Direct synthesis and crystal structure of a novel tetranuclear Co$^{	ext{III}}$Fe$^{	ext{III}}$ Schiff base complex

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ABSTRACT

The title compound, tetra(μ-2-3-(2-oxo- benzylidenamino)-1-hydroxypropan-2-olato)-4-nitropheno ledi-co balt(III)-di iron(III) dimethyl sulfoxide hexasolvate, crystallizes in the monoclinic space group $P2_1/c$ and represent the first example of heterometallic Co$^{	ext{III}}$Fe$^{	ext{III}}$ complex with 3-[(5-nitro-2-hydroxybenzylidene) amino]propane-1,2-diol/2-[(2,3-dihydroxy propyl) iminio)methyl]-4-nitrophenolate - a hydroxyl rich Schiff base ligand which was obtained in situ. Crystal data for $C_{52}H_{74}Cl_{2}Co_{2}Fe_{2}N_{8}O_{26}S_{6}$ ($M = 172.01$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 16.353(3) \, \AA$, $b = 15.234(2) \, \AA$, $c = 15.201(3) \, \AA$, $\beta = 113.99(2)^\circ$, $V = 3460.0(12) \, \text{Å}^3$, $Z = 2$, $T = 173(2) \, \text{K}$, $\mu(\text{MoKα}) = 1.225 \, \text{mm}^{-1}$, $D_{\text{calc}} = 1.651 \, \text{g/cm}^3$, 14130 reflections measured ($5.7^\circ \leq 2\theta \leq 57.266^\circ$), 7748 unique ($R_{int} = 0.1051$, $R_{p} = 0.2148$) which were used in all calculations. The final $R$ was 0.0914 ($I > 2\sigma(I))$ and wR$_{p}$ was 0.2279 (all data). The metal ions have distorted octahedral coordination geometry and are joined in a tetranuclear (Co$_2$Fe$_2$(μ-O)$_4$) core by O-bridging atoms from the ligand. There are numerous intermolecular interactions occurring between the components of the crystal: π-hole interaction between NO$_2^-$, N$_2$O$_5$ groups of the ligands, short S···S, O···O and C···C interactions and weak and strong hydrogen bonds.

1. Introduction

During the past several decades, polynuclear complexes have attracted considerable interest due to their potential for a wide range of physicochemical properties such as magnetic [1], catalytic [2], and useful light- and/or redox-induced functions [3]. High-nuclearity solids may exist in a wide range of shapes and different arrangements of the metal atoms [4,5]. Iron is an important bioelement and is a part of heteronuclear cores in metallobiosites such as in purple acid phosphatase (FeZn) [6], human calcineurin (FeZn) [7] and human protein phosphatase 1 (MnFe) [8]. Fe(III) oxo- and hydroxo-bridged complexes are promising materials in the field of bioinorganic chemistry owing to their relevance as models of the protein active sites [9,10] and their activity in important biological processes [11,12].

In recent years, one of the most widely utilized classes of ligands in metal coordination chemistry are the Schiff bases. Due to their synthetic flexibility, these compounds demonstrate exceptionally rich coordination chemistry and diverse properties in the areas of magnetism, luminescence, chirality, catalysis, cytotoxicity, and ferroelectricity [13-15]. Using of these multipurpose ligands in a synthetic approach named direct synthesis of coordination compounds (which based on spontaneous self-assembly of free metal ions with commonly simple and flexible ligands without significant geometrical restrictions) appears to be an extremely powerful tool for the construction of novel hetero-polynuclear complexes [16]. In this study, we have continued our investigations in the field of direct synthesis and present the synthesis and crystal structure of a novel tetranuclear heterometallic (Fe and Co) complex with a mixed N,O,O-donor hydroxyl rich Schiff base ligand derived from the condensation of 5-nitrosalicylaldehyde with 3-amino-1,2-propanediol and formed in situ.

Keywords: Iron, Cobalt, Schiff base, Direct synthesis, Crystal structure, Heterometallic complexes. view
2. Experimental

2.1. Materials and methods

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard procedures [17]. The synthetic method, direct synthesis, has been intensively used and reported in literature [16,18-20]. Its basis lies in the oxidative dissolution of metal(s) during the synthesis. In our case of the synthesis of a heterometallic complex we use one of the metals in a zero-valent state (Co0), with the other one in the form of a salt (FeCl2) (Scheme 1), which, in general, can be described by Reaction (1).

\[
M'^0 + M''Xy + [Ox] + L \rightarrow [M'^0+M''m + LX] + [Red] \tag{1}
\]

where ligand L is the product of the condensation of 5-nitrosalicylaldehyde with 3-amino-1,2-propandiol, formed in situ.

