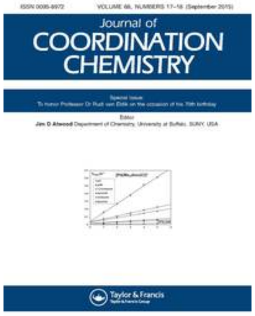

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Transition metal complexes with cage-opened diamondoid tetracyclo[7.3.1.1^{4,12}.0^{2,7}]tetradeca-6.11-diene

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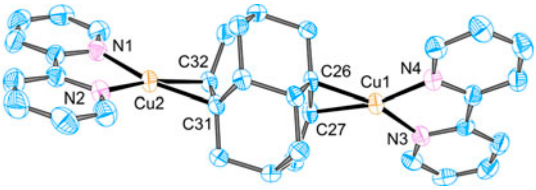

Copper(I) complexes with the diamantane diene tetracyclo[7.3.1.1^{4,12}.0^{2,7}]tetradeca-6.11-diene (**6**) have been prepared and an interesting crystal structure, $[Cu_2(bipy)_2(\mathbf{6})]^{2+}$ (hydrogen atoms, anions, and solvent molecules are omitted for clarity), was obtained.

Cage-opened diamondoid tetracyclo[7.3.1.1^{4,12}.0^{2,7}]tetradeca-6,11-diene forms complexes with $AgNO_3$ and CuCl. The latter crystallized from acetonitrile in polymeric form $[Cu_2Cl_2(CH_3CN)(diene)]_n$; in the presence of 2,2′-bipyridine, a double-charged monomeric Cu(I)-complex $[Cu_2(bipy)_2(diene)]^{2+}$ formed. Both complexes were structurally characterized through X-ray crystal diffraction analysis.

Keywords: Copper complexes; Coordination polymers; Diamantane; Diamondoid; Nanodiamonds; Diene

Introduction

Naturally occurring [1] diamondoids (**1–4**, scheme 1) resemble the part of hydrogen-terminated diamond lattice [2] and occupy an outstanding position among other carbon nano-structures [3] due to their ability to mimic many of the attractive electronic properties of diamond [4]. Additional benefits arise from the rigidity of the diamondoid cages allowing the construction of various 3-D structures with well-defined and predictable topologies

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Dedicated to the 70th birthday of Rudi van Eldik.

[5–13]. Recently discovered diamondoid-based materials [14] exhibit electric current rectification [15] and effective electron emitting properties [16, 17]. These are the characteristics of self-assembled diamondoid derivatives on metal surfaces [18]. The electronic properties of such materials are determined by the diamondoid/metal interfaces that are firmly contacted resulting in well-defined conductance [19]. Generally, the construction of stable hybrid materials based on diamondoid/metal combinations [20] are challenging as metallated diamondoids are reactive toward air and water [21, 22].

One of the approaches to diamondoid/metal hybrids may be incorporation of the metal inside the cage [23]. Unfortunately, theory shows that this results in unstable cage-opened products [24]. More realistic is the preparation of metal complexes of stable diamondoid derivatives with partially opened cages. Among preparatively available building blocks of this type are the unsaturated diamondoid derivatives 3,7-dimethylenebicyclo[3.3.1]nonane (**5**) and open-cage tetracyclo[7.3.1.1^{4,12}.0^{2,7}]tetradeca-6.11-diene (**6**) that are readily available through fragmentations of the respective methyladamantane [25] and diamantane [26] dibromides. It was demonstrated that **5** forms a water and air-stable complex with Ag(I) **7** as well as a bipyramidal complex with Pt(II) [27].

We found that diene **6** forms complexes with Ag(I) and Cu(I) as described in the Experimental section. So far, no crystals were obtained in that way to structurally characterize these compounds. The silver complex was characterized by elemental analysis and NMR measurements (see Experimental section and Supplementary Material). For the copper complexes, this was not possible due to the extreme sensitivity of the compounds toward oxidation. However, we were able to grow crystals of the complex derived from Cu(I) in acetonitrile. The molecular structure of this compound turned out to be a linear polymer, $[Cu_2Cl_2(CH_3CN)(\mathbf{6})]_n$. A part of this coordination polymer is presented in figure 1. Crystallographic data, bond lengths, and angles are presented in tables 1 and 2. The unit cell contains two Cu(I) centers, where Cu(2) is coordinated to one double bond of **6** and a chloride Cl(4). The second copper ion Cu(1) coordinates to nitrogen of one acetonitrile and another double bond of a **6** ligand. Both copper centers are bridged by a choride Cl(3) and form a chain consisting of Cu(I) complex molecules.

