Synthesis of azolyl-substituted adamantane derivatives and their coordination compounds

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Reactions of adamantylazoles with nucleophiles (water, carbon monoxide, acetonitrile) in sulfuric acid were studied. New bifunctional adamantane derivatives containing one heterocyclic substituent and one hydroxyl or acetamide substituent were synthesized. The coordination compounds of copper(II) and zinc(II) with 1-adamantyl-1,2,4-triazole, 4-adamantylpyrazole, and 4-adamantyl-3,5-dimethylpyrazole were synthesized and structurally characterized. These complexes are first examples of coordination compounds of azolyladamantanes.

Key words: adamantane, triazole, pyrazole, zinc, copper, coordination compounds, X-ray diffraction.

Since the discovery of antiviral activity of amantadine, a great diversity of molecules containing an adamantyl moiety were synthesized.[1—5] *N*-Adamantylazoles are a specific class of compounds, which have attracted attention due to their potential biological activity. In particular, adamantylpyrazoles were comprehensively investigated, mainly by Elguero´s research team.[6—10] Despite the fact that the structures of adamantylazoles and their biological activity were studied in sufficient detail,[11] data on the possibility of further functionalization of the adamantane skeleton in adamantylazoles are scarce in the literature. Meanwhile, adamantane is a very popular molecular platform for the construction of rigid non-aromatic ligands, which are used in the synthesis of thermally stable metal organic frameworks (MOFs).[12—15] Most coordination compounds with azoles containing an adamantane moiety belong to transition metal carbene complexes, with 1,3-diadamantylimidazole being their precursor. On the contrary, only a few compounds are known in which monoazolyladamantane is coordinated to a metal ion *via* donor nitrogen atoms. Thus, a series of coordination compounds of cadmium(II) with 4-(1-adamantyl)-1,2,4-triazole and various counterions were synthesized in the study.[16] In all these compounds, the ligands serve as bridges and are coordinated *via* nitrogen atoms of 1,2,4-triazole rings at the 1 and 2 positions. In the anionic ruthenium(III) complex with 1-adamantylimidazole, which has recently been synthesized and structurally characterized,[17] this ligand is coordinated *via* the nitrogen atom at the 3 position of the imidazole ring, and the octahedral coordination environment of ruthenium(III) is completed by four chloride ions in the equatorial plane and a DMSO molecule.

Since unsymmetrically substituted adamantanes bearing a heterocyclic moiety are of interest as ligands for the construction of MOFs or unusual molecular complexes,[18—20] we examined the possibility of further functionalizing the adamantane skeleton in adamantylazoles.

Results and Discussion

The starting adamantylazoles were synthesized according to a known procedure[8,11] with slight modifications. Earlier, the fusion products of 1-bromoadamantane with the corresponding azoles (AzH) were subjected to column chromatography in order to isolate them in the pure form; in the case of fusion with pyrazoles, the column chromatography allowed the separation of 1- and 4-adamantylpyrazoles, the ratio of which depends on the nature of pyrazole, the reagent ratio, and the reaction temperature.[8] We found that the dissolution of the melt, obtained after the reaction, in alcohol followed by the dilution of the alcoholic solution with a large amount of water allowed the extraction of the target compound with boiling hexane. The product obtained after the concentration of the hexane extract does not require additional purification. Upon fusion with pyrazole derivatives, only 1-adamantylpyrazoles can be extracted, unlike 4-adamantylpyrazoles, which are virtually insoluble in hexane, thereby making it

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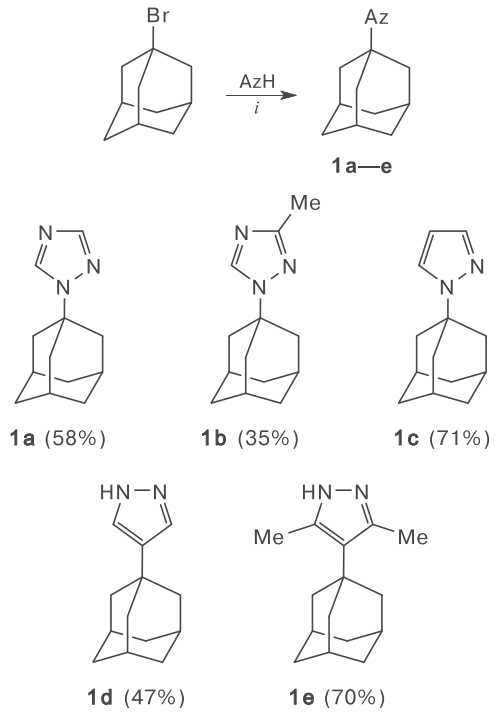
possible to easily separate these isomers without using column chromatography. The synthesized compounds are shown in Scheme 1.

Scheme 1

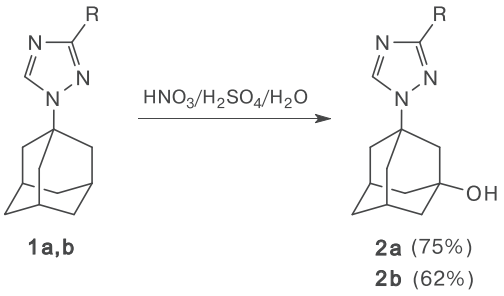


i. Fusion.

We chose carboxyl, hydroxy, and amino groups, which are most popular in coordination chemistry, as potentially interesting functional moieties. In a large number of studies, these groups and some other were introduced into the substituted adamantane skeleton.[18—31]

The reaction of 1-(adamantyl)-1,2,4-triazoles with water in a mixture of sulfuric and nitric acids affords 3-hydroxy-1-(1,2,4-triazol-1-yl)adamantanes (**2a,b**) (Scheme 2).

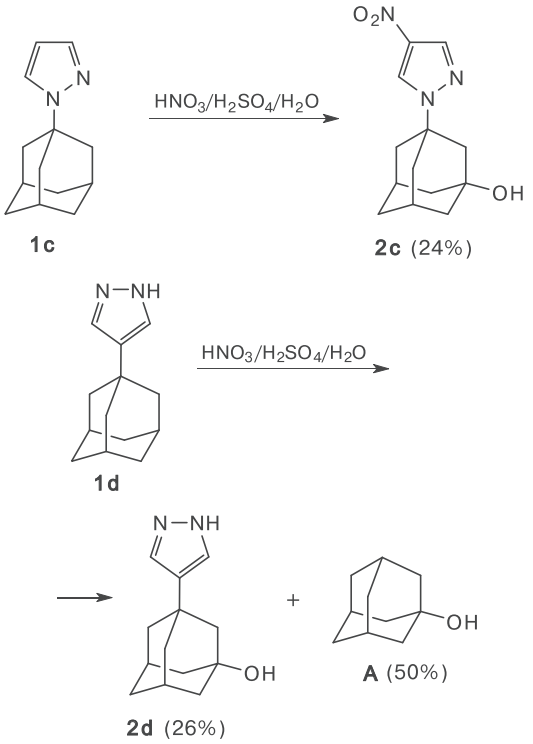
Scheme 2



R = H (**a**), Me (**b**)

Under these conditions, the reaction with 1-adamantylpyrazole is complicated by the nitration of the 4 position of the pyrazole ring susceptible to electrophilic substitution (Scheme 3). In the reactions of 1-adamantylpyrazole **1c** and 4-adamantylpyrazoles **1d,e**, the C—C bond proved to be unstable under the reaction conditions, resulting in that 1-adamantanol (**A**) is produced apart from target 1-(pyrazol-1-yl)-3-hydroxyadamantane (see Scheme 3).

