ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 11, pp. 795–798. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 11, pp. 691–694.

# Spacer-Armed Copper(II) Complex Based on Bis(2-pyidyl-1,2,4-triazol-3-yl)butane and 1-Aminoethane-1,1-Diphosphonic Acid

**V. F. Shul'gin[a], *, N. S. Pevzner[a], M. A. Kiskin[b], E. A. Ugolkova[b], and V. V. Minin[b]**

[a] *Vernadsky Crimean Federal University, Simferopol, 295007 Russia*

[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

**e-mail: shulvic@gmail.com*

Received May 13, 2019; revised May 23, 2019; accepted June 3, 2019

**Abstract**—The new complex $[Cu_4L_2(H_2AEDP)_2(H_2O)_4] \cdot 34H_2O$ was prepared by the reaction of $CuSO_4$ with bis(2-pyridyl-1,2,4-triazol-3-yl)butane ($H_2L$) and 1-aminoethane-1,1-diphosphonic acid ($H_4AEDP$) and studied by X-ray diffraction (CIF file CCDC no. 1913117). The complex is a spacer-armed dimer in which two dimer subunits formed with participation of diphosphonate dianions are linked to each other via two doubly deprotonated bis(pyridyl)triazoles. The bridging diphosphonate anion exists in the zwitter ion form, bis(triazolyl)butane is coordinated via the nitrogen atoms of the pyridyl moiety and the deprotonated triazole ring. Analysis of the ESR spectrum of the polycrystalline sample attests to weak exchange interactions in the dimeric moieties.

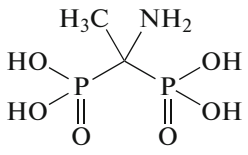
*Keywords:* copper(II), spacer-armed 1,2,4-triazole, X-ray diffraction, ESR spectroscopy

**DOI:** 10.1134/S1070328419100075

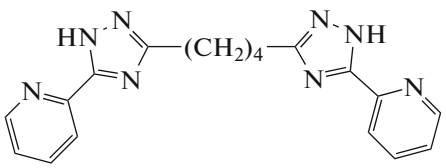
## INTRODUCTION

Diphosphonate ligands are known to implement different binding modes to metal cations; in combination with diverse geometry of coordination polyhedra, this creates conditions for the synthesis of coordination compounds with unusual molecular and supramolecular structures [1–5]. Most of diphosphonates have a layered crystal structure with various layer topology and arrangement of organic radicals in the interlayer voids. The introduction of additional functional groups and organic extra ligands generates more opportunities for the control over the crystal architecture and for the design of unusual small-size clusters [6, 7]. At the same time, spacer-armed 2-pyridyl-1,2,4-triazoles are convenient templates for the assembly of coordination compounds with different number of nuclei and topology [8–10]. Presumably, the use of options provided by the two types of ligands would enable the design of new complexes in which polynuclear moieties are linked by additional organic bridges.

This study addresses the reaction of copper(II) sulfate with 1-aminoethane-1,1-diphosphonic acid ($H_4AEDP$) and bis(2-pyridyl-1,2,4-triazol-3-yl)butane ($H_2L$).



$H_4AEDP$



$H_2L$

## EXPERIMENTAL

Bis(2-pyridyl-1,2,4-triazol-3-yl)butane and 1-aminoethane-1,1-diphosphonic acid obtained by reported procedures [11, 12], distilled water, and reagent grade $CuSO_4 \cdot 5H_2O$ were used in the study.

**Synthesis of $[Cu_4L_2(H_2AEDP)_2(H_2O)_4] \cdot 34H_2O$ (I).** $H_4AEDP$ (0.615 g, 3 mmol) was added to a suspension containing $H_2L$ (0.519 g) in water (30 mL), and the mixture was stirred at 70–80°C for 20 min until the reactants completely dissolved. A solution of

$CuSO_4$ (3 mmol) in water (5 mL) was added to the resulting solution, the mixture was cooled down with stirring, and 1 M NaOH (6 mL) was slowly added dropwise until pH was 6–7. The light blue-colored solution thus formed was filtered and kept for several days at room temperature. The blue crystals that precipitated were separated from the mother liquor by filtration and dried between filter paper sheets. The yield was 0.56 g (38% based on $H_2L$). According to elemental and thermal analyses, the composition of the complex was given by $Cu_4L_2(H_2AEDP)_2 \cdot 34H_2O$ (**I**).