Furthermore, we were able to suppress the formation of the polymeric copper complex using bipyridine as an additional ligand. Thus, we could prepare $[Cu_2(bipy)_2(\mathbf{6})](PF_6)_2$ [28]

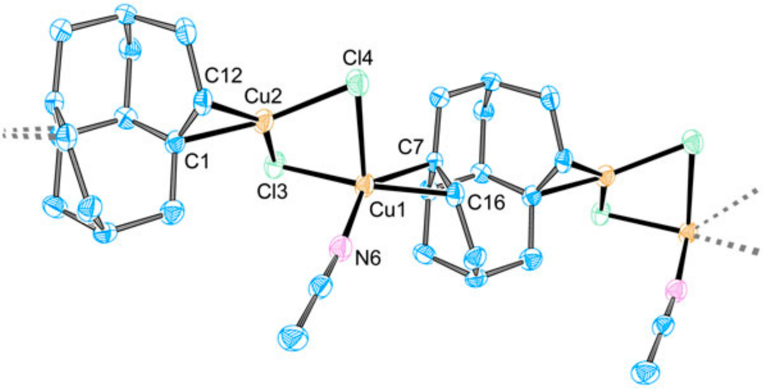


Figure 1. ORTEP plot of a part of the copper polymer $[Cu_2Cl_2(CH_3CN)(\mathbf{6})]_n$. Ellipsoids are drawn at 50% probability level.

Table 1. Crystal data and structure refinement for [$Cu_2Cl_2(CH_3CN)$(**6**)] and [$Cu_2(bipy)_2$(**6**)]$(PF_6)_2$.

Empirical formula	$C_{16}H_{21}Cl_2Cu_2$ N	$C_{37}H_{40}Cu_2F_{12}N_4OP_2$
Formula weight	425.32	973.75
Temperature	190(2) K	193(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 8.420(2)$ Å, $\alpha = 85.68(3)°$ $b = 9.322(2)$ Å, $\beta = 78.77(3)°$ $c = 10.383(2)$ Å, $\gamma = 84.49(3)°$	$a = 8.521(2)$ Å, $\alpha = 91.47(3)°$ $b = 11.312(3)$ Å, $\beta = 92.91(3)°$ $c = 20.487(5)$ Å, $\gamma = 100.83(3)°$
Volume	794.3(3) Å^3	1935.8(9) Å^3
Z, calculated density	2, 1.778 mg/m^3	2, 1.671 mg/m^3
Absorption coefficient	3.004 mm^{-1}	1.277 mm^{-1}
F (0 0 0)	432	988
Crystal size (mm)	0.090 × 0.080 × 0.030	0.280 × 0.280 × 0.080
Theta range for data collection	2.003–27.410°	2.659–28.141°
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-10 \le h \le 11$, $-14 \le k \le 14$, $-24 \le l \le 26$
Reflections collected/unique	13,762/3602 [R(int) = 0.0617]	17,289/8570 [R(int) = 0.0709]
Completeness to theta = 25.242°	99.9%	93.3%
Absorption correction	Empirical	None
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3602/0/274	8570/0/592
Goodness-of-fit on F^2	1.016	0.887
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0331$, $wR2 = 0.0747$	$R1 = 0.0427$, $wR2 = 0.0935$
R indices (all data)	$R1 = 0.0500$, $wR2 = 0.0812$	$R1 = 0.0892$, $wR2 = 0.1120$
Largest diff. between peak and hole	0.436 and −0.569 e Å^{-3}	0.445 and −0.714 e Å^{-3}

Table 2. Selected bond lengths [Å] and angles [°] for [$Cu_2Cl_2(CH_3CN)$(**6**)]$_n$.