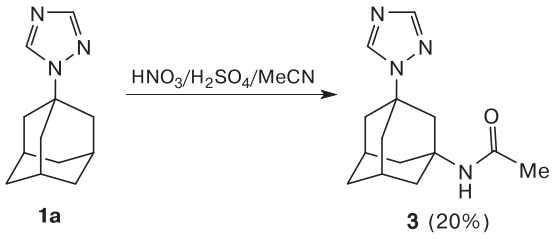
Scheme 3



We intended to synthesize 3-amino-1-azolyladamantanes through the intermediate formation of 3-acetamido-1-azolyladamantanes and subsequent hydrolysis. However, this approach allowed us to prepare only 1-(1,2,4-triazol-1-yl)-3-acetamidoadamantane (**3**) in 20% yield (Scheme 4). It should be noted that compound **3** can be synthesized only using nearly anhydrous (fuming) nitric acid, whereas the reaction with 68% nitric acid affords solely hydroxy derivative **2a**. The reactions with pyrazolyl- and imidazolyladamantanes gave only trace amounts of the target product.

The carboxylation of alkanes is generally performed using the Koch—Haaf reaction.[23] However, the reaction of 1-adamantyl-1,2,4-triazoles with formic acid in a mixture of nitric and sulfuric acids gives 3-hydroxy-1-(1,2,4-triazol-1-yl)adamantanes as the major products. The target product **B** was identified by GC-MS in trace amounts (Scheme 5). The reaction of 1-adamantyl-1,2,4-triazole using fuming nitric acid furnishes a mixture of

Scheme 4



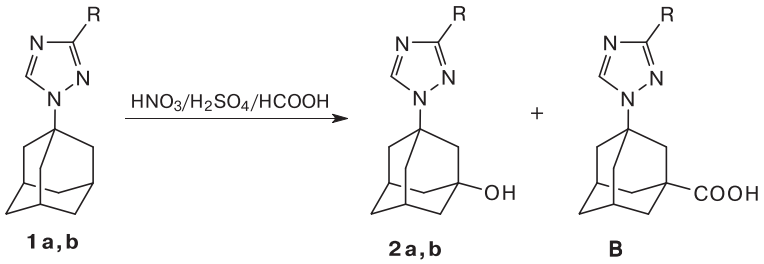
1-adamantanecarboxylic acid and 1,3-di(1,2,4-triazol-1-yl)adamantane. This reaction can be applied as an alternative method for the synthesis of this compound, which we have previously synthesized.[18]

To investigate the coordination ability of the synthesized azolyladamantanes, we performed their reactions with copper(II) and zinc(II) nitrates and chlorides, resulting in the formation of new coordination compounds, which were structurally characterized. Thus, compounds **4** and **5** were prepared by the reaction of ligand **1a** with zinc nitrate or chloride in methanol (Scheme 6).

Complex **6** was synthesized by the reaction of ligand **1e** with copper(II) nitrate in methanol (Scheme 7). In this case, a small amount of complex **7** was isolated. This compound is formed with the participation of 4-bromo-3,5-dimethylpyrazole, which was present as an impurity to compound **1e**. Coordination compound **8** was prepared by the reaction of ligand **1d** with copper(II) chloride in acetone (see Scheme 7).

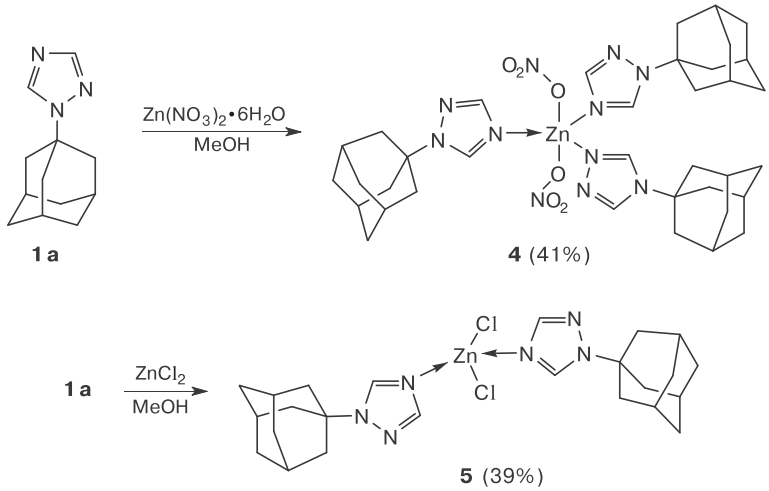
Compound **4** crystallizes in the monoclinic crystal system. The unit cell includes two symmetry-related molecules of the complex. The coordination polyhedron can be described as a distorted trigonal bipyramid (Fig. 1) characterized by the geometry index τ_5 of 0.74 (Table 1); for the ideal trigonal bipyramid, this index is equal to unity.[32] The equatorial positions of the bipyramid are occupied by nitrogen atoms of the 1,2,4-triazole rings (at the 4 position), and the axial positions are occupied by oxygen atoms of monodentate nitrate ions. The interatomic Zn—N distances are typical of such compounds (2.01—2.03 Å). The Zn—O distances are 2.110(2) and 2.239(1) Å. One interatomic Zn—O distance is somewhat larger than the typical value (2.00—2.20 Å) for five-coor-

