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journal homepage: www.elsevier.com/locate/jsscCu(N–N)₂Cl₂ and Cu(N–N–N)Cl₂ and HgCl₂ building blocks in the synthesis of coordination compounds—X-ray studies and magnetic propertiesB. Machura^{a,*}, A. Świtlicka^a, I. Nawrot^a, J. Mroziński^b, R. Kruszynski^c, J. Kusz^d^a Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland^b Wrocław University, F. Joliot-Curie 14 St., 50-383 Wrocław, Poland^c Department of X-ray Crystallography and Crystal Chemistry, Institute of General and Ecological Chemistry, Technical University of Lodz, 116 Żeromski St., 90-924 Łódź, Poland^d Institute of Physics, University of Silesia, 4th Uniwersytecka St., 40-006 Katowice, Poland

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ABSTRACT

A series of complexes containing Cu(N–N)₂Cl₂ (N–N=bis(pyrazol-1-yl)methane (bpzm), bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm), 2,2-dipyridylamine (dpa), 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) and 2,2'-bipyridine (bipy)), Cu(N–N–N)Cl₂ (N–N–N=2,2':6',2''-terpyridine (terpy)) and HgCl₂ building blocks have been synthesized and structurally characterized. Increase in structural dimensionality is observed for [Cu(bpzm)₂][HgCl₄], [Cu(dpa)₂][HgCl₃]₂ and [Cu(terpy)(μ-Cl)HgCl₃] compounds. No coordination polymers have formed in the case of bis(3,5-dimethylpyrazol-1-yl)methane, 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine and 2,2'-bipyridine. The [Cu(bpzm)₂][HgCl₄] and [Cu(terpy)(μ-Cl)HgCl₃] complexes have been studied by magnetic measurements.

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1. Introduction

The design and synthesis of homo- and hetero-metallic coordination polymers is one of the most interesting topics in current coordination chemistry and crystal engineering. Thanks to unique structures, properties and reactivities a lot of hybrid coordination polymers has been employed in catalysis, molecular adsorption, molecular magnetism, nonlinear optics, luminescence or model bioinorganic chemistry [1–6]. Intensive magnetostructural investigations of homo- and heteropolynuclear complexes have contributed to the understanding of the factors governing the sign and the magnitude of the intramolecular exchange interactions between either identical or different paramagnetic centers [6,7].

Generally, the type and topology of the coordination polymers depend on the metal element, valences and geometries needs of the metal ion and functionality of the ligand [8].

In designing polynuclear complexes three important synthetic strategies have been settled: (1) the use of compartmental ligands, which usually leads to oligonuclear complexes; (2) the building-block approach, consisting in the use of complexes with

potentially bridging groups acting as ligands toward a second metal ion; and (3) the use of exo-bidentate ligands, which is a straightforward route towards high-dimensionality systems [9].

To date, numerous mononuclear metal coordination polymers with various nuclearities, dimensionalities, or topologies of the metallic centers have been successfully synthesized and characterized. However, the chemistry of bimetallic coordination polymers has received considerably less attention. During the past decade, a series of very attractive mixed metal coordination polymers have been obtained by using transition metal complex cations and various cyanometallate or thiocyanometallate units. The alteration of the metal center in $M'L_n^{x+}$, $[M''(CN)_n]^{x-}$ or $[M''(SCN)_n]^{x-}$ building blocks and the consequent adjustment of the geometric, magnetic, and electronic properties, provides the control and flexibility required to assemble solids with tunable properties. Other approaches to mixed metal systems have involved the linking of mixed metal polyoxometallates, which leads to the incorporation of two metals into a single framework, albeit on the same site [10–14].

Some multidimensional heteropolynuclear structures has been also prepared in the reactions of HgX₂ (X=Cl, Br or CN) with ML_nCl_2 ($M=Mn^{2+}$, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} ; L =neutral ligands). The HgX₂ moieties accept chloride ligands from the $M(II)$ centers and generate transition metal organoamine double salt mercurates with several different structural motifs including one-dimensional chains, 2D-layers and 3-D extended structures [15–20].

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The $\text{Hg}(\text{CN})_2$ -based coordination polymers studied by Leznoff et al. [20] represent unusual examples of mercury(II) (a diamagnetic d^{10} metal center) mediating a magnetic interaction.

As an extension of this research, we were keen to examine the possibility of synthesis of coordination polymers in the reactions HgCl_2 with $\text{Cu}(\text{N}-\text{N})_2\text{X}_2$ (where $\text{N}-\text{N}=\text{bis}(\text{pyrazol-1-yl})\text{methane}$ (bpzm), $\text{bis}(3,5\text{-dimethylpyrazol-1-yl})\text{methane}$ (bdmpzm), 2,2-dipyridylamine (dpa), 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) and 2,2'-bipyridine (bipy)) and $\text{Cu}(\text{terpy})\text{Cl}_2$. From the structural point of view, the used chelate ligands can be generally divided into two groups. The first group includes bis(pyrazol-1-yl)methane, bis(3,5dimethylpyrazol-1-yl)methane and 2,2-dipyridylamine, and these ligands form a six-membered cycle of boat conformation upon coordination to a transition metal. 5,6-Diphenyl-3-(2-pyridyl)-1,2,4-triazine, 2,2'-bipyridine and 2,2':6',2''-terpyridine form an approximately planar five-membered moiety when they coordinate to a central atom. In the case of terpy two five-membered cycle are conjugated. The compounds $\text{Cu}(\text{N}-\text{N})_2\text{X}_2$ can be easily prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and suitable ligand in methanol, and they have proven to be useful building blocks in the synthesis of multidimensional coordination polymers [21–24]. The geometry around the copper(II) ion in $\text{Cu}(\text{N}-\text{N})_2\text{X}_2$ compounds can be varied by changing the ligand. The copper(II) complexes containing two bis(pyrazol-1-yl)methane molecules are always octahedral, whereas the majority of the others take form $[\text{Cu}(\text{L}-\text{L})_2\text{X}]_n$, in which copper(II) atoms lie in distorted five-coordinate environments of two chelate ligands and unidentate X, but the distorted tetrahedral and octahedral geometries are also possible [25]. By altering the cationic copper(II)-ligand building block we have tried to study the factors influencing the structures of the heterobimetallic species.

Here, we present synthesis and structural studies of the following complexes $[\text{Cu}(\text{bpzm})_2][\text{HgCl}_4]$ (**1**), $[\text{Cu}(\text{bdmpzm})_2][\text{Hg}_2\text{Cl}_6]$ (**2**), $[\text{Cu}(\text{dpa})_2][\text{HgCl}_3]_2$ (**3a**), $[\text{Cu}(\text{dpa})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{dpa})_2(\text{HgCl}_4)_2]$ (**3b**), $[\text{Cu}(\text{dppt})_2(\mu-\text{Cl})\text{HgCl}_3] \cdot \text{H}_2\text{O}$ (**4**) and $[\text{Cu}(\text{bipy})_2(\mu-\text{Cl})_2\text{HgCl}_2]$ (**5**) and $[\text{Cu}(\text{terpy})(\mu-\text{Cl})\text{HgCl}_3]$ (**6**). Increase in structural dimensionality is observed for **1**, **3a** and **6** compounds. In the case of bis(3,5dimethylpyrazol-1-yl)methane, 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine and 2,2'-bipyridine no coordination polymers have formed. The compounds **1** and **6** have been studied by magnetic measurements.

