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Anion-triggered coordination mode of the new chelating ligand 1,3-bis[5-(2-pyrimidinyl)-1,2,4-triazol-3-yl]propane

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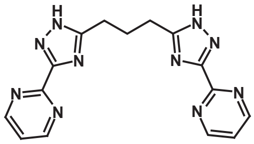
ABSTRACT

The flexible ditopic ligand 1,3-bis[5-(2-pyrimidinyl)-1,2,4-triazol-3-yl]propane H_2L displays remarkable versatility in the coordination mode depending on the counter anion. With copper(II) nitrate H_2L acts as a tetradentate chelate forming a mononuclear complex. The reaction with copper(II) perchlorate gives a centrosymmetric dinuclear complex coordinating the deprotonated form of the ligand. Reaction with copper(II) chloride leads to a pentanuclear complex in which binuclear species are bridged by a $CuCl_2$ fragment. All complexes were crystallographically characterized. Additionally, magnetic properties of bi- and pentanuclear complexes were studied.

1. Introduction

The coordination chemistry of flexible ditopic ligands has attracted recent attention due to their demonstrated versatility forming new attractive coordination structures and topologies and, associate with this, their potential applications [1]. Great attention was paid to coordination compounds on five-membered heterocycles basis primarily triazole and pyrazole derivatives. Although numerous complexes of these ligand have been synthesized, a rational control in the synthesis of coordination compounds has been a great challenge until now [2]. Heteryl ligands with spacer groups such as aliphatic or aryl linkers can produce a wide variety of molecular architectures. Ward and co-workers have described numerous examples of polyhedral cages based on relatively simple bis(pyrazolyl-pyridine) bridging ligands and transition metal cations. Except relatively simple mononuclear complexes numerous high-nuclearity species, and complexes with the structures of double helicates, infinite one-dimensional helicates, molecular rings, and molecular cages have all recently been shown to form from quite simple bis-bidentate ligands containing two pyridyl–pyrazolyl arms [3].

In our previous investigations along these lines, we described new flexible ligands in which pyridine-2-yl-triazolyl chelating 'arms' are linked by a central polymethylene bridge – bis[5-(2-pyridyl)-1,2,4-triazole-3-yl]alkanes [4]. It was found that relatively small changes in the composition and in the structure of bis[5-(2-pyridyl)-1,2,4-triazole-3-yl]alkane ligands are associated with substantial impact on the coordination geometries of the complexes and on their resulting magnetic properties. Here we report the synthesis of a novel, flexible bridging ligand H_2L, containing two bidentate chelating pyrimidyl–trizolyl fragments linked by a flexible propylene spacer, and its co-ordination behavior with Cu(II) ion.



2. Experimental

2.1. Materials and methods

The commercially available $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and $Cu(ClO_4)_2{\cdot}6H_2O$ were used as reactants. 2-Cyanopyrimidine (Aldrich) was used as starting material for ligand preparation.

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The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyser. The IR spectra were recorded on a Nicolet Magna FT-IR 750 spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. UV–Vis spectra were obtained on a Perkin–Elmer Lambda 900 spectrometer using the diffuse reflectance technique, with MgO as a reference. ^1H NMR spectra were recorded on a Bruker VXR-400 spectrometer. The samples for NMR spectral measurements were dissolved in DMSO-d_6. Magnetic measurements were carried out on a Quantum Design PPMS-9 SQUID magnetometer under an external magnetic field of 5000 G in the temperature range of 2–300 K. The diamagnetic contributions of the samples were estimated from Pascal's constants.

2.2. Synthesis

2.2.1. 1,3-Bis[5-(2-pyrimidinyl)-1,2,4-triazol-3-yl]propane

Sodium (0.4 g) was added carefully to 25 cm^3 of methanol followed by addition of 2-cyanopyrimidine (5.3 g, 50 mmol). The solution was left undisturbed for 30 min at room temperature. Glutaryl dihydrazide (3.2 g, 20 mmol) was added to the solution followed by addition of 0.5 cm^3 of acetic acid. The reaction mixture was stirred and refluxed for 7 h. A light yellow solid formed during the reaction was filtered off upon cooling and air dried for 1 day. The product was mixed with 25 ml ethyleneglycol and heated to reflux during 2 h. Upon cooling target ligand were precipitated by adding 200 ml of water. White solids were collected by vacuum filtration, followed by washing with 50 cm^3 water. For purification, target triazole was recrystallized from the MeOH/water solution.

H_2L (4.2 g, 63%). ^1H NMR (300 MHz, DMSO d^6): 8.92 (d, 4H), 7.54 (dd, 2H), 2.86 (dd, 4H), 2.21 (tt, 2H). IR (ν/cm^{-1}): 3367m, 3140m, 3041m, 2922m, 2867m, 1570s, 1517m, 1461m, 1380m, 1324m, 1202m, 1054m, 823m, 739s, 633w. *Anal.* Calc. for $C_{15}H_{14}N_{10}$: C, 53.89; H, 4.22; N, 41.89. Found: C, 53.61; H, 4.16; N, 41.92%.

2.2.2. Coordination compounds. General method

H_2L (0.334 g, 1 mmol) was suspended in a water/MeOH (1:1 v/v) mixture (10 cm^3), and a solution of appropriate Cu(II) salt ($Cu(NO_3)_2·3H_2O$, $Cu(ClO_4)_2·6H_2O$ and $CuCl_2·2H_2O$) (1 mmol) in MeOH (10 cm^3) was added. The reaction mixture was stirred at room temperature during 3 h. Upon stirring clear solution are obtained. After standing for 5–7 days greenish-blue crystals are formed. It was filtered off washed with water and dried on air.