Scheme 5

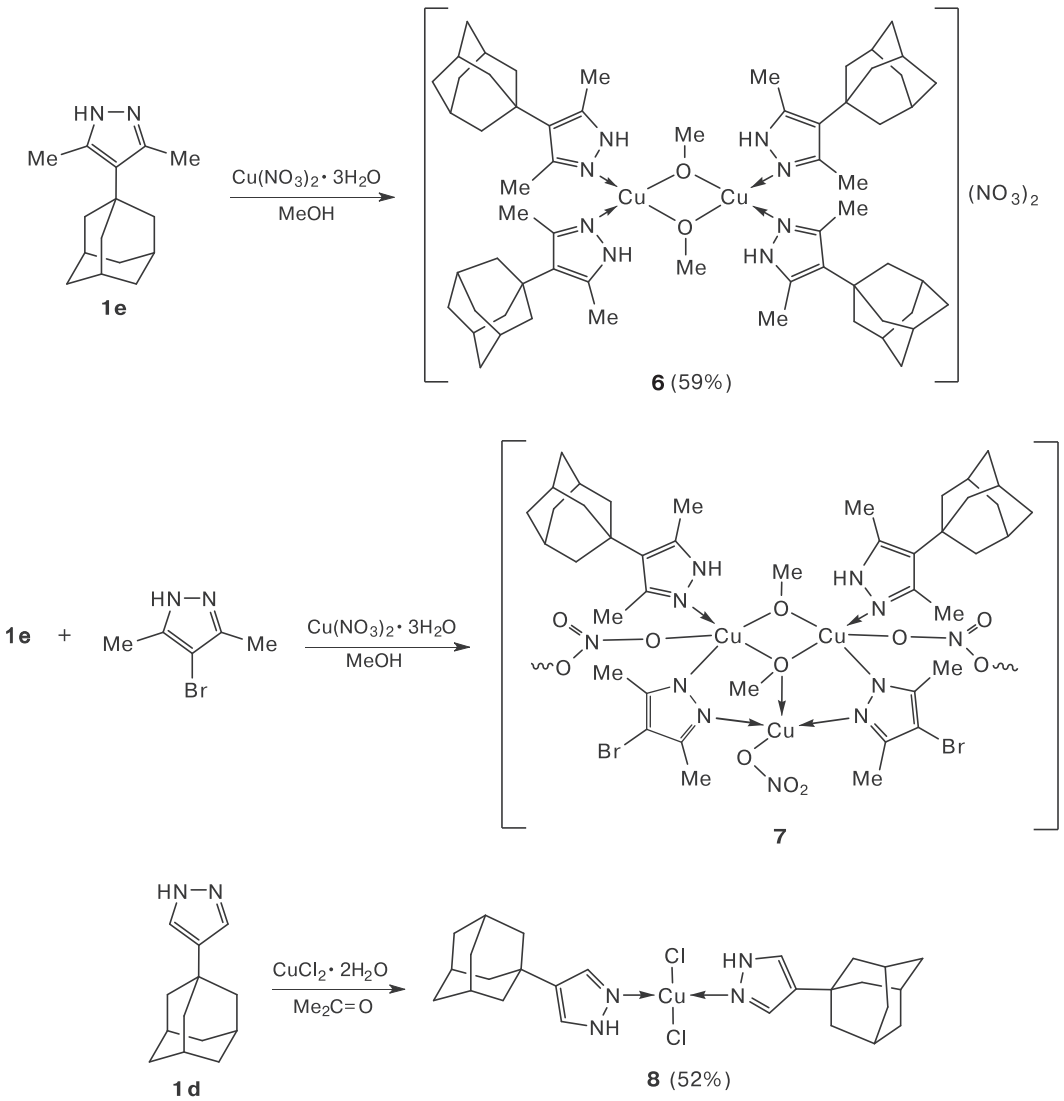


R = H (**a**), Me (**b**)

Scheme 6



Scheme 7



dinate zinc with two nitrate ions due apparently to steric factors.

Compound **5** crystallizes in the orthorhombic crystal system. The unit cell includes four formula units of the complex. There is one-half of the crystallographically independent molecule per asymmetric unit. The zinc atom occupies a special position 4*d* (Wyckoff symbol) with symmetry *2*. The zinc atoms are in a tetrahedral environment (Fig. 2), with the index τ_4[33] close to unity (see Table 1). Two coordination sites are occupied by nitrogen atoms of 1,2,4-triazole rings; two other sites, by chloride ions. The interatomic Zn—N and Zn—Cl distances are 2.019(0) and 2.223(9) Å, respectively. The chlorine atoms form short contacts with hydrogen atoms at the 3 positions of the 1,2,4-triazole rings. The interatomic Cl···H distance is 2.774(0) Å, which is typical of this type of contacts.[34] The molecules are linked *via* these contacts to form supramolecular layers lying parallel to the crystallographic plane *ac* (Fig. 3).

Compound **6** crystallizes in the monoclinic crystal system. The unit cell includes two formula units of the complex. Compound **6** is a binuclear complex. The asym-

Table 1. Geometric parameters of the coordination polyhedra in compounds **4—8**

Compound	α/deg	β/deg	τ index
4	126.2	170.7	$\tau_5 = 0.74$
5	114.2	114.2	$\tau_4 = 0.93$
6	167.9	169.9	$\tau_4 = 0.16$
7	161.9 (Cu(1))	166.2 (Cu(1))	$\tau_5 = 0.07$ (Cu(1))
	161.6 (Cu(2))	168.2 (Cu(2))	$\tau_5 = 0.11$ (Cu(2))
	160.3 (Cu(3))	164.7 (Cu(3))	$\tau_5 = 0.07$ (Cu(3))
8	180.0	180.0	$\tau_4 = 0$

