Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 606–608

Mendeleev Communications

First example of a click-reaction on the aminate copper complexes: effect of reaction parameters

Igor V. Esarev,[a] Vladislav V. Gurzhiy,[b] Artem A. Selyutin,[b] Anastasia V. Laptenkova,[b] Andrey I. Poddel'sky,[c] Nicolay L. Medvedskiy,[a] Alexander I. Ponyaev,[a] Rostislav E. Trifonov[a,b] and Alexey V. Eremin*[a,d]

[a] *St. Petersburg State Institute of Technology (Technical University), 190013 St. Petersburg, Russian Federation. E-mail: ha9room@gmail.com*

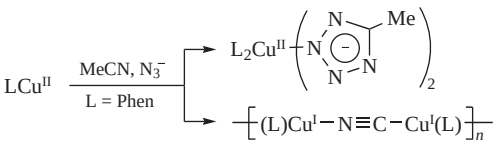
[b] *St. Petersburg State University, 199034 St. Petersburg, Russian Federation*

[c] *G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603137 Nizhnii Novgorod, Russian Federation*

[d] *Peter the Great St. Petersburg Polytechnic University, 195251 St. Petersburg, Russian Federation*

DOI: 10.1016/j.mencom.2018.11.014

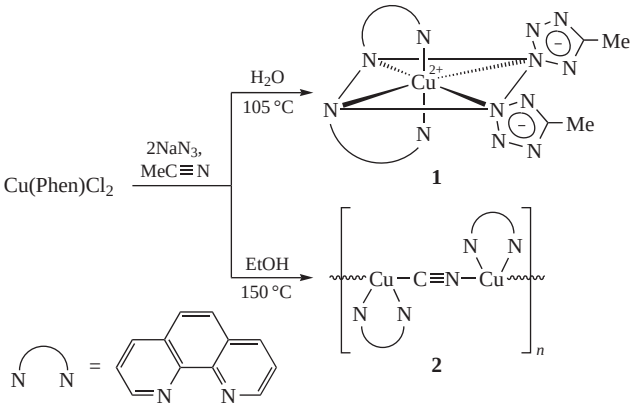
The hydrothermal reaction of NaN_3 with $Cu(Phen)Cl_2$ in acetonitrile solutions results in the formation of two complexes: new d^9 mononuclear *cis*-$[Cu^{II}(Phen)_2(mtz)_2]\cdot H_2O$ and d^{10} coordination polymer *catena*-$[Cu^{I}(Phen)(\mu\text{-}CN)]_n$ (mtz is 5-methyltetrazolate anion and Phen is 1,10-phenanthroline). The process involves *in situ* formation of mtz ligand *via* cycloaddition of acetonitrile and azide (in the case of $[Cu^{II}(Phen)_2(mtz)_2]$) and cleavage of acetonitrile C–C bond (in the case of $[Cu^{I}(Phen)(\mu\text{-}CN)]_n$). Both complexes were fully characterized by a comprehensive set of methods, including the single crystal X-ray diffraction data.



Among various complexes of *d*-elements with nitrogen-containing polydentate ligands,[1] the compounds incorporating tetrazole moieties attract more attention[2] due to the many opportunities provided by coordinated tetrazole, in particular, obtaining mono-, bi- or polynuclear structures[3] capable to act as independent structural units in the synthesis of supramolecular or polymer systems[4] with interesting magnetic properties.[5] On the other hand, azoles and, in particular, tetrazole are attractive as the ligands due to their reactivity and biological activity.[6]

Another interesting aspect of chemistry of the tetrazole complexes is so-called click-reactions,[7–9] which allow one to create nitric fragments directly in the coordination sphere of complexes. Commonly, the click-type reactions involve the most reactive CN-*a* fragment forming the azole ligands *via* [3+2] cycloaddition.[10] However, there are also examples of reactions accompanied by splitting of C–C bonds in nitriles to form free cyano-ligands.[11–14]

