DOI: 10.1002/ejic.200900819

Assembly of Dinuclear Cu^{II} Rigid Blocks by Bridging Azido or Poly(thiocyanato)chromates: Synthesis, Structures and Magnetic Properties of Coordination Polymers and Polynuclear Complexes

Sergey V. Kolotilov,[a,b] Olivier Cador,[b] Konstantin S. Gavrilenko,[a] Stéphane Golhen,[b] Lahcène Ouahab,*[b] and Vitaly V. Pavlishchuk*[a]

Keywords: Exchange interactions / Copper / Chromium / Coordination polymers / N,O ligands

Reaction of a dinuclear cationic copper(II) complex of 4,4′-[2-(3-hydroxyiminobutyl)imino]biphenyl $[Cu^{II}_2(LH)_2]^{2+}$ with N_3^- resulted in the formation of a dinuclear azido $[Cu^{II}_2(LH)_2(N_3)_2(H_2O)_2]$ complex or a 2D coordination polymer $[Cu^{II}_2(LH)_2(N_3)_2]_n$. Reaction of the dinuclear complex with $[Cr^{III}(NCS)_6]^{3-}$ or $[Cr^{III}(NCS)_4(NH_3)_2]^-$ produced a 2D polymer $\{[Cu^{II}_2(LH)_2(CH_3CN)_2]_3[Cr^{III}(NCS)_6]_2\}_n$ or a 1D chain, constructed from tetranuclear units $\{[Cu^{II}_2(LH)_2][Cr^{III}(NCS)_4(NH_3)_2]_2\}_n$. Structures of the compounds were determined by X-ray crystallography and complexes were characterised by the temperature dependency of the magnetic susceptibility and by ESR spectroscopy. Magnetic properties of homometallic compounds were fit with the model of a dimer with the Hamiltonian $\hat{H} = -J\hat{S}_1{\cdot}\hat{S}_2$. For heterometallic complexes $\chi_M T$ curves were fit as the superposition of magnetism resulting from both $[Cu^{II}_2(LH)_2]^{2+}$ and the adjacent Cr^{III}-containing anion. J values for the complexes lie in the range from –12.74(4) to –17.77(8) cm^{-1}. It was shown that the 4,4′-biphenyl bridge efficiently mediates exchange interactions.

Introduction

Polynuclear complexes in which exchange interactions are transferred over long distances have been attracting attention because such compounds may be considered as the basis for the creation of new magnetic materials.[1] In particular, it was shown that the magnetic behaviour of coordination polymers can be changed by inclusion of diamagnetic "guests",[2] which makes such compounds potential candidates for creating the active bodies of sensors[2d,2e] etc. Some attention has been devoted to the properties of coordination polymers where metal-containing "building blocks" were linked by ligands in which donor groups are connected by long rigid organic fragments.[3] The magnetic properties of such systems depend on several factors. Exchange interactions of paramagnetic centres through long bridging ligands control the magnetic properties of coordination polymers, if such paramagnetic centres are based on mononuclear complexes. In contrast, the magnetic properties of a coordination polymer, which contains exchange-coupled polynuclear complexes with long[3a–3e,4] or short[5] metal-to-metal separations, additionally depend on the exchange interactions within the individual block. The situation may be more complex when paramagnetic compounds (both metal-containing and metal-free) are used as the linkers between metal-containing centres.[2a–2c,2e,6] In such a case the magnetic properties of the polymer depend both on the exchange interaction within the polynuclear "building block" and on exchange interactions between such a block and a paramagnetic linker. It was shown that exchange interactions through many "long" organic bridging molecules, in which donor atoms are separated even by a system of single/double bonds (conjugated in some cases), were negligible or not detectable, for example, for polynuclear systems with bridging 4,4′-bipyridine[7] or aromatic dicarboxylates.[8] However, some bridging units (even with the length comparable with the above-mentioned 4,4-bipyridine) are able to transfer exchange interactions over long distances rather efficiently. Recently, for example, a number of anionic dinuclear copper(II) complexes of the metallacyclophane family, in which metal ions were bridged by polyphenyl units, was reported,[9a] and it was shown that the energy of the exchange interactions (absolute values of J) decreased exponentially with an increase in the number of phenyl rings in the bridge between two Cu^{II} ions. In the case of the bridging biphenyl group, the exchange interactions are transferred through the system of conjugated bonds about 1 nm long. Thus, the studies on long-range exchange interactions are important for the creation of coordination polymers for magnetic materials.

---

[a] L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine,
Prospekt Nauki 31, Kiev, 03028, Ukraine
Fax: +38-044-525-62-16
E-mail shchuk@inphyschem-nas.kiev.ua
[b] Equipe Organométalliques et Matériaux Moléculaires, Sciences Chimiques de Rennes, UMR UR1-CNRS 6226, Université de Rennes 1,
Campus de Beaulieu, 35042 Rennes cedex, France
Fax: +33-2-23236840
E-mail lahcene.ouahab@univ-rennes1.fr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900819.

There are some other examples of complexes containing biphenyl bridges between copper(II) ions,[9b–9f] but only for some compounds from this series were exchange interactions characterised.[9b–9d] In these cases, the biphenyl group mediated the nonzero exchange coupling of Cu^{II} ions, thus, polynuclear complexes possessing this kind of bridge can be considered as candidates for the creation of coordination polymers with long-range magnetic interactions. The factors that influence the efficiency of the exchange interactions through such bridging units have not been completely studied. Such factors may include the coordination environment of the paramagnetic ions and the geometry of bridging units, etc.

In this work we report a study of the molecular and crystal structures and the magnetic properties of a number of polynuclear homo- and heterometallic complexes and coordination polymers based on a dinuclear copper(II) "building block" – a complex with a 1:2 Schiff base from 4,4′-diaminodiphenyl and butanedione monoxime (LH_2, Figure 1). The purpose of this work was to elucidate the influence of the structure of the dinuclear $[Cu_2(LH)_2]^{2+}$ unit (coordination environment of the Cu^{II} ions, the dihedral angles between the phenyl groups within the biphenyl bridge and the orientation of phenyl groups towards the Cu-containing chromophore) on the magnetic properties of the resultant polynuclear complex or coordination polymer. The second aim of this study was to determine whether exchange interactions within dinuclear $[Cu_2(LH)_2]^{2+}$ "building blocks" depend on additional bridges between such blocks.

The Cu^{II} dinuclear complexes with a ligand containing the biphenyl fragment {cation of compound $[Cu_2(LH)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$, hereinafter referred to as compound **1**} was chosen as a starting material for several reasons. Besides the above-mentioned interest in the systems where exchange interactions are transferred through long biphenyl bridging units (separation between paramagnetic centres is about 1.2 nm, vide infra), this complex can bind up to four additional ligands in the axial positions of the Cu^{II} ion (2 ligands per copper ion), which enables its suitability as a possible "building block" for the creation of coordination polymers and polynuclear complexes.[9f] Hence, the third aim of this study was to develop the method of preparation for coordination polymers from dinuclear complexes with "rigid" structures and to study the influence of the nature of the bridging units on the structure, topology and magnetic properties of the resultant polymeric network.

Interaction of $[Cu_2(LH)_2(H_2O)_2]^{2+}$ with azide resulted in the formation of the dinuclear complex $[Cu_2(LH)_2(H_2O)_2(N_3)_2]$ (**2**) and the 2D polymer $[Cu_2(LH)_2(N_3)_2]_n$ (**3**). Reaction of the same starting cation with thiocyanatochromates ($[Cr(NCS)_6]^{3-}$ or $[Cr(NCS)_4(NH_3)_2]^-$) led to the 2D polymer $\{[Cu_2(LH)_2(CH_3CN)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O\}_n$ (**4**) or the 1D chain formally consisting of tetranuclear units $\{[Cu_2(LH)_2][Cr(NCS)_4(NH_3)_2]_2\cdot 2H_2O\cdot CH_3OH\}_n$ (**5**), respectively. In both compounds **4** and **5**, the NCS^- group acts as a bridge unit between the Cu^{II} and Cr^{III} ions, which leads to rather long (about 3 Å, vide infra) Cu–S bonds (here, the S atom belongs to the NCS^- group).

Chromium(III) complexes were chosen as linking blocks because of their kinetic inertness and the versatility of the thiocyanatochromate charges in similar Cr^{III} coordination spheres ($[Cr(NCS)_6]^{3-}$ with charge –3 and $[Cr(NCS)_4(NH_3)_2]^-$ with charge –1), which allows the proposal of some conclusions regarding the influence of the bridging thiocyanatochromate charge on the structure of obtained compounds as well as the investigation of whether the exchange interactions between the Cu^{II} and Cr^{III} ions may be transferred through the NCS^- bridging group.

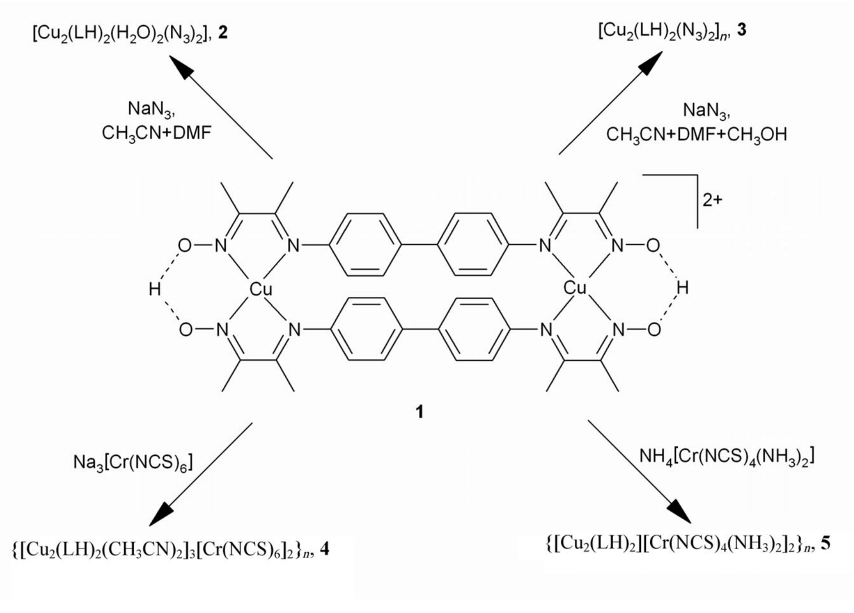

Figure 1. Synthesis of the complexes.

