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Computational and structural studies on the complexation of cobalt(II) acetate by water and pyridine

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ABSTRACT

Four different complexes of the cobalt(II) acetate–pyridine–water system were obtained as dominant species by crystallization from a series of dichloromethane and toluene solutions. The complexes were characterized by terms of X-ray crystal structure determination. Factors in solution properties leading to crystallization of certain complexes are discussed. Furthermore, trends in terms of structure and binding energies in a systematic series of mononuclear cobalt(II) complexes were studied using density functional calculations.

1. Introduction

The coordination chemistry of cobalt has long been the subject of research endeavour [1]. Recently, interest in cobalt complexes has once again risen – particularly in conjunction with the catalysis of water oxidation, or the inverse process of oxygen reduction [2–5]. In this context, especially dinuclear complexes make up important model systems [5]. Oligonuclear cluster complexes of cobalt have also been studied as possible catalysts for the oxidation of organic substrates [6,7].

Another field in which cobalt complexes are of importance is in the catalysis of C–C bond formation reactions such as the aldol reaction [8,9]. In conjunction with our own efforts to develop catalytic cobalt complexes of this type [10], we focussed on the properties of complexes of cobalt(II) with pyridine bases. The factors governing the catalytic activity of these systems is not yet fully understood as, owing (amongst others) to the complex nature of solution equilibria, the structures of the catalytically active cobalt complexes have not been revealed yet.

Although a huge number of complexes, and thereby a wide selection of coordination geometries, of cobalt(II) with simple and common ligands such as water and pyridine have been studied, the trends within this group of compounds have barely been investigated.

We report here the structures of a series of cobalt(II) complexes with varying numbers of aqua and pyridine ligands bound to the metal center. Furthermore, we present a series of DFT calculations investigating the trends in binding energies and structure of the complete series of water/pyridine substituted cobalt(II) complexes.

2. Materials and methods

$Co(OAc)_2·4H_2O$ has been purchased (Merck102530, Darmstadt, Germany) and used without further purification if not described otherwise. Dichloromethane was purified by distillation from calcium hydride; toluene by distillation from sodium. After purification, solvents were stored under inert conditions. (1*R*)-Benzoylcamphor has been prepared as described [10]. IR spectra were recorded as KBr pellets at a resolution of 2 cm^{-1} on a Bruker Tensor-27 Fourier transform spectrometer, running the OPUS 6.5 version of software.

2.1. Crystallisation of the complexes

2.1.1. Diacetato-tetraaqua-cobalt(II) (**1**)

A solution of $Co(OAc)_2·4H_2O$ (69 mg, 0.39 mmol), (1*R*)-benzoylcamphor (100 mg, 0.39 mmol), and pyridine (63 µL, 0.78 mmol) in 1 mL of dichloromethane was prepared. The solvent was allowed to slowly evaporate at room temperature, yielding orange crystals of **1**.

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2.1.2. Tetraaqua-dipyridine-cobalt(II) acetate (**2**)

In 1 mL dichloromethane, $Co(OAc)_2 \cdot 4H_2O$ (69 mg, 0.39 mmol), (1*R*)-benzoylcamphor (100 mg, 0.39 mmol) and pyridine (126 μL, 1.56 mmol) were dissolved. Slow evaporation of the solvent at room temperature gave orange crystals of **2**.

2.1.3. Diacetato-diaqua-dipyridine-cobalt(II) (**3**)

$Co(OAc)_2 \cdot 4H_2O$ (69 mg, 0.39 mmol), (1*R*)-benzoylcamphor (100 mg, 0.39 mmol) and pyridine (63 μL, 0.78 mmol) were dissolved under heating in 1 mL of toluene. Crystals of **3** were grown by slow evaporation of the solvent at room temperature. IR: $\tilde{\nu}$ (cm^{-1}) 3110, 3078, 2896, 1603, 1487, 1450, 1361, 1343, 1219, 1156, 1073, 1039, 1025, 1011, 987, 888, 857, 759, 697, 659, 628, 504, 427. Anal. calc. for $C_{14}H_{20}CoN_2O_6$: C, 45.29%; H, 5.43%; N, 7.55%. Found: C, 45.3%; H, 5.41%; N, 7.57%.

2.1.4. Tetraacetato-tripyridine-dicobalt(II) (**4**)

$Co(OAc)_2 \cdot 4H_2O$ (429 mg, 1.72 mmol) was dehydrated by cautiously heating under vacuum, keeping the temperature well below 200 °C in order to avoid decomposition of the acetate (which is known to take place around 230 °C [11]), until weight loss corresponding to the four aqua ligands was reached. The resulting violet powder was, together with pyridine (0.54 mL, 6.7 mmol) dissolved in 4.3 mL of toluene under heating to the boiling point. From this solution **4** crystallized over a period of several weeks at 4 °C. IR: $\tilde{\nu}$ (cm^{-1}) 3066, 3003, 2931, 1635, 1619, 1601, 1571, 1486, 1447, 1416, 1339, 1218, 1153, 1075, 1038, 1010, 907, 765, 758, 701, 653, 628, 615, 520, 492, 427. Anal. calc. for $C_{51}H_{59}Co_4N_7O_{16}$: C, 48.55%; H, 4.71%; N, 7.77%. Found: C, 47.1%; H, 4.96%; N, 7.5%.[1]

Crystallisation of **1**–**3** was essentially quantitative. Crystallisation of **4**, however, was accompanied by precipitation of an inhomogeneous, mostly pink, powder, prohibiting exact specification of the yield – it is estimated to approximately 50%.