2.2. Measurements

IR spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer (KBr tablet). Elemental analyses for metals were performed with an ICP spectrometer (Fisons Instruments, ARL Model 3410+) and with a Perkin-Elmer 2400 analyzer for C, H, N and Cl. Quantitative determinations of the metals were performed by atomic absorption spectroscopy.

2.3. X-ray crystallography

For the crystal structure determination, the single-crystal of the title compound was used for data collection on an Xcalibur Sapphire 3 diffractometer equipped with graphite monochromatic MoKα radiation (λ = 0.71073 Å). The crystal data, data collection and structure refinement details are summarized in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were added geometrically and refined as riding. The residuals \(R_{	ext{int}} = 0.1225\) and \(U_{	ext{w}} = 1.5U_{	ext{c}}\) were used for carbon atoms of the ligand and \(U_{	ext{w}} = 1.5U_{	ext{c}}\) for methyl atoms of DMSO solvate molecules. For data collection: CrysAlisPro, Agilent Technologies, 2014 [21]; cell refinement: CrysAlisPro, Agilent Technologies, 2014 [21]; data reduction: CrysAlisPro, Agilent Technologies, 2014 [21]; program(s) used to solve structure: SHELXL [22]; program(s) used to refine structure: SHELXL [23]; molecular graphics: SHELXTL [24].

2.4. Synthesis of title compound

3-Amino-1,2-propanediol (0.194 g, 2.5 mmol), 5-nitrosalicyl aldehyde (0.418 g, 2.5 mmol), and triethylamine (0.35 mL, 2.5 mmol) were dissolved in dimethylsulfoxide (DMSO, 25 mL) and stirred until the mixture became yellow. Then Co0 (0.074 g, 1.25 mmol) and FeCl2·4H2O (0.248 g, 1.25 mmol) were added to the resulting solution, mixed for 10 min, and then heated in a water bath (323-333 K) for 3 h. Brown crystals suitable for X-ray analysis (6 h) were filtered off, washed with dry isopropyl alcohol, and finally dried at room temperature. Yield: 0.3 g, 54% (per iron). Anal. calcd. for C52H74N8O26S6Cl2Co2Fe2: C, 36.31; H, 4.34; N, 6.51. Found: C, 36.33; H, 4.41; N, 6.49%. FT-IR (KBr, v, cm⁻¹): 3100 br, 2998 w, 2863 w, 1640 m, 1595 vs, 1544 m, 1481 m, 1439 w, 1390 w, 1311 vs, 1250 m, 1200 w, 1125 w, 1100 m, 1015 m, 945 m, 920 w, 841 w, 794 w, 755 w, 731 w, 688 w, 662 w, 595 v, 544 v, 492 h, 442 w. In the high-frequency region, broad medium-intensity bands in the 3100-2989 cm⁻¹ range can be attributed to ν(CH) due to aromatic C-H stretching, strong bands appearing at 1595 cm⁻¹ were assigned to ν(C=O) stretching vibrations, a very strong absorption at 1311 cm⁻¹ was assigned to ν(NO2). The presence of the solvate molecules (DMSO) is shown by the medium-intensity bands at 1015 and 945 cm⁻¹. The compound is sparingly soluble in DMF and DMSO and insoluble in water.
3. Results and discussion

The X-ray investigation of the title complex showed the molecular structure as determined in the crystalline phase. The crystal and the refinement data are shown in Table 1. It crystallizes in the monoclinic space group \(P2_1/c\). The centrosymmetric unit consists of a complex molecule \([\text{Co}_2\text{Fe}_2]\{\text{HL}\}_3\{\text{Cl}_3\} \cdot 6\text{DMSO}\) in which metal atoms are joined by 0 bridging atoms from the deprotonated Schiff base ligands in the tetranuclear core \(\{\text{Co}_2\text{Fe}_2\{\mu-\text{O}\}_6\}\) forming a nonlinear chain-like arrangement. The structure also contains six DMSO solvent molecules of crystallization (Figure 1). The inversion center is situated at the mid-point of the Fe-O2 unit. The Schiff base ligands, which contains a hexadentate (NNOO) donor set with three hydroxyl groups that provide their chelating and bridging capabilities, compensate for the charges on the metal ions by existing in two forms, doubly deprotonated (dianionic) and triply deprotonated (trianionic).

