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Review

Structural variety and magnetic properties of polynuclear assemblies based on 2-aminoglucose and tritopic triaminoguanidine ligands

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ABSTRACT

Structural features of molecular assemblies determine their magnetic properties. This has been expressed in several qualitative and quantitative magnetostructural correlations. Herein two classes of ligands and there structural and magnetic properties will be discussed. 2-Aminoglucose ligands are 2-aminoalcohols derived from a sugar backbone and therefore provide specific structural and chemical properties which can be used as structural directives. Hence, this allows to control the magnetic properties of related polynuclear complexes. On the other hand, triaminoguanidine derivatives as tritopic ligands preset an equilateral triangular arrangement of metal ions with preferentially antiferromagnetic interactions. This can be utilized to generate higher nuclearity complexes and coordination polymers.

1. Introduction

The magnetic properties of molecular compounds have attracted considerable interest in recent years because of their relevance for the understanding of magnetically coupled active sites in metalloproteins [1]. Most recently additional interest for magnetic molecular assemblies has been generated by their potential applications as magnetic materials [2], such as magnetic memory or as building blocks in quantum devices [3]. Special attention has been devoted to polynuclear assemblies of metal ions [4], which is directly related to the search for strategies to design new systems exhibiting desired physical and chemical properties. In this context two important aspects have been emerged and intensely studied in the past: (i) how to understand and utilize magnetostructural correlations of transition-metal complexes and (ii) how to control structures of polynuclear coordination compounds.

Since the pioneering work of Bleaney and Bowers [5] researchers have been more and more concerned with the first aspect and attempted to rationalize the sign and size of magnetic couplings between metal ions on the bases of structural parameters [6]. As a result this initiated the search for qualitative or quantitative

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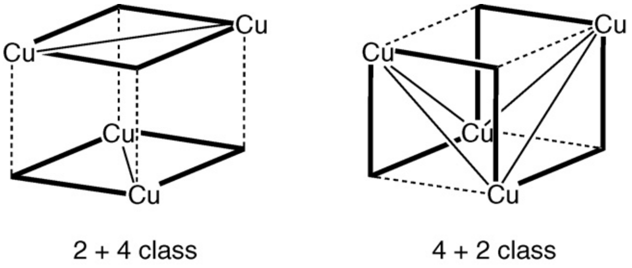
magnetostructural correlations, which are important to understand the mechanism of interaction between metal ions [7]. The first quantitative correlation has been established for planar bis(μ-hydroxo)copper(II) dimers by Hatfield and Hodgson [8]. As in the related bis(μ-alkoxo) and bis(μ-phenoxo)copper(II) dimers, a linear relationship between the coupling constant *J* and the Cu–O–Cu bridging angle is observed with the latter case showing the smallest gradient [9]. Since then correlations for bis(μ-halogeno) dicopper(II) compounds [10], bis(μ-hydroxo)dichromium(III) complexes [11], bis(μ-phenoxo)nickel(II) dimers [12], μ-carboxylate-bridged dinuclear copper(II) complexes [13], dinuclear copper(II) complexes with equatorial diazine/μ-1,1-azide bridge combinations [14], dinuclear hydrogen-bridged copper(II) complexes [15], dimeric oxovanadium(IV) complexes [16], (μ-oxo)diiron(III) species [17], and face-sharing transition-metal complexes with d^3–d^3 electronic configuration [18] have been established. From these correlations a few structural parameters could be identified which determine the type and magnitude of magnetic interaction of a given system. Besides the nature of the bridging unit, these parameters include the metal–metal separation, the bond angles subtended at the bridging atoms, the dihedral angles between coordination planes containing the metal ions, the metal ligand bond lengths, and the stereochemistry of the metal ions involved.

Besides the dinuclear systems, for which detailed experimental and theoretical studies of the correlation between structure and magnetic properties have been reported in the past, there is a clear trend towards polynuclear complexes. For such systems the increased structural complexity together with the presence of different and potentially competing exchange pathways often precludes a detailed study of the exchange interactions. In addition, it should be noted here that for polynuclear complexes an over parametrization in simulations of the magnetic susceptibility data is very likely to occur, and may lead to situations were different sets of solutions similarly fit the experimental data. For larger systems this can be even paired with the limitation given by the currently available computational resources which may prevent fitting or simulation [19]. Nevertheless, in recent years also magnetostructural correlations for oligonuclear systems like mixed-bridged μ-alkoxo-μ-carboxylato trinuclear copper(II) complexes [20], tetranuclear iron(III) butterfly-type complexes [21], and M_4O_4 heterocubanes containing nickel(II) or cobalt(II) ions [22] have been reported. In particular for polynuclear systems such correlations need to be supplemented by theoretical methods based on density functional theory, which have usually been employed to calculate interaction parameters in order to compare them with experimental data and possibly to assist the selection of an appropriate set of fitted values, in case of the presence of ambiguous solutions [19]. Two rare cases of such a theoretical approach have recently been reported. The study on iron(III) butterfly-type complexes, for which a correlation between specific structural parameters and the relevant *J* values was found [21]. The other interesting system is given by Cu_4O_4 heterocubanes, for which the magnetic properties have been related to the number of short and long Cu···Cu distances present in the complex and analyzed according to variations in structural parameters [23]. The two most prominent cases of Cu_4O_4 core structures, the 2 + 4 and the 4 + 2 class, are depicted in Scheme 1 [24].

The second general aspect of interest here, i.e. the design and construction of architectures based on metal complexes, has recently attracted considerable attention in supramolecular chemistry and crystal engineering [25]. A general approach is based on self-assembly reactions between multifunctional organic ligands and metal ions which is driven by the preference of metal ions for a particular geometry and the number, type and arrangement of the ligand binding sites [26]. This classical “node and spacer” approach [27] has led to a wide variety of supramolecular assemblies [28], ranging from oligonuclear complexes to polymeric structures with 1D chains, 2D grids, and 3D frameworks. Additional structuring options are given by the presence of hydrogen bonding interactions, as these allow to extend and cross-link relevant assemblies [29]. Nevertheless, the rational design of complexes directing a specific supramolecular assembly is still a challenge for chemists, in particular as it comes to chirality. Therefore, novel architectures with new ligands need to be synthesized to enrich crystal engineering with new connectivity rules and useful synthetic concepts. In this context metal complexes containing sugar-based salen-type ligands have recently been employed to generate homochiral helical arrays [30]. Moreover, supramolecular architectures mostly contain linear symmetric organic ligands as spacers, whereas the use of C_3 symmetric organic frameworks has been less employed [31]. However, tritopic bridging ligands with a benzene core have also been utilized to generate molecular structures [32]. Nevertheless, with respect to their magnetic properties these ligands have the disadvantage to transmit only rather small exchange couplings.



