Verdazyl-based extended structures: synthesis, structures and magnetic properties of silver(I) one dimensional compounds†

Fabrice Pointillart,[a] Cyrille Train,*[a] Patrick Herson,[a] Jérôme Marrot[b] and Michel Verdaguer*[a]

Received (in Montpellier, France) 5th February 2007, Accepted 21st March 2007
First published as an Advance Article on the web 19th April 2007
DOI: 10.1039/b701686g

The reactions of silver(I) perchlorate with 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide and its oxidized form, the radical 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-6-oxoverdazyl, afford one-dimensional compounds **1** and **2**. Single crystal X-ray diffraction shows that both compounds are built from cationic chains of silver(I) ions bridged by bidentate ligands. The one-dimensional objects are isolated from one another by perchlorate ions and solvent molecules. The oxidation state of the ligands is preserved during the reaction, even under aerobic conditions. The verdazyl derivative presents an intrachain antiferromagnetic exchange interaction $J = -7.5$ cm^{-1} ($H = -J\Sigma S_i \cdot S_{i+1}$) between two radicals through the diamagnetic silver(I) ion.

Introduction

The development of molecular magnetism from magnetochemistry has made intensive use of the classical ligands of coordination chemistry, *e.g.* diamagnetic molecules and ions. This strategy has given numerous examples of strong exchange interaction between the bridged metal ions[1] and has allowed tuning of the dimensionality in a controlled manner. Nevertheless using stable radicals as bridging ligands appeared an attractive way to develop even stronger interactions relying on the unpaired electron of the ligand. The most studied radicals are the (nitronyl) nitroxides,[2,3] nitroxides[4] and semiquinones.[5,6] Another coordinating radical has recently appeared, namely verdazyl. Very strong metal–radical coupling constants have indeed been observed.[7–11] Compared to its predecessors, a bridging verdazyl ligand is bischelating, topologically comparable to an oxalate ligand. The bridge is then constituted of two sets of three atoms. For the radical moiety, the shortening of the bridge allows a good exchange interaction between the linked moieties.

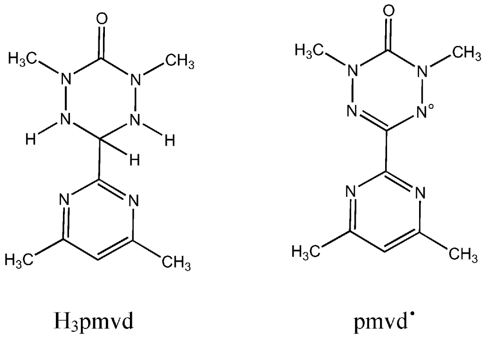
Nitronyl nitroxides have been used to obtain compounds whose dimensionality ranges from 0 to 2.[2,12] In the latter case, it led to a ferromagnet with a Curie temperature as high as 40 K.[12] In contrast, to date, verdazyl-based radicals have mainly led to discrete compounds. The main drawback of these ligands in synthesizing extended structures is their weak Lewis basicity, which imposes either enhancement of the Lewis acidity of the metal ions and/or the introduction of strongly basic pyridine moieties on the ligand.[6–9,13,14] These strategies have until now limited the synthesized products to discrete entities. One noticeable exception has been proposed by Brook *et al.*[15]

Along these lines, we present a strategy based on the use of metal ions free of electron-withdrawing ligands. To preserve as much as possible the Lewis acidity of the metal ion, we use weakly coordinating counter-ions to ease the coordination of 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide (H_3pmvd) and its oxidized radical form, 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-6-oxoverdazyl (pmvd$^•$), to metal ions. We describe the synthesis and structure of one dimensional (1D) compounds where silver(I) ions are bridged either by H_3pmvd or by pmvd$^•$ (Scheme 1). The comparison between the two compounds provides useful information on the chemical reactivity of the two ligands towards Lewis acids and on the influence of the oxidation state on the structural properties as well. The magnetic properties of the radical bridged 1D compound are analysed and discussed.

