

m41.p11

[Co(bppz)₂](ClO₄)₂·MeOH: a new 2,6-bis(pyrazol-1-yl)pyrazine complex

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The crystal structures of only a few iron(II) and silver(I) coordination compounds containing 2,6-bis(pyrazol-1-yl)pyrazine (bppz) ligands have been reported. Most of the iron compounds display a thermochromic spin crossover (SCO) on cooling below room temperature [1]. While the SCO complexes, [Fe(bppz)₂A₂(nCH₃NO₂ {A=BF₄⁻, Co(C₂B₉H₁₁)₂⁻}, were structurally characterized [2,3], solvates containing methanol have not yet been investigated. Solvent effects are however known to dramatically influence the SCO behaviour in the solid state. In the structure of the mononuclear complex [Co(bppz)₂](ClO₄)₂·MeOH, each cobalt(II) ion is coordinated by two chelating bppz ligands. These tridentate ligands are approximately planar with an angle of 88.3° between the two planes. Due to the sterical demands imposed by the ligand, the CoN₆ octahedron is distorted with N-Co-N angles ranging between 74.3 and 117.9° and Co-N distances between 2.0634 and 2.1687 Å. One of the perchlorate units shows a rotational disorder for three of the O atoms with the axis of rotation located on the fourth Cl-O bond.

A view of the molecule arrangement in the unit cell shows that the [Co(bppz)₂]²⁺ cations and the methanol molecules are alternatively arranged in the *bc* plane leading to a chess-board-like pattern composed of the centers of gravity of the methanol molecules and the [Co(bppz)₂]²⁺ cations. These 2D layers are separated by the perchlorate counteranions. The first counteranion layer is essentially planar and lies in the *bc* plane at *x* ≈ 0 with the central Cl atom showing only a slight deviation from the ideal position (0, 0.25, 0.25) for a *p2mm* lattice. The second perchlorate layer shows a marked deviation from the ideal position at *x* = 0.5, resulting in the formation of a puckered mesh structure, which can be derived from the 2D plane group *p2*.

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[2] Elhaik, J., Money, V. A., Barrett, S. A., Kilner, C. A., Radosavljevic Evans, I., Halcrow, M. A. (2003). *Dalton Trans.* 2053-2060.

[3] Elhaik, J., Kilner, C. A., Halcrow, M. A. (2006) *Dalton Trans.* 823-830.

m41.p12

Structure feature of 3-d metal and aluminum trifluoroacetates and their acetates analogs

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A number of trifluoroacetate complexes of the 3-d metals and aluminum were obtained by electrolytic dissolution of metal in CF₃COOH or reaction of metal (or its compounds) with CF₃COOH; crystal structures of more than ten complexes have been investigated by single X-Ray crystallography.

Four independent structure units were found in crystal structure of all obtained compounds.

The first of them is [M(H₂O)₆]³⁺, which could be found in [Al(H₂O)₆][Al(H₂O)₄(CF₃COO)₂](CF₃COO)₄, and it is the only example of stabilization of [M(H₂O)₆]³⁺-ion in crystal structure of carboxylate complexes. The formation of such structure unit was possible due to properties of trifluoroacetic acid as one of the strongest carbonic acids.

The another unit, located in carboxylate complexes of divalent metals and in aluminum trifluoroacetate [Al(H₂O)₆][Al(H₂O)₄(CF₃COO)₂](CF₃COO)₄, is [M(L)₄(CF₃COO)₂]⁰⁺, L = H₂O, py. The influence of H-bonds on the packing crystal structure is would be discussed.

The trinuclear oxocarboxylate complexes [M₃(μ₃-O)(CF₃COO)₆L₃] (M = Cr, Fe; L = CH₃COOH, H₂O, CF₃COO⁻, THF) are known to be formed mostly by trivalent transition metals. For the most active metals (such as iron), the same type complexes could be prepared by a direct reaction of metal with trifluoroacetic acid; however chemical (H₂O₂) or electrochemical oxidation is necessary in the case of less active metals (Cr). As a rule, the trinuclear fragment M₃(μ₃-O)(CF₃COO)₆ retains its structure after crystallization from another solvent. The formation of the homovalent (III, III, III) or heterovalent (III, III, II) complexes may occur differently. The reaction carried out under the similar conditions (M + CF₃COOH + H₂O₂) can produce homo- (Cr (III, III, III)) or heterovalent (Fe (III, III, II)) complexes depending on the nature of metal. Localization of metal atoms in different oxidation states is impossible by means of X-Ray data [1].

The final structure unit in crystal structures of trifluoroacetate complexes is [M₃(CF₃COO)₆(CF₃COOH)₆] where M = Fe²⁺ and Cr²⁺. Trinuclear linear unit is formed by three metal atoms linked by trifluoroacetic bridges.

The influence of the concentration of trifluoroacetic acid on stabilization of the bridged trifluoroacetate groups and the influence of easily protonated ligands on formation of trinuclear linear unit in trifluoroacetate structures was revealed.

A conclusion was made concerning perspectives of application of different trifluoroacetates SBU for design of carboxylate MOF and new methods of synthesis of MOF based on trifluoroacetate complexes.

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[1] Tatyana Yu. Glazunova, Alexander I. Boltalin and Sergey I. Troyanov. Synthesis and crystal structure of trinuclear carboxylate complexes M₃(μ₃-O)(CF₃COO)₆L₃. // *Mendeleev Commun.* 2004. N° 4. P.141.