Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2022, **32**, 471–473

Mendeleev Communications

Copper(II) and zinc(II) complexes with terpene derivatives of ethylenediamine: unexpected ligand transformations

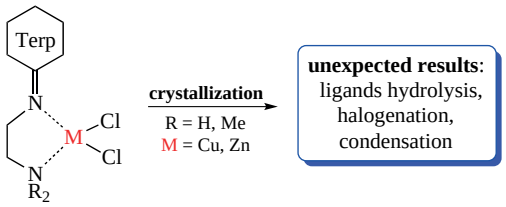
Yana A. Gur'eva,[a] Olga A. Zalevskaya*[a] and Pavel A. Slepukhin[b]

[a] *Institute of Chemistry, Komi Scientific Center, Ural Branch of the Russian Academy of Sciences, 167000 Syktyvkar, Komi Republic, Russian Federation. E-mail: zalevskayaoa@rambler.ru*

[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620108 Ekaterinburg, Russian Federation*

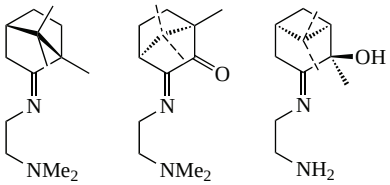
DOI: 10.1016/j.mencom.2022.07.014

Crystallization of copper and zinc complexes with imino terpene derivatives of ethylenediamine causes unexpected chemical transformation of the ligand. Copper(II) chloride catalyzes the hydrolysis of the imine and also acts as a halogenating agent. Crystallization of the zinc complex in acetone is accompanied by the condensation of the ketone with the primary amino group of the ligand.

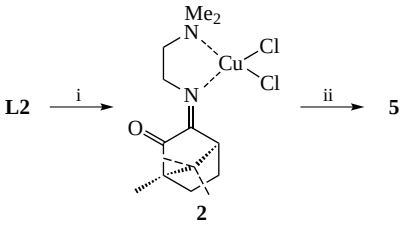


Keywords: copper complexes, zinc complexes, terpenes, ligands, ethylenediamine, imines, crystallization, X-ray diffraction analysis.

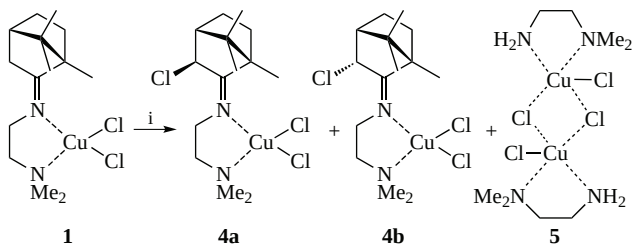
Zinc and copper are essential trace elements that play important roles in the functions of a living organism.[1] The interest in copper and zinc complexes is associated with their potential biological activity.[2–4] Previously,[5–7] for the synthesis of copper and zinc complexes we used terpene derivatives of ethylenediamine **L1**–**L3** when equimolar amounts of metal salt and ligand in methanol or ethanol were reacted at room temperature. After removal of the solvent and precipitation, metal complexes **1**–**3** (Schemes 1–3) were obtained in the form of powders. In this study we have discovered that crystallization of these substances caused some unexpected transformations of their ligands.



Copper complex **1** (see Scheme 1) was previously described and its structure was confirmed by XRD.[8] Herein, we carried out the synthesis and crystallization under different conditions. The crystallization at room temperature from ethanol afforded two types of crystals of different colors and shapes, namely, green and blue prisms. These crystals (**4a**+**4b** mixture and **5**) have been separated by hand. According to XRD data, green prismatic crystals were formed by unexpected co-crystallization of two diastereomers **4a**+**4b** (1:1), and blue prisms were identified as known[9,10] previously described complex **5**. This result can be explained by the fact that copper(II) chloride would catalyze two transformations. Two alternative mechanisms for the formation of diastereomers **4a** and **4b** can be suggested. Free radical chlorination of the terpene moiety of complex **1** is possible, taking into account the formation of molecular chlorine due to the oxidizing ability of Cu^{2+} ion.[11] The ionic mechanism through the intermediate formation of enamine must not be ruled out, which ensures the regioselectivity of nucleophilic chlorination.[12] More research is needed to clarify the mechanism. According to XRD data,† diastereomers **4a**+**4b** (Figure 1) crystallize in the noncentrosymmetric space group $P2_1$ of the monoclinic system



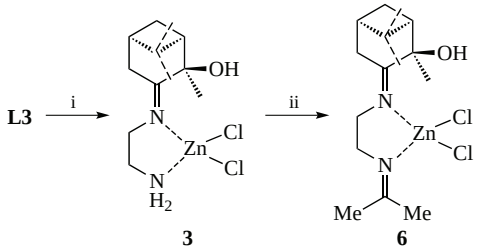
Scheme 2 *Reagents and conditions*: i, $CuCl_2 \cdot 2H_2O$, MeOH, room temperature, 8 h; ii, ethanol, crystallization, room temperature, slow solvent evaporation.