Each ligand spanning the cobalt atom meridionally; thus, the coordination geometry around the Co\textsuperscript{III} ion is slightly distorted octahedral with an N,O,N coordination sphere: two oxygen atoms and one nitrogen atom of the dianionic ligand and one nitrogen atom of the trianionic ligand are in the equatorial plane, apical positions are filled by two oxygen atoms of the trianionic ligand. The chelating fragments coordinated to the Co\textsuperscript{II} ion are twisted, as defined by the dihedral angles of 70.24(2)° between the mean planes of atoms 04/N2/C9/C8/C14 and 01/N1/C7/C1/C2. The Co-O and Co-N bond lengths are within the ranges 1.863(5) - 1.916(5) Å and 1.881(7) - 1.915(6) Å (Table 2), respectively, which are comparable with those for previously reported related compounds (CSD Refcodes: JIJGUH and PENVIQ) [25,26] (Co\textsuperscript{III}-O/N distances which fall in the range 1.880(4) - 1.995(4) Å).

The coordination of the Fe\textsuperscript{III} ion is a highly distorted octahedral OSCI geometry. Three of the four coordination sites in the equatorial plane are occupied by oxygen atoms of the trianionic Schiff base ligand, one of which is symmetry related (O10, O9, O9 (\(i-x+1, -y+1, -z+1\))), and the fourth site is filled by an oxygen atom of the dianionic ligand (O8); octahedral environment being completed with chlorine atom and one oxygen atom of the dianionic ligand in apical positions with an O7Fe1Cl1 angle of 141.69(16)°. (Figure 2) The Fe-O bond lengths are in the range 1.961(5) - 1.995(4) Å. (Table 2). The separation between the Co\textsuperscript{III} and Fe\textsuperscript{III} ions within the binuclear fragment is 3.0321(16) Å and between two symmetry-related Fe\textsuperscript{III} ions is 3.2513(24) Å. Those distances as well as all bonding parameters and the dimensions of the angles in the title complex are in good agreement with those encountered in related complexes [30,31].

As it has been noted [29], one of the forces that make supramolecular system binding blocks stick to one another is π-hole contacts. The shortest reported contact of that type is 2.80 Å [33].

### Table 2. Selected bond lengths and angles *.

| Bond          | Length (Å) | Bond          | Angles (°) |
|---------------|------------|---------------|------------|
| Fe1-O9        | 1.961(5)   | 09-Fe1-O9     | 71.2(2)    |
| Fe1-O9        | 2.037(5)   | 09-Fe1-O7     | 107.2(3)   |
| Fe2-O7        | 2.041(5)   | 07-Fe1-O10    | 74.9(2)    |
| Fe1-O10       | 2.059(5)   | 09-Fe1-C1     | 104.85(17) |
| Fe1-O8        | 2.139(5)   | 09-Fe1-C1     | 102.99(17) |
| Fe2-O7        | 2.303(3)   | 07-Fe1-C1     | 141.69(16) |
| S1S-O1S       | 1.508(7)   | 01S-O1S       | 89.11(17)  |
| S1S-C1S       | 1.753(10)  | 08S-Fe1-C1    | 85.14(17)  |
| S1S-C2S       | 1.764(10)  | 01S-Co1-N1    | 96.2(3)    |
| Co1-O1        | 1.863(5)   | 01S-Co1-04    | 91.2(2)    |
| Co1-N1        | 1.881(7)   | 04S-Co1-07    | 92.5(2)    |
| Co1-O4        | 1.891(6)   | N1-Co1-N2     | 176.9(3)   |
| Co1-O7        | 1.892(5)   | 04S-Co1-N2    | 92.8(3)    |
| Co1-N2        | 1.915(6)   | 07S-Co1-N2    | 89.7(2)    |
| Co1-O10       | 1.916(5)   | 01S-Co1-O10   | 95.0(2)    |
| O1-C2         | 1.283(9)   | N1-Co1-O10    | 85.3(2)    |
| C1-C6         | 1.395(11)  | 04S-Co1-O10   | 170.8(2)   |

