBSQ, S = 1/2** |
| **DBCat, S = 0** | **DBSQ, S = 1/2** |

**where DBSQ – anion-radical of o-quinone,**
**DBCat – dianion of corresponding o-quinone;**
**Y – organic or elementoorganic bridge;**
**R – organic substituent.**

**This paper presents results of thermodynamic studies of some complexes which exhibit redox-isomerism.**

## I. INTRODUCTION

Redox-isomeric complexes combine redox-active ligands and transition metal ions having two or more accessible oxidation states.

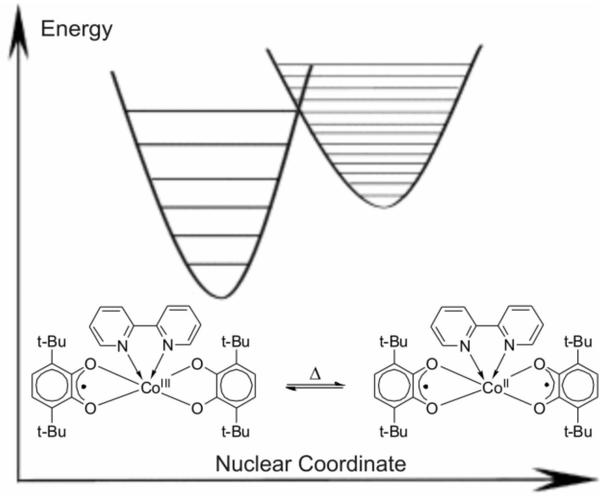


*Fig. 1. Redox-isomerism of (bpy)Co(3,6-DBSQ)$_2$*

Since each electronic isomer exhibits different optical, electronic and/or magnetic properties, these complexes are being proposed as candidates for future application in molecular electronic devices, switches and sensors [4, 5].

In solid state redox-isomerism was discovered in o-semiquinonic cobalt complexes (Fig. 1) [6]. Currently, most of known redox-isomeric complexes were obtained with cobalt, and few of them with nickel, manganese and rhodium [7, 8]. It was revealed that transformation of semiquinon-catecholate form of complex into bis-semiquinonic one is accompanied by phase transition.

So, precise vacuum calorimetry gives very useful quantitative information for the characterization of complexes displaying redox-isomerism as well as of redox-isomeric transformation itself.

The purpose of present work is to measure the low-temperature heat capacity by adiabatic calorimetry over the temperature range 6–350 K and by differential scanning calorimetry in the range 250–420 K of some o-semiquinonic cobalt complexes, to estimate their characteristics, to calculate the standard thermodynamic functions in wide temperature range and to investigate dependence of phase transition characteristics on acceptor ability of quinone fragment and nature of neutral ligands.

## II. EXPERIMENT

### A. Experimental set up

For measuring heat capacity, temperatures and enthalpies of transitions we have used an installation of calorimetric equipment, including adiabatic vacuum and differential scanning calorimeters.

A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range of $6 \leqslant T \leqslant 350$ K [9]. It was established that the apparatus and measurement technique were enable the determination of the heat capacity of substances with an error not exceeding ±2% within the temperature range 6–15 K, ±0.5%, between 15 and 40 K, ±0.2% within the temperature range of $40 \leqslant T \leqslant 350$ K. The phase transition temperatures were measured within about ±0.01 K and the enthalpies of transformations with the error of ±0.2%.

To measure the heat capacity of the sample under study over the range from 250–420 K the differential scanning calorimeter (DSC 204 F1 Phoenix, Netzsch, Germany) was used [10]. The heat capacity error didn’t exceed ±2%. The heating and cooling rates were 5 K/min, the measurements were carried out in argon atmosphere.

Measured samples were also studied with IR and EPR spectroscopies and by magnetic measurements. Elemental analisys reveals that the purity of measured compounds is about 99.5 per cents.

### B. Experimental results

First redox-isomeric complex studied calorimetrically was (bpy)Co(3,6-DBSQ)$_2$, where (bpy) is 2,2-dipiridyl (Fig. 2, curve 2) [11]. Further, in order to try to control the parameters of transition we studied heat capacities of complexes similar to initial, having methoxy and chlorine substituents in position 4 of quinonic fragment (Fig. 2, curves 1, 3). Previously, it was established that methoxy substituent reduces acceptor ability and chlorine substituent increases acceptor ability of quinone compared with non-substituted one (Fig. 3).

Obviously, thermodynamic parameters of phase transition in these complexes depend on acceptor ability of quinonic fragment (Table 1), increasing of acceptor ability of quinones leads to increasing transition temperature, enthalpy and entropy. Transition in (bpy)Co(4-Cl-3,6-DBSQ)$_2$ (Fig. 2, curve 3) doesn’t finish because of thermal destruction of the sample, so, decomposition of the compound makes impossible the determination of transition enthalpy. Data of magnetic measurements, infrared and EPR spectroscopy fully confirm the existence of redox-isomerism in temperature ranges of transitions observed calorimetrically.

