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Heteroligand o-Semiquinonato-Formazanato Cobalt Complexes

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S Supporting Information

ABSTRACT: Two novel heteroligand o-semiquinonato-formazanato cobalt complexes [Co(3,6-SQ)(Form)] (**1**) and [Co(3,6-SQ)$_2$(Form)] (**2**) (3,6-SQ is 3,6-di-*tert*-butyl-o-benzosemiquinonate radical anion; Form is 1,3,5-triphenylformazanate anion) were synthesized and characterized in detail. The molecular structures of [Co(3,6-SQ)(Form)] and [Co(3,6-SQ)$_2$(Form)] were determined by X-ray analysis. Magnetic susceptibility measurements and spectroscopic studies have shown that square-planar complex **1** is diamagnetic with a residual paramagnetism due to antiferromagnetic exchange metal−ligand. Complex **2** includes cobalt(III) in the low-spin state and two anionic-radical o-semiquinonato and one formazanate ligand.

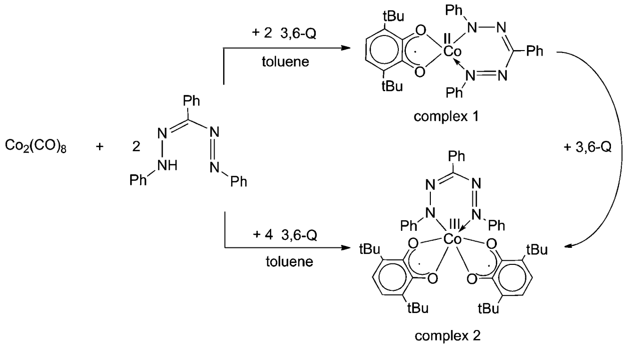
Formazanates (1,2,4,5-tetraazapentadienyls) belong to the well-known class of anionic chelating N-donor ligands. Their metal complexes were successfully applied as eco-friendly textile dyes, components of optical recording media, and polymerization catalysts. Recently, Otten and co-workers[1] have shown that formazanates in the metal coordination sphere can be reversibly reduced to stable "metallaverdazyl" radicals analogous to organic verdazyl radicals. The revealed possibility to use coordinated formazanates as a reversible electron reservoir makes it a prospective redox-active (noninnocent) ligand like well-studied o-quinones and α-diimines. From this viewpoint, formazanate metal complexes are promising for use in catalytic reactions and molecular magnet design.

Metal complexes bearing a formazanate ligand together with other organic ligands have received comparatively little attention in coordination chemistry. For the present time, such types of compounds were found only for ruthenium,[2] boron,[3] and palladium.[4]

The main aim of the present work is a search of the new synthetic methods to the formazanate metal complexes and the attempts to combine the chemistry of cobalt complexes with redox-active o-quinones and formazanate ligands.

The known methods for the preparation of formazanate cobalt complexes are based on rapid mixing of hot ethanol or acetone solutions of a neutral form of the formazane ligand and a corresponding inorganic metal salt.[5] Herein, we show that the interaction of $Co_2(CO)_8$ with 1,3,5-triphenylformazane and 3,6-di-*tert*-butyl-o-benzoquinone leads to formation complex [Co(3,6-SQ)(Form)] (**1**) or [Co(3,6-SQ)$_2$(Form)] (**2**) depending on the reagents' molar ratio (Scheme 1).

Scheme 1. Synthesis of Heteroligand o-Semiquinonato-Formazanate Cobalt Complexes



This method has some preferences in comparison with literature procedures, because the interaction occurs quickly, does not require heating of the reaction mixture (both reactions occur easily even at room temperature), and allows for obtaining formazanate metal complexes in better yield (80−90%). It should be noted that complex **1** reacts with one molar equivalent of 3,6-Q to form complex **2**.

Complexes **1** and **2** were characterized by IR, UV−vis-spectroscopy, elemental analysis, and magnetochemistry. The crystal structures of **1** and **2** have been determined by single-crystal X-ray diffraction (ESI).