C(1)–C(12)	1.376(4)	C(12)–Cu(2)	2.063(3)	Cl(4)–Cu(1)	2.730(2)
C(1)–C(2)	1.512(4)	Cl(3)–Cu(2)	2.294(2)	Cu(1)–N(6)	2.006(2)
C(7)–C(16)	1.389(4)	Cl(3)–Cu(1)	2.295(2)	C(18)–N(6)	1.137(4)
C(1)–Cu(2)	2.062(2)	Cl(4)–Cu(2)	2.247(2)		
C(12)–C(1)–Cu(2)	70.5(2)	Cl(3)–Cu(1)–Cl(4)	90.88(3)		
C(1)–C(12)–Cu(2)	70.5(2)	C(1)–Cu(2)–C(12)	38.9(2)		
C(16)–C(7)–C(8)	122.4(3)	C(1)–Cu(2)–Cl(4)	146.29(8)		
N(6)–C(18)–C(15)	179.3(4)	C(12)–Cu(2)–Cl(4)	108.18(8)		
Cu(2)–Cl(3)–Cu(1)	77.36(3)	C(1)–Cu(2)–Cl(3)	108.36(8)		
Cu(2)–Cl(4)–Cu(1)	69.61(3)	C(12)–Cu(2)–Cl(3)	147.19(8)		
N(6)–Cu(1)–Cl(3)	100.39(7)	Cl(4)–Cu(2)–Cl(3)	104.59(3)		
N(6)–Cu(1)–Cl(4)	98.07(8)	C(18)–N(6)–Cu(1)	172.1(3)		

by applying the same experimental conditions as for the related complex [Cu(bipy)(COD)] PF_6 reported previously [29]. The molecular structure of the cation of [$Cu_2(bipy)_2$(**6**)]$(PF_6)_2$ is shown in figure 2. Crystallographic data, bond lengths, and angles are presented in tables 1 and 3.

The unit cell contains the complex and one acetone molecule as well as two PF_6^- anions. Both copper centers are coordinated by the two bipy nitrogens and one double bond of ligand **6**. Each center has almost square planar coordination geometry, which is common for ternary copper olefin complexes [30–33]. Thus, the Cu–N bond lengths have typical values of about 1.99(3) Å and are in agreement with those found in similar ternary complexes as well as with typical $Cu–C_{olefin}$ distances [30–33]. Due to the coordination with copper,

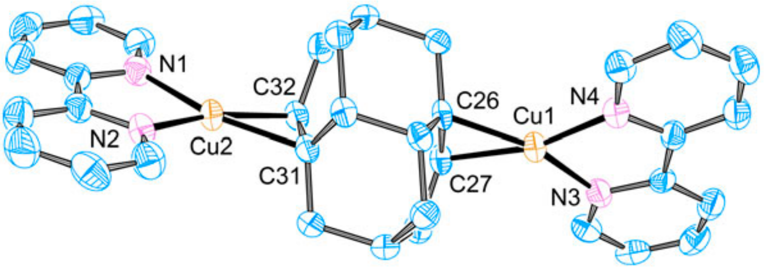
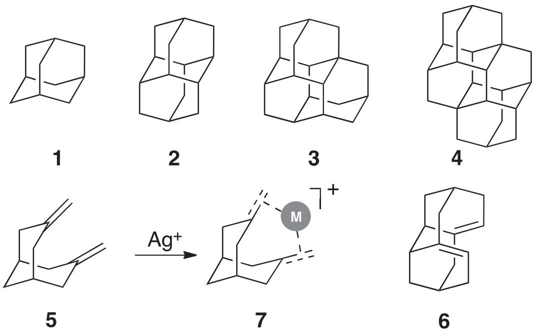


Figure 2. ORTEP plot of $[Cu_2(bipy)_2(\mathbf{6})]^{2+}$; hydrogen atoms, anions, and solvent molecules are omitted for clarity. Ellipsoids are drawn at 50% probability level.



Scheme 1. Adamantane (**1**), diamantane (**2**), triamantane (**3**), [121]tetramantane (**4**), diamondoid dienes **5** and **6**, and stable complexes **7** (M=Ag^+, Pt^{2+}).

Table 3. Selected bond lengths [Å] and angles [°] for $[Cu_2(bipy)_2(\mathbf{6})](PF_6)_2$.

C(32)–C(33)	1.522(5)	C(26)–C(27)	1.398(5)
C(31)–Cu(2)	2.036(3)	C(26)–Cu(1)	2.037(3)
C(32)–Cu(2)	1.997(3)	C(27)–Cu(1)	1.999(3)
Cu(2)–N(1)	1.998(3)	Cu(1)–N(3)	2.247(2)
Cu(2)–N(2)	1.978(3)	Cu(1)–N(4)	1.990(3)
C(32)–C(31)–Cu(2)	68.4(2)	C(27)–C(26)–Cu(1)	69.2(2)
N(2)–Cu(2)–N(1)	83.2(2)	N(4)–Cu(1)–N(3)	83.3(2)
N(2)–Cu(2)–C(32)	160.9(2)	N(4)–Cu(1)–C(27)	161.2(2)
N(1)–Cu(2)–C(31)	156.2(2)	N(3)–Cu(1)–C(26)	155.4(2)

the double bonds' lengths are C(26)–C(27) and C(31)–C(32), with values of 1.398(5) and 1.388(5) Å and show a lengthening as compared to the average value of 1.33 Å for uncoordinated double bonds.