| For $C_{40}H_{114}N_{18}O_{46}P_4Cu_4$ | | |
|---|---|---|
| Anal. calcd., % | C, 24.49 | N, 12.85 |
| Found, % | C, 24.99 | N, 12.43 |

According to thermogravimetric analysis (TGA) data, elimination of water molecules incorporated in complex **I** occurred in two steps with the loss of 31% of the sample weight and was accompanied by minima at 120 and 160°C in the differential thermal curve. The crystals rapidly degraded in air being converted to the hydrate $Cu_4L_2(H_2AEDP)_2 \cdot 20H_2O$ (**II**). The dehydration of complex **II** started at 120°C and was accompanied by minima as 125 and 180°C in the differential thermal curve.

| For $C_{40}H_{66}N_{18}O_{32}PCu_4$ | | |
|---|---|---|
| Anal. calcd., % | C, 28.11 | N, 14.75 |
| Found, % | C, 28.46 | N, 14.61 |

The IR absorption spectra of complex **II** show, apart from the absorption bands for spacered 2-pyridyl-1,2,4-triazole (1615, 1600, 1565, 1508,1482, 1455, 1403, 1350, and 1285 $cm^{-1}$), also broad bands with absorption maxima at 1139, 1093, 1062, 1005, and 923 $cm^{-1}$, corresponding to the phosphorus–oxygen stretching vibrations [13]. The 3500–3000 $cm^{-1}$ range shows a broad enveloping line covering the stretching bands of water and $-NH_3^+$, groups, the bending modes of which give rise to a weak band with a maximum at 1645 $cm^{-1}$.

**Single crystal X-ray diffraction** analysis of **I** was carried out at a temperature of 100 K on a Bruker Smart APEX II diffractometer equipped with a CCD array detector and a monochromatic radiation source ($MoK_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) by a standard procedure [14]. The structure was solved by the direct methods and refined in the full-matrix anisotropic approximation for all nonhydrogen atoms. The calculations were performed using the SHELXL2014 program package [15]. The hydrogen atoms were generated geometrically and refined in the rigid body model. Because of the disorder of some solvate water molecules, X-ray diffraction data were corrected by the Squeeze procedure of the PLATON program package [16].

Crystallographic parameters and structure refinement details for **I**: $C_{40}H_{114}Cu_4N_{18}O_{46}P_4$, $M = 1961.53$, crystal size $0.15 \times 0.05 \times 0.05$ mm, blue crystals, $T = 100(2)$ K, triclinic system, space group $P\bar{1}$, $a = 12.2506(7)$, $b = 13.5754(6)$, $c = 14.9293(7)$ Å, $\alpha = 74.903(2)°$, $\beta = 68.189(2)°$, $\gamma = 71.066(2)°$, $V = 2152.54(19)$ Å$^3$, $Z = 1$, $\rho = 1.513$ g/cm$^3$, $\mu = 1.149$ mm$^{-1}$, $\theta = 1.98°–26.39°$; $-15 \le h \le 15$, $-16 \le k \le 16$, $-18 \le l \le 16$; altogether 20023 reflections, 8757 unique reflections, 6429 reflections with $I \ge 2\sigma(I)$; $R_{int} = 0.041$, $T_{min}/T_{max} = 0.846/0.945$, $S = 1.04$, $R_1 = 0.100$, $wR_2 = 0.223$ (for all data), $R_1 = 0.075$, $wR_2 = 0.203$ (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max} = -1.040/2.546$ e Å$^{-3}$.

The atomic coordinates and other parameters of structure **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1913117); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Elemental analysis was carried out on a EURO Vector 3000A automated analyzer. The thermogravimetric curves were measured on a Termoscan-2 thermal analyzer. IR spectra were recorded on a Spectrum Two FT IR spectrometer equipped with an attenuated total reflectance attachment (Perkin Elmer).