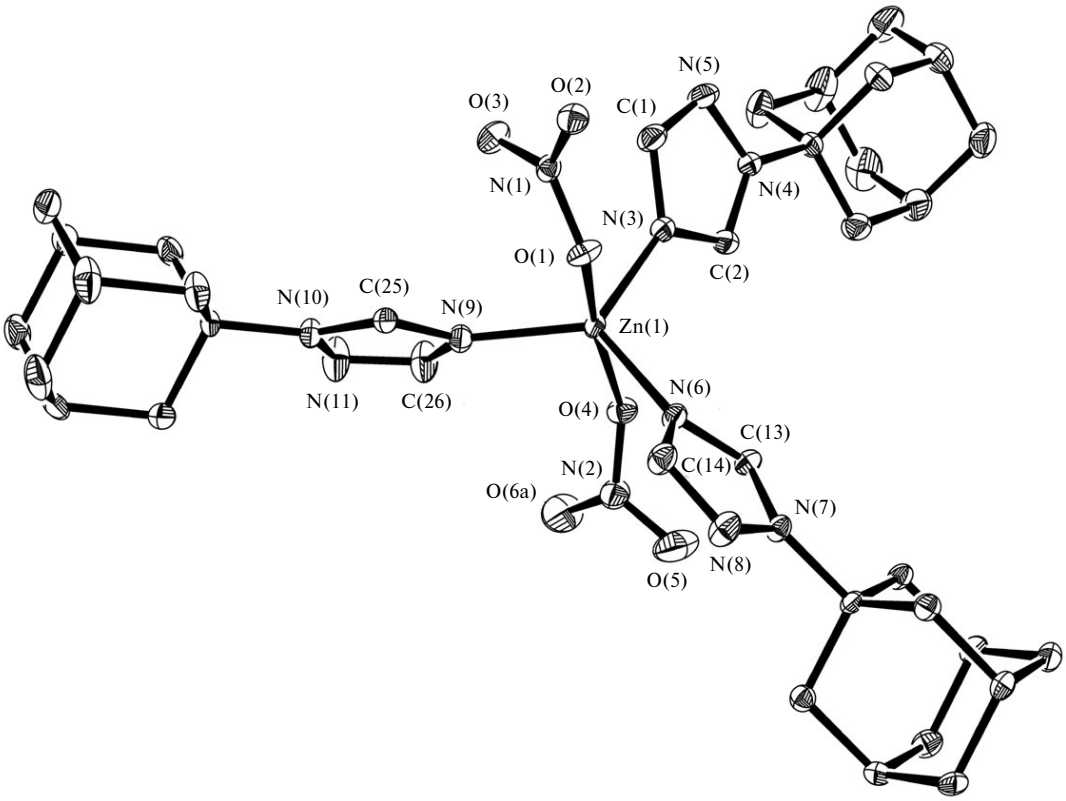


Fig. 1. Molecular structure of compound **4** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and the atom numbering of adamantane moieties are omitted for clarity.

metric unit contains one-half of the molecule located at a center of inversion *2a* (Wyckoff symbol). In this complex, two Cu^{2+} ions are linked by bridging methoxide ions OCH_3^-, two other coordination sites of each copper ion are occupied by neutral organic ligands **1e**, which are not deprotonated during the reaction (Fig. 4). The ligand is coordinated *via* nitrogen atoms at the 2 position of the pyrazole rings. The copper ions are in a distorted square-planar environment ($\tau_4 = 0.16$). The electroneutrality of the complex is provided by two outer-sphere nitrate ions (they are not shown in the figure). The interatomic Cu—N distances are 1.981(3) and 1.967(3) Å; the Cu—O distance is 1.921(2) Å.

Compound **7** crystallizes in the triclinic crystal system. The asymmetric unit contains three crystallographically independent copper(II) ions that form a trinuclear fragment. In this fragment, two deprotonated 4-bromo-3,5-dimethylpyrazole molecules serve as bridging ligands, through which the Cu^{2+} ions are linked along two sides of a non-equilateral triangle; besides, the copper ions are linked by a methoxide ion along the third side of the triangle. Additionally, all three Cu^{2+} ions are coordinated

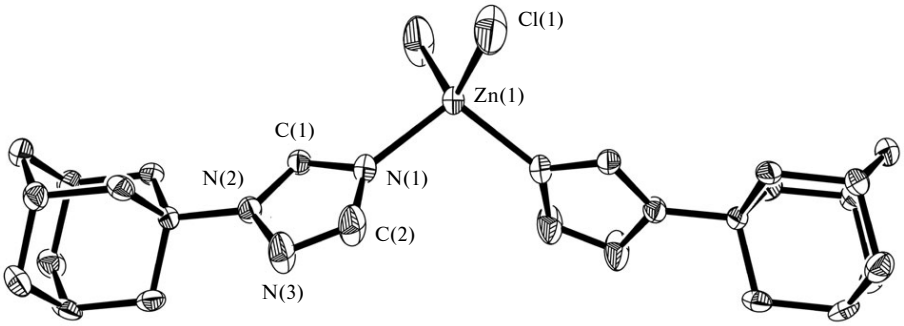


Fig. 2. Molecular structure of compound **5** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and the numbering of symmetry-related atoms and atoms of adamantane moieties are omitted for clarity.

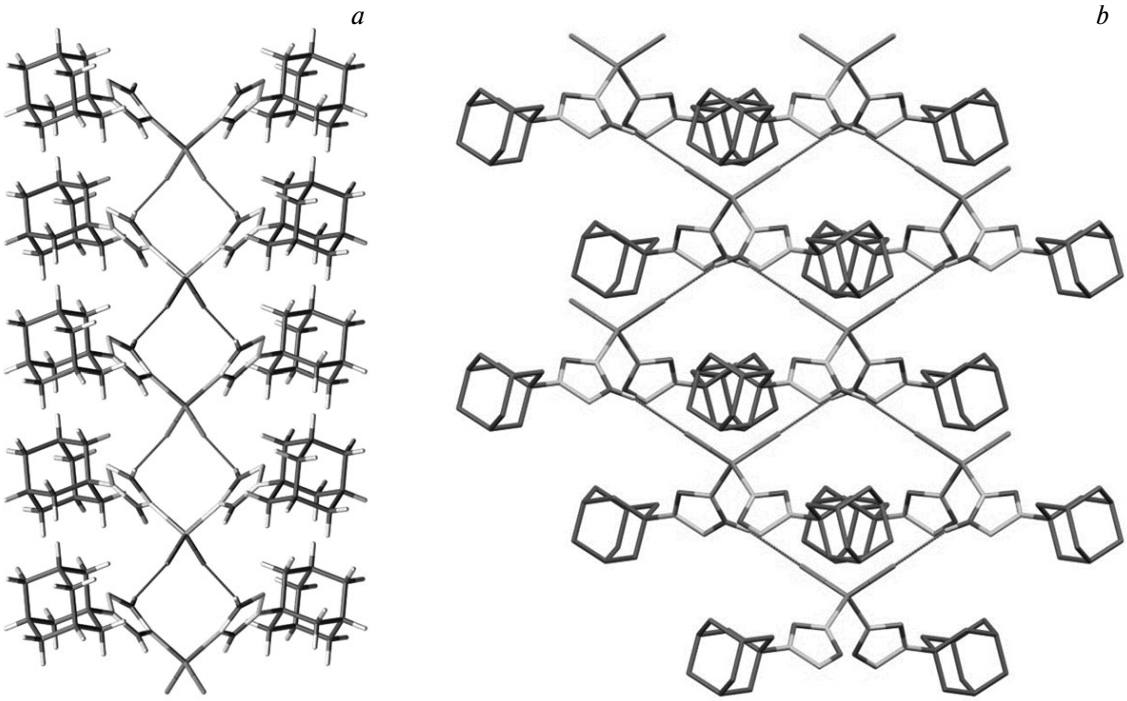


Fig. 3. Supramolecular layer in the crystal structure of compound **5** projected along the *c* (*a*) and *b* axes (*b*).