Here, we report on the reactions between NaN_3 and $Cu(Phen)Cl_2$[15] in MeCN–H_2O or MeCN–EtOH solvents under hydro(solvo)thermal conditions (Scheme 1).† Depending on the reaction conditions, two different copper complexes were obtained: the new *cis*-$[Cu^{II}(Phen)_2(mtz)_2]\cdot H_2O$ **1** (mtz is 5-methyltetrazolate anion) and the well-known coordination polymer $[Cu^{I}(Phen)(\mu\text{-}CN)]_n$ **2**. In the case of **1**, the formation of methyltetrazolate ligand ($MeCN + N_3^- \rightarrow mtz^-$) was accompanied by a disproportionation of initial complex [$2Cu(Phen)^{2+} \rightarrow Cu(Phen)_2^{2+} + Cu_{solv}^{2+}$] that led to the brown precipitate of metallic copper released from



Scheme 1

† All chemicals were purchased from commercial sources (reagent grade, analytical grade or related Russian qualifications) and used as received. $Cu(Phen)Cl_2$ was prepared according to the known procedure.[15]

cis-*[Cu(Phen)$_2$(mtz)$_2$]·H$_2$O* **1**. $Cu(Phen)Cl_2$ (0.2 g, 0.64 mmol) and NaN_3 (0.083 g, 1.28 mmol) were mixed in a water–acetonitrile (1 : 1 v/v, 10 ml) solution. The reaction mixture was sealed in a Teflon-lined stainless steel autoclave and kept at 105 °C for 24 h. After cooling to room temperature, the blue solution was filtered off, and the filtrate was left for evaporation. After several days, the green crystals of **1** were collected. The yield was 57%. IR (4000–350 cm^{-1}): 720 (vs), 855 (s), 1425 (s), 1524 (m), 2371 (w), 3367 (m). Found (%): C, 55.2; Cu, 10.6; N, 27.4; H, 4.1. Calc. for $C_{28}H_{22}CuN_{12}\cdot H_2O$ (%): C, 55.3; Cu, 10.4; N, 27.6; H, 4.0.

[Cu(Phen)(μ-CN)]$_n$ **2**. $Cu(Phen)Cl_2$ (0.2 g, 0.64 mmol) and NaN_3 (083 g, 1.28 mmol) were mixed in ethanol–water (0.95 : 0.05 v/v, 7 ml) solution. Then acetonitrile (5 ml) was added. The mixture was sealed in a Teflon-lined stainless steel autoclave and kept at 150 °C for 72 h. Once it was cooled to room temperature, the red needle-like crystals of **2** were formed and isolated by filtration. The yield was 21% (based on Cu). IR (4000–350 cm^{-1}): 667 (s), 730 (vs), 840 (vs), 1017 (m), 1420 (m), 2360 (w). Found (%): C, 58.0; Cu, 23.2; N, 15.9; H, 2.9. Calc. for $C_{26}H_{16}Cu_2N_6$ (%): C, 57.9; Cu, 23.4; N, 15.7; H, 3.0.

the reaction mixture containing complex **1**. The formation of **2** proceeds *via* a complicated mechanism including C–C bond cleavage of acetonitrile and reduction of Cu^{II} into Cu^{I}. The crystal structure of complex **2** has been previously reported.[16–18]

Suitable crystals for the single crystal X-ray diffraction experiments were selected from the precipitate obtained by the evaporation of reaction solutions. The molecular structures of both complexes were confirmed by X-ray analysis.‡ Copper atom in complex **1** is surrounded by a distorted octahedral environment formed by the four nitrogen atoms of two Phen ligands and two nitrogen atoms of two mtz ligands in their deprotonated form (Figure 1). The Cu–N(Phen) and Cu(1)–N(12) bonds between the two *trans*-located Phen ligands are markedly elongated due to the greater *trans*-effect of Phen as compared to that of mtz ligand (Table S2, Online Supplementary Materials). The crystal structures of **1** and **2** are stabilized by stacking π–π interactions between the Phen ligands (Figure S1, Online Supplementary Materials). Lengths of Cu–N bonds in **1** and the known complexes of copper(II) with tetrazole ligands[19–23] are given in Table S2, while those of Cu–N(Phen) and Cu–(CN) bonds in **2** and some similar compounds are given in Table S3 (see Online Supplementary Materials).[16–18,24,25] Complex **2** synthesized in our work was structurally identical to those reported previously.[16–18] Note that other methods of synthesis involve the direct substitution reaction of Cu^{II} compounds with the donor of CN ligand (*e.g.*, $[Fe(CN)_6]^{3-}$)[16,17] or a reaction of $Cu^{I}CN$ with Phen ligand.[18]