Results and Discussion

Synthesis

The approach employed for preparation of compounds **2**–**5** was based on the utilisation of the dinuclear cation of **1** as a "building block" (Figure 1). The cation of **1**, namely $[Cu_2(LH)_2(H_2O)_2]^{2+}$, contains two Cu^{II} ions in square-pyramidal N_4O donor sets (four N atoms in the equatorial plane and coordinated water molecules in the axial positions, as shown by X-ray structure determination, vide infra). Coordination of two azido anions to the Cu^{II} ions (one N_3^- to each Cu) associated with increase in the coordination number of Cu^{II} from 5 to 6 resulted in the formation of dinuclear compound **2**. If the reaction conditions were changed (vide infra), the azide group could be introduced as a bridging ligand and it could link two copper(II) ions from the "dehydrated" dinuclear "building blocks" $[Cu_2(LH)_2]^{2+}$ to give the 2D polymer **3**. In this compound, all copper(II) ions are located in N_6 donor sets. The result of interaction of **1** with azide – formation of dinuclear complex **2** or polymer **3** – depends on the solvent composition of the reaction mixture: reaction in a DMF/acetonitrile mixture gives **2**, but reaction in a mixture of DMF, acetonitrile and methanol results in precipitation of **3**. It seems that the different solubility of the compounds is the main "driving force" that determines the results of the reaction of **1** with azide.

Dinuclear **1** was linked by two types of Cr^{III} thiocyanato complexes. The reaction of **1** with $[Cr(NCS)_6]^{3-}$ produced the coordination polymer **4**, in which one $[Cr(NCS)_6]^{3-}$ anion forms bonds with three dinuclear cations of **1** (vide infra). Compound **4** contains dinuclear dicopper blocks $[Cu_2(LH)_2(CH_3CN)_2]^{2+}$ with CH_3CN solvent molecules coordinated to the Cu^{II} ions.

Interaction of the same dinuclear cation of **1** with $[Cr(NCS)_4(NH_3)_2]^-$ produced the 1D polymer **5**, which can be formally considered as a chain consisting of tetranuclear units, $\{[Cu_2(LH)_2][Cr(NCS)_4(NH_3)_2]_2\}$. In this compound, two NCS^- groups of each $[Cr(NCS)_4(NH_3)_2]^-$ anion are coordinated to two copper(II) ions from two different $[Cu_2(LH)_2]^{2+}$ units to form one typical and one rather long Cu–S bond (about 2.7 and 3 Å, respectively, vide infra). As in the case of complexes with azido ligands (**2** and **3**), different solvents were used for the synthesis of **4** and **5** (because of the different solubility of **4** and **5**). However, it may be assumed that, in this case, the compositions and the structures of the products (**4** and **5**) mainly depend not on the composition of the solvent mixture but on the difference between the charges of $[Cr(NCS)_6]^{3-}$ and $[Cr(NCS)_4(NH_3)_2]^-$.

Notably, dinuclear complex **1** was prepared in a one-pot synthesis without intermediate isolation of the Schiff base LH_2, which is in contrast to the reported procedure for the preparation of similar compounds with the same ligand, namely $[Cu_2L_2{\cdot}4H_2O]{\cdot}2H_2O$.[9e]

X-ray Structures

Complex 1

In compound **1**, two Cu^{II} ions are linked by two anionic LH^- ligands to form the dimeric dinuclear centrosymmetric cation $[Cu_2(LH)_2(H_2O)_2]^{2+}$ (Figure 2). The positive charge of $[Cu_2(LH)_2(H_2O)_2]^{2+}$ is compensated for by two uncoordinated perchlorate anions. The Cu^{II} ions are located in square-pyramidal N_4O donor sets [$\tau = 0.03$[10]], while the basal positions are occupied by two nitrogen atoms from the azomethine groups and two nitrogen atoms from the oxime groups. One water molecule is coordinated to Cu^{II} in the axial position. The Cu–N and Cu–O bond lengths in **1** are typical for Cu^{II} complexes with nitrogen and oxygen donors (Table 1).[11] Two Cu^{II} ions are linked by rigid biphenyl fragments [Cu1···Cu1 distance 12.317(1) Å]. One oxime group in each molecule of Schiff base is deprotonated and a hydrogen atom links O1 and O2 to forming a pseudomacrocycle, which is typical for complexes with oximes.[12] The oxygen atom O1 of the oxime group is located over the Cu1 ion of a neighbouring dinuclear cation [O1′···Cu1 3.447(4) Å] almost in one line with coordinated O(3) [O1′–Cu1–O3 angle 170.4(1)°]. The distance from Cu1 to O1′ [3.447(5) Å] is too long to represent covalent bonding between these atoms, but the location of the oxygen atom in such proximity to Cu^{II} may be a sign of the tendency of Cu^{II} to increase its coordination sphere to six in **1** as in all other complexes presented in this paper, vide infra. The intermolecular Cu1···Cu1′ separation [4.499(1) Å] is much smaller than the intramolecular one [12.317(1) Å].

There is one uncoordinated H_2O molecule in the crystal per dinuclear cation, which forms an H-bond with an H_2O molecule in the coordination sphere of Cu^{II} [distance O3···O1w 2.733(2) Å].

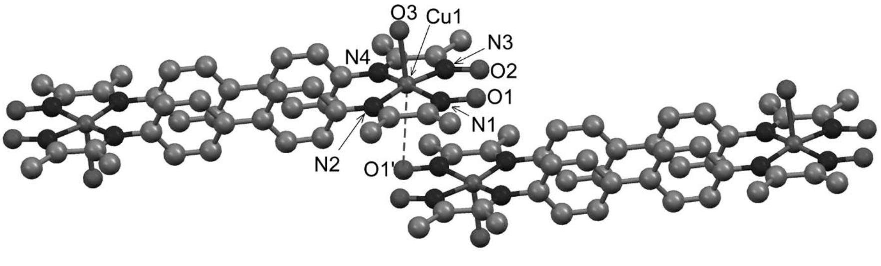

Figure 2. Cation of **1**. Hydrogen atoms, perchlorato anions and uncoordinated water molecules are omitted for clarity. Symmetry equivalent position are the following: *x*, *y*, *z*; –*x*, *y*, –*z* + ½; *x* + ½, *y* + ½, *z*; –*x* + ½, *y* + ½, –*z* + ½; –*x*, –*y*, –*z*; *x*, –*y*, *z* – ½; –*x* + ½, –*y* + ½, –*z*; *x* + ½, –*y* + ½, *z* – ½.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**–**5**.

1			
Cu1–N1	1.987(4)	Cu1–N4	2.040(4)
Cu1–N3	1.996(4)	Cu1–O3	2.264(4)
Cu1–N2	2.034(4)		
N1–Cu1–N3	93.01(17)	N2–Cu1–N4	108.73(15)
N1–Cu1–N2	78.48(16)	N1–Cu1–O3	94.95(18)
N3–Cu1–N2	169.96(16)	N3–Cu1–O3	94.62(17)
N1–Cu1–N4	168.16(18)	N2–Cu1–O3	91.44(16)
N3–Cu1–N4	78.83(16)	N4–Cu1–O3	94.25(17)
2			
Cu1–N4	1.982(4)	Cu1–N5	2.062(4)
Cu1–N6	2.005(4)	Cu1–N1	2.386(5)
Cu1–N7	2.040(4)	Cu1–O3	2.565(5)
N4–Cu1–N6	92.66(17)	N7–Cu1–N1	87.44(19)
N4–Cu1–N7	171.44(17)	N5–Cu1–N1	85.99(17)
N6–Cu1–N7	79.14(16)	N4–Cu1–O3	86.11(15)
N4–Cu1–N5	78.56(17)	N6–Cu1–O3	100.79(15)
N6–Cu1–N5	170.63(17)	N7–Cu1–O3	92.96(15)
N7–Cu1–N5	109.76(16)	N5–Cu1–O3	82.05(15)
N4–Cu1–N1	95.3(2)	N1–Cu1–O3	167.43(15)
N6–Cu1–N1	91.63(17)		
3			
Cu1–N1	1.976(3)	Cu1–N5	2.549(3)
Cu1–N2	2.038(3)		
N1–Cu1–N2	79.22(13)	N2–Cu1–N2′	108.88(17)
N1–Cu1–N1′	92.7(2)	Cu1–N5–Cu1′	147.3(13)
N1–Cu1–N2′	171.88(13)		
4			
Cu1–N1	1.996(4)	Cu1–N5	2.488(3)
Cu1–N2	2.045(3)	Cu1–S1	2.878(3)
Cu1–N3	1.981(4)	Cr1–N6	2.021(5)
Cu1–N4	2.036(3)	Cr1–N7	1.996(5)
N7–Cr1–N7′	91.5(2)	N3–Cu1–N4	79.32(15)
N7–Cr1–N6	92.9(2)	N1–Cu1–N4	171.88(14)
N7–Cr1–N6′	87.6(2)	N3–Cu1–N2	171.28(14)
N7–Cr1–N6	175.5(2)	N1–Cu1–N2	78.83(14)
N6–Cr1–N6′	88.1(2)	N4–Cu1–N2	108.79(14)
N3–Cu1–N1	92.93(16)	S1–Cu1–N5	172.57(14)
5			
Cu1–N1	1.982(5)	Cr1–N12	1.971(6)
Cu1–N5	1.992(5)	Cr1–N10	1.982(6)
Cu1–N6	2.020(5)	Cr1–N11	1.988(6)
Cu1–N2	2.036(5)	Cr1–N9	1.999(6)
Cu1–S1	2.655(2)	Cr1–N13	2.057(6)
Cu1–S4′	3.072(3)	Cr1–N14	2.080(6)
Cu2–N8	1.966(5)	Cr2–N15	1.976(7)
Cu2–N4	2.001(5)	Cr2–N18	1.978(6)
Cu2–N7	2.049(5)	Cr2–N17	1.996(7)
Cu2–N3	2.052(5)	Cr2–N16	1.997(6)
Cu2–S6	2.705(2)	Cr2–N20	2.054(6)
Cu2–S7′	3.029(3)	Cr2–N19	2.075(6)
N1–Cu1–N5	92.7(2)	N11–Cr1–N9	178.2(3)
N1–Cu1–N6	167.5(2)	N12–Cr1–N13	89.7(3)
N5–Cu1–N6	78.8(2)	N10–Cr1–N13	89.2(3)
N1–Cu1–N2	78.6(2)	N11–Cr1–N13	89.7(2)
N5–Cu1–N2	164.5(2)	N9–Cr1–N13	92.0(2)
N6–Cu1–N2	107.42(19)	N12–Cr1–N14	90.5(3)
N1–Cu1–S1	96.81(15)	N10–Cr1–N14	90.7(3)
N5–Cu1–S1	99.54(16)	N11–Cr1–N14	88.4(2)
N6–Cu1–S1	93.65(16)	N9–Cr1–N14	89.9(2)
N2–Cu1–S1	94.24(15)	N13–Cr1–N14	178.1(2)
N8–Cu2–N4	92.9(2)	N15–Cr2–N18	90.1(3)
N8–Cu2–N7	79.0(2)	N15–Cr2–N17	176.2(3)
N4–Cu2–N7	169.7(2)	N18–Cr2–N17	91.0(2)
N8–Cu2–N3	170.4(2)	N15–Cr2–N16	88.3(3)
N4–Cu2–N3	78.5(2)	N18–Cr2–N16	176.9(3)
N7–Cu2–N3	109.00(19)	N17–Cr2–N16	90.8(2)
N8–Cu2–S6	98.34(16)	N15–Cr2–N20	91.6(3)
N4–Cu2–S6	96.11(16)	N18–Cr2–N20	89.4(2)
N7–Cu2–S6	91.40(15)	N17–Cr2–N20	92.0(3)
N3–Cu2–S6	87.03(14)	N16–Cr2–N20	88.0(2)
N12–Cr1–N10	176.0(3)	N15–Cr2–N19	89.2(3)
N12–Cr1–N11	90.5(2)	N18–Cr2–N19	91.6(3)
N10–Cr1–N11	93.4(3)	N17–Cr2–N19	87.2(2)
N12–Cr1–N9	88.9(2)	N16–Cr2–N19	91.0(2)
N10–Cr1–N9	87.3(3)	N20–Cr2–N19	178.7(3)