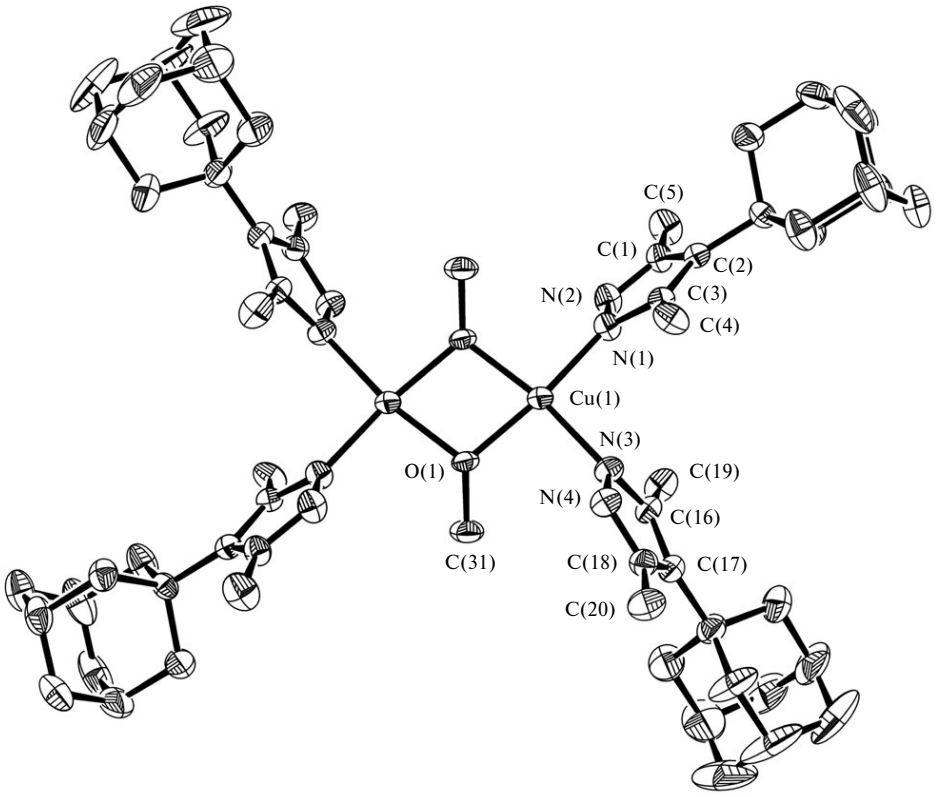


Fig. 4. Molecular structure of compound **6** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms, outer-sphere nitrate ions, and the numbering of symmetry-related atoms and atoms of adamantane moieties are omitted for clarity.

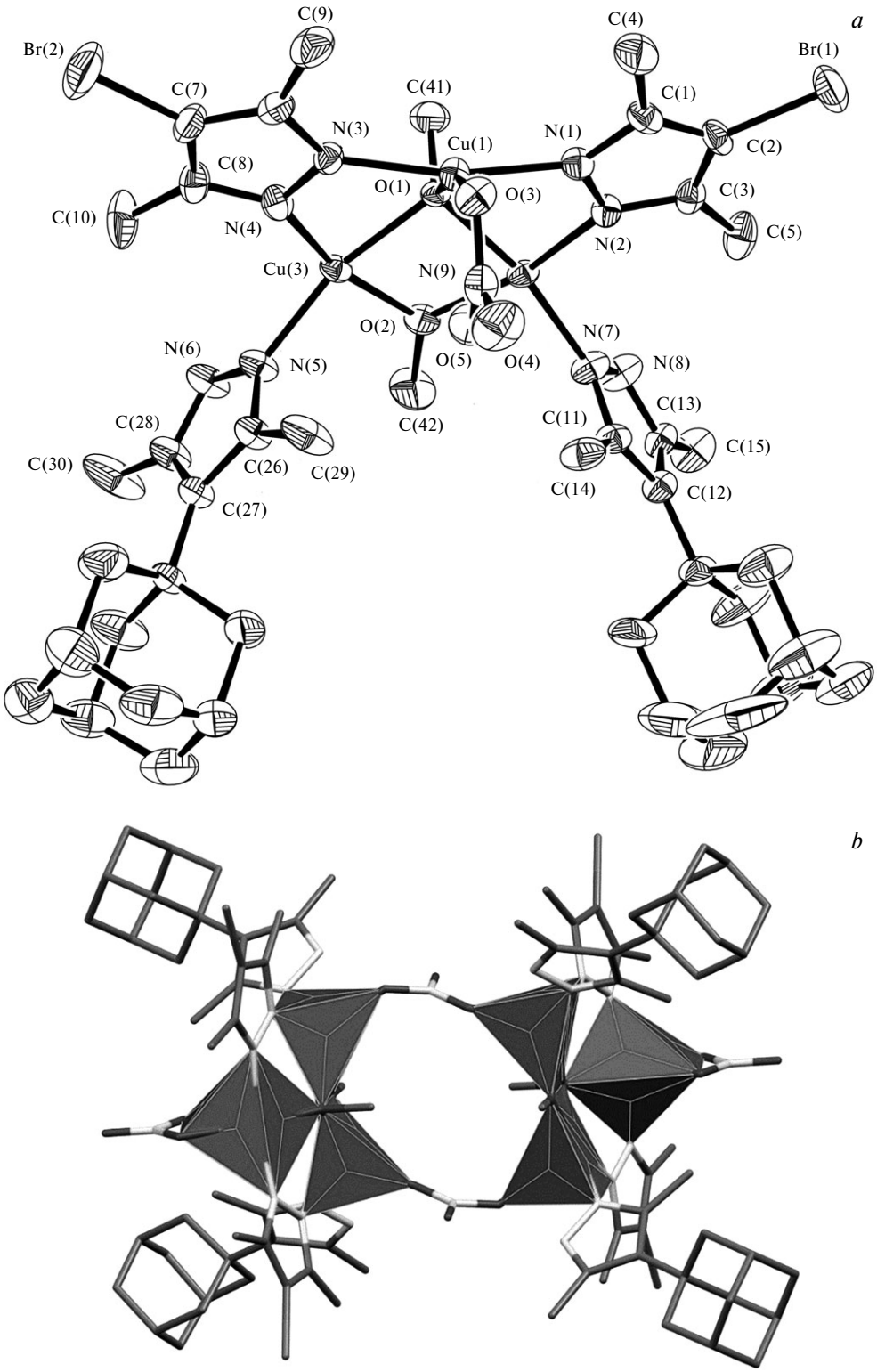


Fig. 5. Asymmetric unit of the crystal structure of compound **7** with thermal ellipsoids drawn at 50% probability level (*a*) and the molecular structure of hexanuclear complex **7** (*b*). Hydrogen atoms and the atom numbering of adamantane moieties are omitted for clarity.

by another methoxide ion (Fig. 5, *a*). The coordination polyhedron of the Cu(1) atom can be described as a distorted square pyramid, with two nitrogen atoms of the 4-bromopyrazolate anion, two oxygen atoms of the anisobidentate chelating nitrate ion, and an oxygen atom of the methoxide ion occupying the vertices. The Cu(2) and