Scheme 1. Classification of tetranuclear cubane-like copper(II) complexes according the Cu–O and Cu···Cu distances of the central Cu_4O_4 core (see text). Thick lines represent short and broken lines long Cu–O distances. Short Cu···Cu distances are indicated by a connecting line.

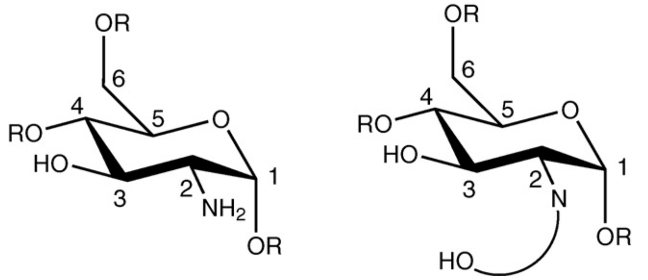
Here a brief survey is given for the latest developments concerning the generation of magnetic assemblies utilizing chiral 2-aminoglucose-based and tritopic triaminoguanidine-based ligands. The structural features of these ligand systems as well as their correlation with the induced molecular assemblies of related transition-metal complexes and their magnetic properties are discussed.

2. 2-Aminoglucose ligands as support for magnetic assemblies

2.1. Complexation behavior of 2-aminoglucose ligands

2-Aminoglucose is the monosaccharide constituting chitosan, the β-(1-4)-linked polysaccharide derived from alkaline deacetylation of chitin. Chitosan is well-known for its adsorption properties towards metal ions [33]. Its biocompatibility and non-toxicity has steamed increasing interest in this material as support and supramolecular ligand for heterogeneous catalysis [34], including Schiff-base-modified derivatives employed in cyclopropanation, alkane oxidation and C–C coupling reactions [35]. Nevertheless, the coordination chemistry of the constituting monosaccharide 2-aminoglucose (see Scheme 2) has been widely unexplored until very recently. The first reported example of a transition-metal complex exhibiting the relevant *trans*-2,3-chelation has been a tetranuclear copper(II) complex with a 4 + 2 cubane-like Cu_4O_4 core (see Scheme 1) [36].

Complexes with 2-aminoglucose ligands generally tend to self-assembly affording oxo-bridged oligonuclear compounds with unexpected magnetic properties [37]. Although such a 2,3-chelation of the donor atoms of the carbohydrate backbone basically resembles that of ethanolamine, distinct differences are imposed by the rigidity and the chirality of the cyclic backbone.



Scheme 2. 2-Aminoglucose (left) and schematic structure of related Schiff-base ligands (right).

Both effects directly reflect in the electronic properties of relevant copper(II) and nickel(II) complexes, for which it was shown that the ligand imposed chirality is transferred to the magnetic centers [37] and that structural distortions can impose rather large zero-field-splitting [38].

In general carbohydrates exhibiting a *trans*-ee or a *cis* configuration of the vicinal donor atoms are ligands suitable for chelation of transition-metal ions [39]. The related steric effects have been modelled in mononuclear nickel(II) complexes with Schiff-base ligands derived from the two epimeric sugars 2-aminoglucose and 2-aminomannose additionally utilizing a capping chelate ligand to prevent self-assembly [40]. As depicted in Fig. 1 both cases afford a 2,3-chelation of the sugar backbone. However, for the mannopyranose system a distortion from the stable $^4C_1$ chair conformation to the $^OS_5$ screw-boat conformation of the pyranose ring is observed, which is imposed by the steric bulk. This clearly shows that the *trans*-ee configuration found in 2-aminoglucose and corresponding polymeric structures should be better suited to accommodate Schiff-base derivatives for complexation of metal ions.

2.2. Structural directives in complexes with 2-aminoglucose ligands

2-Aminoglucose ligands can be regarded as ethanolamine ligands derived from a sugar backbone and therefore provide specific structural and chemical properties which can be used as structural directives. For the copper(II) and nickel(II) complexes unusual structures have been obtained [36,37,41]. This can be attributed to the specific properties of the employed 2-aminoglucose ligands L, which leads to a controlled self-assembly of the basic mononuclear building blocks {Cu(L)} and $\{Ni(L)_2\}$.

For polynuclear copper(II) complexes the structural chemistry is governed by the presence of a Cu_4O_4 core. Such compounds have been classified according their atomic distances within the core structure as depicted in Scheme 1 [24]. Almost all reported structures can be assigned to two classes, which are characterized according their number of short and long Cu···Cu distances within the Cu_4O_4 core as 2 + 4 class and 4 + 2 class (see Scheme 1), with the latter being by far the more common of the two cases.

With the *trans*-2,3-chelating glucose backbone as chelating 2-aminoethanol ligand to set up the mononuclear building blocks it has been possible to selectively generate examples for both major cubane classes as depicted in Fig. 2. The variation of the substitution pattern at C-2 and C-3 positions of the glucose backbone can be utilized to implement specific coordinative and supramolecular presettings and thereby allows for chiral and steric tuning of the Cu_4O_4 core.

2-Aminoglucose with a Schiff base at the C-2 position and a benzylidene acetal protecting group at C-4/C-6 leads to a 4 + 2 class core structure [36]. This can be rationalized by the planarity of the tridentate Schiff-base ligand and the rigidity of the glucose backbone, which bring the O-4 oxygen atom in an ideal position for a possible weak coordination at a neighboring building block. This interaction is favored with respect to the competing one with the μ_2-bridging C-3 alkoxide oxygen atom which is located on the opposite site of the coordination plane. Moreover, due to the lack of appropriate donors, the O-4 oxygen atom cannot undergo any kind of hydrogen bonding interaction.