As shown in Figure 1, the cobalt(II) atom in **1** has a square planar coordination environment; however the plane Co(1)-N(1)N(4)O(1)O(2) is not coplanar with the formazan ligand backbone and lies at an angle of 27.37° relative to it. The bent angle of chelating cycle Co(1)N(1)N(2)C(15)N(3)N(4) along the N(1)...N(4) line is 20.67°. The bond lengths within the formazan backbone indicate that it is fully delocalized (N(1)−N(2), 1.3118(12) Å; N(2)−C(15), 1.3403(13) Å; N(3)−C(15), 1.3401(13) Å; N(3)−N(4), 1.3093(12) Å), consistent with other complexes of anionic formazanate ligands.[6]

The phenyl substituents are twisted with respect to the formazane plane (N2−N1−N3−N4) at torsion angles of

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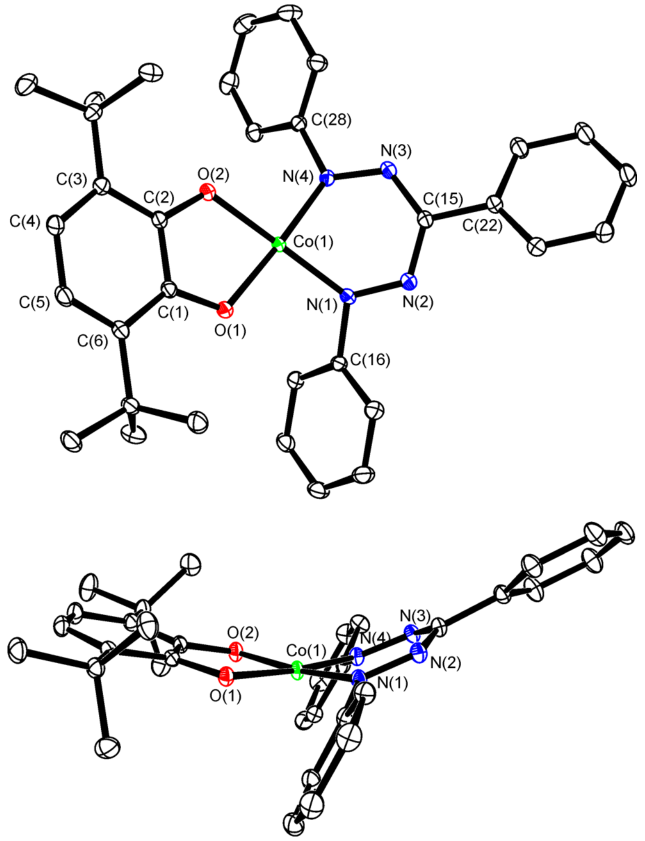

Figure 1. Molecular structure of **1**. Ellipsoids set at 50%; hydrogen atoms are omitted for clarity.

36.35°. It should be noted that a similar geometry was observed for other heteroligand formazanate complex viz. (1,1,1,5,5,5-hexafluoroacetylacetonato)(1,5-p-tolyl-3-nitroformazanato)-palladium.[4] The distances C–O and C–C in O,O′-chelating ligand (C(1)–O(1) is 1.2971(13) Å and C(2)–O(2) is 1.2960(12) Å) lie in the typical range of bond lengths for coordinated radical-anionic o-semiquinonato ligands in different transition metal complexes.[7,8] The C–C distances of the six membered carbon ring of O,O′-chelating ligand in **1** show a quinoid type alternation: bonds C(3)–C(4) and C(5)–C(6) (1.3719(14) and 1.3717(15) Å, respectively) are shorter than other C–C bonds: C(1)–C(6), 1.4263(13) Å; C(1)–C(2), 1.4421(13) Å; C(2)–C(3), 1.4263(15) Å; C(4)–C(5), 1.4240(14) Å. The metrical oxidation state (MOS) of the quinonato ligand was determined based on least-squares fitting of its C–C, C–O, and C–N bond lengths in the accordance with the algorithm of Brown[8] to be −1.15 with a standard deviation of ±0.04. The bond lengths Co–O and Co–N (av. 1.87 and 1.81 Å, respectively) are characteristic for the o-semiquinonato low-spin cobalt(II) complexes.[9] In the related cobalt complex containing dichloro(1,3,5-triphenylformazanato)cobaltate(II) anion reported in the literature,[10] cobalt(II) adopts a tetrahedral geometry causing a high spin state of Co(II), and the corresponding Co–N distances (av. 1.96 Å) are longer than in **1**. Thus, the X-ray analysis has shown that **1** is a low-spin Co(II) complex with one anion-radical o-semiquinonato and one anionic formazanate ligands.

