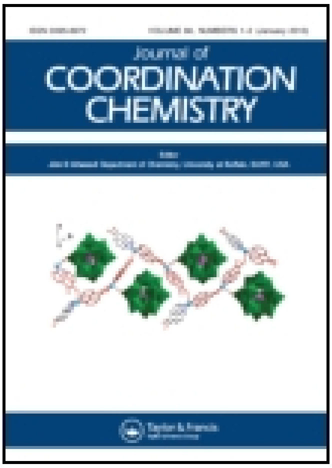

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Cyanuric chloride reagent as a chloride ion donor: synthesis, crystal structure, and magnetic properties of $[Cu_2(2\text{-}APM)_2(\mu\text{-}Cl)_2(\mu\text{-}OCH_3)_2]_n$ coordination polymer

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Cyanuric chloride reagent as a chloride ion donor: synthesis, crystal structure, and magnetic properties of $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n$ coordination polymer

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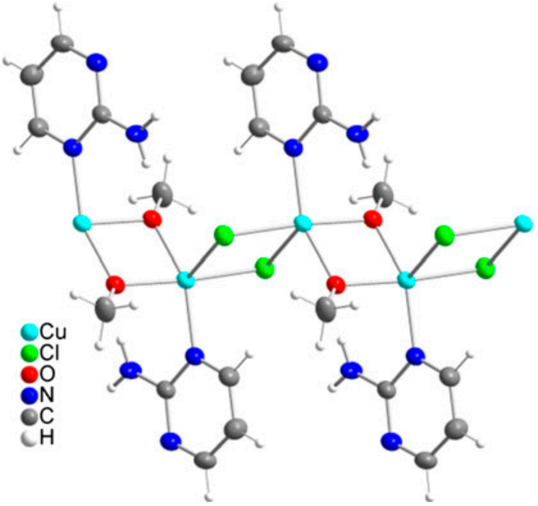

Cyanuric chloride acts as a chloride donor to form a copper(II) coordination polymer.

A new chloro- and methoxo-bridged Cu(II) coordination polymer, $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n \cdot CH_3OH$ (**1**), was prepared using *in situ* formed chloride by the decomposition of cyanuric chloride and 2-aminopyrimidine (2-APM) as a ligand in methanol. Its solid-state structure has been characterized by elemental analysis and single crystal X-ray diffraction. X-ray crystallographic studies reveal that this compound has an extended 2-D supramolecular architecture directed by strong hydrogen bonds and aromatic π–π stacking interactions. Compound **1** shows an antiferromagnetic coupling exchange with coupling constants of −58.2 and −41.4 cm^{-1} between adjacent copper(II) ions, in agreement with the intermetallic distances of 3.0405(5) and 3.6073(5) Å found in the crystal structure.

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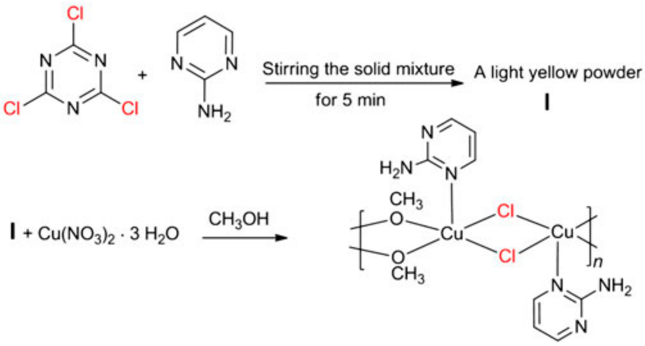
Keywords: Copper(II) coordination polymer; *In situ* reaction; Cyanuric chloride; Structure; Magnetic study

1. Introduction

Inorganic–organic functional materials represent an important interface between synthetic chemistry and materials science [1–3]. Using templates of a metal ion, organic ligands, and inorganic/organic bridges in varied molar ratios, different molecular and crystalline architectures with tunable target properties can be created [4–6]. 2,4,6-Trichloro-1,3,5-triazine, also named cyanuric chloride, tricyanogen chloride, cyanuric trichloride, and cyanuryl chloride, is a white, easy hydrolytic degradation monoclinic crystal of pungent odor. As a useful organic intermediate, cyanuric chloride is often used to produce triazine derivatives with wide usage in the dye industry [7], agriculture chemistry [8], plastic and rubber industry [9], etc. Cyanuric chloride derivatives are widely used as herbicides [10], drugs [11], polymers [12], or ligands in coordination compound systems [13]. Cyanuric chloride has a tendency to hydrolyze with water in the process of triazine derivative production [14, 15], which may generate 2,4-dichloro-6-hydroxy-*s*-triazine, 2-chloro-4,6-dihydroxy-*s*-triazine, or even 2,4,6-dihydroxy-*s*-triazine (cyanuric acid). In protic solvents, cyanuric chloride is solvated and then ionized into a carbocation and a chloride. The chloride may form hydrogen bonds with the –OH hydrogens, and the carbocation may complex with the nonbonding electrons of the –OH oxygen, which is beneficial to the S_{N1} reaction. While cyanuric chloride has been known since 1827, its function as a chloride-generating agent remains practically unexplored.