However, if the same ligand is utilized, but without protecting group at the O-4 oxygen atom, this particular function becomes a potential hydrogen-bond donor. As a consequence the resulting building block can undergo self-aggregation through hydrogen bonding. In contrast to the competing situation found for the former case, the additional hydrogen bonding interactions of the O-4

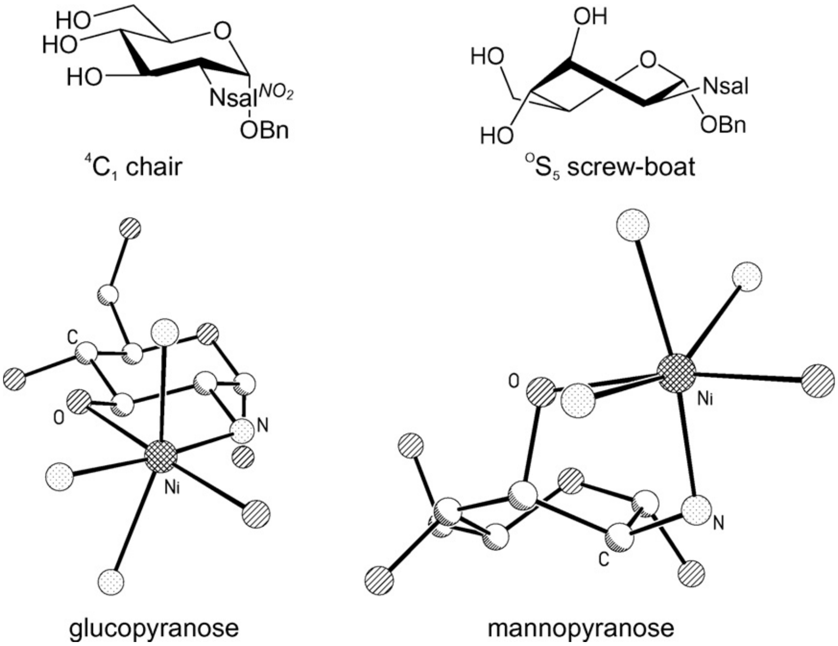


Fig. 1. Comparison of the pyranose ring conformation of nickel(II) complexes with a gluco- and mannopyranose ligand [40]; the first coordination sphere of the chelated nickel(II) ions is included in the structural representations.

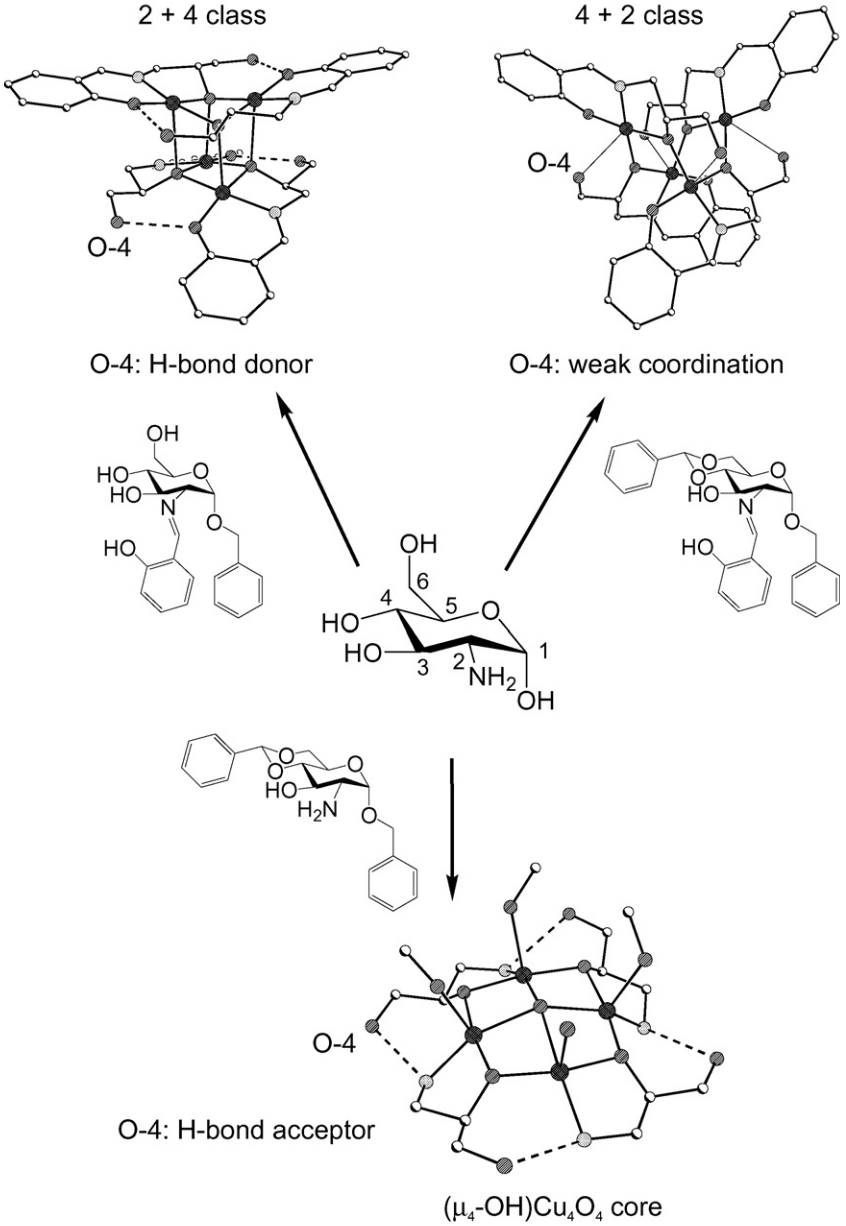


Fig. 2. Structural directives for copper(II) complexes with 2-aminoglucose ligands [41]. Variation of the 2-amino (free amine or Schiff base) and the 4-hydroxy (free or protected) functions at the backbone allows for the specific design of the self-assembly of the tetranuclear core structure (see text). Hydrogen bonds are indicated by dashed lines and weak coordinative bonds at the axial positions by thin lines. In the structural representations the non-coordinating part of the carbohydrate moiety is omitted for clarity.

hydroxy groups synergistically enforce the formation of the μ_3-bridges of the relevant C-3 alkoxide oxygen atoms. Consequently this leads to a $2 + 4$ class core structure [37].

On the other hand, when the protecting group at the hydroxy group at C-4 is retained, but instead a free amino function is employed at the C-2 position, a bidentate ethanolamine is obtained as chelate ligand. Here the O-4 group can only act as hydrogen-bond acceptor or in the absence of an appropriate hydrogen-bond donor as weakly coordinating ligand. Moreover, this leads to a decreased denticity of the employed chelate ligand. If appropriate coligands are present, such bidentate ethanolamine ligands are capable to support the common cubane-like Cu_4O_4 core structures [24]. However, for the assembly of copper(II) building blocks to a tetranuclear core also alternative motifs with a central μ_4-bridge have been reported. The most common is given by the $Cu_4(\mu_4\text{-O})$ core with a tetrahedral assembly of copper(II) ions around a central oxo bridge [42]. Alternatively also a rare second case is observed, containing a central μ_4-OH bridge with a square-planar assembly of the copper(II) ions leading to a $(\mu_4\text{-OH})Cu_4O_4$ core. The latter case has as yet only been reported for complexes supported by macrocyclic Schiff-base ligands [43]. In the absence of coligands, the 2-aminoglucose with protected functional groups at C-1, C-4, and C-6 of the sugar backbone acts as bidentate 2-aminoethanol with interesting structural features. This ligand provides both a hydrogen-bond acceptor (O-4 group) and a hydrogen-bond donor (amino group at C-2) together with a rigid preset orientation of these groups enforced by the glucose backbone. As a consequence this ligand allows for intramolecular hydrogen bonding between the {Cu(L)} building blocks in a self-complementary fashion as depicted in Fig. 2, which leads to a $(\mu_4\text{-OH})Cu_4O_4$ core.