The molecular structure of **2** in crystal is shown in Figure 2. The central cobalt atom has an octahedral environment. Like complex **1**, the geometrical features of O,O′-chelating ligands in

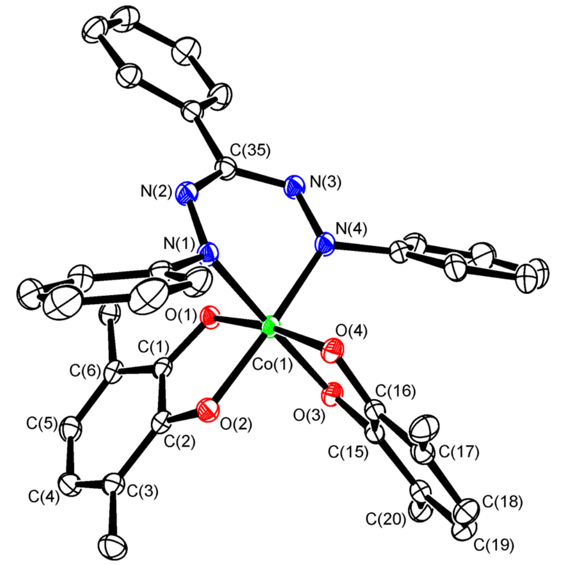

Figure 2. Molecular structure of **2**. Ellipsoids set at 50%; hydrogen atoms and methyl groups of *tert*-butyls are omitted for clarity.

2 are also typical for the radical-anion o-semiquinonato form: the distances C–O lie in the range of 1.2915(18)–1.3053(17) Å; C–C bonds differ in the quinoid pattern (see Table S2 in the Supporting Information). The MOS values calculated according to ref 8 for both ligands are −1.11 and −1.09, respectively, confirming the o-benzosemiquinone form of these ligands. The Co–O bonds lie in the range 1.8831(10)–1.9166(10) Å typical for octahedral cobalt(III) o-semiquinolates.[7,11] The geometrical features of the N,N′-chelating ligand also point out its anionic form. The bent angle of chelating cycle Co(1)N(1)N(2)C(35)N(3)N(4) along the N(1)...N(4) line is 35.12°, which is bigger than in **1** and can be explained by the sterical hindrances between ligands in **2**. So, complex **2** is a cobalt(III) complex with two radical-anionic o-semiquinones and one formazanate anion in accordance with X-ray analysis.

The magnetic properties of **1** and **2** were investigated in the temperature range of 2–300 K. Temperature dependence of the effective magnetic moment (μ_{eff}) for complex **2** is presented in Figure 3. The value of μ_{eff} at 300 K (2.44 μ_B) for complex **2**

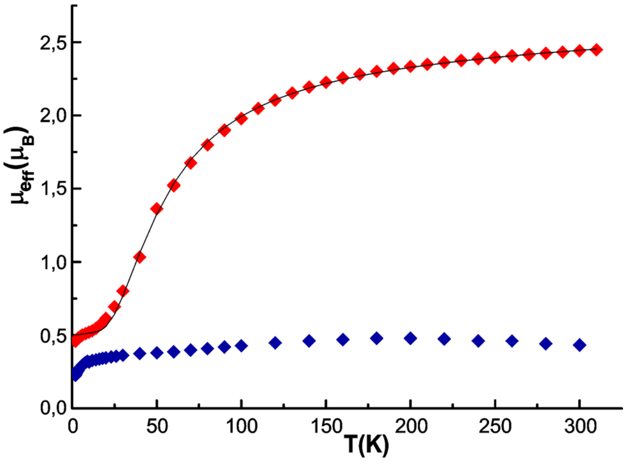

Figure 3. Temperature dependence of magnetic moments of complexes **1** (blue) and **2** (red).