Hydro(solvo)thermal *in situ* ligand synthesis has been rapidly developed over the past several years due to its effectiveness, simplicity, and environmental friendliness [16]. A great number of new coordination compounds, with interesting architectures and properties, have been prepared by *in situ* reactions between organic ligands and metal salts in the reaction mixture [17–20]. In this article, we describe a straightforward route to a chloride/methoxy-bridged copper(II) coordination polymer, $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n\cdot CH_3OH$ (**1**), from the reaction of $Cu(NO_3)_2\cdot 3H_2O$ with a mixture of 2-aminopyrimidine (2-APM) as



Scheme 1. Synthesis of $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n\cdot CH_3OH$ (**1**).

a ligand and cyanuric chloride as a chloride-generating agent in methanol (scheme 1). The reaction involves *in situ* decomposition of cyanuric chloride and subsequent coordination with Cu(II) ions. To the best of our knowledge, this is the first example of a chloride-bridged coordination polymer generated from cyanuric chloride decomposition.

2. Experimental

2.1. *Materials and instruments:*

All starting chemicals were commercially available and used without purification. Magnetic experiments were made on polycrystalline samples using a SQUID magnetometer MPMS XL-5 manufactured by Quantum Design. The temperature dependence of the magnetization from 2 to 300 K was recorded using a constant magnetic field of 0.50 T. The experimental data have been corrected for magnetization of the sample holder (gelatine) and for atomic diamagnetism as calculated from the known Pascal's constants.

2.2. *Synthesis of* $[Cu_2(2\text{-}APM)_2(\mu\text{-}Cl)_2(\mu\text{-}OCH_3)_2]_n\cdot CH_3OH$ (1)

The solid-state reaction of cyanuric chloride (0.5 mM, 0.09 g) with 2-AMP (1.5 mM, 0.14 g) at room temperature gave a light yellow powder after 5 min. It decomposed in the range of 168–175 °C before melting (melting points for cyanuric chloride and aminopyrimidine are 144–146 and 122–125 °C, respectively). Selected FT-IR (KBr, cm^{-1}): 3324 (m, br), 2922 (w), 2852 (w), 1698 (s), 1667 (vs), 1474 (m), 1359 (m), 1245 (m), 1149 (m), 992 (w), 883 (m), 851 (m), 801 (s), and 463 (w). $[Cu_2(2\text{-}APM)_2(\mu\text{-}Cl)_2(\mu\text{-}OCH_3)_2]_n$ (**1**) was prepared from the reaction of the above-mentioned light yellow powder and $Cu(NO_3)_2\cdot 3H_2O$ in a branched tube in methanol. The powder obtained by mixing cyanuric chloride, 2-APM, and $Cu(NO_3)_2\cdot 3H_2O$ (1.5 mM, 0.36 g) was placed in the main arm of a branched tube. Methanol was carefully added to fill the arms, the tube was sealed, and the reagent containing arm was immersed in an oil bath at 60 °C, while the other arm was kept at ambient temperature. After three days, dark blue crystals were deposited in the cooler arm, which were filtered off, washed, and air dried. The yield is 75%. Anal. Calcd for $C_{11}H_{20}C_{12}Cu_2N_6O_3$ ($[Cu_2(2\text{-}APM)_2(\mu\text{-}Cl)_2(\mu\text{-}OCH_3)_2]_n\cdot CH_3OH$, MW = 482.31): C, 27.39; H, 4.18; N, 17.42; and Cu, 26.35%. Found: C, 27.45; H, 4.14; N, 17.51; and Cu, 26.28%. Selected FT-IR (KBr, cm^{-1}): 3995 (vs br), 3152 (m), 2923 (s), 2852 (m), 1745 (w), 1646 (vs), 1591 (m), 1563 (s), 1488 (m), 1384 (m), and 784 (w).