2. Experimental

2.1. General procedure

The bis(pyrazol-1-yl)methane (bpzm) and bis(3,5dimethylpyrazol-1-yl)methane (bdmpzm) were synthesized according to the literature methods [26]. The other reagents and solvents used to the synthesis were purchased from commercial sources and all manipulations were performed in air using materials as received. Elemental analyses (C H N) were performed on a Perkin-Elmer CHN-2400 analyzer.

2.2. Preparation of $[\text{Cu}(\text{bpzm})_2][\text{HgCl}_4]$ (**1**)

HgCl_2 (0.16 g; 0.60 mmol) was dissolved in water (20 ml) and slowly added to the methanolic (20 ml) solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and bis(pyrazol-1-yl)methane (0.18 g; 1.22 mmol), and stirred at room temperature for 6 h. Blue crystalline precipitate of $[\text{Cu}(\text{bpzm})_2][\text{HgCl}_4]$ (**1**) was filtered off and dried in air. X-ray quality crystals of **1** were obtained by slow recrystallization from methanol. Yield 85%.

Found: 23.68; H, 2.23; N, 15.62% Calc. for $\text{C}_{14}\text{H}_{16}\text{N}_8\text{Cl}_4\text{CuHg}$: C, 23.94; H, 2.30; N, 15.96%.

IR (KBr, cm^{-1}) 1641(w), 1519(m) $\nu(\text{C}=\text{N}_{\text{bpzm}})$ and $\nu(\text{C}=\text{C}_{\text{bpzm}})$.

2.3. Preparation of $[\text{Cu}(\text{bdmpzm})_2][\text{Hg}_2\text{Cl}_6]$ (**2**)

A procedure similar to that for **1** was used with HgCl_2 (0.16 g; 0.60 mmol), $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and bis(3,5dimethylpyrazol-1-yl)methane (0.245 g; 1.20 mmol). Violet crystalline precipitate of **2** was collected in 80% yield.

Found: C, 24.15; H, 2.06; N, 10.53% Calc. for $\text{C}_{22}\text{H}_{32}\text{N}_8\text{Cl}_6\text{CuHg}_2$: C, 24.33; H, 2.97; N, 10.32%.

IR (KBr, cm^{-1}) 1613(w) and 1557(s) $\nu(\text{C}=\text{N}_{\text{bdmpzm}})$ and $\nu(\text{C}=\text{C}_{\text{bdmpzm}})$.

2.4. Preparation of $[\text{Cu}(\text{dpa})_2][\text{HgCl}_3]_2$ (**3a**),

$[\text{Cu}(\text{dpa})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{dpa})_2(\text{HgCl}_4)_2]$ (**3b**)

A procedure similar to that for **1** was used with HgCl_2 (0.16 g; 0.60 mmol), $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and 2,2-dipyridylamine (dpa) (0.105 g; 1.23 mmol). Brown precipitate was collected in 90% yield and recrystallized from methanol. Dark red crystals of $[\text{Cu}(\text{dpa})_2][\text{HgCl}_3]_2$ (**3a**) and green crystals of $[\text{Cu}(\text{dpa})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{dpa})_2(\text{HgCl}_4)_2]$ (**3b**) were collected in 60% and 40% yield, respectively. Crystals of **3a** and **3b** were separated using microscope.

Found for **3a**: C, 23.87; H, 1.75; N, 8.16% Calc. For $\text{C}_{20}\text{H}_{18}\text{N}_6\text{Cl}_6\text{CuHg}_2$: C, 23.55; H, 1.78; N, 8.24%.

Found for **3b**: C, 31.56; H, 2.52; N, 10.79% Calc. For $\text{C}_{40}\text{H}_{40}\text{N}_{12}\text{O}_2\text{Cl}_8\text{Cu}_2\text{Hg}_2$: C, 31.35; H, 2.63; N, 10.97%.

IR of **3a** (KBr, cm^{-1}) 3282(m) $\nu(\text{NH})$; 1630(s), 1584(s), 1519(s) $\nu(\text{C}=\text{N}_{\text{dpa}})$ and $\nu(\text{C}=\text{C}_{\text{dpa}})$.

IR of **3b** (KBr, cm^{-1}) 3420(m) $\nu(\text{NH})$; 1632(s), 1583(s), 1516(s) $\nu(\text{C}=\text{N}_{\text{dpa}})$ and $\nu(\text{C}=\text{C}_{\text{dpa}})$.

2.5. Preparation of $[\text{Cu}(\text{dppt})_2(\mu-\text{Cl})\text{HgCl}_3]$ (**4**)

A procedure similar to that for **1** was used with HgCl_2 (0.16 g; 0.60 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) (0.37 g; 1.19 mmol). Green crystalline precipitate of **4** was collected in 75% yield.

Found: C, 45.64; H, 2.80; N, 10.62% Calc. For $\text{C}_{40}\text{H}_{30}\text{N}_8\text{OCl}_4\text{CuHg}$: C, 45.99; H, 2.89; N, 10.73%.

IR (KBr, cm^{-1}) 1607(m), 1598(m), 1579(w) $\nu(\text{C}=\text{N}_{\text{dppt}})$ and $\nu(\text{C}=\text{C}_{\text{dppt}})$.

2.6. Preparation of $[\text{Cu}(\text{bipy})_2(\mu-\text{Cl})_2\text{HgCl}_2]$ (**5**)

A procedure similar to that for **1** was used with HgCl_2 (0.16 g; 0.60 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and 2,2'-bipyridine (0.19 g; 1.21 mmol). Green crystalline precipitate of **5** was collected in 75% yield.

Found: C, 33.21; H, 2.32; N, 19.36% Calc. For $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_6\text{CuHg}$: C, 33.44; H, 2.25; N, 19.74%.

IR (KBr, cm^{-1}) 1599(s), 1575(m), $\nu(\text{C}=\text{N}_{\text{bipy}})$ and $\nu(\text{C}=\text{C}_{\text{bipy}})$.

2.7. Preparation of $[\text{Cu}(\text{terpy})\text{HgCl}_4]$ (**6**)

A procedure similar to that for **1** was used with HgCl_2 (0.16 g; 0.60 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 g; 0.59 mmol) and 2,2':6',2''-terpyridine (terpy) (0.14 g; 0.60 mmol). Green crystalline precipitate of **6** was collected in 80% yield.

Found: C, 28.10; H, 1.79; N, 6.36% Calc. For $\text{C}_{15}\text{H}_{11}\text{N}_3\text{Cl}_4\text{CuHg}$: C, 28.19; H, 1.73; N, 6.57%.

IR (KBr, cm^{-1}) 1598(w), 1605(s), 1575(m) 1500(m), $\nu(\text{C}=\text{N}_{\text{terpy}})$ and $\nu(\text{C}=\text{C}_{\text{terpy}})$.