An X-ray structure determination confirms that the cation of **1** may be considered as a promising "building block" for the assembly of coordination polymers because of the availability of two Cu^{II} centres capable of coordinating additional donors (in the free axial position and/or by substitution of coordinated water molecules).

Complex 2

This compound contains centrosymmetric molecules of $[Cu_2(LH)_2(H_2O)_2(N_3)_2]$, the structure of which is generally similar to that of **1**. The main difference is that Cu^{II} ions in **2** are hexacoordinate, and the sixth position in the coordination sphere of each Cu^{II} is occupied by an azido ion. Thus, the charge of each molecule of **2** is zero, and there are no counterions in the cell. The coordination polyhedra of Cu^{II} in **2** can be represented as distorted octahedra instead of square pyramids as in **1** (Figure 3). There is significant Jahn–Teller distortion of the Cu1 chromophores in **2**: the bonds between Cu1 and the axial N1 of the azido ligand [2.39 Å] and O3 of the coordinated water [2.57 Å] are significantly longer than other Cu–N bonds [average length of Cu–N bonds in the basal plane is 2.02 Å; exact bond lengths involving metal ions and deviations are presented in Table 1]. The intramolecular Cu1···Cu1 separation in **2** [12.297(1) Å] is almost the same as in **1**, whereas the closest intermolecular Cu1···Cu1′ contacts are 6.470(1) Å (along the *a* axis) and 7.278(1) Å (in the *bc* plane).

In the crystal, there are H bonds between neighbouring neutral molecules of **2**, involving an H_2O molecule in the coordination sphere of Cu^{II} and an N atom of an azido group from another molecule of **2** [distance N1···O3 is 2.659(7) Å].

Complex 3

Compound **3** may be formally considered as a polymer built from centrosymmetric fragments of $[Cu_2(LH)_2(N_3)_2]$ in which the azido ions act as bridges between the copper(II) cations from the dinuclear $[Cu_2(LH)_2]^{2+}$ units. The asymmetric unit of **3** contains one Cu^{II} ion, one half of L^{2-} and one azido group (Figure 4, asymmetric non-carbon and non-hydrogen atoms are labelled). Each Cu^{II} ion is located in an axially distorted octahedral N_6 donor set, in which N atoms in the plane are the atoms of the imino and oximato groups of LH^- and the axial positions are occupied by μ-N_3^- ions. The average Cu–N$_{plane}$ distance [2.01 Å] is significantly shorter than the Cu–N$_{azido}$ bond [2.549(3) Å], which is evidence for Jahn–Teller distortion of the Cu^{II} chromophores in **3**, similar to compound **2** (Table 1).

Each $[Cu_2(LH)_2]^{2+}$ unit is linked to four other $[Cu_2(LH)_2]^{2+}$ units by four μ-N_3^- ions. Such polymerisation through μ-N_3^- ions leads to the formation of 2D layers (Figures S1 and S2, Supporting Information). The Cu···Cu separation through the azido group is 4.892(1) Å, the Cu–N–Cu′ angle is 147.3(2)° and the Cu···Cu separation through the biphenyl groups is 12.289(1) Å (similar to **1** and **3**).

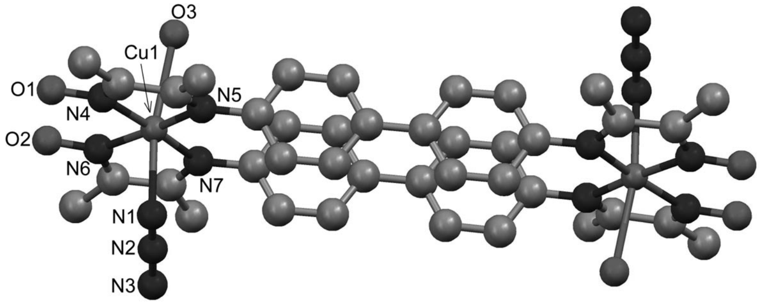

Figure 3. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Symmetry equivalent position are the following: $x, y, z; -x, y + \frac{1}{2}, -z + \frac{1}{2}; -x, -y, -z; x, -y - \frac{1}{2}, z - \frac{1}{2}$.

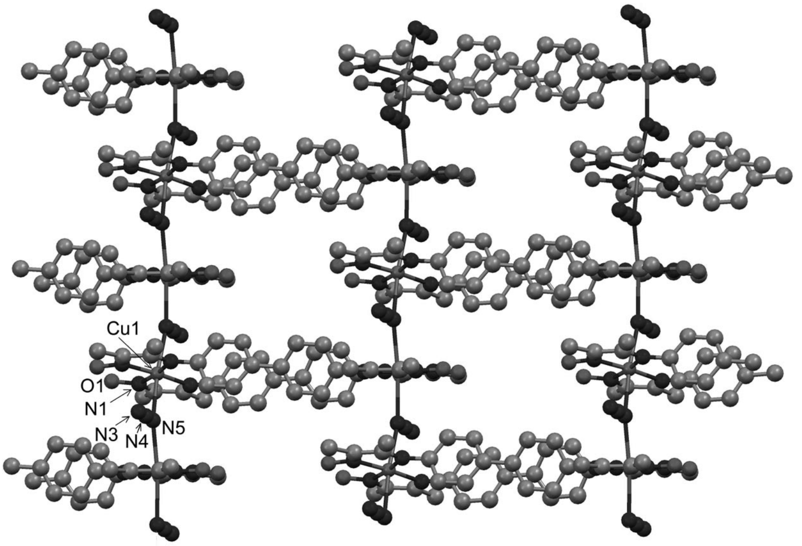

Figure 4. Fragment of the 2D layer of **3**. Hydrogen atoms are omitted for clarity. Symmetry equivalent position are the following: $x, y, z; -x + \frac{1}{4}, -y + \frac{1}{4}, z; x, -y + \frac{1}{4}, -z + \frac{1}{4}; -x + \frac{1}{4}, y, -z + \frac{1}{4}; x, y + \frac{1}{2}, z + \frac{1}{2}; -x + \frac{1}{4}, -y + \frac{3}{4}, z + \frac{1}{2}; x, -y + \frac{3}{4}, -z + \frac{3}{4}; -x + \frac{1}{4}, y + \frac{1}{2}, -z + \frac{3}{4}; x + \frac{1}{2}, y, z + \frac{1}{2}; -x + \frac{3}{4}, -y + \frac{1}{4}, z + \frac{1}{2}; x + \frac{1}{2}, -y + \frac{1}{4}, -z + \frac{3}{4}; -x + \frac{3}{4}, y, -z + \frac{3}{4}; x + \frac{1}{2}, y + \frac{1}{2}, z; -x + \frac{3}{4}, -y + \frac{3}{4}, z; x + \frac{1}{2}, -y + \frac{3}{4}, -z + \frac{1}{4}; -x + \frac{3}{4}, y + \frac{1}{2}, -z + \frac{1}{4}; -x, -y, -z; x - \frac{1}{4}, y - \frac{1}{4}, -z; -x, y - \frac{1}{4}, z - \frac{1}{4}; x - \frac{1}{4}, -y, z - \frac{1}{4}; -x, -y + \frac{1}{2}, -z + \frac{1}{2}; x - \frac{1}{4}, y + \frac{1}{4}, -z + \frac{1}{2}; -x, y + \frac{1}{4}, z + \frac{1}{4}; x - \frac{1}{4}, -y + \frac{1}{2}, z + \frac{1}{4}; -x + \frac{1}{2}, -y, -z + \frac{1}{2}; x + \frac{1}{4}, y - \frac{1}{4}, -z + \frac{1}{2}; -x + \frac{1}{2}, y - \frac{1}{4}, z + \frac{1}{4}; x + \frac{1}{4}, -y, z + \frac{1}{4}; -x + \frac{1}{2}, -y + \frac{1}{2}, -z; x + \frac{1}{4}, y + \frac{1}{4}, -z; -x + \frac{1}{2}, y + \frac{1}{4}, z - \frac{1}{4}; x + \frac{1}{4}, -y + \frac{1}{2}, z - \frac{1}{4}$.