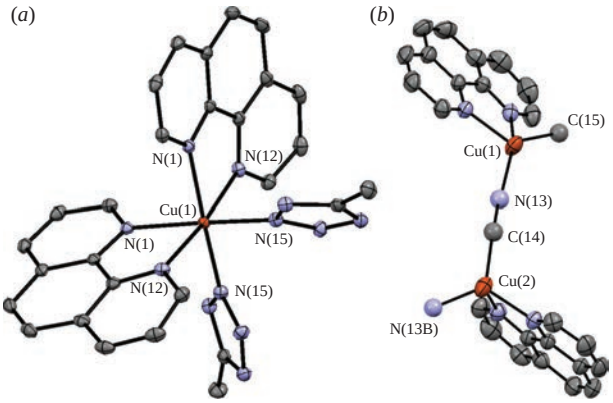


Figure 1 Molecular structures of complexes (*a*) **1** and (*b*) **2** with thermal ellipsoids drawn at the probability level of 50%. Hydrogens are omitted.

However, we have observed the unusual formation of CN ligand that was generated *via* destruction of acetonitrile.

Synthesis of complex **1** is the first reported example of the tetrazolate ligand *in situ* formation within the coordination sphere of copper(II) complex containing other amino ligands. According to other works,[26–28] the mtz anion is formed upon attachment of N_3^- to the nitrile ligand coordinated in the inner sphere of complex. In addition, the reaction mechanism may include the reduction of Cu^{II} into Cu^{I} and also the disproportionation reaction: $2\,Cu^{I} \rightarrow Cu^{II} + Cu^{0}$. The latter reaction pathway is manifested by the presence of two Phen ligands in **1**, which can be caused by partial splitting of initial copper compound along with the reduction of Cu^{I} into Cu^{0} and attachment of released Phen to the formed Cu^{2+}_{solv} species.

The X-band EPR spectrum of polycrystalline sample **1** at 298 K (see Figure S2, Online Supplementary Materials) possesses a rhombic symmetry with *g*-tensor parameters of $g_1 = 2.212$, $g_2 = 2.162$, and $g_3 = 2.004$ ($g_{av} = 2.126$).§ The hyper-fine structure was not observed in the spectrum. The magnitude of *g*-factor and the anisotropy of spectrum are typical of the Cu^{II} complexes bearing the unpaired electron localized on the *d* orbitals of copper(II). The isotropic X-band EPR spectrum of complex **1** in acetonitrile solution at 298 K reveals a quartet typical of Cu^{II} complexes with $g_i = 2.1265$ and HFC constant values on copper nuclei of $a_i(^{63}Cu) = 52.6$ G, $a_i(^{65}Cu) = 56.3$ G (^{63}Cu, 69.15%, $I = 3/2$; ^{65}Cu, 30.85%, $I = 3/2$). The EPR spectral parameters for complex **1** in solid state and in acetonitrile solution were similar and pointed out the preservation of internal coordination sphere of the complex in acetonitrile solution. The isotropic X-band EPR spectrum of **1** in DMSO solution also exhibits a quartet with anisotropy specific for the copper(II) complexes and with parameters: $g_i = 2.136$, $a_i(^{63,65}Cu) \sim 65$ G (Figure S3). It is possible that the structure of complex **1** in DMSO is not the same as that in its solid state (since $g_{av} = 2.126$ in the case of solid, while $g_i = 2.136$ in DMSO solution) due to the strong solvating ability of DMSO. It is also possible that the dissociation of complex **1** providing DMSO-solvated $[Cu^{II}(Phen)_2]^{2+}$ cations and methyltetrazolate anions occurs in the DMSO solution.