Scheme 1 *Reagents and conditions*: i, EtOH, crystallization, room temperature, slow solvent evaporation.

† *Crystal data for* **4a**+**4b** (1:1). $C_{14}H_{25}Cl_3CuN_2$, 391.25 g mol^{-1}, monoclinic, space group $P2_1$, a = 10.6243(18), b = 13.5440(15) and c = 13.5783(16) Å, β = 111.927(17)°, V = 1812.5(5) Å^3, Z = 4, T = 295(2) K, $\mu(MoK_\alpha)$ = 1.640 mm^{-1}, d_{calc} = 1.434 g cm^{-3}, 12568 reflections measured (7.136° ⩽ 2θ ⩽ 61.986°), 8657 unique (R_{int} = 0.0505, R_{sigma} = 0.1160) which were used in all calculations. The final R_1 = 0.0752, wR_2 = 0.1547 [$I > 2\sigma(I)$] and R_1 = 0.1848, wR_2 = 0.2149 (all data). GooF = 0.981. Largest diff. peak/hole 0.56/–0.50 e Å^{-3}.

CCDC 2144267 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



3 **6**

Scheme 3 *Reagents and conditions*: i, $ZnCl_2$, EtOH, room temperature, 8 h; ii, acetone, crystallization, room temperature, slow evaporation.

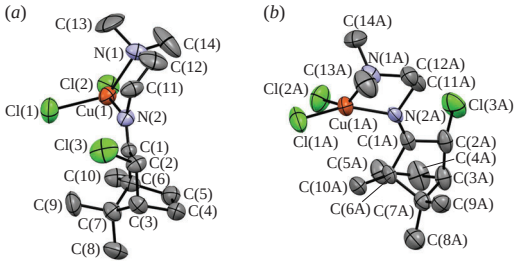


Figure 1 ORTEP drawing of the molecular structure **4a**+**4b**. Thermal ellipsoids are shown at the 35% probability level.

in the form of two crystallographically independent molecules. The molecules have close values of the main bond lengths and bond angles, differing in the configuration of the chlorine-substituted carbon atom. In both molecules, the central copper ion has a highly distorted tetrahedral configuration coordinating two nitrogen atoms of the initial ligand, as well as two chlorine atoms (coordination number 4). The distortions of the tetrahedron concern not only the natural differences in the Cu–N and Cu–Cl bond lengths, but also the bond angles [in particular, the bond angle N(2)Cu(1)Cl(2) = 153.3°]. As a result of the coordination interaction of the Cu^{2+} ion with the ligand, the five-membered chelate cycle CuN_2C_2 is closed. On the whole, both molecules are characterized by rather high values of the thermal parameters of atoms, and the overall quality of the data does not allow direct localization of hydrogen atoms.

The formation of complex **5** may be explained by the fact that $CuCl_2$ being the Lewis acid promotes the hydrolysis of the imine ligand in complex **1** with the liberation of *N*,*N*-dimethylethylenediamine and final formation of compound **5**. A similar process of catalytic solvolysis of the imine is also observed when trying to synthesize copper complex **2** (see Scheme 2). The prediction of the structure **2** was made by analogy with the corresponding palladium complex, whose formation is accompanied by a change in the configuration of the C=N bond of the initial ligand **L2**.[7] As a result, crystallization of the substance obtained upon the reaction product between **L1** and copper(II) chloride from ethanol afforded compound **5** whose structure was verified by X-ray diffraction (crystal data for **5** are described[9,10]).

Unlike unstable copper complexes **1** and **2**, the corresponding zinc complexes are more stable. Their description is beyond the scope of this publication. However, while collecting unexpected transformations, we consider it appropriate to give here the following interesting example. The interaction of **L3** ligand with $ZnCl_2$ in ethanol gives complex **3** with the yield 92% (see Scheme 3). The structure of new compound **3** is confirmed by ^1H, ^{13}C NMR and IR spectroscopy as well as elemental analysis data. Slow crystallization of zinc complex **3** from acetone at room temperature is accompanied by the condensation reaction of the primary amino group with acetone and the formation of complex **6**. This result is not unusual, since zinc chloride is known to be used as a catalyst for the condensation reactions of carbonyl compounds with amines.[13] There are examples of such metal ion directed template synthesis.[14] Structure **6** was verified

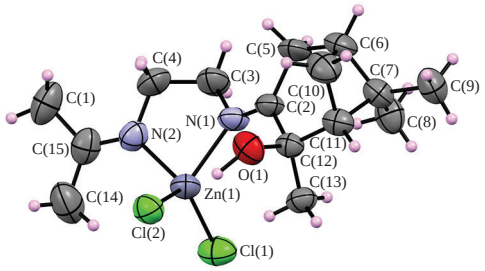


Figure 2 ORTEP drawing of the molecular structure **6**. Thermal ellipsoids are shown at the 35% probability level.