Results and discussion

Synthesis

Tetrazane 6-oxide molecules are usually spontaneously oxidized in their verdazyl radical form in air in the presence of metal ions such as Co(II) or Cu(I).[11,13] Instead, H_3pmvd



Scheme 1

---

[a] *Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Unité CNRS 7071, IFR 2769, Université Pierre et Marie Curie—Paris 6, 4 place Jussieu, case 42, 75252 Paris Cedex 05, France*

[b] *Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France*

† The HTML version of this article has been enhanced with colour images.

Table 1 Crystal data for **1** and **2**

Compound	$Ag(H_3pmvd)_n{}^+n(ClO_4{}^-)n(CH_3CN)$ **1**	$Ag(pmvd^\bullet)_n{}^+n(ClO^-)n(H_2O)$ **2**
Formula	$C_{12}H_{19}N_7O_5ClAg$	$C_{10}H_{15}N_6O_6ClAg$
M/g mol^{-1}	484.65	458.6
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*, $Z = 8$	$P2_1/n$, $Z = 4$
Cell parameters	$a = 12.2251(7)$ Å	$a = 10.3656(4)$ Å
	$b = 15.406(9)$ Å	$b = 14.7041(6)$ Å
	$c = 19.7291(10)$ Å	$c = 11.0971(4)$ Å
		$\alpha = \gamma = 90°$
	$\alpha = \beta = \gamma = 90°$	$\beta = 111.493(2)$
Volume V/Å^3	3716(2)	1573.8(2)
T/K	250	100 (2)
Number of variables	174	221
R_1, wR_2	0.114, 0.110	0.0523, 0.1313
Goodness of fit	1.071	1.039

showed itself to be stable towards oxidation when crystallizing $Ag(H_3pmvd)_n{}^+n(ClO_4{}^-)n(CH_3CN)$ (**1**) in aerobic conditions. This stability has been exploited to obtain, for the first time, similar coordination compounds with the reduced and oxidized forms of the ligand.

The ability of both forms of the ligand to bind a metal ion can appear surprising. The oxidation of H_3pmvd to $pmvd^\bullet$ weakens the σ-donating activity of the ligand but opens the possibility of back-bonding with the now singly occupied π* orbitals of the ligand. The synthesis of **1** and $Ag(pmvd^\bullet)_n{}^+n(ClO^-)n(H_2O)$ (**2**) indicates that the two phenomena tend to cancel one another out.

It remains that, following the published results emphasizing the difficulty in the synthesis of coordination compounds including verdazyl-containing ligands, these two ligands are weak Lewis bases. Up to now, the synthesis of such compounds followed two strategies to overcome the problem. The first relies on the enhanced acidity of the metal center by electron-withdrawing ligands like (1,1,1,5,5,5)-hexafluoroacetylacetonate ($hfac^-$) or trifluoroacetate ligands initially proposed in the coordination chemistry of other radicals.[16] A complementary strategy is the use of chelating ligands including one[7,14,17–19] or two[8,11] pyridine moieties whose Lewis basicity is much higher than that of the pyrimidine[20] moiety. In the former strategy, the presence of blocking ligands limited the chemistry to the formation of discrete homometallic dinuclear complexes where verdazyl radicals bridge the two metal ions. In the latter case, mononuclear species are obtained. In the present work, the reaction of the metal ion with poor Lewis bases was made possible by the choice of perchlorate,[21] a weakly coordinating counter-ion. The absence of the electron-withdrawing ligands in the coordination sphere of the metal ion together with the use of pyrimidine substituted verdazyl-based species has left open all the potential connections. As silver(I) can be bound to two bidentate ligands[22] and bis(bidentate) H_3pmvd and $pmvd^\bullet$ are linear connectors, one dimensional (1D) extended structures can be obtained, as demonstrated by the single crystal structures of **1** and **2**.

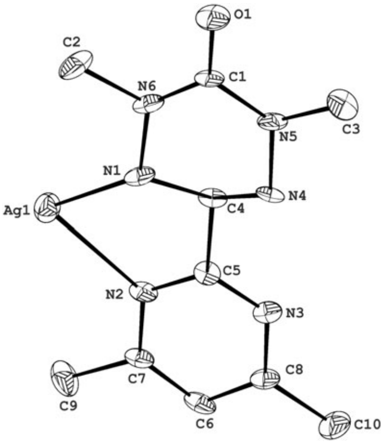


Fig. 1 Molecular structure of **1**: the atoms of the asymmetric unit that form the cationic moiety are shown as thermal ellipsoids at the 30% probability level; perchlorate ion and acetonitrile molecule are omitted for clarity.