There are approximate square cavities (about 5 Å in dimension) between the biphenyl groups of neighbouring dinuclear units (Figure 4). In the crystal, neighbouring 2D layers of **3** are "shifted" along the *a* axis on *a*/2 (or maybe similarly considered to be "shifted" along the *b* axis on *b*/2). Thus, the cavities of adjacent layers are not located one over another, and no channel is observed. However, the total volume of accessible voids in **4**, calculated with the PLATON software[13] for a probe molecule with a radius of 1.4 Å (like H_2) is 9.4%.

Complex 4

This compound is built from $[Cu_2(LH)_2(CH_3CN)_2]^{2+}$ cations linked by $[Cr(NCS)_6]^{3-}$ anions, which are coordinated to copper(II) ions through S atoms of the NCS^- groups. The NCS^- groups act as bridges between the Cr^{III} and Cu^{II} ions. Each $[Cr(NCS)_6]^{3-}$ unit is bonded to three Cu^{II} ions of three $[Cu_2(LH)_2(CH_3CN)_2]^{2+}$ moieties, and each $[Cu_2(LH)_2(CH_3CN)_2]^{2+}$ block in turn is bonded by two $[Cr(NCS)_6]^{3-}$ anions (Figure 5). Coordinated CH_3CN molecules were captured from the reaction mixture (acetonitrile was a component of the solvents mixture). The ratio of $[Cr(NCS)_6]^{3-}$ to $[Cu_2(LH)_2]^{2+}$ corresponds to the charge balance between anionic and cationic units (two anions with charge –3 are counterbalanced by three cations with charge +2, which results in the formation of a neutral net).

The structure of the $[Cu_2(LH)_2]^{2+}$ unit in **4** is similar to the structures of such dinuclear units in **2** and **3**. The $[Cu_2(LH)_2(CH_3CN)_2(SCN)_2]$ fragment is centrosymmetric, and the coordination polyhedron of each Cu^{II} may be represented by axially distorted octahedra. Four nitrogen atoms of imino and oximato groups of LH^- are located in the plane [average Cu–N_{plane} distance is 2.02 Å], and one axial position of each Cu^{II} is occupied by a nitrogen atom of acetonitrile [Cu–N 2.488(3) Å] and the other by a sulfur atom from an NCS^- group [Cu–S 2.878(3) Å] (Table 1). The Cu–S bond in **4** is significantly longer than the Cu–N bond, but it is quite typical for a bond between Cu^{II} and an S atom in the axial position. Cu–S bond lengths, reported for

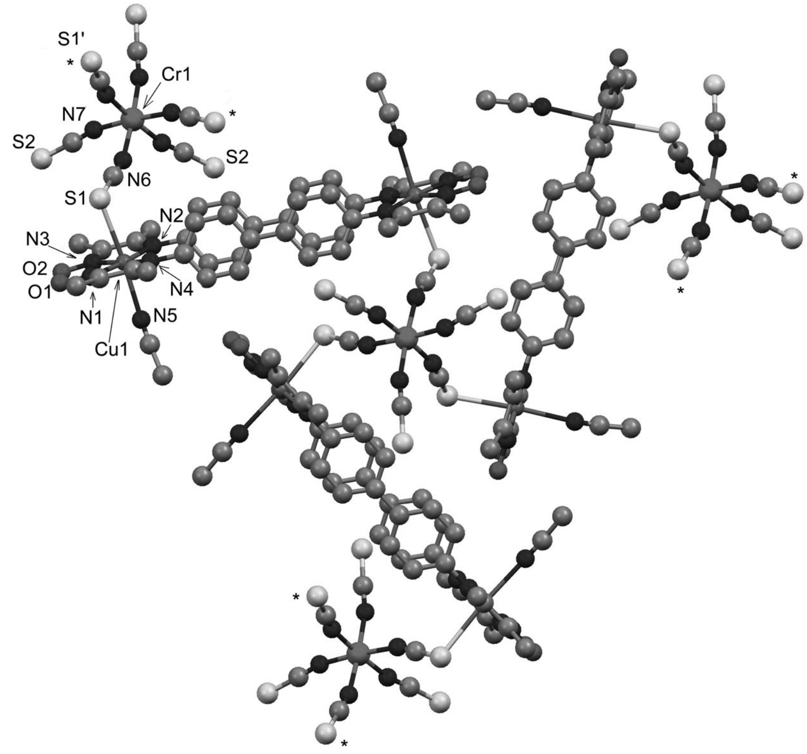

Figure 5. Fragment of the 2D layer of **4**, * indicates the S atoms that are coordinated to the Cu^{II} ions. Hydrogen atoms are omitted for clarity. Symmetry equivalent position are the following: x, y, z; $-y, x - y, z$; $-x + y, -x, z$; $x + {}^{2}/_{3}, y + {}^{1}/_{3}, z + {}^{1}/_{3}$; $-y + {}^{2}/_{3}, x - y + {}^{1}/_{3}, z + {}^{1}/_{3}$; $-x + y + {}^{2}/_{3}, -x + {}^{1}/_{3}, z + {}^{1}/_{3}$; $x + {}^{1}/_{3}, y + {}^{2}/_{3}, z + {}^{2}/_{3}$; $-y + {}^{1}/_{3}, x - y + {}^{2}/_{3}, z + {}^{2}/_{3}$; $-x + y + {}^{1}/_{3}, -x + {}^{2}/_{3}, z + {}^{2}/_{3}$; $-x, -y, -z$; $y, -x + y, -z$; $x - y, x, -z$; $-x + {}^{2}/_{3}, -y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; $y + {}^{2}/_{3}, -x + y + {}^{1}/_{3}, -z + {}^{1}/_{3}$; $x - y + {}^{2}/_{3}, x + {}^{1}/_{3}, -z + {}^{1}/_{3}$; $-x + {}^{1}/_{3}, -y + {}^{2}/_{3}, -z + {}^{2}/_{3}$; $y + {}^{1}/_{3}, -x + y + {}^{2}/_{3}, -z + {}^{2}/_{3}$; $x - y + {}^{1}/_{3}, x + {}^{2}/_{3}, -z + {}^{2}/_{3}$.

Cu^{II} complexes with NCS^- groups, vary in the range from 2.412 Å to 3.286 Å, as was highlighted in the review of Kabešová et al.[14a] In several compounds reported later, Cu–S bonds (where S is the atom of the NCS^- group) were found to be longer than 3 Å[14b] or 2.808(13) Å (in this case, the NCS^- group was called "semi-coordinated"; however, the authors indicated that such NCS^- groups mediated nonzero exchange interactions).[14c] The Cu–S bond in the first example of a copper(II) complex with Reinecke's anion, $[(HL)Cu(SCN)Cr(NCS)_3(NH_3)_2]$ [H_2L = 3,3-trimethylenedinitrilobis(2-butanoneoxime)], was found to be 2.643(1) Å.[14d] Similar Cu–S bonds were reported for some other Cu^{II} complexes with thiocyanatochromates.[14e]

Each Cr^{III} ion in compound **4** is located in an octahedral N_6 donor set with approximately equal Cr–N bonds [2.021(5) and 1.996(5) Å]. The NCS^- groups are almost linear, and the angle between the Cu–S bond and the NCS^- group in compound **4** is 103.1(1)°, while the angle between the Cr–N bond and the NCS^- anion is significantly higher [158.8(1)°].

Complex **4** possesses a layered structure; each layer contains "honeycomb" cavities with local C_6 symmetry (Figure S3, Supporting Information). Similarly to the structure of **3**, neighbouring layers of **4** are shifted in the *ab* plane, and, instead of channels, there are cavities of dimensions of about $15 \times 10 \times 10$ Å in the structure (Figure S3). These cavities are "capped" by $[Cr(NCS)_6]^{3-}$ units, and their "walls" are constructed from asymmetric halves of $[Cu_2(LH)_2]^{2+}$ blocks. CH_3CN molecules, coordinated to Cu^{II} ions, are directed towards the internal part of the cavity (Figure S3). In addition, there are nonbonded H_2O molecules in the cavities.

The closest Cu···Cr distance in one layer (through the NCS^- group) is 6.370(1) Å, whereas the Cu···Cu separation through the biphenyl bridge is 12.331(1) Å. The total volume of accessible voids in **4**, calculated as above,[13] is 20.2% for a compound containing no acetonitrile molecules coordinated to the Cu^{II} ions (assuming that the cell volume does not change upon CH_3CN removal) or 10.5% for a compound with coordinated CH_3CN.

Complex 5

Compound **5** may be considered as a 1D chain formed from tetranuclear neutral $\{[Cu_2(LH)_2][Cr(NCS)_4(NH_3)_2]_2\}$ units. Dinuclear $[Cu_2(LH)_2]^{2+}$ cations are linked by $[Cr(NCS)_4(NH_3)_2]^-$ anions, and the NCS^- groups act as bridges between the Cu^{II} and Cr^{III} atoms. Two neighbouring $[Cu_2(LH)_2]^{2+}$ cations are bridged by two $[Cr(NCS)_4(NH_3)_2]^-$ groups.