by X-ray diffraction analysis (Figure 2).‡ According to the XRD data, complex **6** crystallizes in the noncentrosymmetric space group of the monoclinic system. The central zinc ion coordinates two nitrogen atoms of the initial ligand, as well as two chlorine atoms in a distorted tetrahedral configuration (coordination number 4) with the closing of the five-membered ZnN_2C_2 chelate ring. The chelate ring is not planar, the C(3) atom deviates from the Zn(1)N(1)N(2)C(4) plane by 0.579 Å. Double and single C–N bonds in the structure are clearly distinguishable, and their lengths are close to the expected values. The OH group of the terpene fragment forms an intramolecular hydrogen bond with the Cl(2) atom with the following parameters: O(1)–H(1) = 1.1(1) Å, H(1)···Cl(2) = 2.1(1) Å, O(1)···Cl(2) = 3.151(6) Å, O(1)H(1)Cl(2) = 167(9)°. Significantly shortened intermolecular contacts are absent in the crystal, the molecules are packed into stacks along the helical axes.

In conclusion, the described examples of unexpected ligand transformations of copper and zinc complexes with terpene derivatives of ethylenediamine will be of interest to researchers in the field of coordination chemistry. However, the fact of chlorination of the terpene moiety in copper(II) complexes that we have discovered (see Scheme 1) requires further research.

This work was supported by the Russian Foundation for Basic Research (project no. 20-03-00027) and by the Ministry of Science and Higher Education of the Russian Federation (state assignments no. 1021062211116-4-1.4.1). Crystal structure determination was performed using equipment of the Center for Joint Use ‘Spectroscopy and Analysis of Organic Compounds’ at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.014.

References

1 R. Crichton, in *Biological Inorganic Chemistry*, 3rd edn., ed. R. Crichton, Academic Press, Cambridge, MA, 2019, ch. 22, pp. 599–623.
2 M. Porchia, M. Pellei, F. Del Bello and C. Santini, *Molecules*, 2020, **25**, 5814.
3 S. Nasiri Sovari and F. Zobi, *Chemistry*, 2020, **2**, 418.
4 O. A. Zalevskaya and Ya. A. Gur’eva, *Russ. J. Coord. Chem.*, 2021, **47**, 861.

‡ *Crystal data for* **6**. $C_{15}H_{26}Cl_2N_2OZn$, 386.65 g mol^{-1}, monoclinic, space group $P2_1$, a = 8.0706(6), b = 9.6426(9) and c = 11.8445(10) Å, β = 90.131(8)°, V = 921.76(13) Å^3, Z = 2, T = 295(2) K, μ(MoK$_\alpha$) = 1.622 mm^{-1}, d_{calc} = 1.393 g cm^{-3}, 6596 reflections measured (7.424° ⩽ 2θ ⩽ 61.72°), 4017 unique (R_{int} = 0.0414, R_{sigma} = 0.0630) which were used in all calculations. The final R_1 = 0.0484, wR_2 = 0.1101 [$I > 2\sigma(I)$] and R_1 = 0.0807, wR_2 = 0.1480 (all data), GooF = 1.027. Largest diff. peak/hole 0.58/–0.60 e Å^{-3}.

CCDC 2144266 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

5 Ya. A. Gur'eva, O. A. Zalevskaya, I. N. Alekseev, P. A. Slepukhin and A. V. Kutchin, *Russ. J. Org. Chem.*, 2018, **54**, 1285 (*Zh. Org. Khim*., 2018, **54**, 1274).
6 Ya. A. Gur'eva, I. N. Alekseev, O. A. Zalevskaya, P. A. Slepukhin and A. V. Kutchin, *Russ. J. Org. Chem*., 2016, **52**, 781 (*Zh. Org. Khim*., 2016, **52**, 796).
7 O. A. Zalevskaya, Y. A. Gur'eva, A. V. Kutchin, Yu. R. Aleksandrova, E. Yu. Yandulova, N. S. Nikolaeva and M. E. Neganova, *Inorg. Chim. Acta*, 2021, **527**, 120593.
8 K. S. Kwon, S. Nayab and J. H. Jeong, *Polyhedron*, 2017, **130**, 23.
9 D. W. Phelps, W. H. Goodman and D. J. Hodgson, *Inorg. Chem*., 1976, **15**, 2266.
10 I. Warad, *J. Mol. Struct.*, 2021, **1236**, 130371.
11 D. Lennon and J. M. Winfield, *Molecules*, 2017, **22**, 201.
12 X. Zhou, C. Yu, Z. Feng, Y. Yu, J. Wang, E. Hao, Y. Wei, X. Mu and L. Jiao, *Org. Lett.*, 2015, **17**, 4632.
13 A. S. Sokolova, O. I. Yarovaya, A. V. Shernyukov, Y. V. Gatilov, Y. V. Razumova, V. V. Zarubaev, T. S. Tretiak, A. G. Pokrovsky, O. I. Kiselev and N. F. Salakhutdinov, *Eur. J. Med. Chem*., 2015, **105**, 263.
14 A. Ahmedova, S. Zareva and A. Dołega, *Mendeleev Commun*., 2020, **30**, 519.

Received: 26th January 2022; Com. 22/6796