These specific hydrogen-bonding features of the C-1, C-4, and C-6 protected 2-aminoglucose ligand are ideally suited to also

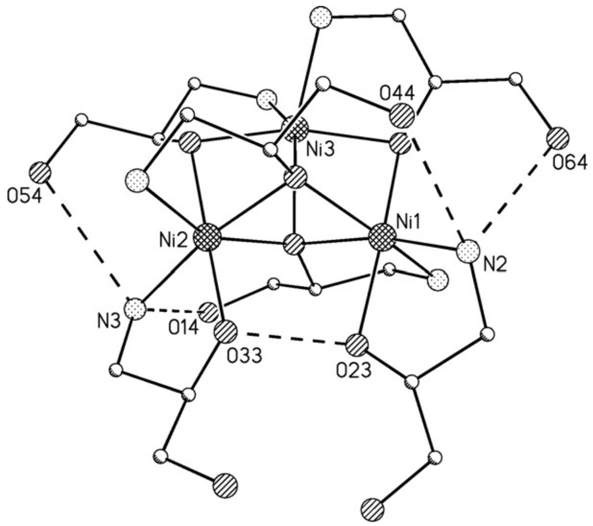


Fig. 3. Hydrogen bonding for the trinuclear nickel(II) complex with $(\mu_3\text{-OR})_2(\mu_2\text{-OR})_2Ni_3$ core structure derived from a chelating C-1, C-4, and C-6 protected 2-aminoglucose ligand [41]. Hydrogen bonds are indicated by dashed lines. All atoms except the chelate part of the glucose backbone as well as the C-4 and O-4 atoms are omitted for clarity. Pertinent distances: N2···O44 302, N2···O64 307, N3···O14 297, N3···O54 316, O23···O33 244 pm.

support the self-assembly of the mononuclear building blocks $\{Ni(L)_2\}$ to the rare case of an isosceles Ni_3 triangular structure with a $(\mu_3\text{-OR})_2(\mu_2\text{-OR})_2Ni_3$ core (see Fig. 3). Of particular importance for the support of the core structure are the two terminal chelate ligands at the Ni1 and Ni2 centers. The relevant amino groups (N2 and N3) are oriented towards the O-4 oxygen atoms of the adjacent $\{Ni(L)_2\}$ building blocks, leading to hydrogen bonds of N2 (Ni1) with O44 (Ni2) and O64 (Ni3) as well as N3 (Ni2) with O14 (Ni1) and O54 (Ni3) (for relevant distances see Fig. 3). As a consequence, the two O-3 oxygen atoms (O23 and O33) of these terminal chelate ligands are oriented towards each other. This makes the resulting M–(R)O···O(R)–M fragment susceptible for protonation [15], leading to a strong hydrogen bond with an O···O distance of 244 pm along the elongated basal edge of the isosceles triangle (Ni1···Ni2 316.4, Ni1···Ni3 280.4, and Ni2···Ni3 283.4 pm).

2.3. Magnetic properties of complexes with 2-aminoglucose ligands

Due to the steric constraints given by the glucose backbone, ligands derived from 2-aminoglucose not only support unusual structures in self-assembly processes of mononuclear $\{Cu(L)\}$ and $\{Ni(L)_2\}$ building blocks, but also lead to compounds with exceptional magnetic properties. As described in the previous section, three different basic structural motifs have been observed for copper(II) and nickel(II) complexes with 2-aminoglucose-based ligands. For the tetranuclear copper(II) complexes with Cu_4O_4 core structure extensive experimental and theoretical magnetic data have been reported in literature [23]. However, such data is neither available for tetranuclear copper(II) complexes with square-planar $(\mu_4\text{-OH})Cu_4O_4$ core, nor for trinuclear nickel(II) complexes with $(\mu_3\text{-OR})_2Ni_3$ core.

The magnetic behavior of alkoxo-bridged tetranuclear copper(II) complexes is basically given by their core structure (see Scheme 1). For non-sugar-based complexes with a 4 + 2 core exclusively ferromagnetic interactions are observed along the short Cu···Cu distances [44], whereas for non-sugar-based complexes with a 2 + 4 core exclusively antiferromagnetic interactions have as yet been reported [45]. Interestingly, for the corresponding copper(II) complexes with Schiff-base ligands derived from 2-aminoglucose an inverse behavior is observed, leading to ferromagnetic coupling for a 2 + 4 core and antiferromagnetic coupling for a 4 + 2 core, respectively. This behavior is obviously determined by the steric presettings established by the sugar backbone of the Schiff-base ligands. Therefore the question arises, which are the governing features in this context. According to magnetostructural correlations derived from a theoretical study the magnetic interactions within tetranuclear copper(II) complexes with cubane-like core structure can be related to geometrical parameters [23]. The two most prominent are the Cu–O–Cu bridging angles and the Cu···O distances within the Cu_4O_4 core structure.

For 4 + 2 cubane-like structures an additional increase of the four already elongated Cu···O distances as well as a concomitant increase in the Cu–O–Cu bridging angles eventually leads to antiferromagnetic coupling along the short Cu···Cu distances and almost vanishing interactions along the long Cu···Cu distances (cf. Scheme 1) [23]. This allows to rationalize the fairly large antiferromagnetic coupling constant of $J = -130\,\text{cm}^{-1}$ observed for the complex with 4 + 2 core structure, as extremely elongated long Cu···O distances of 293–321 pm within the heterocubane and large Cu–O–Cu bridging angles of 121–127° are present in this case [36]. Two structural features related to the rigid chiral backbone of the sugar ligand can account for this observation.

First the steric repulsion introduced by the hydrogen atoms at the C-3 and C-4 position pointing towards the neighboring copper fragment. Second the additional donor function O-4, which is competing for the weak axial interaction at the copper(II) ions against the *trans* positioned μ_3-bridging oxygen atoms O-3 of the glucose backbone of a neighboring $\{Cu(L)\}$ building block in the Cu_4O_4 core structure at distances of 265–303 pm (cf. Fig. 4).