We conclude that diamantane diene **6** is well suited for the complexation with transition metals and forms linear oligomeric structures. This is the first example of metal/diamondoid (nanodiamond) molecular scaffold with rather long rigid organic bridges between the transition metals. Addition of a bipyridine suppresses the oligomerization and allows isolation of a single molecular entity, which formally contains a metal-connected p-n-p-conductivity junction. Such molecules can find applications in the development of new metal–organic materials for nanoelectronics. Since lipophilic hydrocarbon moieties are considered as highly “pharmacophoric” [34, 35], such Cu-complexes may also find applications as pharmaceutically active agents [36, 37].

Experimental

Materials and reagents

Commercial reagents were used as obtained without purification. Solvents were dried according to the standard procedures. All handling of oxygen sensitive compounds was carried out in a glove box (M. Braun, Garching, Germany; $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) within an argon atmosphere.

Preparation of the complexes of 6 with $AgNO_3$ and CuCl

Complex with Ag(I). Diene **6** was obtained as previously described [26]. A solution of **6** (84 mg, 0.5 mmol) in 1 mL of diethyl ether and 1 mL of saturated solution of $AgNO_3$ was added. The reaction mixture was filtered immediately; the precipitate was washed with water and diethyl ether, and then dried in vacuo to give 137 mg (75%) of the silver complex monohydrate as a colorless solid (mp > 184 °C, dec.). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K): δ 5.57 (d, $J = 6.0$ Hz, 2H), 2.32 (bs, 2H), 2.32–2.27 (m, 1H), 2.27–2.22 (m, 1H), 2.18 (dt, $J = 12.0$, 4.2 Hz, 2H), 1.95–1.87 (m, 4H), 1.83–1.76 (m, 2H), 1.76–1.66 (m, 3H), 1.66–1.61 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, 300 K): δ 138.57 (C), 118.71 (CH), 43.94 (CH_2), 42.27 (CH), 31.91 (CH_2), 31.73 (CH_2), 29.27 (CH). Elemental analysis: Calcd for $C_{14}H_{20}AgNO_4$: C: 44.9, H: 5.4, N: 3.7; found: C: 44.8, H: 5.0, N: 3.7.

Complex with Cu(I). A solution of **6** (645 mg, 3.5 mmol) in 3.3 mL of ethyl acetate with 547 mg (2.8 mmol) of freshly prepared CuCl was stirred under reflux for 9 h and then cooled to RT. The precipitate obtained was filtered, washed with ethyl acetate (2 × 5 mL), and dried in vacuo at 40 °C to give 0.94 g (95%) of a slightly greenish solid.

Crystallization of $[Cu_2Cl_2(CH_3CN)(6)]$

Crystals suitable for X-ray diffraction studies were obtained by recrystallization of the copper complex obtained from acetonitrile as mentioned above.

Synthesis of $[Cu_2(bipy)_2(6)](PF_6)_2$

To a stirred solution of 37 mg (0.07 mmol) $[Cu(CH_3CN)_4]PF_6$ in 3 mL of acetone, 15.6 mg (1.0 mmol) of 2,2′-bipyridine was added. The resulting red solution was stirred for 2 h and then an excess of **6** (160 mg, 0.9 mmol) was added. The solution was filtered through a pad of zeolite. Diffusion of diethyl ether into the solution at room temperature resulted in the formation of light yellow crystals suitable for X-ray structure determination.

Crystallography

Single crystals suitable for X-ray diffraction were mounted on the tip of a glass rod using inert perfluoropolyether oil. The X-ray crystallographic data were collected on a BRUKER NONIUS FR591 Kappa CCD diffractometer and with a STOE IPDS one-circle diffractometer. Both diffractometers were equipped with low temperature systems. Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator were used. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F2 (SHELXL-2014) [38].

Supplementary material

CCDC 1056381 and CCDC 1057184 contain the supplementary crystallographic data for $[Cu_2Cl_2(CH_3CN)(\mathbf{6})]_n$ and $[Cu_2(bipy)_2(\mathbf{6})](PF_6)_2$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Furthermore, NMR spectra are reported.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1071802].

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