2.8. Crystal structures determination and refinement

The X-ray intensity data of **1**, **2**, **4** and **6** were collected on a KM-4-CCD automatic diffractometer equipped with CCD detector and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$). The X-ray intensity data of **3a**, **3b** and **5** were collected on a Gemini A Ultra diffractometer at room temperature using graphite monochromated $\text{MoK}\alpha$ radiation. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and absorption correction [27] were applied. The structures were solved by the Patterson method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their adjacent atoms and assigned isotropic temperature factors equal 1.2 times the value of equivalent temperature factor of the aromatic parent atoms and equal 1.5 times the value of equivalent temperature factor of the methyl parent carbon atom. SHELXS97 [28], SHELXL97 [29] and SHELXTL [30] programs were used for all the calculations. Atomic

scattering factors were those incorporated in the computer programs.

2.9. IR and EPR spectra

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range $4000\text{--}400 \text{ cm}^{-1}$ with the samples in the form of KBr pellets.

EPR spectra of compounds **1** and **6** were recorded at room temperature and 77 K on a Bruker ESP 300 spectrometer operating at X-band equipped with an ER 035 M Bruker NMR gaussmeter and HP 5350B Hewlett-Packard microwave frequency counter.

2.10. Magnetic measurement

Variable-temperature magnetic measurements of polycrystalline samples of **1** and **6** were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5-type) at a magnetic field of 0.5 T over the temperature range 1.8–300 K. Correction are based on subtracting the sample-holder signal and contribution χ_{Dia} estimated from Pascal constants [31] equal $-330 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ for complex **1** and $-284 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ for complex

Table 1
Crystal data and structure refinement for **1**, **2**, **3a**, **3b**, **4**, **5** and **6** complexes.

	1	2	3a	3b	4c	5	6
Empirical formula	$\text{C}_{14}\text{H}_{16}\text{N}_8\text{Cl}_4\text{CuHg}$	$\text{C}_{22}\text{H}_{32}\text{N}_8\text{Cl}_6\text{CuHg}_2$	$\text{C}_{20}\text{H}_{18}\text{N}_6\text{Cl}_6 \text{ Cu Hg}_2$	$\text{C}_{40}\text{H}_{40}\text{Cl}_8\text{N}_{12}\text{O}_2\text{Cu}_2\text{Hg}_2$	$\text{C}_{40}\text{H}_{30}\text{N}_8\text{OCl}_4\text{CuHg}$	$\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_4\text{CuHg}$	$\text{C}_{15}\text{H}_{11}\text{N}_3\text{Cl}_4\text{CuHg}$
Formula weight	702.28	1085.98	1019.82	1532.70	1044.65	718.30	639.20
Temperature (K)	150(2)	293(2)	293(2)	293(2)	150(2)	293(2)	293(2)
Wavelength (\AA)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P-1	P2(1)/c	P-1	P2(1)/c	C2/c	P-1
Unit cell dimensions (\AA , $^\circ$)	$a=10.0397(3)$ $b=14.7961(5)$ $c=14.3794(5)$ $\beta=94.381(3)$	$a=9.3640(7)$ $b=9.9892(9)$ $c=14.7153(5)$ $\alpha=113.723(8)$ $\beta=101.397(6)$ $\gamma=96.299(7)$	$a=8.5400(17)$ $b=21.0546(4)$ $c=7.5037(15)$ $\beta=95.214(18)$	$a=8.9877(2)$ $b=11.2372(3)$ $c=12.8652(3)$ $\alpha=78.981(2)$ $\beta=83.760(2)$ $\gamma=77.313(2)$	$a=15.5148(7)$ $b=16.0972(6)$ $c=15.9348(6)$ $\beta=93.537(4)$	$a=21.3693(18)$ $b=9.1276(2)$ $c=15.6161(15)$ $\beta=131.660(15)$	$a=7.3187(9)$ $b=9.1689(13)$ $c=13.4880(12)$ $\alpha=83.784(10)$ $\beta=81.715(9)$ $\gamma=86.501(11)$
Volume (\AA^3)	2129.80(12)	828.14(11)	1343.6(4)	1241.2(2)	3972.1(3)	2275.6(3)	889.44(18)
z	4	1	2	1	4	4	2
Density (calculated) (mg/m^3)	2.190	2.178	2.521	2.050	1.747	2.097	2.387
Absorption coefficient (mm^{-1})	8.718	10.394	12.802	7.490	4.709	8.158	10.418
F(000)	1332	511	942	734	2044	1364	598
Crystal size (mm)	$0.10 \times 0.14 \times 0.18$	$0.08 \times 0.12 \times 0.44$	$0.04 \times 0.15 \times 0.17$	$0.03 \times 0.06 \times 0.10$	$0.03 \times 0.05 \times 0.20$	$0.10 \times 0.15 \times 0.19$	$0.05 \times 0.14 \times 0.22$
θ range for data collection ($^\circ$)	2.76 to 25.00	3.23 to 25.00	3.34 to 25.00	3.37 to 25.00	2.81 to 25.00	3.49 to 25.05	2.82 to 25.00
Index ranges	$-10 \leq h \leq 11$ $-17 \leq k \leq 17$ $-17 \leq l \leq 15$	$-11 \leq h \leq 11$ $-11 \leq k \leq 6$ $-11 \leq l \leq 11$	$-10 \leq h \leq 10$ $-25 \leq k \leq 24$ $-8 \leq l \leq 8$	$-10 \leq h \leq 10$ $-13 \leq k \leq 13$ $-15 \leq l \leq 15$	$-18 \leq h \leq 18$ $-10 \leq k \leq 19$ $-18 \leq l \leq 18$	$-25 \leq h \leq 25$ $-10 \leq k \leq 10$ $-18 \leq l \leq 18$	$-8 \leq h \leq 6$ $-10 \leq k \leq 10$ $-15 \leq l \leq 16$
Reflections collected	6914	5141	12,387	23,810	24,556	10,301	5459
Independent reflections ($R_{\text{int}}=0.0160$)	1882	2812 ($R_{\text{int}}=0.0500$)	2353 ($R_{\text{int}}=0.0369$)	4372 ($R_{\text{int}}=0.0289$)	6961 ($R_{\text{int}}=0.0551$)	2010 ($R_{\text{int}}=0.0247$)	3001 ($R_{\text{int}}=0.0219$)
Completeness to 2θ (%)	99.9	96.7	99.8%	99.7	99.4	99.8	95.9
Max. and min. transmission	0.421 and 0.227	0.428 and 0.230	0.531 and 0.138	0.804 and 0.594	0.870 and 0.757	0.439 and 0.242	0.603 and 0.195
Data/restraints/parameters	1882/0/131	2812/0/182	2353/0/160	4372/0/305	6961/0/496	2010/0/137	3001/0/217
Goodness-of-fit on F^2	1.047	1.036	1.051	1.024	0.911	1.096	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0110$ $wR_2=0.0280$	$R_1=0.0433$ $wR_2=0.1103$	$R_1=0.0298$ $wR_2=0.0743$	$R_1=0.0167$ $wR_2=0.0343$	$R_1=0.0389$ $wR_2=0.0987$	$R_1=0.0275$ $wR_2=0.0676$	$R_1=0.0350$ $wR_2=0.0940$
R indices (all data)	$R_1=0.0116$ $wR_2=0.0281$	$R_1=0.0489$ $wR_2=0.1126$	$R_1=0.0376$ $wR_2=0.0762$	$R_1=0.0211$ $wR_2=0.0348$	$R_1=0.0719$ $wR_2=0.1126$	$R_1=0.0314$ $wR_2=0.0687$	$R_1=0.0429$ $wR_2=0.0968$
Largest diff. peak and hole (e \AA^{-3})	0.467 and -0.356	3.788 and -0.970	1.453 and -1.989	0.337 and -0.535	4.463 and -0.885	0.412 and -1.402	2.110 and -0.846

6. The value $60 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ was used for the temperature-independent paramagnetism of copper(II) center. The effective magnetic moment was calculated from the equation: $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}(\text{B.M.})$

Magnetization versus magnetic field measurements were carried out at 2 K in the field range 0–5 T.

