A Novel Dinuclear Nickel(II) Complex with Three Bridges of Cl−, OAc− and (-OCH2CH2O-) Group of N, N, N′, N′-Tetrakis(2-benzimidazolyl methyl-1, 4-di-ethylene amino) Glycol Ether

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Abstract. The novel dinuclear Ni2+ complex [Ni2(μ-Cl)(μ-OAc)(EGTB)]Cl·ClO4·2CH3OH, where EGTB is N, N, N′-tetrakis(2-benzimidazolyl methyl-1, 4-di-ethylene amino)glycol ether, crystallizes in the orthorhombic space group Pmn21 with a = 15.272(2), b = 14.768(2), c = 22.486(3) Å, V = 5071.4(12) Å3, Z = 4. Dcalc = 1.414 g cm−3, and is bridged by triply bridging agents of a chloride ion, an acetate and an intra-ligand (-OCH2CH2O-) group. The nickel coordination geometry is that of a slightly distorted octahedron with a NiN4Cl2 arrangement of the ligand donor atoms.

There is growing interest in the active site structures and catalytic functions of multi-nuclear metal complexes containing multi-benzimidazole for the purpose as superoxide dismutase (SOD) enzyme and nucleic mimics [1–3]. Previous research has showed that some EGTB-metal complexes can simulate SOD enzyme and catalyze the dismutation of superoxide radical [4]. Several complexes have been crystallographically characterized to date, such as [Ni2-(EGTB-Et)(CH3CN)4](ClO4)4 [5], [Co2Cl2(EGTB)(ClO4)2·5H2O [4] and [Zn2Cl2(EGTB)(ClO4)2·CH3OH·3H2O] [6]. We synthesized the dinuclear triply bridged Ni2-EGTB complex [Ni2(μ-Cl)(μ-OAc)(EGTB)]Cl·ClO4·2CH3OH (1), and characterized by single crystal X-ray diffraction method.

X-ray structural analysis of 1 confirmed that the compound contained a dinuclear complex with a crystallographic imposed mirror symmetry (Symmetry code: A x, 0.5–y, z) with triply bridging agents of a chloride ion, an acetate and an intra-ligand (-OCH2CH2O-) group (Fig. 1), counter-ions Cl− and ClO4−, and two solvate molecules CH3OH. In the dinuclear complex, both Ni2+ cations have distorted octahedral coordination. Each identical Ni2+ cation is coordinated by a chloride ion, an oxygen atom from the acetate, an ether oxygen atom from the ligand and three nitrogen atoms from two benzimidazole groups and an aliphatic amine group of the same ligand, leading to two positive charges at the [Ni2(μ-Cl)(μ-OAc)(EGTB)]2+ coordination moiety. A chloride and a perchlorate ions act as the counter-ions, therefore the complex is electroneutral. This is somewhat different from [Ni2(EGTB-Et)(CH3CN)4](ClO4)4 complex, in which the two Ni2+ cations are coordinated by a perchloride ions act as the counter-ions, therefore the complex is positive charges cationic complex [5].

The Ni−Cl distance is 2.361(2) Å, and two Ni−O distances are 1.996(5) and 2.279(6) Å. The three Ni−N distances are 2.033(7), 2.060(6), and 2.166(6) Å with the Ni−N bond trans to an ether oxygen the shortest, the Ni−N bond trans to an acetate oxygen the middle and the Ni−N bond trans to Cl the longest.

Keywords: Nickel; Dinuclear Ni2+ complex; Crystal structure; Benzimidazole

![Fig. 1](Image) The molecular structure of the [Ni2(μ-Cl)(μ-OAc)(ETGB)] cation of 1 (Symmetry code: A x, 0.5–y, z).

Selected distances Å and angle°: Ni1−O2 1.996(5), Ni1−N4 2.033(7), Ni1−N2 2.060(6), Ni1−N1 2.166(6), Ni1−O1 2.279(6), Ni1−Cl1 2.361(16), N1...Ni1A 3.85(1), O2...Ni1−N4 90.1(2), O2...Ni1−N2 166.8(2), N4...Ni1−N2 93.7(2), O2...Ni1−N1 86.8(2), N4...Ni1−N1 79.4(3), N2...Ni1−N1 81.4(3), O2...Ni1−O1 84.7(2), N4...Ni1−O1 156.7(3), N2...Ni1−O1 156.7(3), N2...Ni1−O1 156.7(3), O2...Ni1−Cl1 79.4(3), N4...Ni1−Cl1 102.1(2), N2...Ni1−Cl1 97.8(2), N1...Ni1−Cl1 178.4(2), O1−N1...Cl1 100.9(2).