2.2. Crystal structure determination

Single crystal X-ray diffraction data were collected using a Bruker D8 three circle diffractometer with Smart Apex CCD detector, Oxford Cryostream low temperature device and fine focus Mo Kα sealed tube with graphite monochromator.

180° ω-scans for a total of 2400 frames (0.3°-scan correlated) per measurement with four different ϕ positions ($\Delta\phi = 90°$) were collected. Data reduction and empirical absorption correction were carried out with the program packages SAINT and SADABS [12].

Solution of phase problem and structure refinement were performed with SHELXS and SHELXL, Graphics are from SHELXP [13].

2.3. Electronic structure calculations

All calculations were performed using the Gaussian09 [14] program package. In all cases the B3LYP [15] functional with a LanL2TZ (f) [16–20] basis set for cobalt and a 6-311+G(d,p) [21,22] basis set for all other atoms was used. All cobalt(II) complexes were assumed to exist in high-spin configuration. Geometry optimizations were conducted using the default convergence criteria implemented in the program. Optimized geometries were confirmed to represent energetic minima by frequency calculations yielding only real frequencies.

Interaction energies were calculated as difference between the electronic energy of the complex with the ligand in a bound state and the energies of the relaxed structures of the isolated ligand and remaining complex fragment.

3. Results and discussion

We have previously reported efforts to develop molecularly imprinted polymers [23] with class-II aldolase-like activity [10]. The use of analogs of transition states (or reaction intermediates) – (1*R*)-benzoylcamphor in the present case – as templates in the polymer synthesis is intended to yield recognition sites capable of facilitating the conversion of substrates to aldol products. While spectroscopic studies by us [10] and others [24] point toward a direct coordination of the template cobalt center, the nature of the embedded complexes remains elusive.

In order to evaluate the structures of different cobalt(II) complexes, we prepared a series of solutions of cobalt(II) acetate (mostly the tetrahydrate was used) in different solvents, containing between 0 and 6 equivalents of pyridine and generally one equivalent of (1*R*)-benzoylcamphor. Slow evaporation of the solvent from these solutions resulted in the formation of crystalline material that could be investigated by single crystal structure determination (see Table 1).

Although our spectroscopic investigations [10] suggested otherwise analysis of compounds **1**–**3** revealed, that the (1*R*)-benzoylcamphor was not incorporated into the structures, rather already reported structures [25–27] were obtained as crystalline material. Compound **1** has been reported twice according to CCDC database entries COAQAC (RT, R1 = 14%) [28] and COAQAC1 (153 K, R1 = 1.8%) [25]; we reinvestigated the structure at 100 K resulting in a very low *R*-factor of just 1.46% up to $2\theta = 60°$. While our structure of compound **2** is comparable to reported data, complex **3** has previously been investigated at higher temperature and different experimental setup resulting in an inferior *R*-factor compared to our structure. Geometric parameters for compounds **1**–**3** are summarized in Table 2.

Complex **1** crystallizes from a dichloromethane solution of cobalt acetate tetrahydrate with (1*R*)-benzoylcamphor and up to two equivalents of pyridine. While solution spectroscopy experiments indicate a coordination of the (1*R*)-benzoylcamphor, it was not incorporated in the solid state. The complex **1** crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The cobalt atom is located on a center of inversion. Two acetato ligands are bound *trans* to each other and four water molecules are bound in a planar arrangement (Fig. 1) completing a sixfold coordination environment. Short distances of Co–O1 of 208.84 pm, and Co–O3 of 208.82 pm and a longer distance Co–O4 of 211.73 pm, and angles of O–Co–O of close to 90° are indicative of an axial distortion of the coordination geometry, resulting in a distorted octahedron with two axial water molecules and two water and two acetato ligands in the equatorial plane. The difference in Co–O distances of the coordinated water molecules O3, O4 and their symmetry equivalents are attributed to the hydrogen bonds between O3 (donor) and O2 (acceptor, see below). The water ligand O4, involved in an intermolecular hydrogen bond to an acetate ligand, exhibits the longest Co–O distance.

Upon increase of the pyridine concentration the two acetato ligands were substituted by two pyridine ligands (complex **2**, Fig. 2). The two acetato ligands remain in the outer sphere coordination environment of the complex [26]. The pyridine ligands are coordinated trans to each other (Co–N1 = 215.53 pm, Co–N2 = 215.15 pm), thus it appears that no coordinative rearrangement can be observed upon substitution of the two acetato ligands. This surprises, as the water ligands, due to their π-donor

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[1] The elemental composition was calculated assuming exactly 0.5 pyridine molecules per complex molecule, corresponding to maximum occupation of the pyridine site found in the crystal structure. This, however, can, due to the strong disordering of the pyridine, not be fully established from the crystal structure. The deviation of the found composition from the calculated values can be explained by incomplete occupation of this site.