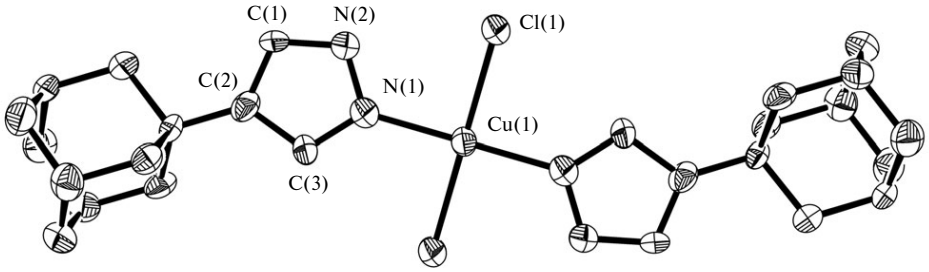


Fig. 6. Molecular structure of compound **8** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and the numbering of symmetry-related atoms and atoms of adamantane moieties are omitted for clarity.

Cu(3) atoms are also in a distorted square-pyramidal environment, each atom being coordinated by one ligand **1e** and two methoxide ions; the fifth coordination site is occupied by an oxygen atom of the bridging nitrate ion, through which the trinuclear moieties are linked together to form a hexanuclear neutral complex (Fig. 5, *b*).

Compound **8** crystallizes in the monoclinic crystal system. The unit cell contains four formula units of the neutral complex. There is one crystallographically independent copper(II) ion, one chloride ion, and one ligand molecule per asymmetric unit. The copper(II) ion is in a nearly ideal square-planar environment (Fig. 6), the index τ_4 is equal to zero. In the inner coordination sphere of the complex, two ligand molecules are coordinated in the protonated form *via* nitrogen atoms at the 2 position of the pyrazole rings; two other *trans* positions are occupied by chloride ions. The interatomic Cu—N distance is 1.99 Å, and the Cu—Cl distance is 2.256 Å. The angle between the plane of the pyrazole rings and the plane of the coordination unit is 14.5°. It is worth noting that ten of fourteen known complexes of pyrazole derivatives (in the protonated form) with copper(II) chloride have a distorted tetrahedral coordination environment and only in four compounds, the copper atom is in a planar environment.[35—38]

To summarize, we modified the procedure for the preparation of 1- and 4-adamantylazoles and examined the applicability of the Ritter and Koch—Haaf reactions for the functionalization of the adamantane skeleton in 1- and 4-adamantylazoles. It was shown that these procedures are suitable only for the synthesis of hydroxy-substituted azolyladamantanes. Acetonitrile and carbon(II) monoxide are not sufficiently nucleophilic for the successful reactions giving products in high yields. The C—C bond in 4-adamantylpyrazoles is unstable and is cleaved in acidic media. New coordination compounds of zinc(II) and copper(II) with 1-adamantyl-1,2,4-triazoles and 4-adamantylpyrazoles were synthesized, and their structures were determined by X-ray diffraction.

Experimental

Solvents and reagents of reagent grade were used as received. Anhydrous formic acid was prepared by freeze-drying of the commercial 95% acid solution. Acetonitrile was dried over 4 Å molecular sieves. The NMR spectra were recorded on a BRUKER AVANCE III HD spectrometer (400 MHz). The GL-MS analysis was performed on a Agilent 7890A GC gas chromatograph equipped with an Agilent 5975C quadrupole mass spectrometer. The IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with an attenuated total reflectance accessory with diamond crystal.

Synthesis of adamantylazoles (general procedure). 1-Bromoadamantane (2.16 g, 10 mmol) was mixed with an appropriate azole (10 mmol) in a thick-walled flask with Teflon screw cap. The flask was closed and placed in an oven for 12 h at 120 °C to prepare 1-adamantylazoles or at 180 °C to prepare 4-adamantylpyrazoles. After cooling, the melt was dissolved in ethanol (20 mL) and poured to distilled water (200 mL). The precipitate was filtered off and dried. The products were extracted with boiling hexane (3×20 mL). The combined extracts were concentrated. The resulting products did not require additional purification. In the synthesis of 4-adamantylpyrazoles, the precipitate, which remained after the heating of the reaction products in hexane at reflux, was filtered off, dried, and used in the next step without additional purification.

Functionalization of adamantylazoles (general procedure). Adamantylazole (1 mmol) was dissolved in 98% sulfuric acid (1 mL). Then fuming nitric acid (98%, 5 mmol) was added on cooling. The mixture was stirred at room temperature for 2—4 h. Then a water—anhydrous acetonitrile— anhydrous formic acid mixture was added dropwise (10 mmol) depending on the target product. The mixture was stirred for 12 h, poured onto ice, filtered, and extracted with chloroform. The extract was concentrated, and the target product with high purity was obtained.

1-(1-Adamantyl)-1,2,4-triazole (1a). Colorless crystals. Yield 59%, m.p. 89—90 °C (hexane; *cf.* lit. data[39]: m.p. 87—88 °C). ^{1}H NMR (DMSO-d_6), δ: 1.72 (m, 6 H, Ad); 2.10 (m, 6 H, Ad); 2.17 (m, 3 H, Ad); 7.97 (s, 1 H, C_{Tr}(3)H); 8.58 (s, 1 H, C_{Tr}(5)H). IR, ν/cm^{-1}: 3319 (m), 2907 (s), 2853 (s), 1743 (w), 1497 (m), 1452 (m), 1308 (m), 1275 (s), 1211 (m), 1153 (s), 1102 (m), 1055 (w), 1042 (s), 958 (m), 870 (s), 665 (s).

1-(1-Adamantyl)-3-methyl-1,2,4-triazole (1b). Colorless crystals. Yield 35%, m.p. 55—57 °C (hexane; *cf.* lit. data[40]: m.p. 52—53 °C). ^{1}H NMR (DMSO-d_6), δ: 1.70 (m, 6 H, Ad); 2.07 (m, 6 H, Ad); 2.15 (m, 3 H, Ad); 2.23 (s, 3 H, CH_3); 8.36 (s, 1 H, C_{Tr}(5)H). IR, ν/cm^{-1}: 2906 (s), 2850 (s), 1517 (m), 1355 (m), 1309 (m), 1204 (m), 1104 (w), 1006 (m), 834 (w).