is close to the spin-only value of 2.45 μ_B typical for a system with two noninteracting paramagnetic centers with $S = 1/2$. With lowering temperature, the μ_{eff} value of complex **2** decreases insensibly in the range 300−150 K and more suddenly below 150 K and reaches 0.46 μ_B at 2 K. It indicates the domination of antiferromagnetic exchange interactions between unpaired electrons of o-semiquinonato ligands. Estimation of exchange interaction parameters was carried out using the model of exchange coupled dimer ($H = -2JS_1S_2$). The optimal values of interaction parameters are $J = -65.4$ (±0.4) K (45.4 ± 0.3 cm^{-1}) and $g = 2.04$ (±0.01). The related octahedral o-semiquinonato cobalt(III) complex $Co(3,6\text{-}SQ)_3$ also demonstrates the antiferromagnetic SQ−SQ exchange with $J_{SQ-SQ} = -39.1$ cm^{-1}; in zinc(II) complex $Zn(tmeda)(3,6\text{-}SQ)_2$, $J_{SQ-SQ} = -33.7$ cm^{-1}.[11]

Complex **2** was also characterized by EPR spectrum; the apparent signal (solid state, 298 K) is very broad (line width >1000 G) with $g = 2.02$. In contrast to complex **2**, the polycrystalline sample of **1** demonstrates only residual paramagnetism at the rate of about 0.4 μ_B; however, neither EPR nor NMR signals for complex **1** were observed. The most probable reason for a singlet ground state of **1** is antiferromagnetic exchange between low-spin cobalt(II) (d^7, $S = 1/2$) and o-semiquinonato radical anion ($S = 1/2$), and the residual paramagnetism is caused by the admixture of the exited states with higher spin multiplicity.

Optical absorption spectra of complexes **1** and **2** were recorded in toluene solutions at room temperature (Figure 4).

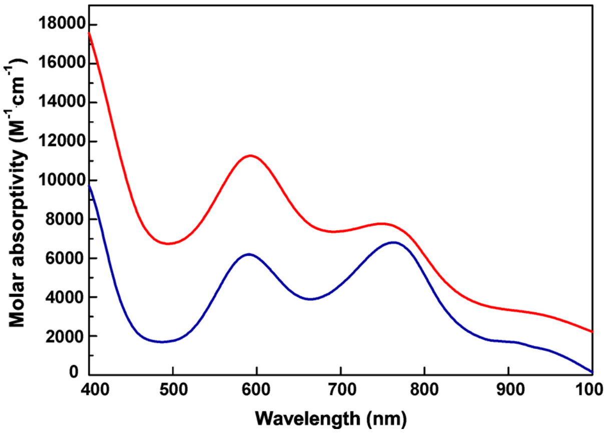

Figure 4. Optical absorption spectra of **1** (blue) and **2** (red) (toluene, RT, $C = 1 \times 10^{-4}$ M).

Both complexes have very intense absorption bands in the range of 350−400 nm ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}). These were assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions in o-semiqiunonate ligands. The spectra also display intense broad bands in the visible range at 590 and 593 nm, for **1** and **2**, respectively, in agreement with the presence of anionic formazanate ligands in these compounds. The absorption bands observed in the range of 750−770 nm ($\varepsilon \sim 7 \times 10^3$ M^{-1} cm^{-1}) are characteristic for heteroligand o-semiquinonato cobalt complexes with nitrogen donor ligands[9,12] and correspond to charge transition between metal and o-semiquinonate ligands.

In summary, we have successfully synthesized the first examples of heteroligand o-semiquinonato-formazanato cobalt complexes. The crystal structures of complexes have been established by single crystal X-ray crystallographic measurement. Complex **1** adopts square planar geometry and contains low-spin Co(II) and two chelating ligands: o-semiquinonate and formazanate. Due to the presence in **1** of two radical centers with strong antiferromagnetic exchange, this complex demonstrates diamagnetic behavior. Compound **2** is the low-spin Co(III) complex supported by formazanate and two anionic-radical o-semiquinonato ligands. Magnetic properties of **2** were specified by the domination of antiferromagnetic exchange interactions between unpaired electrons of o-semiquinonato ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental data; Tables S1 and S2 with structural information; Figures S1 (the dependence χ-T), S2 (the dependence χT-T), and S3 (EPR of **2** in solid state); and X-ray crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00912.

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Notes

The authors declare no competing financial interest.

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