Also for 2 + 4 cubane-like structures the Cu–O–Cu angles have been found to be important in determining the magnetic properties of the tetranuclear complexes, as could be expected from the well-known magnetostructural correlations described for dinuclear copper(II) complexes with Cu_2O_2 core. For such cases the Cu–O–Cu angle confines the range of ferromagnetic coupling,

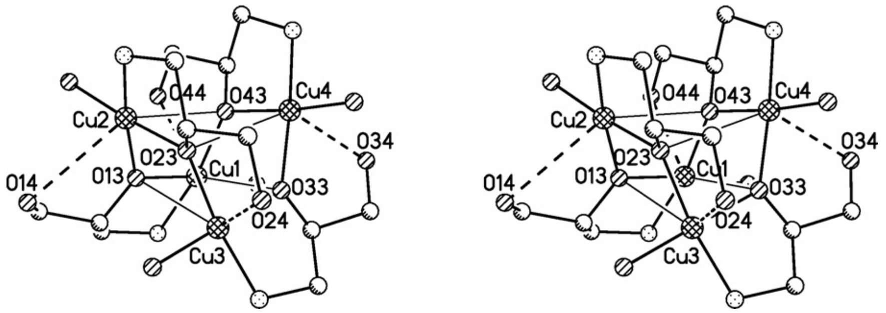
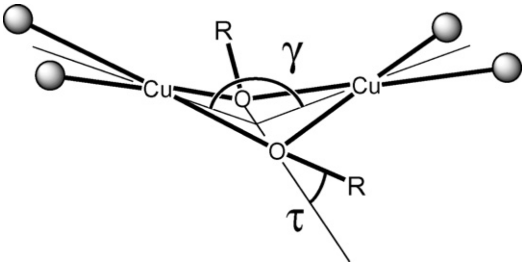


Fig. 4. Stereo view of the core structure of the 2-aminoglucose-based tetranuclear copper(II) complex of 4 + 2 class (see Fig. 2) [36]. Thin lines represent the long Cu···O edges of the Cu_4O_4 core and broken lines the second potential axial Cu···O contacts at the square-planar copper(II) centers.

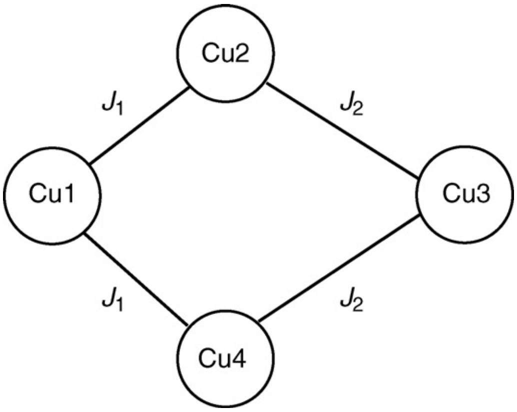


Scheme 3. Representation of hinge (γ) and out-of-plane distortion (τ) of a Cu_2O_2 core.

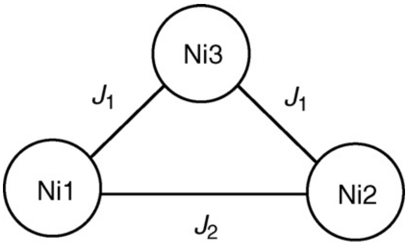
which is found below the limiting values of 95.7 ($J = 7857–82.1\alpha$) and 97.5° ($J = 7270–74.53\alpha$) for alkoxo- and hydroxo-bridged complexes, respectively [9]. In agreement with the observed antiferromagnetic interactions all relevant alkoxo-bridged tetranuclear copper(II) complexes with a 2 + 4 core structure show Cu–O–Cu angles clearly larger than the limiting value. It is interesting to note here, that there is one report on a similar hydroxo-bridged tetranuclear copper complex with a weak ferromagnetic coupling and an angle of 96.6° [46], which is somewhat smaller than the corresponding confining borderline value.

Based on these magnetostructural correlation the ferromagnetic coupling of 64 cm^{-1} observed within the two dimeric units of the 2 + 4 complex nicely agrees with the very small Cu–O–Cu bridging angles in the range of 89.8 and 94.4° [41], which is well below the limiting value for alkoxo-bridged dinuclear complexes. However, the situation is a little more complex, as there are two additional effects on this intra-dimer coupling constant working in opposite direction. The first is characteristic for Cu_4O_4 cubanes and leads to an overestimation of the antiferromagnetic nature of the intra-dimer coupling constant, whereas it nicely accounts for the observed rather small but ferromagnetic inter-dimer coupling constant of 4 cm^{-1}. On the other hand, the geometrical distortion of the Cu_2O_2 core, induced by the rigid glucose backbone, leads to an increase in the ferromagnetic character of the relevant copper–copper coupling constant [47]. The related geometrical parameters are the so-called hinge (γ) and out-of-plane distortion (τ) as depicted in Scheme 3. The actual values of γ and τ found for the 2 + 4 complex with 2-aminoglucose ligand are in excellent agreement with the magnitude of the observed ferromagnetic couplings [37].

A completely different spin topology is found for the tetranuclear copper(II) complexes with square-planar (μ_4-OH)Cu_4O_4 core, as depicted in Scheme 4. The differentiation in two coupling interactions with values of 205 and 260 cm^{-1} is due to the variation of the substitution pattern at the axial positions of the four copper ions.



Scheme 4. Spin topology of the tetranuclear copper(II) complex with (μ_4-OH)Cu_4O_4 core derived from a 2-aminoglucose ligand (see Fig. 2) [41].



Scheme 5. Spin topology of the trinuclear nickel(II) complex with (μ_3-OR)$_2$$Ni_3$ core derived from a 2-aminoglucose ligand (see Fig. 3) [41].

Nevertheless, also in this case the magnetostructural correlations deduced for Cu_2O_2 core structures seem to be effective. In fact, the observed magnetic couplings can be understood in terms of predominate interactions along the μ-alkoxido bridges of the four mixed hydroxido- and alkoxido-bridged Cu_2(μ-OH)(μ-OR) fragments. Together with the well-known effects of the already discussed hinge and out-of-plane distortions also observed in this case the moderate antiferromagnetic coupling constants can be rationalized (see Scheme 3) [41]. Even though this gives a consistent qualitative picture, the two bridges present within the Cu_2(μ-OH)(μ-OR) edge fragments may very well also partially compensate their ferro- and antiferromagnetic effects in a sort of counterbalance mechanism, leading to a moderately antiferromagnetic coupling along the edges [48].