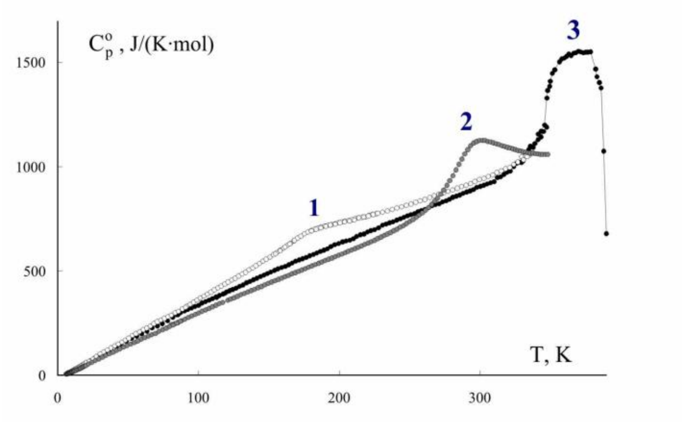


*Fig. 2. Temperature dependence of heat capacity of (bpy)Co(4-MeO-3,6-DBSQ)$_2$ [**I**] (1), (bpy)Co(3,6-DBSQ)$_2$ [**II**] (2), (bpy)Co(4-Cl-3,6-DBSQ)$_2$ [**III**] (3)*

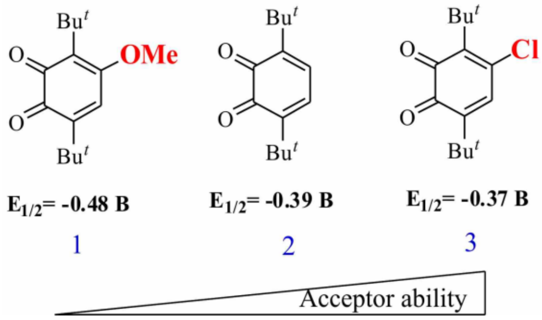


*Fig. 3. Reduction potentials of 4-MeO-3,6-DBQ (1), 3,6-DBQ (2) and 4-Cl-3,6-DBQ (3)*

*Table 1. Thermodynamic parameters of phase transition in **I**, **II** and **III***

| | ΔT, K | $T^o_{tr}$ ($C^o_{p,\ max}$), K | $\Delta H^o_{tr}$, kJ/mol | $\Delta S^o_{tr}$,J/K·mol |
|---|---|---|---|---|
| **I** | 134–222 | 178.0 | 2.14 | 11.9 |
| **II** | 250–375 | 299.9 | 15.0 | 48.8 |
| **III** | 309– | 370.0 | – | – |

If to use the 1,10-phenanthroline as neutral ligand instead of 2,2-dipiridyl we will obtain complex which heat capacity is presented in Fig. 4.

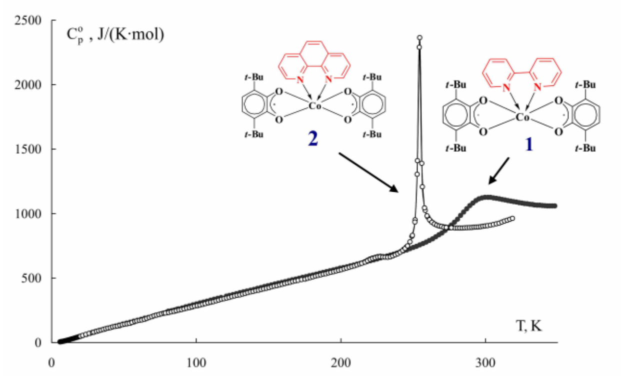


*Fig. 4. Temperature dependence of heat capacity of (bpy)Co(3,6-DBSQ)$_2$ [**II**] (1) and (phen)Co(3,6-DBSQ)$_2$ [**IV**] (2)*

As we can see, minor distinction (of 2 carbon atoms) in neutral ligand leads to significant change in phase transition temperature, interval and steepness (Table 2).

*Table 2. Thermodynamic parameters of phase transition in **II** and **IV***

| | $\Delta T$, K | $T^{o}_{tr}(C^{o}_{p,\,max})$, K | $\Delta H^{o}_{tr}$ , kJ/mol | $\Delta S^{o}_{tr}$ , J/K·mol |
|---|---|---|---|---|
| **II** | 250–375 | 299.9 | 15.0 | 48.8 |
| **IV** | 234–281 | 254.5 | 6.32 | 24.8 |

For explaining different steepness (cooperativity) domain model proposed by Sorai and Seki for spin-crossover transitions was used [12]. Extent of cooperativity of transitions is highly important characteristics which should be studied in order to be able to control it for creating molecular devices, switches and sensors. Precise vacuum calorimetry is one of suitable methods which allow us to investigate cooperativity of redox-isomeric transitions.

## III. CONCLUSIONS

The temperature dependence of heat capacity for some *o*-semiquinonic cobalt complexes was studied by methods of calorimetry in 6–350(420) K temperature range.

Thermodynamic parameters of phase transition which accompanies redox-isomeric transformation of semiquinone-catecholate form of the complex into bis-semiquinonic one were determined. It was revealed, that increasing of acceptor ability of quinones leads to increasing transition temperature, enthalpy and steepness.

Substitution of neutral ligand dipyridil on phenanthroline leads to increasing the cooperativity extent of phase transition and decreasing the values of its enthalpy and enthropy.

On the basis on experimental data the standard thermodynamic functions were calculated for studied complexes in wide temperature range.

These studies contribute to development an approach of “tuning” properties of redox-isomeric systems for use in specific practical purposes. Peculiar redox-active character of semiquinonic transition metal complexes makes them appealing to design materials of potential technological interest.

## IV. ACKNOWLEDGMENTS

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