1-(1-Adamantyl)pyrazole (1c). Colorless crystals. Yield 80%, m.p. 54—55 °C (hexane; *cf.* lit. data[41]: m.p. 52—54 °C). ^{1}H NMR ($CDCl_3$), δ: 1.76 (m, 6 H, Ad); 2.17 (m, 6 H, Ad); 2.22 (m, 3 H, Ad); 6.23 (t, 1 H, C_{Pz}(4)H, J = 1.0); 7.51 (d, 1 H, C_{Pz}(3)H,

Table 2. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **4—6**

Parameter	**4**	**5**	**6**
Molecular formula	$C_{36}H_{51}N_{11}O_6Zn$	$C_{24}H_{34}Cl_2N_6Zn$	$C_{62}H_{94}Cu_2N_{10}O_8$
M/g mol^{-1}	799.24	542.84	1234.55
T/K	150(2)	150(2)	150(2)
Space group	*Pc*	*Pnna*	$P2_1/c$
a/Å	10.6787(8)	10.1574(6)	16.102(6)
b/Å	13.1761(9)	28.4931(16)	14.077(5)
c/Å	13.0883(9)	8.8107(5)	13.938(5)
α/deg	90	90	90
β/deg	91.549(2)	90	93.436(13)
γ/deg	90	90	90
V/Å^3	1840.9(2)	2550.0(3)	3154(2)
Z	2	4	2
d_{calc}/g cm^{-3}	1.442	1.414	1.300
μ/mm^{-1}	0.730	1.197	0.735
F(000)	844.0	1136.0	1316.0
Crystal size/mm	0.4×0.35×0.32	0.39×0.27×0.08	0.18×0.16×0.12
2θ-Scan range/deg	3.816—55.898	4.84—51.398	3.846—50.308
h, k, l ranges	$-14 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 17$ $-16 \leqslant l \leqslant 17$	$-12 \leqslant h \leqslant 11$, $-34 \leqslant k \leqslant 34$, $-10 \leqslant l \leqslant 10$	$-19 \leqslant h \leqslant 17$, $-14 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 15$
Number of reflections			
measured	20393	16872	29077
unique	8518	2421	5557
R_{int}	0.0275	0.0456	0.0730
R_σ	0.0441	0.0315	0.0617
Number of refined parameters	498	150	
Number of restraints	14	0	0
GOOF based on F^2	1.034	1.075	1.036
R-фактор ($I > 2\sigma(I)$)			
R_1	0.0216	0.0362	0.0436
wR_2	0.0548	0.0802	0.1030
R factor (all data)			
R_1	0.0224	0.0502	0.0750
wR_2	0.0550	0.0859	0.1166
Residual electron density ($\Delta\rho_{max}/\Delta\rho_{min}$)/e Å^{-3}	0.39/−0.22	0.91/−0.41	0.31/−0.32
Flack parameter	0.022(7)	—	—

J = 1.0 Hz); 7.54 (d, 1 H, $C_{Pz}(5)H$, J = 1.0 Hz). IR, ν/cm^{-1}: 2905 (s), 2845 (s), 1448 (m), 1397 (m), 1309 (m), 1102 (m), 1055 (m), 743 (s).

4-(1-Adamantyl)pyrazole (1d). Colorless crystals. Yield 47%, m.p. 208—209 °C (hexane; *cf.* lit. data[39]: m.p. 208—210 °C). ^{1}H NMR ($CDCl_3$), δ: 1.76 (m, 6 H, Ad); 1.85 (m, 6 H, Ad); 2.07 (m, 3 H, Ad); 7.47 (s, 2 H, $C_{Tr}(3)H$). IR, ν/cm^{-1}: 3153 (m), 2900 (s), 2847 (s), 1450 (s), 1345 (m), 1153 (m), 1138 (m), 1102 (w), 1084 (m), 1038 (m), 989 (s), 958 (s), 934 (w), 852 (s), 804 (s), 676 (s), 632 (s).

3,5-Dimethyl-4-(1-adamantyl)pyrazole (1e). Colorless crystals. Yield 70%, m.p. 219—220 °C (hexane; *cf.* lit. data[42]: m.p. 220—221 °C). ^{1}H NMR (DMSO-d_6), δ: 1.72 (m, 6 H, Ad); 2.10 (m, 6 H, Ad); 2.17 (m, 3 H, Ad); 7.97 (s, 1 H, $C_{Tr}(3)H$); 8.58 (s, 1 H, $C_{Tr}(5)H$). IR, ν/cm^{-1}: 3167 (s), 2907 (s), 2898 (s), 2847 (s), 1433 (m), 1407 (m), 1292 (w), 1183 (w), 1027 (m), 816 (w).

1-(1,2,4-Triazol-1-yl)-3-hydroxyadamantane (2a). Pale-brown powder. Yield 75%, m.p. 97—98 °C (MeOH). ^{1}H NMR (DMSO-d_6), δ: 1.55 (m, 2 H, Ad); 1.64 (m, 4 H, Ad); 1.98 (t, 6 H, Ad); 2.28 (t, 2 H, Ad); 4.77 (s, 1 H, OH); 7.94 (s, 1 H, $C_{Tr}(3)H$); 8.53 (s, 1 H, $C_{Tr}(5)H$). ^{13}C NMR (DMSO-d_6), δ: 30.0, 34.3, 41.0, 43.7, 49.7, 60.0, 67.4, 140.5, 150.7.

3-Methyl-1-(1,2,4-triazol-1-yl)-3-hydroxyadamantane (2b). Yield 62%, m.p. 78—79 °C (MeOH). ^{1}H NMR (DMSO-d_6), δ: 1.63 (s, 4 H, Ad); 1.96 (s, 4 H, Ad); 2.00 (s, 6 H, Ad); 2.27 (s, 3 H, $C_{Tr}(3)CH_3$); 4.72 (s, 1 H, OH); 8.36 (s, 1 H, $C_{Tr}(5)H$).

1-(1,2,4-Triazol-1-yl)-3-acetamidoadamantane (3). Yield 20%. ^{1}H NMR (DMSO-d_6), δ: 1.63 (s, 2 H, Ad); 1.77 (s, 3 H, CH_3); 1.86 (m, 2 H, Ad); 2.03 (m, 4 H, Ad); 2.09 (m, 2 H, Ad); 2.28 (s, 2 H, Ad); 2.33 (s, 2 H, Ad); 7.55 (s, 1 H, NH); 7.96 (s, 1 H, $C_{Tr}(3)H$); 8.56 (s, 1 H, $C_{Tr}(5)H$).