3. Results and discussion

3.1. Preparation and infrared data

The compounds $[\text{Cu}(\text{bpzm})_2][\text{HgCl}_4]$ (**1**), $[\text{Cu}(\text{bdmpzm})_2][\text{Hg}_2\text{Cl}_6]$ (**2**) $[\text{Cu}(\text{dppt})_2(\mu\text{-Cl})\text{HgCl}_3] \cdot \text{H}_2\text{O}$ (**4**), $[\text{Cu}(\text{bipy})_2(\mu\text{-Cl})_2\text{HgCl}_2]$ (**5**) have been obtained in high yield and purity in the reaction of aqueous solution of HgCl_2 with a methanolic solution of CuCl_2 containing 2 equivalents of bis(pyrazol-1-yl)methane (bpzm), bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm), 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt), 2,2'-bipyridine (bipy), respectively. The reaction of HgCl_2 with a methanolic solution of CuCl_2 containing 2 equivalents of 2,2-dipyridylamine (dpa) leads to the formation of a mixture of $[\text{Cu}(\text{dpa})_2][\text{HgCl}_3]_2$ (**3a**) and $[\text{Cu}(\text{dpa})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{dpa})_2(\text{HgCl}_4)_2]$ (**3b**). The complex $[\text{Cu}(\text{terpy})(\mu\text{-Cl})\text{HgCl}_3]$ (**6**) is a product of the analogous reaction of HgCl_2 with $\text{Cu}(\text{terpy})\text{Cl}_2$.

The selected frequencies observed in the IR spectra of **1–6** complexes are given in the Experimental part. The characteristic bands of the C=C and C=N stretching modes of bpzm, bdmpzm,

dpa, dppt, bipy and terpy are observed in the range 1640–1500 cm^{-1} . The medium intensity bands at $\sim 3300 \text{ cm}^{-1}$ in the IR spectrum of **3a** and **3b** are assignable to $\nu(\text{NH})$ vibration of the coordinated 2,2-dipyridylamine [32].

3.2. Crystal structure analysis

The crystallographic data of **1**, **2**, **3a**, **3b**, **4**, **5** and **6** are summarized in Table 1. The single-crystal X-ray diffraction studies reveal that **1**, **3a** and **6** adopt supramolecular framework structures, whereas the compounds **2**, **3b**, **4** and **5** are molecular complexes. The short intra- and intermolecular contacts [33] detected in the structures **1**, **2**, **3a**, **3b**, **4**, **5** and **6** are collected in Table 2.

The compound **1** creates a one-dimensional zigzag chain along $[10\bar{1}]$ crystallographic axis in which the adjacent units $[\text{Cu}(\text{bpzm})_2]^{2+}$ and HgCl_4^{2-} are conjoined through the bridging chloride ion (Fig. 1), and the intra-chain $\text{Cu}\cdots\text{Hg}$, $\text{Cu}\cdots\text{Cu}$ and $\text{Hg}\cdots\text{Hg}$ contacts are 4.586, 9.078 and 9.172 Å, respectively. The polymer chains are connected via the intermolecular C–H \cdots Cl contacts (which can be classified as weak hydrogen bonds) to the three dimensional net. The Cu(II) ions of **1** are six-coordinate and the coordination geometry is best described as distorted tetragonal bipyramid with chloride ions in the axial positions and the equatorial plane defined by four nitrogen atoms of the bis(pyrazol-1-yl)methane. The six-membered rings formed upon coordination of bis(pyrazol-1-yl)methane molecules to the central ion show a boat conformation with the copper and the carbon atoms off the plane defined by the four nitrogen atoms. The Hg(II) ions are tetrahedrally coordinated with four chloride ions and each Hg(II) ion is bridged with two copper ions via the single chloride bridge.

Table 2

Hydrogen bonds for **1**, **2**, **3a**, **3b**, **4**, **5** and **6** complexes.

D	A	H \cdots A	D \cdots A	D–H \cdots A
1				
C(1)	Cl(1)#1	2.74	3.471(2)	137.0
C(3)	Cl(2)#2	2.83	3.527(2)	133.0
C(7)	Cl(2)#3	2.59	3.430(2)	145.0
C(7)	Cl(1)#4	2.63	3.555(2)	160.0
2				
C(11)	Cl(3)#5	2.64	3.583(8)	164.0
3a				
N(2)	Cl(2)#6	2.36	3.313(5)	162.0
C(1)	Cl(4)#7	2.81	3.674(7)	156.1
3b				
O(1)	Cl(3)	2.28	3.188(3)	152.0
O(1)	Cl(1)	2.69	3.434(3)	152.0
O(1)	N(3)	2.51	2.956(4)	116.0
N(3)	O(1)	2.25	2.956(4)	135.0
N(3)	Cl(1)#7	2.56	3.394(3)	155.0
N(5)	Cl(4)	2.50	3.177(2)	132.0
N(5)	Cl(2)#8	2.42	3.253(3)	154.0
C(1)	Cl(2)#9	2.79	3.528(3)	137.0
C(17)	Cl(3)#10	2.72	3.606(4)	158.0
4				
O(1)	Cl(4)	2.43	3.263(19)	180.0
C(8)	Cl(3)	2.80	3.657(8)	153.00
C(27)	Cl(2)#11	2.69	3.609(8)	171.0
C(36)	Cl(3)	2.77	3.692(8)	170.0
5				
C(1)	Cl(2)#12	2.68	3.366(6)	131.0
C(3)	Cl(1)#13	2.82	3.731(8)	168.0
C(4)	Cl(2)#14	2.78	3.692(5)	166.0
C(7)	Cl(2)#15	2.79	3.669(8)	159.00
6				
C(2)	Cl(1)#16	2.76	3.685(9)	171.0
C(7)	Cl(4)#17	2.77	3.672(8)	163.0
C(9)	Cl(2)#18	2.67	3.544(8)	156.0

#1: $1/2+x, -1/2+y, z$; #2: $2-x, y, 1/2-z$; #3: $3/2-x, 1/2-y, -z$; #4: $1+x, y, z$; #7: $-x, 1-y, 1-z$; #5: $-x, 1-y, 1-z$; #6: $x, 3/2-y, 1/2+z$; #7: $-x, -y, 2-z$; #8: $-x, -y, 1-z$; #9: $-x, 1-y, 2-z$; #10: $x, -1+y, z$; #11: $-x, 1-y, 2-z$; #12: $-x, y, 1/2-z$; #13: $1/2-x, 1/2+y, 1/2-z$; #14: $1/2-x, 1/2-y, 1-z$; #15: $1/2-x, 1/2-y, 1-z$; #16: $-1-x, -y, 1-z$; #17: $-1+x, 1+y, z$; #18: $-x, 1-y, -z$.