In a contrast to the dinuclear $[Cu_2(LH)_2]^{2+}$ units in **1**–**4**, such a unit in compound **5** is not centrosymmetric. The coordination sphere of each Cu^{II} may be represented as a distorted octahedron in which the equatorial positions are occupied by four nitrogen atoms from the imine and oxime groups [Cu–N bonds are 2.01 Å on average] and the axial

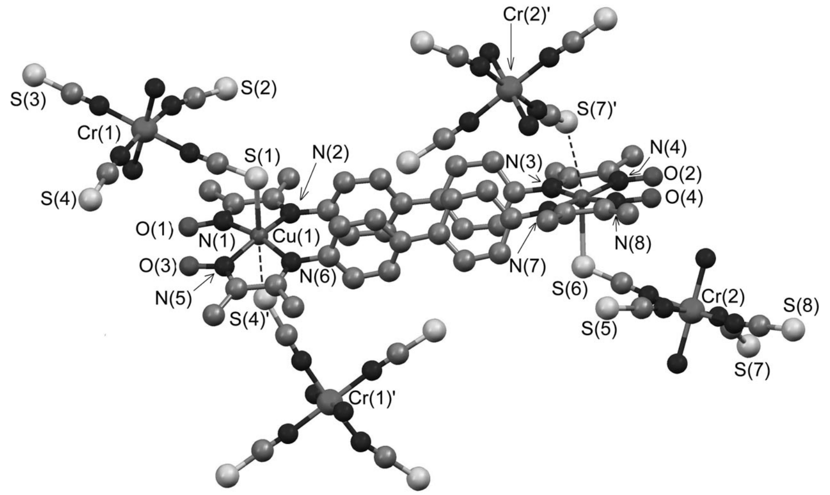

Figure 6. Fragment of the polymeric chain of **5**. Hydrogen atoms and uncoordinated water molecules are omitted for clarity. Symmetry equivalent position are the following: *x*, *y*, *z*; –*x*, *y* + ½, –*z* + ½; –*x*, –*y*, –*z*; *x*, –*y* – ½, *z* – ½.

positions are occupied by sulfur atoms from the NCS^- groups. The coordination sphere of each Cu^{II} ion contains two S atoms (from the NCS^- groups), but there is a significant difference in the Cu^{II}–S bond lengths. In the coordination sphere of each copper(II) ion, one S atom is located much closer to Cu^{II} [Cu–S bonds 2.655(2) and 2.705(2) Å] than the second S atom [Cu–S bonds 3.072(3) and 3.029(3) Å] (Figure 6, Table 1).

The average angle between "short" Cu–S bonds [2.7 Å] and linear NCS^- groups is 103.8° (the same as in **4**; however, two such angles in **5** are not equal, and the difference between them is about 10°). The Cr^{III} ions are located in tetragonally distorted chromophores, and the amino groups of $[Cr(NCS)_4(NH_3)_2]^-$ occupy *trans* positions in the coordination polyhedra. Intramolecular Cu···Cr distances are 5.995(1) and 5.905(1) Å, whereas the Cu···Cu separation through the biphenyl bridge is 12.268(1) Å. The S–Cu–S′ angles are 169.2(7)° and 174.3(7)°.

Compound **5** contains 3.3 solvate H_2O molecules per Cu_2Cr_2 formula unit. One of the H_2O molecules fills its position with an occupancy factor of 0.3 and probably forms an H bond with the NCS^- group [distance O1w···S5 is 2.231(20) Å]. One H_2O fills its position with an occupancy factor of 1, whereas two H_2O molecules are disordered over 4 positions with occupancy factors of 0.7, 0.3, 0.7 and 0.3. Notably, CHN analysis of the bulk sample is consistent with the presence of CH_3OH, and it may be assumed that disordered solvent atoms may correspond to disordered methanol (which in no way changes the positions of nonsolvent atoms).

ESR Spectroscopy of the Complexes

ESR spectra were measured for the homometallic complexes **1**–**3** at room temperature in the solid state. Compound **1** gives a spectrum containing one line centred at $g = 2.092$. In the case of **2**, two lines could be distinguished, which correspond to $g_\perp = 2.064$ and $g_\parallel = 2.209$ ($g_{av.} = 2.112$). The ESR spectrum of complex **3** shows a broad line, which may correspond to a $g_\parallel$ value of about 2.15–2.18, and a sharp line corresponding to $g_\perp = 2.064$.

These values are consistent with the *g* value found for the similar copper(II) complex $[Cu_2L_2]\cdot 6H_2O$, where L is the same ligand as in **1**–**3**, i.e. 4,4′-(2-(3-hydroxyiminobutyl)imino)biphenyl ($g_\perp = 2.05$, $g_\parallel = 2.31$),[9e] and fall in the range typical for Cu^{2+} complexes with N donor ligands.[15]

Magnetic Properties of the Complexes

Magnetic properties of complexes **1**–**5** were characterised by the temperature dependence of the molar magnetic susceptibility, χ_M, in the range from 2 to 300 K. For all complexes, $\chi_M T$ decreases on lowering the temperature, which implies that the dominating interactions in all compounds are antiferromagnetic. For the homometallic complexes **1**–**3**, it may be clearly concluded that they possess a diamagnetic ground state.

Complex 1

At 300 K, $\chi_M T$ for **1** is 0.74 $cm^3\,K\,mol^{-1}$, which is close to the spin-only value expected for two noninteracting Cu^{II} ions with $g = 2$ (0.75 $cm^3\,K\,mol^{-1}$). The $\chi_M T$ vs. T curve for **1** was fitted with the use of the Heisenberg Hamiltonian for two spins [Equation (1)]:[16]

$$\hat{H} = -J\hat{S}_1\cdot\hat{S}_2 \tag{1}$$

The thermal variation of $\chi_M T$ can then be expressed as follows [Equation (2)]:

$$\chi_M T = (1-x)\frac{2Ng^2\beta^2}{k}\frac{\exp\left(\frac{J}{kT}\right)}{1+3\exp\left(\frac{J}{kT}\right)} + x\frac{Ng_{imp.}{}^2\beta^2}{3k}s(s+1) \tag{2}$$

where *J* is the superexchange interaction parameter and the other parameters have their usual meanings. The parameter *x* is the content of paramagnetic $S = ½$ impurities and $g_{imp.}$

Table 2. Structural and magnetochemical parameters of dinuclear Cu^{II} complexes containing a bridging group with the biphenyl unit (J recalculated for the Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$).

Complex[a]	d(Cu–Cu)[b] [Å]	α[c] [°]	β [°]	J [cm^{-1}]	g	Ref.
1	12.317(1)	77.4	2.1	–13.44(6)	2.022(1)	this work
2	12.297(1)	87.4	2.8	–12.74(4)	2.022(1)	this work
3	12.289(1)	75.0	30.2	–17.77(8)	2 (fixed)	this work
4	12.331(1)	72.0	2.9	–15.8(2)	g_{Cu} = 2.1 (fixed) g_{Cr} = 1.94(6)	this work
5	12.268(1)	80.5	35.6	–12.8(2)	g_{Cu} = 2.1 (fixed) g_{Cr} = 1.9314(5)	this work
$Na_4[Cu_2(bpba)_2]$	12.19	60.7	19.7	–9.5	2.11	[9a]
$[Cu_2(tren)_2(BZD)](NO_3)_4$	12.172(4)[d]	–	18.4[d]	–6.4	2.030, 2.124, 2.191[e]	[9b]
$[Cu_2(tren)_2(BZD)](ClO_4)_4$				–6.0		[9b]
$[Cu_2(tren)_2(BZD)](PF_6)_4$				–5.2		[9b]
$[Cu_2Cu^{I}L'_2(HL')]$	11.5	–	20.5	+11.9	2.17	[9d]

[a] bpba = *N*,*N*′-4,4′-biphenylenebis(oxamate), tren = bis(2,2′,2′′-triaminotriethylamine), BZD = 4,4′-diaminobiphenyl, H_2L' = bis(*N*-salicylidene-4,4′-diphenylamine). [b] Intramolecular separation through the biphenyl bridge. [c] α is the average angle between the N_4 plane and the plane of adjacent phenyl ring, β is the average angle (if two angles are different) between the two phenyl rings in the biphenyl bridge. [d] Average value for two crystallographically independent molecules. [e] Calculated from ESR spectroscopy.

is taken to be equal to g observed in the ESR spectrum. The quantity of impurities could be estimated from $\chi_M T$ at 2 K, and for **1**, such an estimation gave $x = 0.054$ (or 5.4 %). This value of x was fixed, and the best fit was obtained with $J = -13.44(6)\ cm^{-1}$, $g = 2.022(1)$ and $R^2 = 1.2 \times 10^{-4}$ [hereinafter $R^2 = \Sigma(\chi T_{calcd.} - \chi T_{obs.})^2 / \Sigma(\chi T_{obs.})^2$, Figure 7]. The g value for complex **1** is quite consistent with the result of the ESR measurements ($g = 2.092$). Though the data were fitted as $\chi_M T$ vs. T, fitting of the χ_M vs. T curve gives the same parameters (Supporting Information, Figures S4–S6).

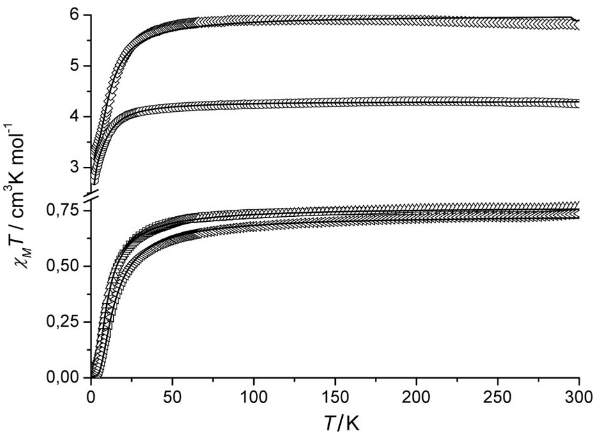

Figure 7. Experimental magnetic susceptibilities and calculated curves for complexes **2** (open triangle), **3** (open sideways triangle), **4** (open diamond) and **5** (open circle). The curves for compounds **1** and **2** almost coincide.

The value of J for compound **1** is rather high (in absolute terms) despite the large Cu···Cu separation (Table 2) which suggests that the biphenyl group efficiently transmits a superexchange interaction.