The reaction mechanism in the case of complex **2** is also of interest. There was no any reported example of obtaining the cyanide anion in the Cu^{II}–MeCN systems under the reaction conditions similar to that revealed in the present work. However, it is believed that acetonitrile can react with water in the presence of Cu^{2+}_{solv} with a cyanohydrin formation: $MeCN + H_2O \rightarrow HOCH_2CN + H_2$. Under the conditions of hydrothermal synthesis, the resulting

‡ *Crystal data for* **1**. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Eos CCD area detector operating with a monochromated MoKα radiation (λ = 0.71073 Å) at 100(2) K. The unit-cell parameters for $C_{28}H_{24}CuN_{12}O$, M = 608.13, monoclinic, *C*2/*c*, at 100 K: a = 9.5063(3), b = 15.4116(6) and c = 17.5253(7) Å, β = 93.945(3)°, V = 2561.50(16) Å^3, Z = 4, μ = 0.903 mm^{-1}. The parameters were refined by the least-squares method using 8250 reflections in the 2θ range of 5.43–55.00°. The structure was solved by direct methods and refined to R_1 = 0.031 (wR_2 = 0.071) for 2630 unique reflections with $|F_0| \geqslant 4\sigma_F$ using the SHELX software[31] incorporated in the OLEX2 software package.[32]

Crystal data for **2**. Data were collected using a Rigaku Oxford Diffraction Xtalab diffractometer equipped with a semiconductor HyPix-3000 area detector operating with microfocused monochromated CuKα radiation (λ = = 1.54184 Å). The unit-cell parameters for $C_{26}H_{16}Cu_2N_6$, M = 539.53, monoclinic, $P2_1/c$, at 100 K: a = 18.4775(8), b = 8.3433(3), and c = 16.5648(8) Å, β = 110.044(5)°, V = 2399.01(19) Å^3, Z = 4, μ = = 2.389 mm^{-1}. The parameters were refined by the least-squares method using 14089 reflections in the 2θ range of 5.09–140.00°. The structure was solved by direct methods and refined to R_1 = 0.041 (wR_2 = 0.105) for 3919 unique reflections with $|F_0| \geqslant 4\sigma_F$ using the SHELX software[31] incorporated in the OLEX2 software package.[32] The unit cell contains disordered ethanol molecules, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON:[33] total potential solvent accessible void volume is 250 Å^3 and electron count voids per cell is 69e that is approximately equal to 0.5 ethanol molecule per formula unit of **2**. Both cyanide fragments in the structure of **2** are mutually positionally disordered (CN/NC) and their occupancies were refined as 0.55/0.45 and 0.58/0.42.

Absorption correction for both structures was applied in CrysAlisPro software complex[34] using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The carbon-bound H atoms were geometrically located and included in the refinement according to the 'riding' model approximation, with U_{iso}(H) set to 1.5U_{eq}(C) and C–H of 0.96 Å for the Me groups and U_{iso}(H) set to 1.2U_{eq}(C) and C–H of 0.93 Å for the CH groups. Hydrogen atoms of water molecules in **1** were localized from difference Fourier maps and refined with individual isotropic ADPs. The crystallographic data and refinement parameters for **1** and **2** are summarized in Table S1 (see Online Supplementary Materials).

CCDC 1836717 and 1837839 contain 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.

§ The spectra were recorded on a Bruker EMX spectrometer (working frequency 9.75 GHz). The spectral parameters were obtained by the simulation using the WinEPR SimFonia Software (v. 1.25, Bruker).

cyanohydrin can be decomposed releasing formaldehyde and HCN.[14,29] It was assumed in some works[11,13,30] that the presence of reducing agents in the reaction system contributes to the methyl radical elimination from MeCN, while the formation of CN^- from tetrazole looks unlikely due to a high stability of copper(I) complexes with azole ligands under the reaction conditions.[10]

In conclusion, the obtained results are of general interest since they expand knowledge of the ligand effect on the click reaction providing the tetrazole compounds and coordination polymers.

This work was in parts supported by the Ministry of Education and Science of Russian Federation (grant no. 4.4697.2017/6.7) and by the Russian Foundation for Basic Research (grant no. 16-08-01299). The single crystal X-ray diffraction experiments were carried out at the X-ray Diffraction Centre of St. Petersburg State University. The EPR investigations were performed using the equipment of Analytical Centre at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.014.