Structure‡

Compound **1** crystallizes in the *Pbca* space group (Table 1). The asymmetric unit is composed of one silver(I) ion, one H_3pmvd ligand, one perchlorate anion and one acetonitrile molecule (Fig. 1). Because of thermal agitation, the two latter were refined isotropically. The presence of a hydrogen atom on the C(4) carbon atom induces a tetrahedral geometry around this atom and a non coplanarity of the 4,6-dimethyl-2-pyrimidyl and the 1,5-dimethyl-1,2,4,5-tetrazane 6-oxide rings (Fig. 2a). Two H_3pmvd ligands are bound to the silver ion. The dihedral angle between the mean plane of the ligands is 128.1° (Fig. 2b). The average distance between the nitrogen atoms of the pyrimidine moiety and the silver atom is 2.293 Å while it is 2.445 Å for the tetrazane 6-oxide moiety (Table 2). The mean N–Ag–N bite angle is 69.2°. The coordination polyhedron around the silver atom is best described as a flattened tetrahedron (Fig. 3). The mirror symmetry with respect to the (100) plane generates a 1D structure with H_3pmvd ligands bridging silver(I) ions (Fig. 3). A significant change is observed upon coordination of the organic ligand to the silver(I) ion. In the solid state, the two rings of the free H_3pmvd are almost perpendicular.[23] In **1**, upon coordination to silver(I), the H_3pmvd molecule, though not perfectly planar, is strongly flattened compared to the free ligand (Fig. 2).

---

‡ CCDC reference numbers 634853 and 635223. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701686g

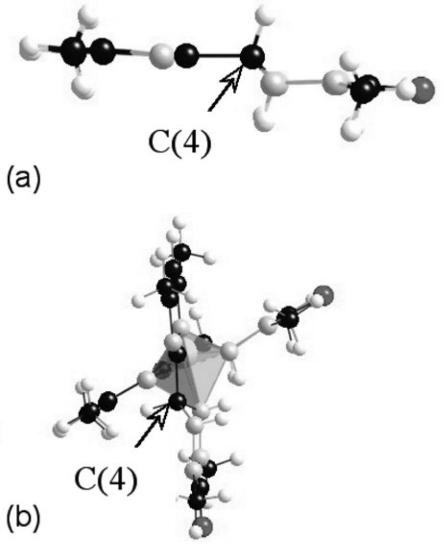


Fig. 2 (a) Tetrahedral geometry around the C(4) atom of the ligand in **1**. (b) View along 100 of the cationic chains in **1** illustrating the flattening of the ligand upon coordination.

Compound **2** crystallizes in the $P2_1/n$ space group (Table 1). The asymmetric unit is composed of one silver(I) ion, one pmvd$^\bullet$ molecule, one perchlorate anion and one water molecule (Fig. 4a). The absence of hydrogen atoms on C(7), N(8) and N(12) and the planar geometry around the C(7) atom confirms that the molecule is in its oxidized pmvd$^\bullet$ radical form. The two rings of pmvd$^\bullet$ are coplanar. The silver(I) ion is surrounded by two pmvd$^\bullet$ ligands. The coordination of the silver atom is a nearly regular tetrahedron. The dihedral angle between the two verdazyl rings coordinated to the silver(I) ion is 95.0° (Fig. 4b). The nitrogen atoms from the pyrimidine moiety are located at an average distance of 2.286 Å from the silver ion while this mean distance is 2.309 Å for the oxoverdazyl moiety (Table 3). The mean N–Ag–N bite angle is 71.8°. The mirror symmetry with respect to the (1$\bar{1}$1) plane generates a one-dimensional structure where verdazyl ligands bridge silver(I) ions (Fig. 5). The planarity of the oxoverdazyl radical and the observed bond lengths and angles are close to those observed for other oxoverdazyl radicals coordinated to metal atoms.[9,15,24]