Complex 2

At high temperature (300 K), $\chi_M T$ for **2** is $0.77\ cm^3 K mol^{-1}$, which is close to the spin-only value expected for two noninteracting Cu^{II} ions with $g = 2$. The $\chi_M T$ curve was fitted by using exactly the same approach as in the case of compound **1**. The ratio of impurities, x, was estimated to be 0.0215 (2.15 %). The best fit was obtained with $J = -12.74(4)\ cm^{-1}$, $g = 2.022(1)$ and $R^2 = 5.8 \times 10^{-5}$ (Figure 7). The g value, obtained from the magnetic data, is slightly lower than g obtained from ESR spectroscopy.

Complex 3

In contrast to complexes **1** and **2**, at high temperatures (300 K), $\chi_M T$ for **3** is about $0.72\ cm^3 K mol^{-1}$, which is slightly lower than the spin-only value expected for two noninteracting Cu^{II} ions with $g = 2$ ($0.75\ cm^3 K mol^{-1}$).

Generally, no analytical expressions exist for fitting of magnetic interactions in a 2D system that takes into account coupling in two perpendicular directions (namely, through the biphenyl bridge and through the azido group in **3**). Thus, in order to estimate the values of the exchange couplings in **3**, some simplifications should be made. From a structural point of view, compound **3** is made of 2D lattices, but from a magnetic point of view, the situation is more ambiguous. Cu^{II} ions are connected by azido bridges in a 1,1-mode along the a axis. However, the $Cu1–N5_{(azido)}$ distance is 2.549(2) Å, which corresponds to a Jahn–Teller distortion along the z axis of octahedral Cu^{II}. In such a case, the single electron lies in a magnetic orbital located in the xy plane. Therefore, delocalisation of the spin density towards the azido ligand is expected to be very small, and, as a first approximation, the magnetic properties of compound **3** should be consistent with the magnetic behaviour of isolated dinuclear Cu^{II} units as in compound **2**. Nevertheless, two possible models were checked to fit the magnetic properties of **2**: the model of isolated dimers (interactions through the azido group are neglected) and the model of infinite chains (interactions through the biphenyl group are neglected).

Fitting of the $\chi_M T$ vs. T curve within the model of isolated dimers as in Equation (1) gives an agreement with $J = -17.77(8)\ cm^{-1}$, $g = 1.976(1)$ and $R^2 = 1.4 \times 10^{-4}$. The quantity of impurities in this and the following fits of the data for **3** was estimated from the low-temperature $\chi_M T$ value to be $x = 0.011$ (1.1%). This fit produced a g value much lower than expected for Cu^{II} ions, and this makes no physical sense. There may be two reasons for an unrealistically low g value: the model of the dimer, Equation (1), is not suitable for the fitting of data for a 2D system like compound **3**, or the formula weight of the compound has been underestimated because of possible capture of water molecules from air in the pores of **3** (as was shown above, compound **3** contains pores, which are potentially accessible for small molecules like H_2O, and the total volume of accessible voids is about 9%). To check this assumption, we used a model with a weighting factor a, which was introduced as follows [Equation (3)]:

$$\chi_M T_{\text{weighted}} = a{\cdot}\chi_M T + \chi T_{\text{impurity}} \tag{3}$$

The weighting factor a indicates an increase (if $a < 1$) in the formula weight of a compound, the magnetic properties of which have been measured, relative to the formula weight of the compound analysed by elemental analysis and X-ray diffraction. To some extent this factor allows us to take into account the increase in the formula weight caused by water molecules being adsorbed from air, the quantity of which may vary and is difficult to predict. The fit for complex **3** gives $J = -17.77(8)$ cm^{-1}, $g = 2$ (fixed) and $a = 0.976(1)$ with $R^2 = 1.4 \times 10^{-4}$. The J value did not change when the value for g was not fixed and with $a = 1$ [Equation (2)], which indicates that the J value is determined by the shape of the $\chi_M T$ vs. T curve but not by the high-temperature value of $\chi_M T$.

The J value, which characterises the coupling through the diaminobiphenyl group, is slightly higher in **3** than in **2** (in absolute terms). However, while the phenyl rings are almost parallel in **2**, the angle between the two phenyl rings in **3** is about 30° about the central C–C bond (Table 2). From this simple comparison, it may be concluded that this angle does not play a significant role in the exchange coupling transfer through the biphenyl bridge.

The second possible alternative to fit the data for **3** (different from the above dimer model) is to use the model of linear chains [Equation (4)]:[17]

$$\hat{H} = -J\sum_i \hat{S}_i\hat{S}_{i+1} \tag{4}$$

In this approach, interactions through the biphenyl bridge are neglected and only coupling through azido groups is taken into account (apparently, it is just an approximation because the coupling though the biphenyl bridge is not negligible, as was shown above for compounds **1** and **2** for which the model of two interacting Cu^{II} ions was completely adequate). The term representing the molecular field was introduced, which may correspond to all other interactions not included in the above Hamiltonian.[18] However, good fits corresponded to the parameter sets where $|J|$ is comparable with $|zJ'|$, thus it may be concluded that this model is not adequate.

Complex 4

The $\chi_M T$ value for compound **4** at 300 K is 5.81 cm^3 K mol^{-1}, which is slightly lower than the expected spin-only value (6 cm^3 K mol^{-1} for a $Cu^{II}_6Cr^{III}_2$ system with all g factors equal to 2.00). On cooling, $\chi_M T$ increases slightly to 5.91 cm^3 K mol^{-1}, reaching this value at 140 K, and on further cooling to 50–60 K, the decrease in $\chi_M T$ is insignificant ($\chi_M T$ = 5.8 cm^3 K mol^{-1} at 53 K). Further cooling caused a rapid decrease in $\chi_M T$ down to 3.25 cm^3 K mol^{-1} at 2 K.

For similar complexes in which Cr^{III} and Cu^{II} are connected through NCS$^-$ bridges with a similar bridging geometry, the observed coupling between the chromium and copper spins is low, typically, J is less than two wavenumbers in absolute terms (for a Hamiltonian $H = -JS_1S_2$).[14c,14d] In addition, the Cu–S bond (S is the sulfur atom from a bridging NCS$^-$ group) in **4** is long [2.878(3) Å], and it is therefore natural to neglect this exchange pathway with respect to the dominating exchange coupling in dinuclear Cu^{II} units. The magnetism of complex **4** can be summed up as being the result of (i) three dinuclear units, the magnetic properties of which obey Equation (1) and (ii) two isolated octahedral Cr^{III} ions (S_{Cr} = 3/2) with a small zero-field splitting (ZFS) [Equation (5)]:[18]

$$\hat{H}_{Cr} = D_{Cr}[S_z^2 - \frac{1}{3}S(S+1)] \tag{5}$$

The fitting procedure of the $\chi_M T$ vs. T curve produces $g_{Cr} = 1.94(6)$, $J = -15.8(2)$ cm^{-1}, $|D_{Cr}| = 1.4(1)$ cm^{-1} and $R^2 = 1.6 \times 10^{-4}$. To avoid overparametrisation, g_{Cu} was fixed at the level of 2.1, a value typical for copper complexes with S donors.[15,19] Notably, a decrease in g_{Cu} results in an increase in g_{Cr} at a comparable final R^2 value. The value of D_{Cr} is consistent with D_{Cr} calculated for other Cr^{III} complexes from magnetochemical measurements.[14c,20] However, this D_{Cr} value is significantly higher than D_{Cr} found for Cr^{III} mononuclear complexes from ESR spectroscopy, which have typical values <0.5 cm^{-1}.[21] The discrepancy between the D_{Cr} values, extracted from the fitting of the magnetic data and from ESR measurements, may be evidence that precise determination of D_{Cr} from magnetic data analysis is not always possible and that consideration of D_{Cr} in calculations unavoidably includes other effects such as intermolecular exchange. In order to verify this, we fitted the same $\chi_M T$ vs. T curve for **4** with the approximation that $\chi_M T$ of the Cr^{III} component does not depend on T and that $\chi_M T$ of the compound is a superposition of $\chi_M T$ of the Cu^{II}_2 and Cr^{III} components. In this case, in contrast to the previous fit, introduction of a molecular field[18] improved the fit. The lowest R^2 value corresponds to $J = -15.1(3)$ cm^{-1}, $zJ' = -0.047(7)$ cm^{-1}, $g_{Cr} = 1.94(2)$ and $R^2 = 1.9 \times 10^{-4}$, while g_{Cu} was fixed at the level of 2.1, i.e. the same as in the fit with nonzero D_{Cr}. The assumption that in this case D_{Cr} cannot be reliably calculated from the $\chi_M T$ vs. T curve seems to be correct because the two fits gave almost the same J and g_{Cr} values.

Complex 5

The $\chi_M T$ value for compound **5** is 4.26 $cm^3 K mol^{-1}$ at 300 K (spin-only value for this system is 4.5 $cm^3 K mol^{-1}$ at $g_{Cu} = g_{Cr} = 2.000$). As in the case of **4**, on cooling, the $\chi_M T$ value for **5** increases to 4.30 $cm^3 K mol^{-1}$, reaching this value at 200–220 K. $\chi_M T$ remains above 4.1 $cm^3 K mol^{-1}$ in the temperature range from 300 to 30 K and on further cooling rapidly decreases to 2.75 $cm^3 K mol^{-1}$ at 2 K. To fit the data, two paramagnetic Cr^{III} centres per dinuclear Cu^{II} unit were taken into account. The fit was performed by using the approach similar to that applied for compound **4**: $\chi_M T$ for complex **5** was taken as a sum of $\chi_M T$ for the dinuclear Cu^{II}_2 unit, calculated according to Equation (3), and $\chi_M T$ for two isolated Cr^{III} ions. The value of g_{Cu} was fixed at the level 2.1 to avoid overparametrisation. The best fit corresponds to the following set of parameters: g_{Cr} = 1.93(3), J = –17.0(2) cm^{-1}, $|D_{Cr}|$ = 3.17(3) cm^{-1} and R^2 = 1.1×10^{-4}. Again, similarly to complex **4**, D_{Cr} for **5** falls in range of reported D_{Cr} values determined from magnetochemical measurements,[14c,20b,20c] but significantly exceeds the values usually calculated from ESR spectroscopy for Cr^{III} complexes.[21] However, the fit of the $\chi_M T$ vs. T curve with zero D_{Cr} gives J = –12.8(2) cm^{-1}, zJ' = –0.195(3) cm^{-1} and g_{Cr} = 1.9314(5) and a lower R^2 value (1.5×10^{-5}) at a fixed g_{Cu} = 2.1, which is in agreement with the above supposition that, in this case, D_{Cr} cannot be reliably calculated from the $\chi_M T$ vs. T curve. Notably, J of this fit is much lower (in absolute terms) than J calculated for **5** with a nonzero D_{Cr} value.