Tris(1-adamantyl-1,2,4-triazole)dinitratozinc (4). Zinc(II) nitrate, $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), was mixed with compound **1a** (1 mmol) and methanol (10 mL) in a 20 mL vial with screw cap. The reaction solution was kept at room temperature for two days. Then the colorless crystals that formed were filtered off and

Table 3. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **7** and **8**

Parameter	**7**	**8**
Molecular formula	$C_{43}H_{66}Br_2Cu_3N_{10}O_9$	$C_{26}H_{36}Cl_2CuN_4$
M/g mol^{-1}	1217.49	539.03
T/K	150(2)	298(2)
Space group	$P\bar{1}$	$P2_1/c$
a/Å	12.3332(12)	16.067(8)
b/Å	15.9699(16)	10.879(6)
c/Å	16.2701(17)	7.143(4)
α/deg	118.656(4)	90
β/deg	92.101(4)	95.366(16)
γ/deg	106.963(4)	90
V/Å^3	2629.5(5)	1243.1(11)
Z	2	2
d_{calc}/g cm^{-3}	1.538	1.440
μ/mm^{-1}	2.781	1.116
F(000)	1246.0	566.0
Crystal size/mm	0.36×0.23×0.12	0.45×0.33×0.03
2θ-Scan range/deg	2.978—51.358	3.744—48.814
h, k, l ranges	$-15 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 19$, $-19 \leqslant l \leqslant 19$	$-18 \leqslant h \leqslant 18$, $-12 \leqslant k \leqslant 12$, $-8 \leqslant l \leqslant 5$
Number of reflections		
measured	22984	6533
unique	9919	1987
R_{int}	0.0475	0.0554
R_σ	0.0749	0.0649
Number of refined parameters	616	152
Number of restraints	12	0
GOOF based on F^2	1.043	1.251
R factor ($I > 2\sigma(I)$)		
R_1	0.0490	0.0968
wR_2	0.1222	0.2651
R factor (all data)		
R_1	0.0750	0.1187
wR_2	0.1339	0.2961
Residual electron density ($\Delta\rho_{max}/\Delta\rho_{min}$)/e Å^{-3}	1.24/−0.99	2.13/−0.75

washed with a small amount of methanol and diethyl ether. Yield 41%. Found (%): C, 54.3; H, 6.4; N, 19.2. $C_{36}H_{51}N_{11}O_6Zn$. Calculated (%): C, 54.1; H, 6.4; N, 19. ^{1}H NMR (DMSO-d_6), δ: 1.71 (m, 6 H, Ad); 2.10 (m, 6 H, Ad); 2.17 (m, 3 H, Ad); 7.96 (s, 1 H, C_{Tr}(3)H); 8.54 (s, 1 H, C_{Tr}(5)H). ^{13}C NMR (DMSO-d_6), δ: 28.8, 35.4, 41.9, 57.8, 140.5, 150.6. IR, ν/cm^{-1}: 3150 (s), 3113 (s), 2928 (s), 2860 (s), 1522 (s), 1489 (s), 1460 (s), 1443 (s), 1395 (s), 1362 (s), 1304 (s), 1279 (s), 1250 (m), 1202 (m), 1136 (s), 1103 (m), 1042 (w), 1013(w), 1001 (s), 997 (s), 984 (w), 899 (m), 876 (m), 837 (m), 816 (m), 770 (m), 667 (s), 656 (s), 642 (m).

Bis(1-adamantyl-1,2,4-triazole)dichlorozinc (5) was synthesized in a similar way to compound **4** starting from compound **1a** and $ZnCl_2$. Yield 39%. Found (%): C, 53.5; H, 6.0; N, 15.2. $C_{24}H_{34}Cl_2N_6Zn$. Calculated (%): C, 53.1; H, 6.3; N, 15.5. ^{1}H NMR (DMSO-d_6), δ: 1.72 (m, 6 H, Ad); 2.10 (m, 6 H, Ad); 2.17 (m, 3 H, Ad); 7.99 (s, 1 H, C_{Tr}(3)H); 8.60 (s, 1 H, C_{Tr}(5)H). ^{13}C NMR (DMSO-d_6), δ: 28.7, 35.4, 41.8, 58.0, 140.5, 150.4. IR, ν/cm^{-1}: 3150 (w), 3319 (w), 2911 (s), 2850 (w), 1521 (s), 1450 (w), 1286 (m), 1142 (s), 1101 (m), 994 (s), 683 (w), 836 (m), 683 (m), 655 (s).

Di-μ-methoxobis[bis(3,5-dimethyl-4-adamantylpyrazole)-copper] (6). Copper(II) nitrate, $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol), was mixed with compound **1c** (1 mmol) and methanol (10 mL) in a 20 mL vial with screw cap. The solution was kept at 80 °C overnight. Then the blue-green crystals were filtered off and washed with a small amount of methanol and diethyl ether. Several crystals of compound **7** were simultaneously obtained. Found (%): C, 59.9; H, 7.4; N, 11.0. $C_{62}H_{94}Cu_2N_{10}O_8$. Calculated (%): C, 60.3; H, 7.7; N, 11.4. IR, ν/cm^{-1}: 3189 (w), 2897 (s), 2850 (s), 1559 (w), 1522 (w), 1342 (s), 1282 (s), 1202 (m), 1035 (s), 815 (w), 683 (w).

Bis(4-adamantylpyrazole)dichlorocopper (8). A solution of $CuCl_2 \cdot 2H_2O$ (0.2 mmol) in acetone (5 mL) was added to a solution of compound **1b** (0.2 mmol) in acetone (10 mL). The reaction solution was kept at room temperature overnight. The pale-green plate-like crystals that precipitated were filtered off,

washed with acetone, and dried. Yield 52%. Found (%): C, 58.3; H, 6.4; N, 10.3. $C_{26}H_{36}Cl_2CuN_4$. Calculated (%): C, 57.9; H, 6.7; N, 10.4. IR, ν/cm^{-1}: 3287 (s), 2903 (s), 2847 (s), 1454 (s), 1400 (w), 1348 (w), 1341 (w), 1313 (w), 1287 (w), 1115 (s), 1092 (m), 1049 (s), 988 (s), 964 (s), 874 (s), 845 (w), 812 (m), 721 (s), 667 (m), 606 (m), 465 (w).

X-ray diffraction studies were performed by a standard procedure on a Bruker Apex DUO automated four-circle diffractometer equipped with a CCD detector and a graphite monochromator using molybdenum radiation (λ = 0.71073 Å). The intensities of reflections were measured by φ- and ω-scanning of narrow frames (0.5°). Absorption corrections were applied using the SADABS program.[43] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXT[44] and SHEXL program suites[45] *via* the Olex2 graphical interface.[46] Hydrogen atoms were positioned geometrically and refined using a rigid-body model. The O atom of one nitrate ion of complex **7** was disordered over two positions and refined using SIMU restraints. Crystallographic parameters and the X-ray data collection and structure refinement statistics are given in Table 2. The relatively high R factor and large residual electron density peaks for structure **8** are attributed to the fact that the crystal was a twin, and it was refined using the twin matrix (1 0 0.4 0 -1 0 0 0 -1) with BASF = 0.25 in the final refinement steps. The X-ray diffraction data were deposited with the Cambridge Crystallographic Data Centre (CCDC 1956464—1956468), can be obtained from the authors, and are available at http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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