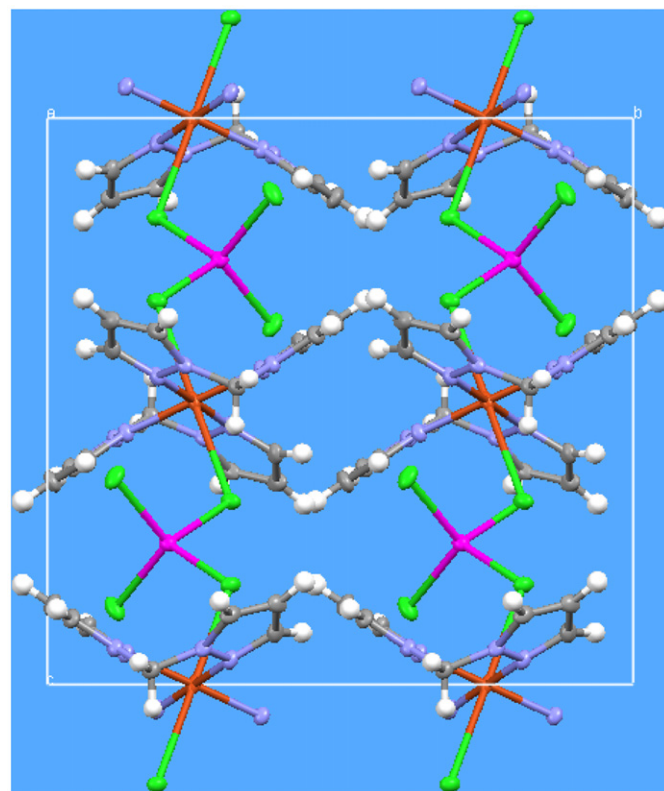


Fig. 1. The 1D structure of **1** viewed along crystallographic a -axis. Color codes: orange, Cu; pink, Hg; green, Cl; purple, N; gray, C; white, H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The crystal structure of **2** consists of $[\text{Cu}(\text{bdmpzm})_2]^{2+}$ cations and $[\text{Hg}_2\text{Cl}_6]^{2-}$ anions in a molar ratio 1:1 connected via the intermolecular C–H...Cl contacts to the one-dimensional chains extending along crystallographic [001] axis (Fig. 2). Similar to **1**, bis(3,5-dimethylpyrazol-1-yl)methane molecules bind to the Cu(II) ion forming two six-membered cycles with a *boat* conformation. However, in this case the cations and anions remain isolated, probably due to the presence of the bulky methyl group in the coordinated bdmpzm ligands. The distance from the Cu(1) of $[\text{Cu}(\text{bdmpzm})_2]^{2+}$ to the terminal chloride of the nearest $[\text{Hg}_2\text{Cl}_6]^{2-}$ anion is equal to 5.247 Å. The centrosymmetric dinuclear anion $[\text{Hg}_2\text{Cl}_6]^{2-}$ contains two bent Cl(1)–Hg(1)–Cl(2)

units bridged by two Cl(3) atoms with distorted tetrahedral coordination for Hg and a four-membered Hg_2Cl_2 ring.

The polymer net of **3a** creates 2,3-c two nodal net with described by $\{8^3\}2\{8\}$ Schlafli symbol [34]. Considering each of metal atoms as a separate independent point node leads to extended point symbols $[8(2)]$ and $[8.8.8]$, respectively, for Cu and Hg ions. In case of considering of polymer as an uninodal net with centers located at net binding points (Hg ions), the net is expressed by $\{6^3\}$ Schlafli symbol corresponding to 3-c uninodal net described by $[6.6.6]$ extended point symbol.

The formation of the two-dimensional structure of **3a** can be explained as follows: the chloride ligands migrate from Cu(II) center to HgCl_2 to form a HgCl_3^- anions, which form a 1-D chain of $[\text{HgCl}_3]_n^-$ along the [001] crystallographic axis with Hg(1)–Cl(4) bond lengths of 2.6634(14) Å, and such chains are further bridged by $[\text{Cu}(\text{dpa})_2]^{2+}$ cations into a 2-D layer extending along crystallographic (100) plane (Fig. 3). The polymer sheets of **3a** are connected via the intermolecular N–H...Cl hydrogen bonds to the three dimensional net, and the presence of C–H...Cl intramolecular hydrogen bonds provide additional stabilization to the polymer net. Each Cu(II) ion of **3a** is six-coordinate and its coordination geometry is best described as distorted tetragonal bipyramid with chloride ions in the axial positions and the equatorial plane defined by four nitrogen atoms of the 2,2-dipyridylamine. Likewise as bis(pyrazol-1-yl)methane, the coordinated 2,2-dipyridylamine molecules form with the central atom two six-membered cycles with a *boat* conformation.

Fig. 4 presents the cell packing of **3b** viewing along [100] crystallographic direction. The Cu(1) and Cu(2) central ions of **3b** are six-coordinate and their coordination geometries are the best described as distorted tetragonal bipyramids with equatorial planes defined by four nitrogen atoms of the 2,2-dipyridylamine. The Cu(1) coordination sphere is completed by two water molecules in the apical positions, whereas the Cu(2) center links two tetrahedrally coordinated mercury ions HgCl_2^{2-} through a single chloride bridge. The presence of medium strength and weak hydrogen bonds within structure of **3b** leads to formation of three-dimensional network linking cations and anions.

The perspective drawing of **4** with atomic numbering is shown in Fig. 5. The Cu(1) ion is five-coordinate coordinated by four N donors from the two dppt ligands and chloride anion. The angular structural index parameter τ [35] expressed here as the difference between the bond angles N(8)–Cu(1)–N(4) and N(2)–Cu(1)–N(6) divided by 60 has a value of 0.52. Compared with the ideal values

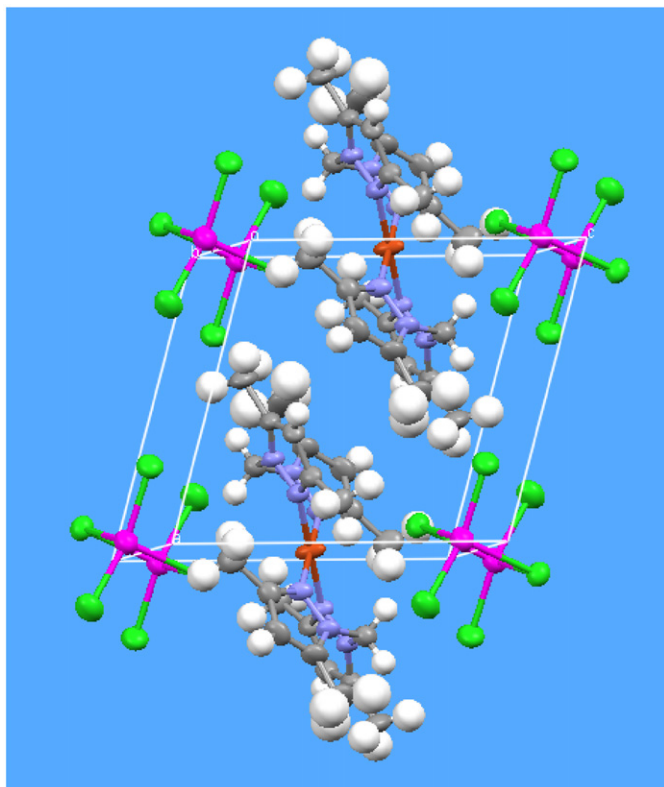


Fig. 2. The cell packing of **2**.