Summary from Magnetic Properties

The magnetic properties of all complexes described in this paper could be treated by using the model for Cu^{II} dimers. The J values for the Cu···Cu coupling in these compounds are presented in Table 2 along with some structural parameters. For all compounds presented in this paper, the J values lie in range from –12.74(4) to –17.77(8) cm^{-1}.

Table 2 also contains a summary of the magnetic properties of the Cu^{II} complexes with 4,4′-biphenyl bridging units. In all cases, except for one,[9d] exchange was found to be antiferromagnetic, and in the trinuclear $Cu^{II}_2Cu^{I}$ complex with Schiff bases from 4,4′-diaminodiphenyl and 2-hydroxybenzaldehyde, J was found to be positive on the basis of susceptibility measurements in the temperature range from 77 to 300 K.[9d] There are π–π stacking interactions between the trinuclear units in the crystal structure of this compound, and, thus, the temperature dependence of χ_M cannot be undoubtedly assigned to exchange through the biphenyl bridge. Also, though the χ_M vs. T curve was fitted, this temperature range does not seem to be sufficient for reliable determination of J for weakly coupled systems.

In six compounds (**1**–**5** and $Na_4[Cu_2(bpba)_2]$[9a]), two Cu^{II} ions are linked by two 4,4′-biphenyl groups which are the parts of the chelating ligands (ligand abbreviations are given in the notes to Table 2). Three compounds, $[Cu_2(tren)_2(BZD)](NO_3)_4$, $[Cu_2(tren)_2(BZD)](ClO_4)_4$ and $[Cu_2(tren)_2(BZD)](PF_6)_4$, contain one 4,4′-biphenyl group between the two Cu^{II} ions. However, only one of them was structurally characterised.[9b,9c] In any case, the lower J values (in absolute terms) for the latter three complexes in this series may be explained by the presence of only one exchange pathway between the paramagnetic centres.

Generally, for the compounds with biphenyl bridges, the efficiency of exchange coupling through the biphenyl bridge is expected to depend on several factors, among which the following seem to be the most important: (i) the electronic density on the Cu^{II} ions and the bridging group, i.e. the nature of the coordination environment and substituents on the ligands, (ii) conjugation within the C_6H_5–C_6H_5 unit, which, in turn, should depend on the angle between two adjacent phenyl rings (β) and (iii) the angle between the plane of the magnetic orbital of copper(II) (which is approximately the same as the N_4 plane) and the plane of the conjugated π system of the phenyl ring (i.e. the plane of phenyl ring, angle α). However, a simple analysis of the relationship between α, β and J shows that there is no direct correlation; at least, the quantity of experimental points is not enough to find it.

Conclusions

It was shown that linking of the dinuclear copper(II) complex **1** by appropriate bridging agents enabled the preparation of polymeric or polynuclear complexes. All these compounds are characterised by antiferromagnetic behaviour. The magnetic properties of compounds **1**–**5** are determined by exchange coupling within the dicopper unit and may be described as a superposition of magnetism of this cationic building block and the adjacent anion. The magnitude of the exchange coupling of two Cu^{II} ions is significant despite the high separation of these paramagnetic centres. The biphenyl bridge efficiently transmits exchange coupling between metal centres at a distance of about 12 Å.

Experimental Section

Materials and Measurements: Commercially available reagents and solvents (Aldrich, Merck) were used as received. $Na_3[Cr(NCS)_6]\cdot 4H_2O$ and $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2H_2O$ were synthesised as described.[22] Magnetic measurements were performed by using a Quantum Design MPMS SQUID magnetometer operating in the temperature range 2–300 K with a DC magnetic field of up to 5 T. Samples were measured in Teflon capsules, diamagnetic corrections were calculated by using Pascal's constants.[19]

Crystallographic Data Collection and Structure Determination: Single crystals of the title compounds were mounted on a Nonius four-circle diffractometer equipped with a CCD camera and a graphite monochromated Mo-K_α radiation source (λ = 0.71073 Å) at the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data were collected at 293 K. An effective absorption correction was performed (SCALEPACK). The structures of complexes **1**–**5** were solved by using direct methods with the Sir-97[23] or SHELXS-97[24] software and were refined with full-matrix least-squares methods on F^2 by using the SHELXL-97 program.[24] Compound **5** contains disordered water molecules. One of the water molecules is disordered over 2 positions with occupancy fac-

Table 3. Crystal data and structure refinement for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{40}H_{40}Cl_2Cu_2N_8O_{16}$	$C_{40}H_{41}Cu_2N_{14}O_6$	$C_{40}H_{42}Cu_2N_{14}O_4$	$C_{72}H_{72}Cr_1Cu_3N_{21}O_7S_6$	$C_{48}H_{54}Cr_2Cu_2N_{20}O_{7.30}S_8$
Formula weight [$g\,mol^{-1}$]	1086.78	940.00	909.96	1778.58	1515.58
Temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	trigonal	monoclinic
Space group	$C2/c$	$P2_1/c$	$Fddd$	$R\bar{3}$	$P2_1/c$
a [Å]	26.8321(8)	6.4699(6)	9.7733(2)	24.031(3)	17.9240(2)
b [Å]	12.9544(5)	28.980(3)	24.1003(5)	24.031(3)	22.6660(4)
c [Å]	13.6241(4)	11.2999(9)	37.2051(10)	26.102(4)	18.2790(3)
β [°]	99.180(3)	105.743(2)	90.0000	90.0000	112.1040(10)
Volume [$Å^3$]	4675.0(3)	2039.2(3)	8763.3(3)	13054(3)	6880.32(18)
Z	4	2	8	6	4
Calculated density [$g\,cm^{-3}$]	1.544	1.533	1.379	1.357	1.463
Absorption coefficient [mm^{-1}]	1.102	1.110	1.027	1.049	1.220
$F(000)$	2224	431	3760	5496	2992
θ range for data collection [°]	0.998 to 25.682	0.996 to 27.54	2.546 to 27.485	0.996 to 27.50	0.998 to 25.35
Reflections collected	8183	17649	25124	74405	43511
Reflections unique	4213	4700	2518	6648	12534
R(int)	0.0387	0.0696	0.0742	0.0576	0.0929
Parameters	316	301	138	331	796
Goodness-of-fit on F^2	0.940	1.016	1.104	1.090	1.022
R_1 ($[I > 2\sigma(I)]$)[a]	0.0595	0.0684	0.0572	0.0550	0.0618
wR_2 $[I > 2\sigma(I)]$[b]	0.1750	0.1886	0.1791	0.1843	0.1574

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

tors of 0.7 and 0.3 each, and one fills its position with an occupancy factor of 0.3. Crystallographic data are summarised in Table 3. CCDC-696861 (**1**), -696862 (**2**), -696863 (**3**), -696864 (**4**) and -696865 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution! Though we did not have any problems working with perchlorates and azides, such compounds are potentially explosive.

Synthesis of $[Cu_2(LH)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (1): 4,4-Diaminodiphenyl (0.050 g, 2.72×10^{-4} mol) was dissolved in methanol (2 mL). To this solution was added butanedione monoxime (0.055 g, 5.44×10^{-4} mol), and the reaction mixture was heated at 50 °C for 20 min. After this, a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.101 g, 2.72×10^{-4} mol) in methanol (0.5 mL) was added, which resulted in the immediate formation of dark-brown precipitate. The reaction mixture was left for 24 h during which time the initial precipitate dissolved and dark-brown crystals formed. The product was filtered, washed with methanol (3 mL) and dried in air. Yield 85% (0.127 g). $C_{40}H_{50}Cl_2Cu_2N_8O_{16}$ (1096.88): calcd. C 43.8, H 4.59, N 10.2; found C 43.6, H 4.44, N 10.1.

Synthesis of $[Cu_2(LH)_2(H_2O)_2(N_3)_2]$ (2): Compound **1** (0.100 g, 9.12×10^{-5} mol) was dissolved in dimethylformamide (1.0 mL), the solution was diluted with acetonitrile (8 mL) and solid NaN_3 was added (0.013 g, 2.0×10^{-4} mol, 10% excess). Transparent green crystals formed in 1 d, which were filtered and dried in air. Yield 50% (0.043 g). $C_{40}H_{46}Cu_2N_{14}O_6$ (945.99): calcd. C 50.8, H 4.90, N 20.7; found C 50.7, H 4.80, N 20.7.

Synthesis of $[Cu_2(LH)_2(N_3)_2]_n$ (3): Compound **1** (0.100 g, 9.12×10^{-5} mol) was dissolved in dimethylformamide (1.0 mL), the solution was diluted with acetonitrile (4 mL) and methanol (4 mL) and solid NaN_3 (0.013 g, 2.0×10^{-4} mol, 10% excess) was then added. Black–green crystals formed in 1 d, which were filtered and dried in air. Yield 80% (0.066 g). $C_{40}H_{42}Cu_2N_{14}O_4$ (909.96): calcd. C 52.8, H 4.65, N 21.5; found C 53.0, H 4.55, N 21.5.

Synthesis of $\{[Cu_2(LH)_2(CH_3CN)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O\}_n$ (4): Compound **1** (0.070 g, 6.39×10^{-5} mol) was dissolved in dimethyl sulfoxide (1 mL), the solution was diluted with acetonitrile (6 mL) and a solution of $Na_3Cr(NCS)_6\cdot 4H_2O$ (0.023 g, 4.26×10^{-5} mol) in acetonitrile (2 mL) was added. Black crystals formed in several minutes. The mixture was left for 3 h, the crystals were filtered off, washed with acetonitrile and dried in air. Yield 90% (0.068 g). $C_{144}H_{148}Cr_2Cu_6N_{42}O_{14}S_{12}$ (3561.09): calcd. C 48.6, H 4.19, N 16.5; found C 48.6, H 4.13, N 16.4.