The ESR spectra were measured on a Spinscan X spectrometer (ADANI). The spin Hamiltonian (SH) parameters were found by best fit procedure between the experimental and simulated spectra. The spectra were simulated as described in [17]. The sum of Lorentzian and Gaussian functions was used as the line shape function [18]. Minimization involved variation of the *g*-factor, line width and line shape parameters, and fine structure tensor parameters.

## RESUILTS AND DISCUSSION

The reaction of $H_2L$, $H_4AEDP$, and $CuSO_4$ (in 1 : 2 : 2 ratio) in water with addition of a solution of NaOH to pH 6–7 resulted in the isolation of the crystals of $Cu_4L_2(H_2AEDP)_2 \cdot 34H_2O$ (**I**) (the solvation number was determined from elemental analysis and TGA data). The structure of **I** was determined by X-ray diffraction. It was shown that the complex crystallizes as a hydrate with 30 water molecules and the molecule is tetranuclear and centrosymmetric (Fig. 1). In the polynuclear complex, one can distinguish two binuclear $\{Cu_2(H_2AEDP)(H_2O)_2\}$ moieties (Cu(1)···Cu(2), 3.60(1) Å), which are connected by a pair of $H_2AEDP^{2-}$ bridging anions, with the inversion center being located between the dimers (Cu(1)···Cu(2a), 9.69(1) Å).

Each phosphonate group of $H_2AEDP^{2-}$ and two Cu(II) cations form six-membered chelate rings in a nearly chair conformation (Fig. 2). One phosphonate group binds Cu(II) cations via two O atoms of the

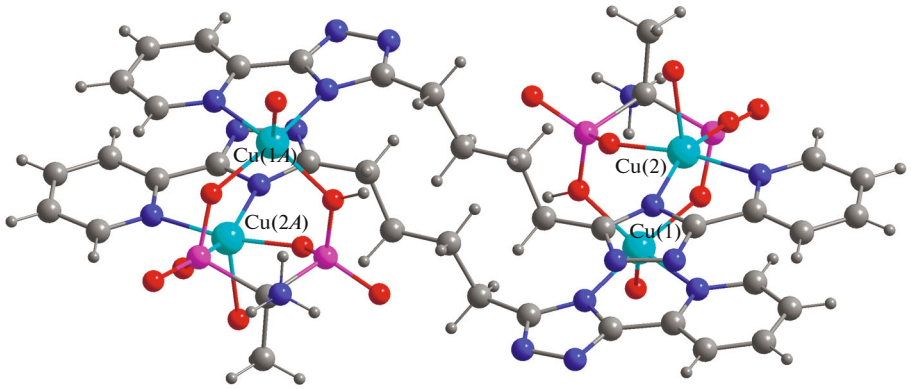



**Fig. 1.** Molecular structure of complex **I**.

deprotonated hydroxyl groups. The second phosphonate group is partly deprotonated and one hydroxyl binds the Cu(II) cation being in the protonated state. The copper–protonated oxygen bond (1.970(4) Å) is somewhat elongated in comparison with the bonds between Cu(II) cations and the oxygen atoms of the deprotonated phosphoryl groups (1.936(4)–1.951(4) Å). One proton migrates to the amino group and, hence, the biphosphonate ligand acquires a zwitter-ion structure and the total charge of –2.

The residual positive charge of the copper cation is counterbalanced via hydrogen atom elimination from the NH group of the triazole ring; consequently, the bis-triazole ligand acts as a dianion, being coordinated to two Cu(II) cations of two dimers through nitrogen atoms of the pyridyl moiety and the triazolate anion. The bonds between Cu(II) and the triazolate moiety (2.003(5)–2.009(5) Å) are somewhat shorter than the bonds with the pyridyl nitrogen atoms (2.056(4)–2.059(4) Å). The nitrogen–carbon bond lengths within the triazolate anions are roughly equal (1.318(5) and 1.313(5) Å for N(3) and N(4); 1.338(5) and 1.354(5) Å for N(2)), which attests to negative charge delocalization within the triazole ring. The bond lengths and bond angles in the ligands are close to usual values [19].