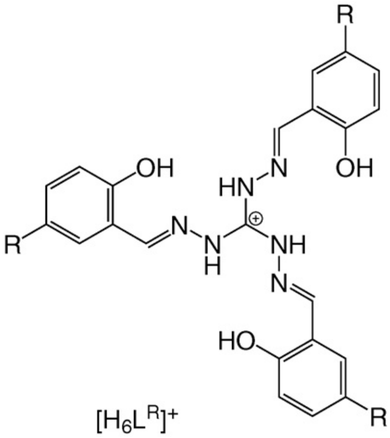
The trinuclear nickel(II) complex with (μ_3-OR)$_2$$Ni_3$core, obtained from {$Ni(L)_2$} building blocks with a 2-aminoglucose-based ligand (cf. Fig. 3), is the first example that exhibits ferromagnetic interactions. As the core structure represents an isosceles triangle, a two-*J* model needs to be employed as spin topology (see Scheme 5), with the two coupling constants found to be 11.0 and 16.4 cm^{-1}. To obtain a sufficient agreement with the experimental data zero-field splitting needed to be employed for the nickel(II) centers, which can be assumed to be approximately axial symmetric and equal for the nickel centers Ni1 and Ni2 along the elongated axis with values of $D_{1,2} = 3.7\,cm^{-1}$ and $D_3 = 1.8\,cm^{-1}$ (cf. Scheme 5).

Although for linear trinuclear nickel(II) complexes examples with ferromagnetic interactions between the adjacent ions have long been known [49], this is in contrast to the generally observed antiferromagnetic interactions in the case of triangular systems, which are found independent of the molecular symmetry for both isosceles [50] and equilateral Ni_3 triangles [51,52]. Nevertheless, the observed ferromagnetic behavior can be explained on the basis of magnetostructural correlations which have been put forward for di- [12] and tetranuclear [22] nickel(II) complexes. These correlations indicate Ni–O–Ni border line angles of about 93.5 and 99.0° for the corresponding μ_2-O and μ_3-O bridged di- and tetranuclear systems, respectively, below which a ferromagnetic interaction is observed. Interestingly, the Ni–(μ_2-O)–Ni and Ni–(μ_3-O)–Ni angles of the 2-aminoglucose-based trinuclear nickel(II) complex are found within the range of 82–99°, which clearly is consistent with the observed overall ferromagnetic interactions within the isosceles Ni_3 triangle.

3. Triaminoguanidine ligands as support for magnetic assemblies

3.1. Complexation behavior of triaminoguanidine ligands

The organic framework of tris(2-hydroxybenzylidene)triaminoguanidine depicted in Scheme 6 provides a planar structure

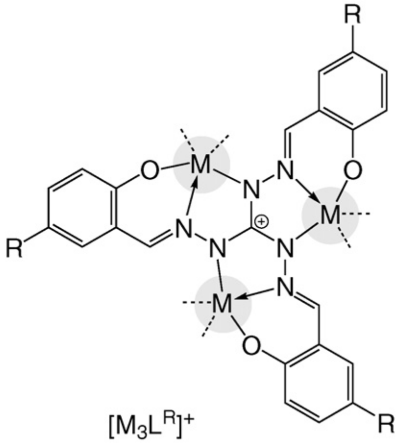


Scheme 6. Triaminoguanidine ligand.

with three equivalent binding pockets and overall C_3 symmetric arrangement. Moreover, this tritopic ligand is capable of chelating transition-metal ions leading to rather short metal–metal distances. Besides the rare example of a mononuclear dioxomolybdenum complex [53], this ligand system has been found to support trinuclear transition-metal complexes [52–55]. Their general schematic structure is depicted in Scheme 7.

In addition to the tridentate coordination by the $[N_2O]$ donor sets of the three coordination pockets of the triaminoguanidine ligand system depicted in Scheme 7, for the coordinatively rather flexible zinc(II) ion also other coordination modes have been observed. If the aromatic hydroxy groups of the ligand system are protected as methoxy groups, the ligand acts as threefold $[N_2]$ donor set only utilizing the nitrogen donors of the triaminoguanidine CN_6 core [55]. Moreover, the bromo derivative (see Scheme 6 with R = Br) under specific reaction conditions leads to a pentanuclear system $[Zn\{Zn_2(H_2O)_3(NH_3)L^{Br}\}_2]$ with a zinc(II) ion bridging two fragments.

Utilizing the tritopic triaminoguanidine ligand system and divalent metal ions like zinc(II), cadmium(II), and palladium(II) several discrete cage molecules with interesting topologies have been synthesized. Besides the most common tetrahedral coordination cages also octahedral and trigonal-bipyramidal cages have been reported [55–59]. If instead appropriate coligands are present, the aggregation of the trinuclear building blocks can be prevented. An example with the paramagnetic nickel(II) ion is shown in Fig. 5[52].



Scheme 7. Trinuclear complex fragment based on triaminoguanidine ligand.

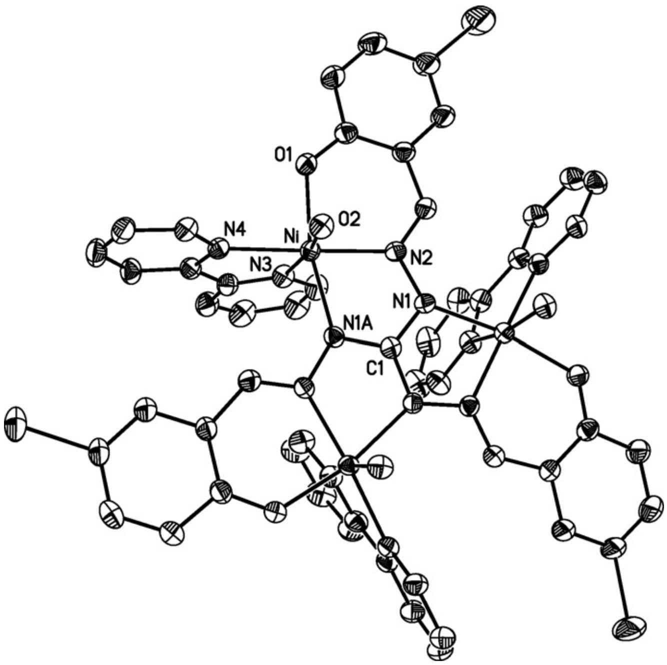


Fig. 5. Molecular structure of the nickel(II) complex cation $[Ni_3L^{Br}(bipy)_3(H_2O)_3]^+$ containing bipy coligands [52]; thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity.