$[Cu(H_2L)NO_3]NO_3$ (**1**). *Anal.* Calc. for $C_{15}H_{14}CuN_{12}O_6$: C, 34.52; H, 2.70; N, 32.21. Found: C, 34.23; H, 2.98; N, 32.36%.

$[Cu_2(HL)_2](ClO_4)_2·3H_2O$ (**2**). *Anal.* Calc. for $C_{30}H_{32}Cl_2Cu_2N_{20}O_{11}$: C, 34.42; H, 3.08; N, 26.76. Found: C, 34.37; H, 3.17; N, 26.54%.

$[\{\mu\text{-}CuCl_2\}\{(\mu\text{-}Cl)Cu(HL)(H_2O)Cl_2\}_2]·H_2O$ (**3**). *Anal.* Calc. for $C_{30}H_{32}Cl_8Cu_5N_{20}O_3$: C, 27.25; H, 2.44; N, 21.19. Found: C, 27.29; H, 2.31; N, 21.09%.

2.3. X-ray crystallography

An experimental array of reflection was obtained by the standard method [5] on a Bruker SMART APEX II automated diffractometer equipped with a CCD detector and a monochromatic radiation source (Mo Kα radiation, λ = 0.71073 Å). The structures of **1**–**3** were solved by a direct method and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms of the carbon-containing ligands were geometrically generated and refined in the riding model. The calculations were performed using the SHELX-97 program package. The crystallographic parameters and X-ray diffraction experimental-parameters are given in Table 1.

3. Results and discussion

3.1. Synthesis and structure

The bispyrazolyl ligand H_2L was synthesized by the reaction of 2-CN-pyrimidine and glutaric acid's hydrazide. The product is obtained in good yield and is easily purified. The structure of 1,3-bis[5-(2-pyrimidinyl)-1,2,4-triazol-3-yl]propane is established from the NMR and IR spectra. In order to evaluate the potential of H_2L as a precursor to produce Cu(II) complexes, we explore the syntheses of coordination complexes by varying counter-anions. Target complexes were obtained by the reaction of H_2L with equimolar amount of a $Cu(NO_3)_2·3H_2O$, $Cu(ClO_4)_2·6H_2O$ and $CuCl_2·2H_2O$ in water–methanol solution, namely $[Cu(H_2L)NO_3]NO_3$ (**1**), $[Cu_2(HL)_2](ClO_4)_2·3H_2O$ (**2**) and $[\{\mu\text{-}CuCl_2\}\{(\mu\text{-}Cl)Cu(HL)(H_2O)Cl_2\}_2]·H_2O$ (**3**). These three complexes were prepared in same conditions but have remarkable different structures as result of different coordination mode of ligands.

The reaction of H_2L with $Cu(NO_3)_2·3H_2O$ yields big blue crystals of composition $[Cu(H_2L)NO_3]NO_3$ in moderate yield. IR-spectra show several bands assigned to NO_3^- anion stretching which indicated about different nature of nitrate-anions in crystalline lattice: at 1384 cm^{-1} (non-coordinated nitrate-anion) and at 1423 and 1328 cm^{-1} (coordinated nitrate-anion). Spectral data were confirmed crystallographically (Fig. 1). The compound **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one of the complex cation and a lattice nitrate-anion as a counter.

Complex **1** have mononuclear structure/ Copper(II) ion is five-coordinated by the four donor atoms from triazolyl–pyridyl chelating fragments and oxygen from nitrate-anion. The planes of the two bidentate triazolyl–pyridyl arms are inclined at an angle of 41.5° to one another. This constitutes a significant distortion towards ideal geometry. According to the Addison's method for five-coordinate geometries [6] title complex demonstrate geometry intermediate between square pyramidal and trigonal bipyramidal (τ = 0.51). The coordination bonds lengths Cu–N are quite similar (1.95–2.02 Å) and remarkably contrasted with more long Cu–N9 bond (2.198 Å). An interesting feature of the NO_3 anion is additional weak 'semi-co-ordinate' interactions O2 atom with copper ion (2.602 Å). In this way Cu(II) demonstrate variable coordination number between five and six. Such phenomena was described in our early work on an example of zinc complexes [7]. Non-coordinated nitrate anion occupies the cavity of the crystal lattice and held apart from electrostatic attraction hydrogen bonds with the nitrogen atoms of the triazole ring.

Reaction of H_2L with $Cu(ClO_4)_2·6H_2O$ afforded a greenish-blue solution. Single crystals of target complex suitable for X-ray diffraction were obtained upon slow evaporation of reaction mixture on air. $[Cu_2(HL)_2](ClO_4)_2·3H_2O$ crystallize in the monoclinic space group $C2/c$. Unfortunately crystals had a poor quality which affects to large value of *R*-factor. General structure of complex is shown in Fig. 2.

Complex has binuclear structure with mono-deprotonated form of triazole ligand. Similar structures have been found for copper(II) complex with 1,3-bis(5-(pyridine-2-yl)-1,2,4-triazol-3-yl)propane [4] but in this case no base were added to reaction mixture for deprotonation. It is seems that as a proton acceptor acts itself ligand. The distances between the copper ions within dimer is 3.79 Å. The 5-fold coordination spheres of the copper(II) ions having distorted square pyramidal geometry (τ = 0.42–0.47), provided by three nitrogen atoms of one pyridyltriazole arm of first ligand and by two nitrogen atoms from second ligand. The triazolate groups bridging Cu1 and Cu2 form a rigid, non-planar 6-membered {Cu–N–N–Cu–N–N} ring with boat conformation. Metallocycle is quite distorted arising from a distortion in the copper-triazolate angels, which have 135.4–137.0 and 119.8–121.2 values. It seems