References

1 *Comprehensive Coordination Chemistry II*, 2nd edn., eds. J. A. McCleverty and T. J. Meyer, Elsevier, Amsterdam, 2003.
2 (*a*) G. Aromí, L. A. Barrios, O. Roubeau and P. Gamez, *Coord. Chem. Rev*., 2011, **255**, 485; (*b*) E. A. Popova, R. E. Trifonov and V. A. Ostrovskii, *Arkivoc*, 2012, **i**, 45; (*c*) C.-C. Du, J.-Z. Fan, X.-F. Wang, S.-B. Zhou and D.-Z. Wang, *J. Mol. Struct*., 2017, **1133**, 348; (*d*) A. Takayama, T. Suzuki, M. Ikeda, Y. Sunatsuki and M. Kojima, *Dalton Trans*., 2013, **42**, 14556.
3 (*a*) Q. Lin, T. Wu, S.-T. Zheng, X. Bu and P. Feng, *J. Am. Chem. Soc*., 2012, **134**, 784; (*b*) X. Li, Z. Li, X. Xu and X. Guo, *J. Coord. Chem*., 2015, **68**, 195.
4 (*a*) S. Jeong, X. Song, S. Jeong, M. Oh, X. Liu, D. Kim, D. Moon and M. S. Lah, *Inorg. Chem*., 2011, **50**, 12133; (*b*) S. Xiong, Y. Gong, H. Wang, H. Wang, Q. Liu, M. Gu, X. Wang, B. Chen and Z. Wang, *Chem. Commun*., 2014, **50**, 12101; (*c*) P. Cui, H.-S. Hu, B. Zhao, J. T. Miller, P. Cheng and J. Li, *Nat. Commun*., 2015, **6**, 6331; (*d*) T. Wu, B-H. Yi and D. Li, *Inorg. Chem*., 2005, **44**, 4130.
5 (*a*) Y.-B. Lu, M.-S. Wang, W.-W. Zhou, G. Xu, G.-C. Guo and J.-S. Huang, *Inorg. Chem*., 2008, **47**, 8935; (*b*) F.-H. Zhao, Y.-X. Che and J.-M. Zheng, *Inorg Chem*., 2012, **51**, 4862; (*c*) A. B. Gaspar, V. Ksenofontov, M. Seredyuk and P. Gütlich, *Coord. Chem. Rev*., 2005, **249**, 2661; (*d*) J. Liu, H.-M. Dong, E.-C. Yang and X.-J. Zhao, *Z. Anorg. Allg. Chem*., 2014, **640**, 201.
6 (*a*) E. Łukowska-Chojnacka, J. Mierzejewska, M. Milner-Krawczyk, M. Bondaryk and M. Staniszewska, *Bioorg. Med. Chem*., 2016, **24**, 6058; (*b*) M. S. Surendra Babu, B. Umamaheswara Rao, V. Krishna, S. Mustafa and G. Nageswara Rao, *J. Saudi Chem. Soc*., 2017, **21**, 291; (*c*) V. A. Ostrovskii, E. A. Popova and R. E. Trifonov, *Adv. Heterocycl. Chem*., 2017, **123**, 1.
7 (*a*) Z. P. Demko and K. B. Sharpless, *J. Org. Chem*., 2001, **66**, 7945; (*b*) K. Stawicka, K. Drazkiewicz and M. Ziolek, *Micropor. Mesopor. Mater*., 2018, **258**, 41; (*c*) L. Liang and D. Astruc, *Coord. Chem. Rev*., 2011, **255**, 2933.
8 M. Aldhoun, A. Massi and A. Dondoni, *J. Org. Chem*., 2008, **73**, 9565.
9 J. C. Jewett and C. R. Bertozzi, *Chem. Soc. Rev*., 2010, **39**, 1272.
10 (*a*) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z. Xue, *Angew. Chem. Int. Ed*., 2002, **41**, 3800; (*b*) R. Nasani, M. Saha, S. M. Mobin and S. Mukhopadhyay, *Polyhedron*, 2013, **55**, 24; (*c*) L. Ma, Y. C. Qiu, G. Peng, J. B. Cai and H. Deng, *Eur. J. Inorg. Chem*., 2011, 3446; (*d*) H. Gerhards, A. Krest, P. J. Eulgem, D. Naumann, D. Rokitta, M. Valldor and A. Klein, *Polyhedron*, 2015, **100**, 271; (*e*) F. Dehghani, A. R. Sardarian and M. Esmaeilpour, *J. Organomet. Chem*., 2013, **743**, 87.