Synthesis of $\{[Cu_2(LH)_2][Cr(NCS)_4(NH_3)_2]_2\cdot 2H_2O\cdot CH_3OH\}_n$ (5): Compound **1** (0.100 g, 9.12×10^{-5} mol) was dissolved in acetonitrile (5 mL), and methanol (5 mL) was then added, followed by a solution of $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2H_2O$ (0.074 g, 2.0×10^{-4} mol, 10% excess) in methanol (3 mL). Brown crystals formed within several minutes. The mixture was left for 3 h, the crystals were filtered off, washed with methanol and dried in air. Yield 70% (0.098 g). $C_{49}H_{62}Cr_2Cu_2N_{20}O_7S_8$ (1530.77): calcd. C 38.4, H 4.08, N 18.3; found C 38.6, H 4.10, N 18.2.

Supporting Information (see footnote on the first page of this article): The crystallographic data, figures demonstrating the crystal packing of compounds **3** and **4** and the fits of the χ_M vs. T curves are presented.

Acknowledgments

This work was partially supported by the exchange program of the CNRS-NAS of the Ukraine. S. V. K. thanks la Région Bretagne for post-doctoral support. This work also was supported in part by the EU through MAGMANet.

---

[1] a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, *73*, 3–14; c) D. Maspoch, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2004**, *14*, 2713–2723; d) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; e) B. Moulton,

M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117–123; f) L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **2002**, *124*, 12096–12097; g) J. A. McCleverty, M. D. Ward, *Acc. Chem. Res.* **1998**, *31*, 842–851; h) R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu, S. Shova, *Chem. Eur. J.* **2006**, *12*, 187–203.

[2] a) N. Yanai, W. Kaneko, K. Yoneda, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 3496–3497; b) W. Kaneko, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 13706–13712; c) B. Nowicka, M. Rams, K. Stadnicka, B. Sieklucka, *Inorg. Chem.* **2007**, *46*, 8123–8125; d) L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772; e) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.* **2003**, *2*, 190–195; f) A. S. Lytvynenko, S. V. Kolotilov, O. Cador, K. S. Gavrilenko, S. Golhen, L. Ouahab, V. V. Pavlishchuk, *Dalton Trans.* **2009**, 3503–3509.

[3] a) R. Robson, *Dalton Trans.* **2008**, 5113–5131; b) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288; c) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247; d) M. J. Rosseinsky, *Microporous Mesoporous Mater.* **2004**, *73*, 15–30; e) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; f) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; g) W. Mori, S. Takamizawa, *J. Solid State Chem.* **2000**, *152*, 120–129; h) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4900–4904.

[4] a) M. E. Kosal, J.-H. Chou, S. R. Wilson, K. S. Suslick, *Nat. Mater.* **2002**, *1*, 118–121; b) E. Deiters, V. Bulach, M. W. Hosseini, *Chem. Commun.* **2005**, 3906.

[5] a) S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millangea, G. Férey, *Chem. Commun.* **2006**, 284–286; b) C. Serre, F. Millange, S. Surblé, G. Férey, *Angew. Chem. Int. Ed.* **2004**, *43*, 6285–6289; c) A. C. Sudik, A. P. Côté, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 2998–3000; d) S. V. Kolotilov, D. Schollmeyer, L. K. Thompson, V. Golub, A. W. Addison, V. V. Pavlishchuk, *Dalton Trans.* **2008**, 3007–3014; e) K. Nakata, H. Miyasaka, K. Sugimoto, T. Ishii, K. Sugiura, M. Yamashita, *Chem. Lett.* **2002**, 658–659.

[6] a) N. Roques, D. Maspoch, F. Luis, A. Camón, K. Wurst, A. Datcu, C. Rovira, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2008**, *18*, 98–108; b) M. Ohba, H. Ōkawa, *Coord. Chem. Rev.* **2000**, *198*, 313–328.

[7] a) H. W. Park, S. M. Sung, K. S. Min, H. Bang, M. P. Suh, *Eur. J. Inorg. Chem.* **2001**, 2857–2863; b) M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Moratal, A. Monge, E. Gutierrez-Puebla, *Inorg. Chem.* **1987**, *26*, 3520–3527; c) M. S. Haddad, D. N. Hendrickson, J. P. Cannady, R. S. Drago, D. S. Bieksza, *J. Am. Chem. Soc.* **1979**, *101*, 898–906; d) S. V. Kolotilov, O. Cador, S. Golhen, O. Shvets, V. G. Ilyin, V. V. Pavlishchuk, L. Ouahab, *Inorg. Chim. Acta* **2007**, *360*, 1883–1889.

[8] A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Coôté, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110–7118.

[9] a) E. Pardo, J. Faus, M. Julve, F. Lloret, M. C. Muñoz, J. Cano, X. Ottenwaelder, Y. Journaux, R. Carrasco, G. Blay, I. Fernández, R. Ruiz-García, *J. Am. Chem. Soc.* **2003**, *125*, 10770–10771; b) T. R. Felthouse, E. N. Duesler, D. N. Hendrickson, *J. Am. Chem. Soc.* **1978**, *100*, 618–619; c) T. R. Felthouse, D. N. Hendrickson, *Inorg. Chem.* **1978**, *17*, 2636–2648; d) G. Dong, Q. Chun-qi, D. Chun-ying, P. Ke-liang, M. Qingjin, *Inorg. Chem.* **2003**, *42*, 2024–2030; e) A. S. El-Tabl, *Transition Met. Chem. (London)* **2002**, *27*, 166–170; f) E. A. Mikhalyova, S. V. Kolotilov, K. S. Gavrilenko, P. G. Nagornyi, S. Golhen, L. Ouahab, V. V. Pavlishchuk, *Theor. Exp. Chem.* **2008**, *44*, 245–251.

[10] A. Addison, T. N. Rao, J. Reedijk, J. Rijn, G. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[11] a) L. K. Thompson, S. K. Mandal, E. J. Gabe, F. L. Lee, A. W. Addison, *Inorg. Chem.* **1987**, *26*, 657–664; b) A. M. Duda, A. Karaczyn, H. Kozlowski, I. O. Fritsky, T. Glowiak, E. V. Prisyazhnaya, T. Yu. Sliva, J. Swiatek-Kozlowska, *J. Chem. Soc., Dalton Trans.* **1997**, 3853–3860.

[12] a) M. J. Prushan, A. W. Addison, R. J. Butcher, *Inorg. Chim. Acta* **2000**, *300–302*, 992–1003; b) V. V. Pavlishchuk, A. W. Addison, R. J. Butcher, R. P. F. Kanters, *Inorg. Chem.* **1994**, *33*, 397–399.

[13] a) A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34 (Supplement); b) A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

[14] a) M. Kabešová, R. Boča, M. Melník, D. Valigura, M. Dunaj-Jurčo, *Coord. Chem. Rev.* **1995**, *140*, 115–135; b) S. Ferlay, G. Francese, H. W. Schmalle, S. Decurtins, *Inorg. Chim. Acta* **1999**, *286*, 108–113; c) V. M. Nikitina, O. V. Nesterova, V. N. Kokozay, E. A. Goreshnik, J. Jezierska, *Polyhedron* **2008**, *27*, 2426–2430; d) K.-L. Zhang, W. Chen, Y. Xu, Z. Wang, Z. J. Zhong, X.-Z. You, *Polyhedron* **2001**, *20*, 2033–2036; e) V. M. Nikitina, O. V. Nesterova, V. N. Kokozay, R. I. Zubatyuk, V. V. Dyakonenko, O. V. Shishkin, E. A. Goreshnik, C. J. Gómez-García, J. M. Clemente-Juan, J. Jezierska, *Inorg. Chim. Acta* **2009**, *362*, 2237–2246.

[15] A. W. Addison, T. N. Rao, E. Sinn, *Inorg. Chem.* **1984**, *23*, 1957–1967.

[16] E. Sinn, *Coord. Chem. Rev.* **1970**, *5*, 313–347.

[17] J. Carranza, C. Brennan, J. Sletten, F. Lloret, M. Julve, *J. Chem. Soc., Dalton Trans.* **2002**, 3164–3170.

[18] O. Kahn, *Molecular Magnetism*; Wiley-VCH: Weinheim, Germany, **1993**.

[19] A. W. Addison, P. J. Burke, K. Henrick, T. N. Rao, E. Sinn, *Inorg. Chem.* **1983**, *22*, 3645–3653.

[20] a) F. Thétiot, F. Bérézovsky, S. Triki, J. S. Pala, C. J. Gómez-García, A. A. Hajem, S. Bouguessa, J.-M. Fabre, *C. R. Chim.* **2003**, *6*, 291–300; b) Y. Journaux, O. Kahn, J. Zarembowitch, J. Galy, J. Jaudt, *J. Am. Chem. Soc.* **1983**, *105*, 7585–7591; c) E. Coronado, M. C. Giménez, C. J. Gómez-García, F. M. Romero, *Polyhedron* **2003**, *22*, 3115–3122; d) G. Marinescu, M. Andruh, R. Lescouëzec, M. C. Muñoz, J. Cano, F. Lloret, M. Julve, *New J. Chem.* **2000**, *24*, 527–536; e) M. C. Muñoz, M. Julve, F. Lloret, J. Faus, M. Andruh, *J. Chem. Soc., Dalton Trans.* **1998**, 3125–3132.

[21] a) E. Pedersen, H. Toftlund, *Inorg. Chem.* **1974**, *13*, 1603–1612; b) B. R. McGarvey, *J. Chem. Phys.* **1964**, *41*, 3743–3758; c) J. Krzystek, A. Ozarowski, J. Telser, *Coord. Chem. Rev.* **2006**, *250*, 2308–2324.

[22] Manual on inorganic preparative chemistry; Moscow, IL, **1956**, p. 630.

[23] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[24] G. M. Sheldrick, *SHELX-97*, University of Göttingen, Göttingen, Germany, **1997**.

Received: August 20, 2009
Published Online: February 3, 2010