The geometry of the copper coordination polyhedron corresponds to a slightly distorted tetragonal pyramid with the Addison parameter $\tau \approx 0.15$ [20]. The base of the pyramid is composed of two oxygen atoms of the binucleating diphosphonate anion and two nitrogen atoms of spacered bis(2-pyridyl-1,2,4-triazole). The apex of the pyramid is occupied by the coordinated water molecule, the oxygen atom of which is located at a distance of 2.213(4) or 2.205(4) Å from the Cu(1) or Cu(2) atom, respectively. The Cu(II) cation deviates from the pyramid base; its deviation from the root-mean-square plane of $N_2O_2$ is 0.286 and 0.204 Å for Cu(1) or Cu(2), respectively.

The hydrate water molecules fill the voids of the crystal lattice and participate in the complex hydrogen bond system involving the ammonium and heterocyclic nitrogen atoms (N···O, 2.76–3.17 Å) and oxygen atoms of the phosphoryl groups (O···O, 2.66–2.93 Å) and coordinated water molecules (O···O 2.71–2.85 Å).

The ESR spectra of partly dehydrated complex **I** (compound **II**, $Cu_4L_2(H_2AEDP)_2 \cdot 20H_2O$) were recorded for solid samples at 77 and 300 K (Fig. 3). The spectra were simulated by spin Hamiltonian (1) with fine structure for $S = 1$.

$$\hat{H} = \beta(g_x S_x H_x + g_y S_y H_y + g_z H_z S_z) + D\left(S_z^2 - S(S+1)/3\right) + E\left(S_x^2 - S_y^2\right), \quad (1)$$

where $S_x$, $S_y$, $S_z$ are total spin to the *x, y,* and *z* axes, respectively; $D$, $E$ are components of the fine structure tensor, $g_x$, $g_y$, $g_z$ are *g*-tensor components; and $H$ is the applied magnetic field. The calculated SH parameters

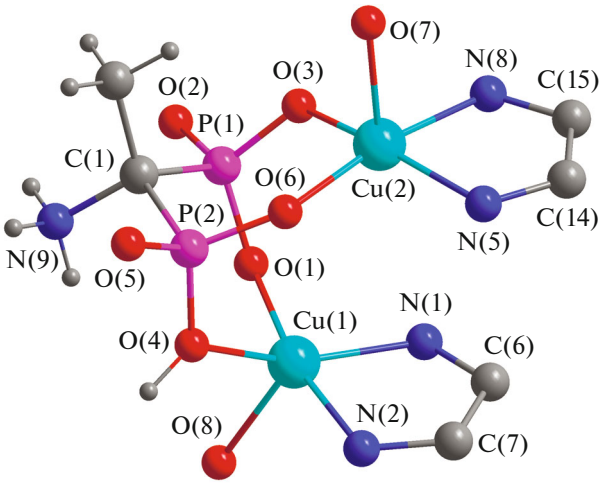



**Fig. 2.** Dimeric moiety of complex **I**. Bond lengths within coordination polyhedra: Cu(1)–O(1), 1.939(4); Cu(1)–O(4), 1.970(4); Cu(1)–N(2), 2.002(5); Cu(1)–N(1), 2.056(5); Cu(1)–O(8), 2.212(5); Cu(2)–O(3). 1.936(4); Cu(2)–O(6), 1.951(4); Cu(2)–N(5), 2.009(5); Cu(2)–N(8), 2.058(5); Cu(2)–O(7), 2.204(4) Å.

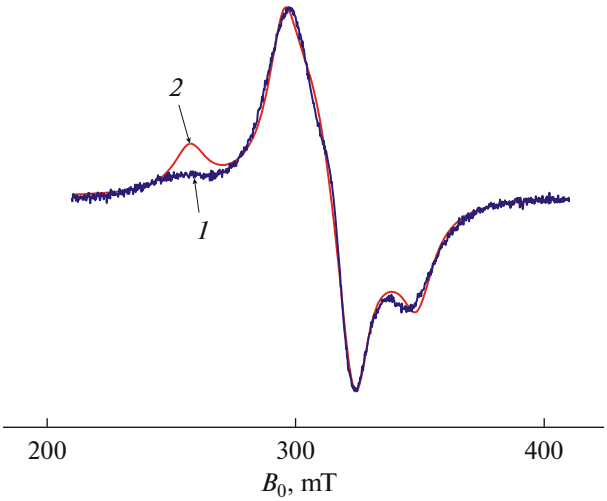



**Fig. 3.** ESR spectrum of compound **II** (solid sample) at 300 K: (*1*) experiment, (*2*) simulation.

are as follows: $g_z = 2.316$, $g_x = 2.081$, $g_y = 2.085$, $D = 0.0355$ cm$^{-1}$, $E = 0.0054$ cm$^{-1}$.