2.3. *X-ray crystallography*

X-ray diffraction data for **1** were collected at 120 K by the ω-scan technique on a Gemini ultra diffractometer equipped with an Atlas CCD detector using mirror collimated Cu-Kα radiation ($\lambda = 1.5418$ Å). The data integration and the numerical absorption corrections were carried out with the CrysAlis program [21]. The structure was solved by charge flipping methods using the Superflip program [22] and refined using Jana 2006 software [23]. The crystal data and refinement parameters are presented in table 1.

Table 1. Crystal data and refinement details for **1**.

Formula	$C_{11}H_{20}Cl_2Cu_2N_6O_3$
Formula weight	482.3
Crystal size	0.39 × 0.32 × 0.29
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	5.8517(3)
b (Å)	8.5609(4)
c (Å)	9.5186(5)
α (°)	110.627(5)
β (°)	97.711(5)
γ (°)	91.011(4)
V (Å^3)	441.15(4)
Z	1
Dx (g cm^{-3})	1.815
F(0 0 0)	244
μ(Cu-Kα) (mm^{-1})	5.98
Rint	0.032
Measured reflections	3922
Obs. reflections [$I > 2\sigma(I)$]	3523
R [obs. reflns]	0.034
wR (all data)	0.106

3. Results and discussion

3.1. *Syntheses, spectroscopy, and X-ray structure*

The solid state reaction of cyanuric chloride with 2-AMP gave a light yellow powder after five minutes. Chloride is formed *in situ* during the reaction [16, 24]. Presumably, the cyanuric chloride forms some chloro adduct with 2-APM and the light yellow color results from charge transfer in the adduct. TLC analysis showed a weak interaction between the starting materials in the yellow product; its spot was separated easily into 2-AMP and cyanuric chloride spots. IR spectrum of the yellow product is consistent with this finding (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.969250); it shows characteristic bands of 2-AMP and cyanuric chloride. $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n$ (**1**) was prepared from the reaction of the above-mentioned light yellow powder and $Cu(NO_3)_2{\cdot}3H_2O$ in a branched tube in methanol.

The infrared spectrum of **1** displays characteristic bands at 3395, 3152, and 1646 cm^{-1} which are assigned to v(O–H), v(N–H), and v(N=C) of the amine functionalities, respectively. The molecular structure of **1** was determined by X-ray crystallography. A plot of the centrosymmetric complex with atom numbering scheme is shown in figure 1; selected bond lengths and angles are provided in table S1. The structural analysis reveals that crystals of **1** are built of a neutral 1-D polymeric chain of Cu(II) complex with the copper ions linked by a pair of double μ_2-Cl- and μ_2-methoxy-bridging groups. The copper is five-coordinated by two bridging oxygens of methanol, two bridging chlorides, and a nitrogen from 2-APM. Two copper(II) centers and two bridging groups create exactly planar four-membered Cu_2Cl_2 and Cu_2O_2 cyclic units, where the planarity is kept by the symmetry. The NCl_2O_2 coordination set defines a distorted square-pyramidal coordination arrangement. The structural index, $\tau[\tau = (\alpha - \beta)/60$, where α and β are the two largest coordination angles; $\tau = 0$ for ideal square pyramidal geometry, and $\tau = 1$ for trigonal bipyramidal geometry], has a value of 0.327 [25]. In this description, the Cl1^{i} occupies the axial position and O1m/O1m^{ii}/N1/Cl1 forms the basal plane. The long Cu1–Cl1^{i} bond with 2.7215(8) Å

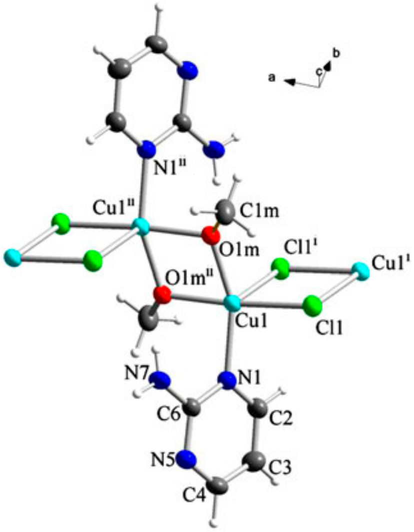


Figure 1. Extended asymmetric unit of $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n\cdot CH_3OH$ (**1**) (50% probability ellipsoids, 120 K), with full coordination spheres of copper. The CH_3OH is omitted for clarity. Symmetry transformations: (i) $1-x$, $2-y$, $1-z$; (ii) $2-x$, $2-y$, $1-z$.