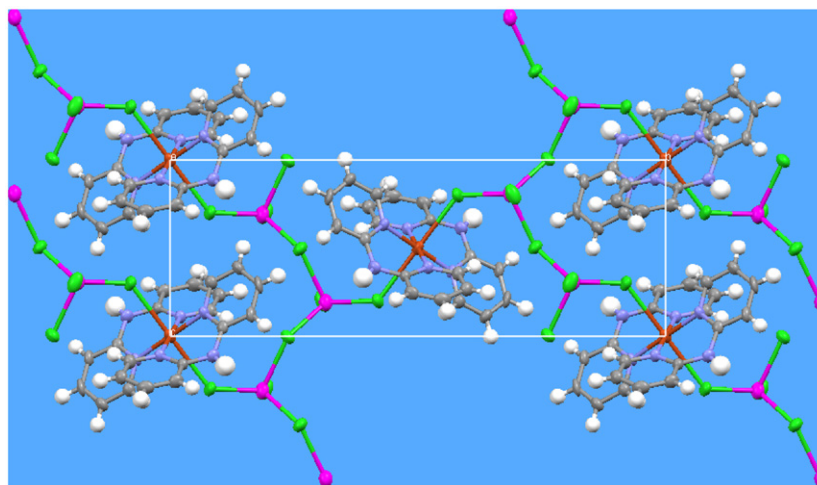


Fig. 3. The 2D structure of **3a** viewed along crystallographic *a*-axis. Color codes: orange, Cu; pink, Hg; green, Cl; purple, N; gray, C; white, H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of 1 for an equilateral bipyramid and 0 for a square pyramid, the τ descriptor of the examined structure suggests a stereochemistry intermediate between equilateral-bipyramidal and square-pyramidal. The medium strength intermolecular O–H...N hydrogen bond in structure **4** links water molecule and complex cation. An additional weak C–H...Cl intramolecular hydrogen bonds link these moieties to dimers. Beside mentioned, in the structure of **4** exist some short intramolecular interactions, which can be classified as a weak hydrogen bonds.

X-ray crystal structure of **5** reveals a simple molecular complex in which the coordinatively unsaturated HgCl₂ unit is bound to the chloride ligands of Cu(bipy)₂Cl₂ (Fig. 6). The chloride ligands

bridge the Cu(II) and Hg(II), and the Cu...Hg separation equal to 3.832 Å indicates that there is no metal–metal bonding between the two metal centers. The Cu(II) coordination geometry is best described as a distorted octahedron with two *cis*-oriented molecules of 2,2'-bipyridine and two chloride ions completing the coordination sphere. The four-coordinated Hg(II) center has a distorted seesaw coordination geometry with structural index parameter $\tau_4 = (360^\circ - (\alpha + \beta)) / 141^\circ$ equal to 0.78 [36].

The structure **6** reveals a one-dimensional chain motif of [Cu(terpy)HgCl₄]_n that runs parallel to the [100] crystallographic axis, and the intra-chain Cu...Hg and Cu...Cu contacts are 3.923 and 7.319 Å, respectively (Fig. 7). The polymer chains of **6** are connected *via* the intermolecular C–H...Cl contacts (which can be classified as weak hydrogen bonds) to the three-dimensional nets. Each Cu(II) atom is connected with two mercury ions through a single chloride bridge. The Hg(II) center is four-coordinated by Cl ions and the angular structural index parameter τ_4 equal to 0.72 indicates a distorted square-pyramidal coordination geometry around Hg(II) ions [36]. The Cu(II) center is five-coordinated by three N donors from the terpy ligand and two chloride anions. The angular structural index parameter τ [35] equal to 0.01 indicates a square-pyramidal coordination geometry around Cu(II) ions with the three N atoms of terpy ligand and one chloride ligand in the basal square plane.

The Cu–N, Cu–Cl and Cu–O distances of the examined structures fall within the normal range, and they are in good agreement with the bond lengths found in the related structures [37–41]. The Hg–Cl bond lengths are in the range of 2.29–3.19 Å confirmed for chloro complexes of Hg(II) [16–20].

3.3. EPR spectra

The EPR powder spectra of the complex **1** recorded in the X-band indicates single line only, at room temperature with parameter $g_{\text{average}} = 2.07$ and poorly resolved line at 77 K with $g_{\perp} = 2.07$ and $g_{\parallel} = 2.22$. The EPR powder spectra of the complex **6** recorded in the X-band and indicate three single lines at 293 and 77 K with the *g*-parameters given in Table 3. This type of three *g*-value signals is reasonable for the square-pyramidal symmetry

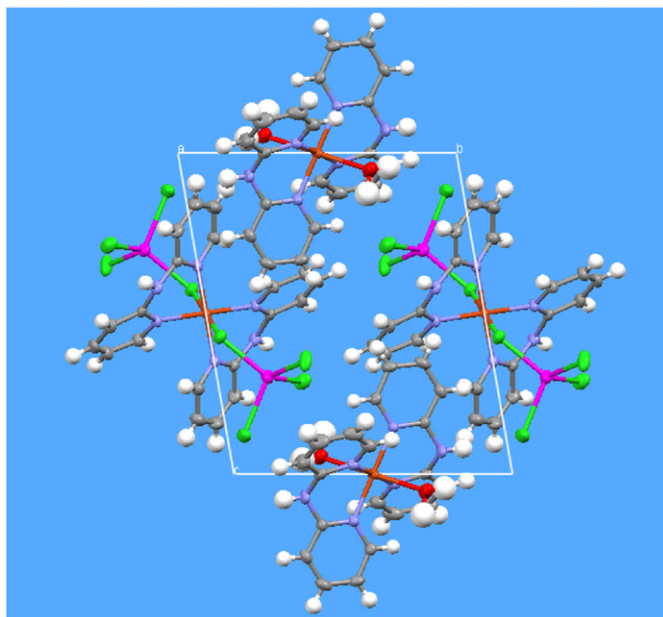


Fig. 4. The cell packing of **3b** viewing along the *a* direction. Color codes: orange, Cu; pink, Hg; green, Cl; purple, N; gray, C; red, O; white, H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

