

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A NOVEL THREE-DIMENSIONAL Cu(II) AZIDO COORDINATION POLYMER

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The structural and magnetic properties of polymetallic complexes bridged by azido ligands have received considerable attention. The two main reasons for this interest are (i) the remarkable ability of the azido ligand to transmit magnetic interactions when adopting different bridging modes; (ii) its great versatility as a ligand which affords a great variety of structural types spanning from discrete molecules to three-dimensional networks. We report herein a unique three-dimensional Cu(II) compound bridged by azido ligands with (1,3) bridged mode. The title complex was prepared by slow diffusion in an H-shape tube of methanolic solution of NaN₃ on one arm, and Cu(ClO₄)₂ and the ligand on the other arm in CHCl₃, deep green crystals were formed after one week. Crystal data: orthorhombic, space group *Pna*2₁, a = 6.379(2) Å b = 10.060(3) Å c = 27.232(9) Å V = 1747.3(10) Å³, Z = 4. Each Cu(II) center is six-coordinated to two nitrogen atoms from two ligands and four other nitrogen donors from four azido anions. It is interesting that one pair of the azido anions act as bridged ligands, while the other only as the terminal ligands. The ligands link the Cu(II) centers to form a one-dimensional structure, and these chains are further connected through N₃⁻ to form this unique three-dimensional network with large cavities as depicted above (from b-direction). The shortest Cu-Cu separation in the chains along c-direction is 13.616 Å and the corresponding values for those in the ac plane and b-direction are 6.378 and 5.957 Å respectively.

Keywords: CRYSTAL STRUCTURE AZIDO COORDINATION POLYMER

STRUCTURE COMPARISON OF THE PHOSPHAZENES [Cl_{4-n}P(NPCl₃)_n][PCl₆] (n = 1-4)

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After the structure determination of [Cl₃P-NPCl₃][PCl₆] (**P1**) [1, 2], [Cl-P(NPCl₃)₃][PCl₆] (**P3**) [3] and [P(NPCl₃)₄][PCl₆] (**P4**) [4] the X-ray crystal structure analysis of [Cl₂P(NPCl₃)₂][PCl₆] (**P2**) at 90K now completes the series of phosphazenes [Cl_{4-n}P(NPCl₃)_n][PCl₆] (n = 1-4). As the cations of **P1** those of **P2** adopt all-*trans* conformations. The comparison of these phosphazenes resulted mainly in the following:

In **P1**, **P2**, and **P4** all the NPCl₃ groups are *trans* oriented, but *cis* and *gauche* orientations are observed in **P3**. By the gradual substitution of Cl atoms by NPCl₃ groups the P-Cl bond lengths as well as the P-N bond lengths to the central P atom are significantly increased and the P-N bond lengths of the NPCl₃ groups are decreased. The P-N-P angles show a very high variability: they range from 132.5(2)° to 157.2(2)°. There is a large negative correlation between the N-P-Cl bonding angles and the corresponding P-N-P-Cl torsion angles of the NPCl₃ groups. The intermolecular coordination angles P_{anion}-Cl...Cl_{cation} [99.00(4)-117.38(10)°] are distinctly smaller than the angles P_{cation}-Cl...Cl_{anion} [141.86(5)-180°].

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THE TWO STRANDED HELICAL SILVER(I) POLYMERS WITH 1,4-BIS(2-PYRIDOXY)BENZENE

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The researches in the area of supramolecular arrays based on bipyridyl ligands with different flexible spacers continues to attract interest[1-3] It is because they can easily coordinate with many metals to form structural diversified coordination polymer. Steel and coworker had used 1,4-bis(2-pyridoxy)benzene (bpob) to react with silver nitrate to produce a [2 + 2] ring compound. However, we got a two stranded helical polymers [Ag(bpob)(MeCN)]ClO when using AgClO react with bpob in MeCN to investigate the effect of anion toward the coordination behavior on bpob ligand. X-ray structure analysis reveals it is an infinitely one-dimension chain. Each Ag(I) is coordinated by two N atoms from two bpob ligands and, less strongly, by an acetonitrile nitrogen atom, to form linear chain. Two such chains form a helical configuration around 2₁ screw axis (Figure 1). The bpob ligand in 1 lie in a *cis*-configuration and the two pyridine rings are nearly parallel to each other with 15.1(4)° of dihedral angle, while they are nearly perpendicular to benzene ring with 88.9(3)° and 77.7(4)° respectively. The Ag-Ag distances separated by the *cis*-bpob bridge is 10.463(8)Å. There are close π-π interactions (3.33Å) between two benzene rings of two chains in helices.

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THE NOVEL OCTATHALLIUM-SELENOBORATO-CLOSO-DODECABORATE

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Isolated [B₂BSe]⁻ anions are stabilized by Tl cations to give the novel compound TlB₂BSe another example for the selenoborato-closo-dodecaborates of general formula M₃B₂BSe (M = Rb, Cs) [1,2]. The present octathallium-selenoborato-closo-dodecaborate TlB₂BSe crystallizes in the triclinic space group *P*-1 with the lattice parameters a = 9.765(2) Å, b = 10.394(2) Å, c = 20.621(4) Å, α = 79.55(3)°, β = 82.83(3)° and γ = 75.81(3)°. In the structure B12-icosahedra, which are also observed in elementary boron [3] as well as in various closo-boranes, are completely coordinated by BSe units. In this case boron emerges in a trigonal-planar co-ordination which is quite rare in selenoborate chemistry [4]. Like the above mentioned analogues this cluster does fully obey Wade's rules, i.e. 2n+2 binding electrons per B₂ moiety lead to the closo-configuration.

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