* Symmetry code: (i) \(-x+1, -y+1, -z+1\).
In the title complex π-hole interaction occur between NO$_2$ groups of the ligands forming O···N and O···C contacts with, respectively, distances for [O5-N3] and [O5-C5] distances of 3.4878(38) Å which is essentially shorter than the sum of the Van der Waals radii for the atoms involved. There are also a number of weak C-H···O, C-H···Cl, C-H···S, C-H···N contacts that link the components in the crystal as shown as dashed lines.

In the title complex π-hole interaction occur between NO$_2$ groups of the ligands forming O···N and O···C contacts with, respectively, distances for [O5-N3] and [O5-C5] distances of 3.0226(108) Å and 3.0894(110) Å, respectively. These are in a good agreement with previously reported for analogous contacts [32].

In addition, in the crystal, all units are connected by a number of short connections and hydrogen bonds (Table 3, Figure 2). Thus, the solvent DMSO molecules connected with each other by short S···S (1-2, 2.45 Å) contact [S2S···S3S = 3.4878(38) Å] which is essentially shorter than the sum of the Van der Waals radii for the atoms involved. There are also connections with the complex units through strong O-H···O [O8···O3S (1-x, 0.5+y, 0.5-z) = 2.562(8) Å], O-H···S [O8···S3S(1-x, 0.5+y, 0.5-z) = 3.596(6) Å] and a number of weak C-H···O, C-H···N, C-H···Cl and C-H···hydrogen bonds (Table 3). These data are in good agreement with previously published data [33-36].

4. Conclusion

The direct synthesis method for preparation of coordination compounds was successfully used for the open-air preparation of the novel tetranuclear heterometallic complex with polydentate Schiff base ligands formed in situ as a product of condensation between 5-nitrosalicylaldehyde and 3-amino-1,2-propanediol. The molecular structure of the newly tetranuclear heterometallic (Fe and Co) complex with a mixed N, O-donor hydroxyl rich Schiff base ligand was examined by spectroscopic (IR) and X-ray crystallography techniques.

**Table 3. Hydrogen geometric parameters (Å, °) of the title compound.**

| D-H     | D-H     | H-A     | D-A     | zD-H-A    |
|---------|---------|---------|---------|-----------|
| O8-H8-O3S | 0.82    | 11.74   | 22.562(8) | 1173.9    |
| C4-H4-C1  | 0.95    | 2.89    | 3.762(9)  | 153.1     |
| C6-H6-O15  | 0.95    | 2.40    | 3.203(12) | 154.5     |
| C7-H7-O15  | 0.95    | 2.46    | 3.326(11) | 152.0     |
| C14-H14-O2S | 0.95   | 2.49    | 3.274(11) | 139.7     |
| C15-H15B-S3S | 0.99   | 2.85    | 3.758(9)  | 152.7     |
| C18-H18A-O3S | 0.99   | 2.48    | 3.279(9)  | 138.0     |
| C15-H15B-O3 | 0.98    | 2.42    | 3.289(12) | 147.0     |
| C25-H25C-O3 | 0.98    | 2.20    | 3.101(12) | 152.4     |
| C45-H45C-O2S | 0.98    | 2.39    | 3.357(13) | 168.0     |
| C55-H55A-O2S | 0.98    | 2.45    | 3.192(11) | 132.5     |

* Symmetry codes: (i) x+1, y+1/z, z+1/2; (ii) x, y+1/z, z+1/2; (iii) x, y+1/2, z+1/2; (iv) x+1, y+1/2, z+1/2; (v) x+y+1/2, z+1/2; (vi) x, y+1/2, z+1/2; (vii) x, y+1/2, z+1/2; (viii) x+1, y+1/2, z+1/2.

**Figure 2.** The crystal packing of the title compound (along a axis). Several C-H···O hydrogen bonds and C-H···Cl, C-H···S, C-H···N contacts that link the components in the crystal are shown as dashed lines.

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**Supporting information**

CCDC-2019437 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

**Disclosure statement**

Conflict of interests: The authors declare that they have no conflict of interest.

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