Despite the presence of the dimeric moieties, the signal for the low-field forbidden transition [17] is not observed, indicating the presence of weak exchange interactions between the copper(II) cations.

Thus, it was shown that the use of the 1-aminoethane-1,1-diphosphonate dianion, which promotes the formation of polynuclear structure, in the presence of ditopic spacered bis(2-pyridyl-1,2,4-triazolyl)butane for the reaction with copper(II) ions gives rise to dimeric moieties connected by two aliphatic spacers.

## ACKNOWLEDGMENTS

X-ray diffraction analysis was carried out using the research equipment of the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

## FUNDING

The study of complex compounds was carried out within the state assignment of the Kurnakov Institute of General and Inorganic Chemistry, RAS, in the field of fundamental scientific research and was supported by the Russian Science Foundation (project no. 18-13-00024).

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## REFERENCES

1. Maeda, K., *Microporous Mesoporous Mater.* 2004, vol. 73, p. 47.
2. Matczak-Jon, E. and Videnova-Adrabinskav, V., *Coord. Chem. Rev.*, 2005, vol. 249, p. 2458.
3. Fu, R., Hu, S., and Wu, X., *Cryst. Growth Des.*, 2014, vol. 14, p. 6197.
4. Mao, J.-G., *Coord. Chem. Rev.*, 2007, vol. 251, p. 1493.
5. Bao, S.-S. and Zheng, L.-M., *Coord. Chem. Rev.*, 2016, vol. 316, p. 63.
6. Pan, L., Yuan, Y., Xiao, Y., et al., *J. Mol. Struct.*, 2008, vol. 892, p. 272.
7. Bouhsina, S., Buglyo, P., Abiaad, E., et al., *Inorg. Chim. Acta*, 2004, vol. 357, p. 305.
8. Klingele, M.H. and Brooker, S., *Coord. Chem. Rev.*, 2003, vol. 241, p. 119.
9. Gusev, A.N., Shul'gin V.F., and Kiskin, M.A., *J. Stuct. Chem.*, 2019, vol. 60, no. 3, p. 335.
10. Gusev, A.N., Shul'gin, V.F., Ryush, I.O., et al., *Eur. J. Inorg. Chem.*, 2017, no. 3, p. 704.
11. Gusev, A.N., Shul'gin, V.F., Meshkova, S.B., et al., *Inorg. Chim. Acta*, 2012, vol. 387, p. 321.
12. Kabak, L.V., Kuz'mina, N.E., Khudenko, A.V., et al., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 10, p. 1673.
13. Pan Ling Ling, Yuan Yi-Xuan, Xiao, Y., et al., *J. Mol. Struct.*, 2008, vol. 892, p. 272.
14. *SMART (control) and SAINT (integration) Sofware. Version 5.0*, Madison: Bruker AXS Inc., 1997.
15. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
16. Spek, A.L., *Acta Crystallogr., Sect D: Biol. Crystallogr.*, 2009, vol. 65, no. 2, p. 148.
17. Rakitin, Yu.V., Larin, G.M., and Minin, V.V., *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* (Interpretation of ESR spectra of Coordination Compounds), Moscow: Nauka, 1993.
18. Lebedev, Ya.S. and Muromtsev, V.I., *EPR i relaksatsiya stabilizirovannykh radikalov* (ESR and Relaxation of Stabilized Radicals), Moscow: Khimiya, 1972, p. 25.
19. Allen, F.H., Kennard, O., Watson, D.G., et al., *J. Chem. Soc., Perkin Trans.*, 1987, vol. 12, p. 1.
20. Addison, A.W. and Rao, T.N., *J. Chem. Soc., Dalton Trans.*, 1984, p. 1349.

*Translated by Z. Svitanko*