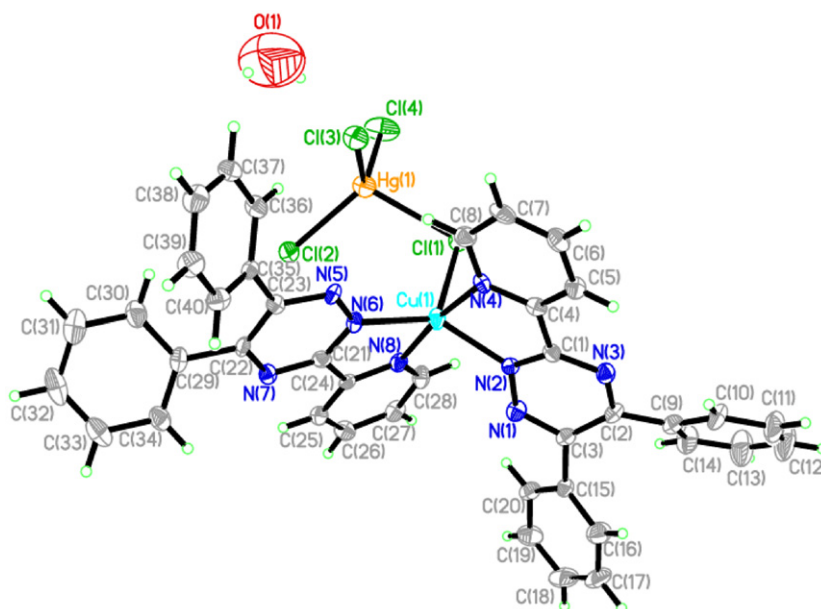


Fig. 5. The molecular structure of **4**.

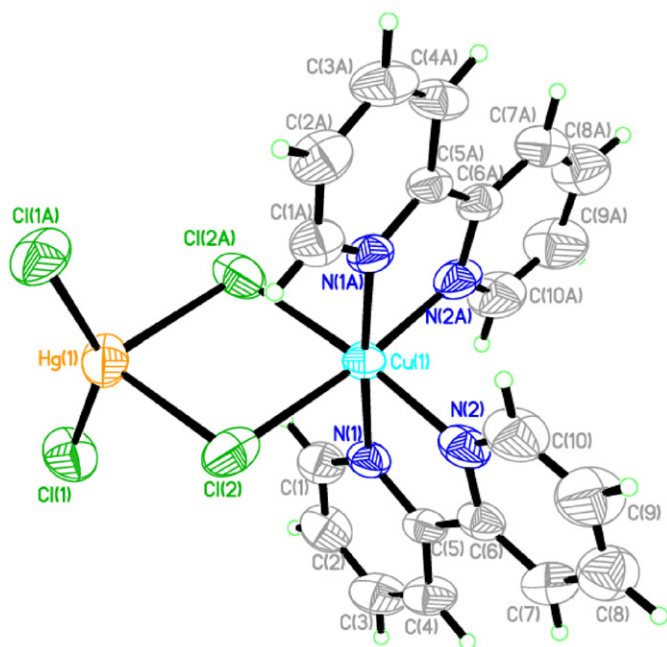


Fig. 6. The molecular structure of 5.

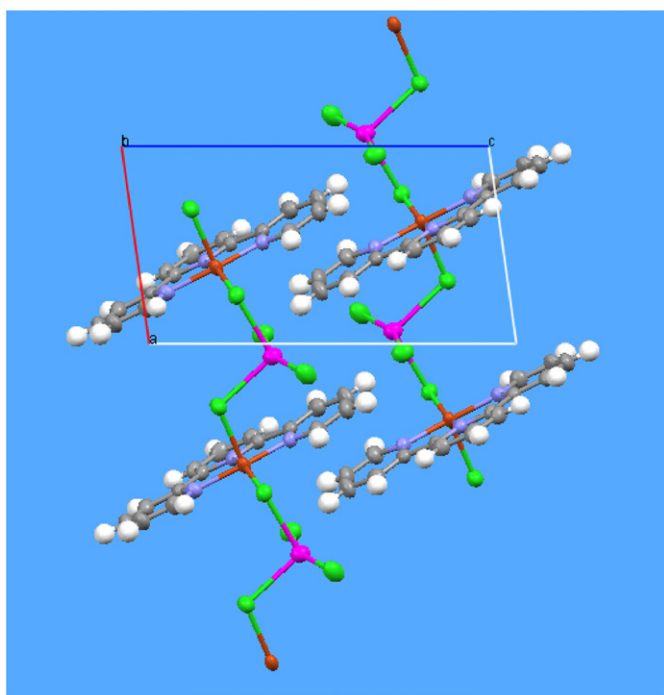


Fig. 7. The 1D structure of 6 viewed along crystallographic *b*-axis. Color codes: orange, Cu; pink, Hg; green, Cl; purple, N; gray, C; white, H.

Table 3
EPR data of 6.

Temperature (K)	<i>g</i>		
293	$g_1=2.23$	$g_2=2.16$	$g_3=2.05$
77	$g_1=2.23$	$g_2=2.14$	$g_3=2.05$

that is found for the copper(II) sites. Up to liquid helium temperature (4.2 K) EPR data indicated only signals typical for monomeric centers.

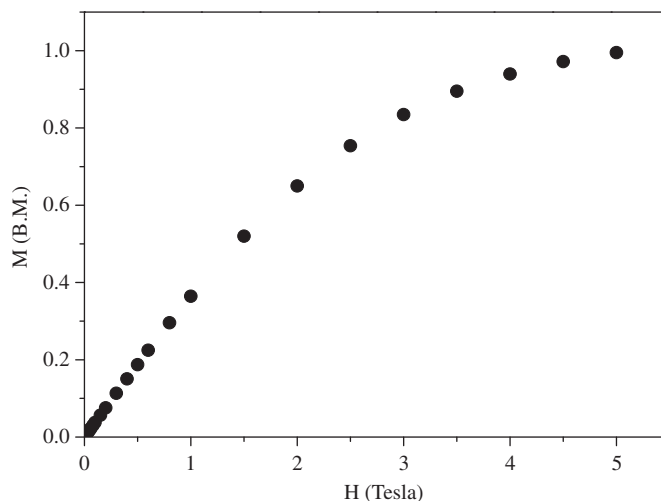


Fig. 8. The variation of the magnetization *M* versus the magnetic field *H* for complex 1.

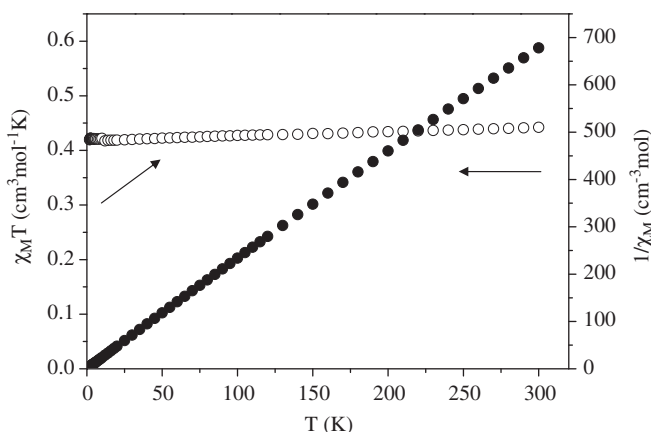


Fig. 9. Experimental magnetic data plotted as $\chi_M T$ (o) and $1/\chi_M$ (•) versus *T* for complex 1.