corresponds to weak bonding of the chloride to copper due to the Jahn–Teller effect [26]. The two methoxide-O1m atoms bridge asymmetrically with two copper ions [Cu1–O1m 1.9247(17)/Cu1–O1m^{i} 1.9544(18) Å]. The length of the axial Cu–Cl bond is 2.722(1) Å, which is longer than other bonds. The Cu–Cl and Cu–O distances are close when compared to those found in other Cu(II) complexes containing $Cu_2Cl_2(OMe)_2$ units [27, 28]. The Cu–Cl–Cu and Cu–O–Cu bond angles are 92.147(25)° and 103.22(8)°, respectively, which are in a normal range in comparison with similar polymeric networks [27]. The Cu–N bond is close to reported complexes of Cu(II) with 2-AMP ligand [29–31].

Due to the presence of NH_2 and also uncoordinated methanol molecules in the crystal packing of **1**, there are strong and directed hydrogen bonds (table 2). A 2-D supramolecular architecture (figure 2) is formed by the presence of reasonable π–π stacking and N–H···N and N–H···O interactions seen in **1**, that is, for π–π with centroid–centroid distances 3.7968 (2) Å between the exactly parallel ring planes (by symmetry) [32].

3.2. *Magnetic properties*

Since copper coordination polymers containing dinuclear units are good candidates for study on magnetic interactions [33–36], the magnetic behavior of **1** was studied from 2 to 300 K.

Table 2. Hydrogen bonding parameters in **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N7–H1n7···N5^{i}	0.81(4)	2.19(4)	2.995(4)	172(4)
O2m–H1o2···Cl1^{iii}	0.87(5)	2.32(6)	3.165(8)	164(7)

Note: Symmetry codes: (i) $-x+2$, $-y+1$, $-z$; (iii) x, $y-1$, z. The O2m atom belongs to solvent CH_3OH.

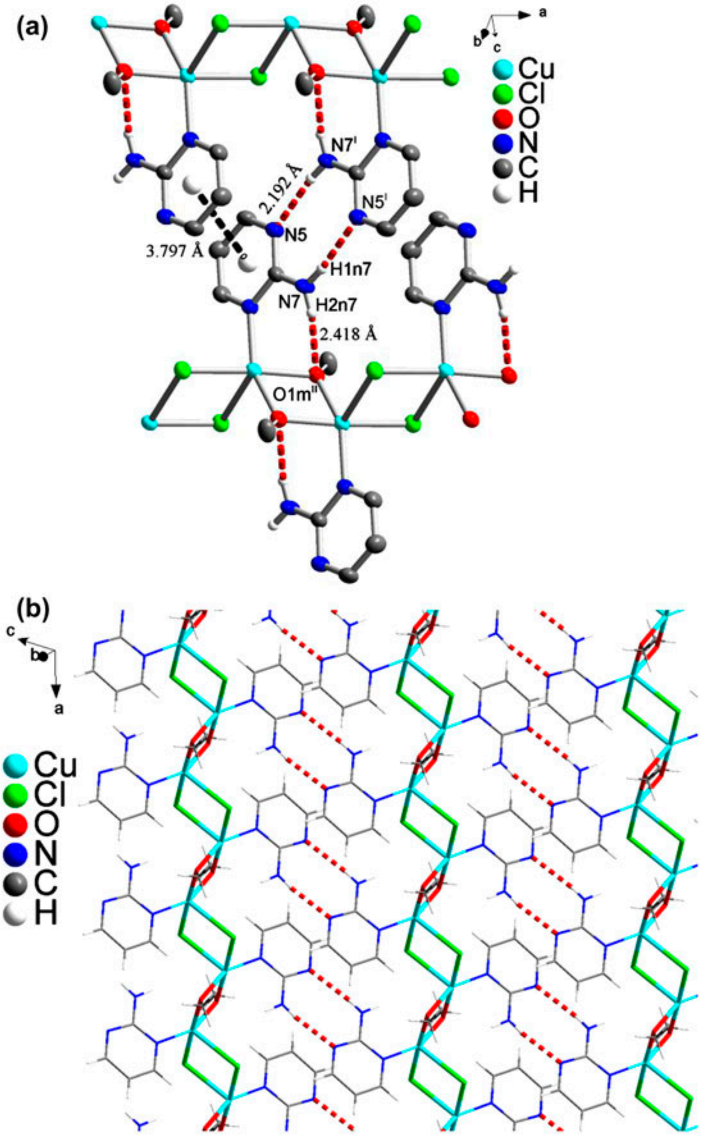


Figure 2. (a) 2-D supramolecular architecture formed by $\pi \cdots \pi$ interactions (black dashed line between 2-APM rings), N–H···N and N–H···O interactions (H bonds: red dashed line). Solvent molecules and hydrogens except N–H are omitted for clarity. Symmetry transformations: (i) $2 - x$, $1 - y$, $-z$; (ii) $2 - x$, $2 - y$, $1 - z$. (b) The extended structure of **1** (see http://dx.doi.org/10.1080/00958972.2014.969250 for color version).