3.2. *Triaminoguanidine ligands as tritopic building blocks*

Trinuclear complexes based on tritopic triaminoguanidine ligands have been employed as building blocks in the synthesis of supramolecular cage compounds. These complexes are generally homonuclear. For these compounds three basically different bridging mode situations have been observed, which depend on the nature of the constituting metal ion utilized in the synthesis. Whereas for the cadmium(II) cages solely a bis(μ-phenoxide)-bridged Cd_2O_2 unit with an additionally coordinating chloride coligand at the fifth coordination site has been observed [58], the cases of the palladium(II) cages are characterized by the presence of a barbiturate as ditopic bridging ligand between the palladium centers [56,57]. A somewhat different situation is observed for the zinc(II) cages, due to the coordinatively more flexible character of their underlying metal centers. This leads on the one hand to bis(μ-phenoxide)-bridges as in the cadmium case, and on the other hand to mixed phenoxide/chloride bridges between zinc(II) centers of neighboring building blocks. Moreover, for supramolecular zinc(II) complexes also a situation is found where three μ_2-hydroxides are bridging two trinuclear building blocks [55,59].

It is interesting to note here, that in an attempt to utilize $[Co(en)_3]^{3+}$ as a counter cation to prepare an octahedral palladium cage, a substitution reaction takes place resulting in a heterometallic pentanuclear complex with a cobalt(III) ion bridging two $\{Pd_2(L)\}$ fragments. This two pentanuclear fragments are further linked by two barbiturate ligands affording a rectangular box-like cage [57].

If copper(II) ions are coordinated by triaminoguanidine ligands in the absence of potentially capping coligands, coordination polymers are obtained through aggregation via bis(μ-phenoxide)-bridges formed between metal centers as depicted in Fig. 6[60]. A symmetric planar bridging mode typically observed for bis(phenoxide)-bridged binuclear copper(II) units is prevented due to the steric requirements of the given ligand, which leads to a dihedral angle of 138° and a Cu–Cu distance of 297 pm for the Cu_2O_2 bridging unit. This asymmetric bridging unit leads to pentacoordinate square-pyramidal coordination environments for both

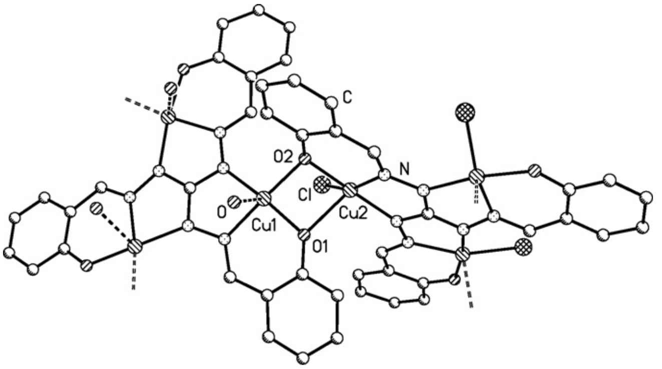
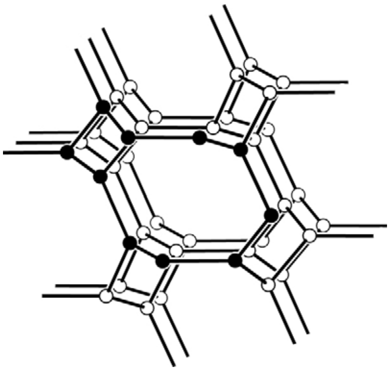


Fig. 6. Molecular structure of the interlocked $\{Cu_6L_2\}$ building unit of the three-dimensional coordination polymer [60]. Hydrogen atoms and solvent molecules are omitted for clarity; the DMF molecule is represented by the coordinating oxygen atom; open broken lines represent connections to neighboring $\{Cu_3L\}^+$ units.



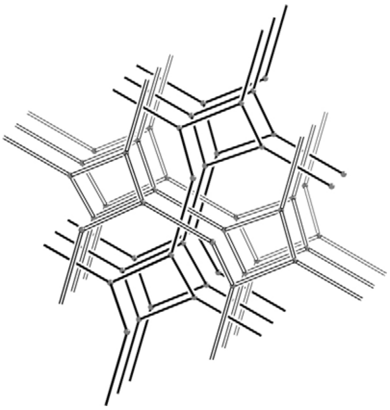
Scheme 9. Topology of the porous framework of the copper coordination polymer with $\{Cu_3L^{OH}\}^+$ building blocks (nodes represent the central carbon atoms of the triaminoguanidine ligands) with one of the 10-membered rings of the (10,3)-a network highlighted [61].

crystallographically distinct $\{Cu_3L\}^+$ units. For one of the copper ions (Cu2) the square-planar coordination is completed by a chloride ion, whereas a DMF molecule occupies the axial position at the other copper ion (Cu1). The observed distortions eventually lead to a dihedral angle between the interlinked $\{Cu_3L\}^+$ units of about 70°.

The resulting coordination polymer is composed of two interpenetrating (10,3)-a networks of opposite handedness. A schematic representation is depicted in Scheme 8. Although two different $\{Cu_3L\}^+$ trigonal building blocks assemble the frameworks, no considerable distortion of the archetype (10,3)-a network is observed. This is consistent with the small deviations from the ideal 120° angles between the intercentroid vectors of the (10,3)-a networks, with values of about 119° at the trigonal building blocks.

By variation of the substitution pattern of the triaminoguanidine ligand (R = OH, cf. Scheme 6) it is possible to generate even a porous chiral 3D network [61]. The same basic bridging situation is observed as it is depicted in Fig. 6 for the interpenetrated example. However, the additional hydroxy substituent at the aromatic rings in *para* position to the coordinating phenolate group prevents the filling of the resulting 3D channels by a second interpenetrated network of opposite handedness. This leads to a porous framework for the copper coordination polymer with $\{Cu_3L^{OH}\}^+$ building blocks. The schematic representation of the topology of the porous (10,3)-a network is shown in Scheme 9.

The size-limiting feature of the 3D channels within the $\{Cu_3L^{OH}\}$ coordination polymer are pseudotetrahedral cavities which are defined by the non-coordinating hydroxy groups of the ligand with a diameter of about 0.8 nm for an inscribed sphere. This leads to a hydrophilic character of the solvent-accessible free volume (about 56%). A representation of the void space is given in Fig. 7.



Scheme 8. Topology of the two interpenetrated (10,3)-a nets of a copper coordination polymer with $\{Cu_3L\}^+$ building blocks (nodes represent the central carbon atom of the triaminoguanidine ligands) [60].