As the result of the existence of three bridges between the both Ni2+ cations, the Ni...Ni separation in 1 is only 3.851 Å, obviously much shorter than those in other EGTB metal complexes with only one bridging intra-ligand (-OCH2CH2O-) group, [Ni2(EGTB-Et)(CH3CN)4](ClO4)4, Co2-EGTB and Zn2-EGTB, in which the Ni...Ni distance is 7.072 Å [5], Co...Co 5.713 Å [4] and Zn...Zn 5.689 Å [6], respectively; but close to the distances of dinuclear Ni2+ complexes [Ni2(bim)-μ-μ(OAc)]2+ 3.422 Å [7], [Ni2(Hshi)(pyr)4(OAc)]2+ 3.016 Å [8] and [{Ni2(pppepO)(C6H5COO)}-CH2COOH]2+ 3.387 Å [9].

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Then added NaOOCCH₃/H₂O (0.25 mmol) in 10 ml ethanol to the ethanol was mixed and stirred for half hour at room temperature. The EGTB was synthesized by a modification from the Beijing Chemical Reagent Company of China without further purification. The EGTB was reported for [Ni₂(EGTB-Et)(CH₃CN)]₄⁺ 2.078 Å [5].

The Ni-N distance in 1 is different. The Ni-N bonds between Ni²⁺ cations and aliphatic amine groups is 2.166(6) Å, slightly longer than the Ni-N bonds between Ni²⁺ cations and benzimidazole groups, with bond lengths ranging from 2.033(7) to 2.060(6) Å. The average Ni-N distance 2.086(6) Å is typical of Ni-N distance of several crystallographically characterized Ni²⁺ complexes [7–8, 10–11] and compare favorably with the average Ni-N distance 2.078 Å [5] for [Ni₂(EGTB-Et)(CH₃CN)]₄⁺. The different Ni-N bond length is likely due to the sp²-hybridized benzimidazole N atom forms a shorter Ni-N bond than the sp³-hybridized aliphatic amine N atom. Furthermore, the Ni-O distances vary considerably also. The Ni-O bonds between Ni²⁺ cations and acetate group is 1.996(5) Å, significantly shorter than the Ni-O bonds between Ni²⁺ cations and ether oxygen atom from the EGTB ligand, with bond length 2.279(6) Å. In complex 1 the chloride ion bridges two Ni²⁺ cations, and the Ni-Cl bond length of 2.361(2) Å is slightly shorter than the Ni₂Cl₁ distance 2.451(2) Å for related dinickel complex of Ni₂(L-O)Cl₁(L-OH) = 2.6-Bis[(bis[2-aminoethoxy]aminomethyl)phenol] [12], in which the chloride ion bridges two Ni²⁺ cations also. The structure of 1 is stabilized by N—H...Cl hydrogen bonds. The hydrogen bonds of 1 link the complex each other and form platelike structure (Fig. 2.).

**Experimental Section**

**Synthesis of [μ-Cl μ-OAc -N, N', N'-tetrakis (2-benzimidazolyl methyl-1, 4-diethylen amino) glycol ether] dinickel(II) chloride perchloride dimethanol (1)**

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagent Company of China without further purification. The EGTB was synthesized by a modification of the published procedures [13]. EGTB (0.125 mmol) in 20 ml absolute methanol and NiCl₂·6H₂O (0.25 mmol) in 20 ml absolute ethanol was mixed and stirred for half hour at room temperature. Then added NaOOCCH₃/H₂O (0.25 mmol) in 10 ml ethanol to the flask in 10 minutes, and stirred for 6 hours. The resulting green solution was filtered and the filtrate was left to stand at room temperature. Green crystals were obtained after a few days.

**Crystal structure determination of 1**

Crystal data: Molecular formula C₄₂H₃₀Cl₁₀O₁₀Ni₂, formula weight 1079.70 g mol⁻¹, a = 15.272(2), b = 14.768(2), c = 22.486(3) Å, V = 5071.4(12) Å³, orthorhombic, T = 298(2) K, space group Pnma. Data collection: Bruker SMART 1K CCD, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, crystal size 0.22x0.04x0.02 mm³, 298(2) K, ω-scan, 3.22°, 20 < 43.18°, −15 < h < 15, −15 < k < 7, −23 < l < 23, Z = 4, 3084 reflection measured, 1463 independent, R(Mo-Kα) 0.96 mm⁻¹, experimental absorption correction with SADABS [14]. Structure analysis and refinement: The structure was solved by direct methods (SHELXS-97), refinement was done by full-matrix least-squares on F² using the SHELXS-97 program suite [15]. In final cycles all non-hydrogen positions were refined anisotropic temperature factors with hydrogen riding in ideal positions; the isotropic thermal parameters for the methyl and hydroxo protons were refined with 1.5 times and for all other hydrogen atoms with 1.2 times the Ueq values of the bonding atoms. 319 refine parameters, final R₁ = 0.0524, wR₂ = 0.1393 for 1461 reflections with I > 2σ(I), final R₁ = 0.0960, wR₂ = 0.1479 for all data, largest difference peak and hole 0.88/−0.31 e Å⁻³ in the vicinity of the Ni atom. The structure data has been deposited with the Cambridge Crystallographic Data Center (No. 260658).

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