11 F. Xu, W. Huang and X.-Z. You, *Dalton Trans*., 2010, **39**, 10652.
12 (*a*) J. L. Burmeister and L. M. Edwards, *J. Chem. Soc*., 1971, 1663; (*b*) X.-C. Huang, S.-L. Zheng, J.-P. Zhang and X.-M. Chen, *Eur. J. Inorg. Chem*., 2004, 1024; (*c*) X. Zhang, G. Y. Dong, B.Y. Yu, K. Van Hecke and G. H. Cui, *Transition Met. Chem*., 2015, **40**, 907.
13 T. Lu, X. Zhuang, Y. Li and S. Chen, *J. Am. Chem. Soc*., 2004, **126**, 4760.
14 Y.-Y. Liu, Z.-X. Wang, X. He, M. Shao and M.-X. Li, *Inorg. Chem. Commun*., 2017, **80**, 46.
15 S. Chandraleka, K. Ramya, G. Chandramohan, D. Dhanasekaran, A. Priyadharshini and A. Panneerselvam, *J. Saudi Chem. Soc*., 2011, **18**, 953.
16 X. He, C.-Z. Lu, D.-Q. Yuan, S.-M. Chen, J.-T. Chen, *Eur. J. Inorg. Chem*., 2005, 2181.
17 A. Kaur and T. Pintauer, *Eur. J. Inorg. Chem*., 2013, 3297.
18 J. Nie, J. Wang and C. Dai, *Acta Crystallogr*., 2010, **E66**, m1538.
19 Z.-H. Shao, J. Luo, R.-F. Cai, X.-G. Zhou, L.-H. Weng and Z.-X. Chen, *Acta Crystallogr*., 2004, **E60**, m225.
20 C. Wang, J. Li, X. Fan, F. Zhao, W. Zhang, G. Zhang and Z. Gao, *Eur. J. Inorg. Chem*., 2015, 1012.
21 B. Szafranowska and J. Beck, *Eur. J. Inorg. Chem*., 2013, 3167.
22 Y. J. Zhang, X. Fang, M. L. Cao, H. Y. Yu and J. D. Wang, *Acta Crystallogr*., 2007, **E63**, m2630.
23 X.-H. Huang, T.-L. Sheng, S.-C. Xiang, R.-B. Fu, S.-M. Hu, Y.-M. Li and X.-T. Wu, *Jiegou Huaxue (J. Struct. Chem.)*, 2007, **26**, 161.
24 J.-H. Yu, J.-Q. Xu, Q.-X. Yang, L.-Y. Pan, T.-G. Wang, C.-H. Lu and T.-H. Ma, *J. Mol. Struct*., 2003, **658**, 1.
25 F.-Y. Dong, Y.-T. Li, Z.-Y. Wu, Y.-M. Sun, W. Sun, Z.-Q. Liu and Y.-L. Song, *J. Inorg. Organomet. Polym. Mater*., 2008, **18**, 398.
26 H. Zhao, Z.-R. Qu, H.-Y. Ye and R.-G. Xiong, *Chem. Soc. Rev*., 2008, **37**, 84.
27 F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc*., 2002, **124**, 12210.
28 V. A. Ostrovskii, G. I. Koldobskii and R. E. Trifonov, in *Comprehensive Heterocyclic Chemistry III*, eds. A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven and R. J. K. Taylor, Elsevier, Amsterdam, 2008, vol. 6, pp. 257–423.
29 D. E. Feierman and A. I. Cederbaum, *Chem. Res. Toxicol*., 1989, **2**, 359.
30 W. Hu, F. Teng, H. Peng, J. Yu, S. Sun, J. Cheng and Y. Shao, *Tetrahedron Lett*., 2015, **56**, 7056.
31 G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.
32 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.
33 A. L. Spek, *Acta Crystallogr*., 2015, **C71**, 9.
34 *CrysAlis(Pro)*, *Rigaku Oxford Diffraction*, 2017, Version 1.171.39.35a.

Received: 18th May 2018; Com. 18/5585