3.3. *Magnetic properties of triaminoguanidine-based assemblies*

From the magnetochemistry point of view tritopic ligands can provide several promising features. The probably most employed concept in this context is spin polarization, which for tritopic aromatic ligands with a methylene bridged benzene core should give rise to ferromagnetic coupling schemes, allowing the generation of high-spin molecules [32]. However, such ligands have shown to transmit only rather small exchange interactions leading to only very weakly coupled systems. An alternative option aims at the contrary, i.e. the generation of antiferromagnetically coupled systems. Here transition-metal ions with half-integer spin are of particular interest, as they afford trinuclear metal complexes with a resulting non-zero spin ground state. Besides the fundamental interest in the properties of spin-frustrated systems [62], such a situation is proposed to enable new perspectives in fields like quantum computing with magnetic molecules exhibiting relevant electronic properties [63].

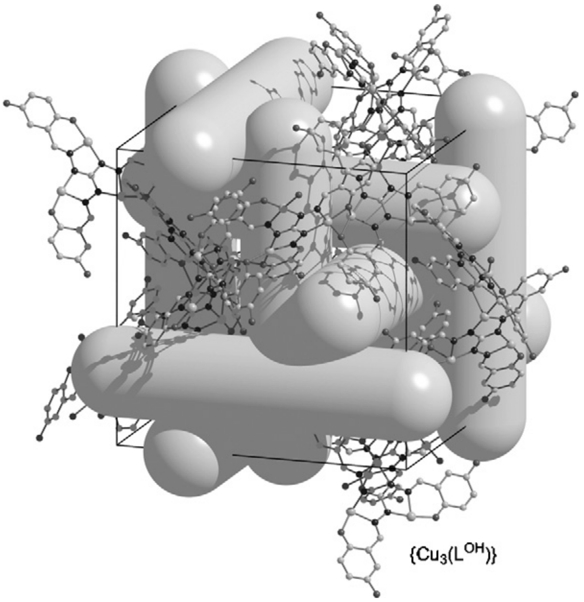


Fig. 7. Representation of the unit cell of the coordination polymer based on $\{Cu_3L^{OH}\}$ building blocks with the pseudo-tetragonal channels illustrated as cylinders with a diameter of 0.8 nm; all building units originating within the cell are generated [61].

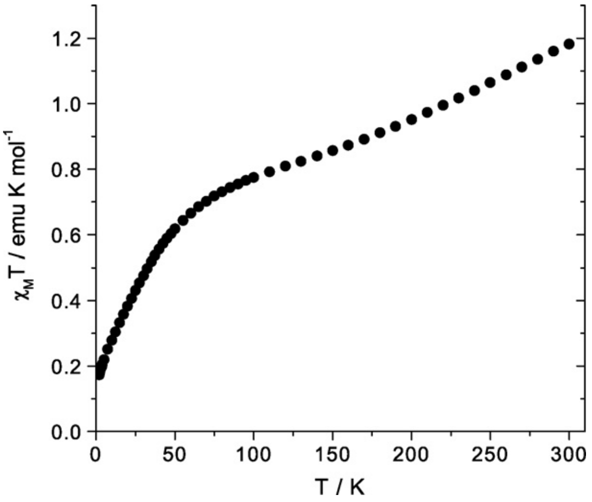


Fig. 8. Temperature dependence of $\chi_M T$ for the three-dimensional coordination polymer with {Cu$_3$L}$^+$ building blocks [60].

Trinuclear complex fragments based on the tritopic triaminoguanidine framework (see Scheme 7) exhibit rather short metal–metal distances of about 500 pm within a planar π-bonded CN$_6$ bridging core unit. For nickel(II) complexes this leads to rather strong antiferromagnetic interactions of about −30 cm^{-1} between the metal ions [52]. This is well within the range generally observed for diazine bridged binuclear nickel(II) complexes [64]. Nevertheless, it should be noted here, that in contrary to the usually observed *Z* configuration of the M–N=N–M diazine bridge, for the triaminoguanidine core an *E* configuration is present. Due to the C_3 symmetry of the trinuclear nickel(II) complex a non-magnetic $S = 0$ ground state is obtained.

The magnetic properties of the three-dimensional coordination polymers obtained by the assembly of the trinuclear copper(II) building blocks {Cu$_3$L} also exhibit antiferromagnetic interactions. Moreover, the temperature dependence of the $\chi_M T$ data depicted in Fig. 8 is indicative of a strong coupling within spin-frustrated Cu$_3$ triangles of the building blocks in the order of about 320 cm^{-1} [60]. Moreover, from the observed plateau in the $\chi_M T$ diagram it is evident that the interactions within the spin frustrated trinuclear {Cu$_3$L}$^+$ units dominate the system and that the exchange coupling along the interlocking binuclear copper(II) units (see Fig. 6) must be considerably lower in magnitude.

An estimate for the interbuilding block coupling interaction of the bis(phenoxide)-bridged copper(II) centers can be derived from the magneto-structural correlation between the Cu–O(Ph)–Cu bridging angle and the coupling constant J ($J = 2462–31.95\alpha$) [9]. The derived value of about −500 cm^{-1} based on an average angle of 93° clearly overestimates the actual exchange coupling constant. This is in line with the well-known hinge distortion (cf. Scheme 3), which increases the ferromagnetic character of the relevant coupling constant. However, even more important might be the fact, that the bridging oxygen atom O1 is in axial position with respect to the square-planar arrangement at the Cu2 center (see Fig. 2) and hence not capable of transmitting an efficient overlap between the relevant magnetic orbitals of the two copper(II) centers.

4. Conclusions

The use of 2-aminoglucose-modified ligands allows the generation of a series of oligonuclear copper(II) and nickel(II) complexes with exceptional magnetic properties. Although 2-aminoglucose ligands can be regarded as analog for simple 2-aminoalcohols, their chiral and rigid sugar backbone provides specific structural and chemical properties which can be utilized as structural directives. As a consequence the substitution pattern of 2-aminoglucose derivatives allows to control the magnetic properties of their relevant polynuclear complexes. Moreover, in the case of copper(II) ions this enables the synthesis of a tetranuclear complex combining a ferromagnetic ground state with optical activity. Utilizing triaminoguanidines as tritopic ligands it is possible to synthesize trinuclear complexes with strong antiferromagnetic exchange coupling between the metal ions. This allows to generate building blocks with a magnetic ground state, that show spin-frustration within the triangular arrangement. The assembly of such trinuclear copper(II) building blocks leads to polymeric materials, which clearly indicate the efficient exchange coupling through the bridging triaminoguanidine ligand system. By variation of the substitution pattern at the ligand system it is possible to even generate a porous magnetic coordination polymer. The magnetic properties of the relevant complexes can be related to well-known magneto-structural correlations, which in turn might allow for a deliberate design of new compounds and materials utilizing the ligand systems described here.

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