3.4. Magnetic properties

The variation of the magnetization *M* versus the magnetic field *H* for complex 1 has been measured at 2 K and indicates linear relation to ~ 1 T and then continues Brillouin function (Fig. 8). Value of magnetization 0.99 B.M. at 5 T evidences presence of one unpaired electron in the complex molecule.

Magnetic properties of the complex 1 were determined over the temperature range 1.8–300 K. Plots of reciprocal $\chi_M^{-1}=f(T)$ and $\chi_M T$ product versus *T* are given in Fig. 9. The value of $\chi_M T$ at 300 K is equal $0.442 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with effective magnetic moment 1.88 B.M. The values of Weiss constants θ determined from the relation $\chi_M^{-1}=f(T)$ over the temperature range 1.8–300 K are equal to -0.05 K. This unusually low value of θ is characteristic for an isolated copper(II) magnetic center.

Magnetic properties of the complex 6 were determined in the range 1.8–300 K. Plots of reciprocal $\chi_M^{-1}=f(T)$ are given in Fig. 10. The value of $\chi_M T$ at 300 K is equal $0.473 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with effective magnetic moment 1.95 B.M.

The relation $\chi_M^{-1}=f(T)$ over the temperature range 50–300 K indicate constant values of $\chi_M T \approx 0.48 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. At the lower temperatures (1.8–50 K) Weiss constant is equal -1.2 K as a results of weak antiferromagnetic coupling copper centers through $[\text{HgCl}_4]^{2-}$ bridges.

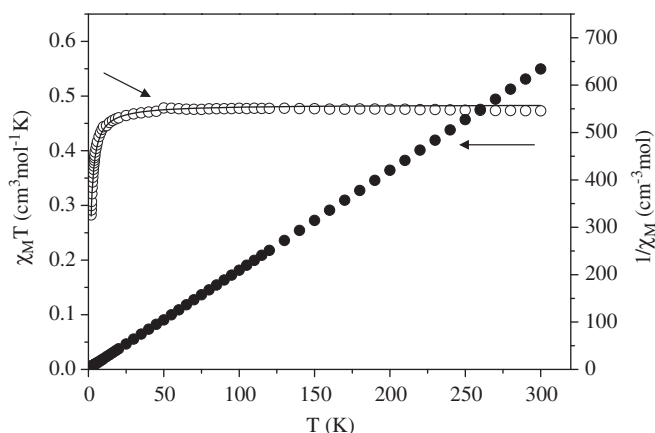


Fig. 10. Experimental magnetic data plotted as $\chi_M T$ (○) and $1/\chi_M$ (●) versus T for complex **6**. The solid line is the calculated curve for $\chi_M T$ vs. T .

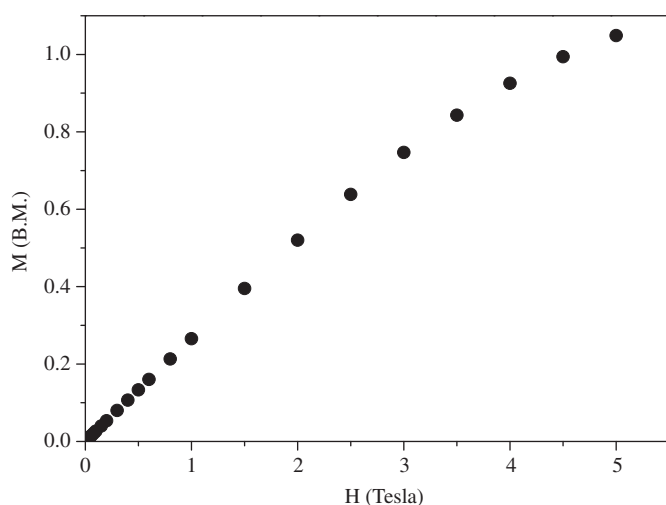


Fig. 11. The variation of the magnetization M versus the magnetic field H for complex **6**.

The variation of the magnetization M versus the magnetic field H for complex **6** has been measured at 2 K and indicates linear relation to ~ 1 T and then continues Brillouin function (Fig. 11). Value of magnetization of 1.04 B.M. at 5 T evidences presence of one unpaired electron in the complex molecule.

Magnetic data of the infinite linear chain of Cu^{2+} centers were analyzed using the 1D-expression [42–44] in the temperature range 1.8–50 K.

$$\chi_{\text{Cu}} = \frac{N\beta^2 g_{\text{av}}^2}{4kT} e^{J/kT}$$

where Hamiltonian with nearest neighbor interactions is equal $H = -2J \sum_n S_n S_{n+1}$, J value characterizes intra-chain interactions, N is the Avogadro's number, T the absolute temperature, β the Bohr magneton, k the Boltzmann's constant and g_{av} average spectroscopic splitting factor. Infinite chain indicate very weak antiferromagnetic interaction of copper centers with $J = -0.64 \text{ cm}^{-1}$, $g = 2.27$ and

$$R = \sqrt{\frac{\sum_{i=1}^n [(\chi_M^{\text{exp}})_i - (\chi_M^{\text{calc}})_i]^2 / (\chi_M^{\text{exp}})_i^2}{\sum_{i=1}^n 1 / (\chi_M^{\text{exp}})_i^2}} = 2.96 \times 10^{-5}$$

was the criterion used to determine the best fit.

4. Conclusions

HgCl_2 moiety accepts chloride ligands from the $\text{Cu}(\text{II})$ center of $\text{Cu}(\text{N}-\text{N})_2\text{Cl}_2$ ($\text{N}-\text{N} = \text{bis}(\text{pyrazol}-1\text{-yl})\text{methane}$ (bpzm), bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm), 2,2-dipyridylamine (dpa), 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) and 2,2'-bipyridine (bipy)) or $\text{Cu}(\text{N}-\text{N}-\text{N})\text{Cl}_2$ ($\text{N}-\text{N}-\text{N} = 2,2':6',2''\text{-terpyridine}$) and generates binuclear or polynuclear complexes.

Increase in structural dimensionality is observed for $[\text{Cu}(\text{bpzm})_2][\text{HgCl}_4]$, $[\text{Cu}(\text{dpa})_2][\text{HgCl}_3]_2$ and $[\text{Cu}(\text{terpy})(\mu\text{-Cl})\text{HgCl}_3]$ compounds. For the last one, the magnetic measurements reveal very weak antiferromagnetic interaction of copper centers of the one-dimensional chain $[\text{Cu}(\text{terpy})\text{HgCl}_4]_n$.

Supplementary data

Supplementary data for $\text{C}_{14}\text{H}_{16}\text{N}_8\text{Cl}_4\text{CuHg}$, $\text{C}_{22}\text{H}_{32}\text{N}_8\text{Cl}_6\text{CuHg}_2$, $\text{C}_{20}\text{H}_{18}\text{N}_6\text{Cl}_6\text{CuHg}_2$, $\text{C}_{40}\text{H}_{40}\text{Cl}_8\text{N}_{12}\text{O}_2\text{Cu}_2\text{Hg}_2$, $\text{C}_{40}\text{H}_{30}\text{N}_8\text{OCl}_4\text{CuHg}$, $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_4\text{CuHg}$ and $\text{C}_{15}\text{H}_{11}\text{N}_3\text{Cl}_4\text{CuHg}$ are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 769819–769825.

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