The temperature dependence of χT per copper is shown in figure 3. The room temperature value of 0.346 cm^3 K mol^{-1} is very close to the expected value of 0.375 cm^3 K mol^{-1} for the isolated S = ½ copper(II) ion. On cooling, this value steadily decreases to 0.006 cm^3 K mol^{-1} at 2 K. This behavior is compatible with an antiferromagnetic coupling exchange between the neighboring copper(II) ions.

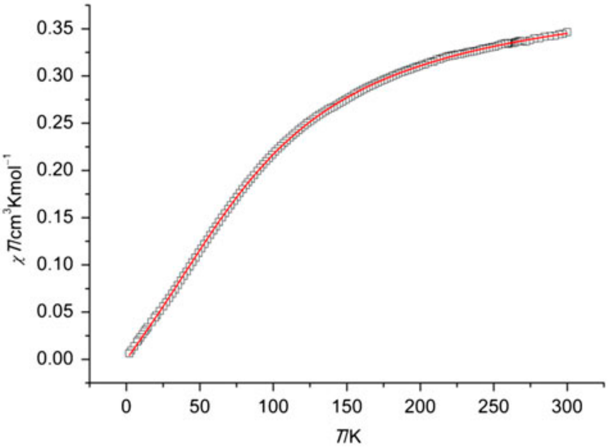


Figure 3. Temperature dependence of χT for **1**. The solid line represents the best fit using the equation and parameters described in the text.

According to the 1-D character of the structure, the experimental data were fitted to an alternating Heisenberg linear chain model, $H = -J\Sigma(S_{2i-1}S_{2i} + \alpha S_{2i}S_{2i+1})$, where J is the exchanging coupling constant for the copper ions and α is a parameter that takes into account the distortion in the chain and can vary from $\alpha = 0$, corresponding to isolated dimers, to $\alpha = 1$, corresponding to a uniform chain of $S = ½$ spins. The analytical expression used in the fit was as follows:

$$\chi T = \frac{\mathrm{N}g^2\beta^2}{K}\frac{A + Bx + Cx^2}{1 + DxEx^2 + Fx^3}$$

where N stands for the Avogadro's number, β the Bohr magneton, k the Boltzmann constant, g the Landé factor, $x = |J|/kT$ and A–F are functions of α [37]. The best fit was obtained for $g = 2.030(8)$, $\alpha = 0.71(2)$, and $J = -58.2(4)$ cm^{-1} with $R^2 = 0.99992$. This fit corresponds to antiferromagnetic coupling constants of −58.2 and −41.4 cm^{-1} between the adjacent copper ions along an alternating chain of $S = ½$ spins and in complete agreement with the intermetallic distances of 3.0405(5) and 3.6073(5) Å found in the crystal structure. The antiferromagnetic coupling of **1** is similar to those for the linear chain antiferromagnetic compound $Cu(pzdo)Cl_2(H_2O)_2$ (pzdo = pyrazinedioxide) [33, 38] and azido derivative of Cu(II) complex with macrocyclic building block of the type $[CuLN_3]_n \cdot [ClO_4 \cdot 3/2H_2O]_n$ (L = 3,10-bisbenzyl-1,3,5,8,10,12-hexaazacyclotetradecane) [39].

4. Conclusion

A straightforward route to a chloride- and methoxo-bridged Cu(II) coordination polymer, $[Cu_2(2\text{-APM})_2(\mu\text{-Cl})_2(\mu\text{-OCH}_3)_2]_n \cdot CH_3OH$, was developed. Cyanuric chloride is an *in situ* chloride donor in this method. The antiferromagnetic coupling found in **1** is similar to the magnetic behavior found in other chloro-bridged Cu(II) coordination polymers.

Supplementary material

CCDC-982793 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supporting information for this article is available at http://dx.doi.org/10.1080/00958972.2014.969250 or from the author.

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