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Ag(1)–N(1)#1	2.401(10)	C(4)–N(1)	1.469(15)
Ag(1)–N(4)	2.498(10)	C(4)–N(4)	1.459(14)
Ag(1)–N(2) #1	2.307(9)	N(4)–N(5)	1.423(13)
Ag(1)–N(3)	2.279(11)	N(1)–N(6)	1.429(14)
C(5)–N(2)–Ag(1)#2	119.1(7)	N(1)–C(4)–C(5)	109.8(9)
N(2)#1–Ag(1)–N(1)#1	69.3(3)	C(4)–C(5)–N(2)	117.3(9)
N(3)–Ag(1)–N(4)	69.1(3)	Ag(1)#2–N(1)–C(4)	108.3(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - 3/2, y - 1, -z - 1/2$; #2 $x - 1/2, y, -z + 1/2$.

The four nitrogens of the verdazyl moiety are separated from the oxygen atom of the neighbouring water molecule by distances ranging from 3.032 to 3.469 Å. These distances are in accordance with hydrogen bonds between the water molecule and the verdazyl ring. This water molecule has no other close neighbour. As is shown in Fig. 5, the nearest pmvd$^\bullet$ radicals of neighbouring chains are perpendicular to one another excluding π-interactions. Together with the absence of interchain hydrogen bonds or any other noticeable interchain interactions, this means that the chains can be considered as isolated.

It is worthwhile to briefly compare the structures of **1** and **2**. When going from **1** to **2**, a shortening of respectively 0.140 Å and 0.071 Å of the mean C–N and N–N bond lengths is observed related to the change from the tetrazane to verdazyl moiety. The other distances within the tetrazane/verdazyl moiety decrease by less than 0.03 Å. At the same time, the bond distances within the pyrimidine ring increase by less than 0.03 Å. This development is due to the transformation of the highest occupied molecular orbital into a singly occupied one upon oxidation whose electron density is concentrated on the NNCNN fragment of the verdazyl moiety.[25] The mean bond length between Ag(I) and the pyrimidine moiety remains practically unchanged when going from **1** to **2**. At the same time, the bond lengths between the silver atom and the nitrogen atoms of the second moiety of the ligand decrease by 0.140 Å while the bite angle increases by 2.6°. This indicates that the loss of σ-donating capability upon oxidation is overcome by the appearance of strong π-back donation from the metal to the SOMO of the ligand.[17] The flattening of the tetrahedron around silver(I) when going from **2** (Fig. 4b) to **1** (Fig. 3) can be attributed to the mismatch between the two rings of the ligands (Fig. 2) appearing in H_3pmvd compared to their coplanarity in pmvd$^\bullet$.

1 is the first compound where a verdazyl-based ligand appears in its reduced form while **2** is the first extended

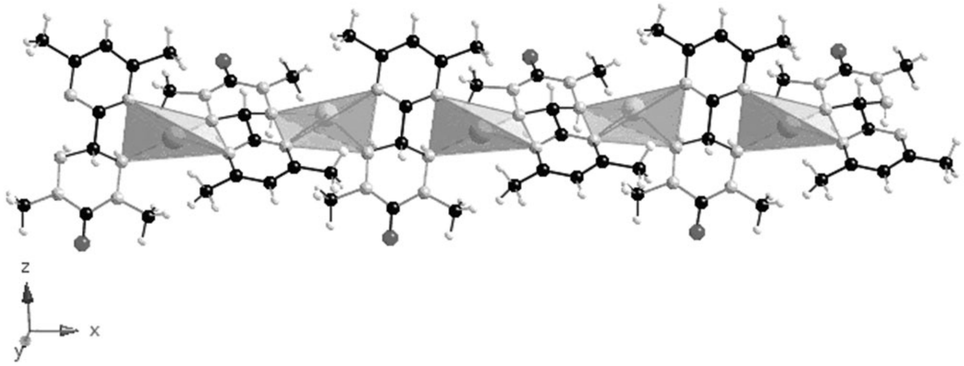


Fig. 3 The flattened tetrahedral geometry of silver(I) ion in the cationic chains of **1**. Perchlorate ions and acetonitrile have been omitted for clarity.

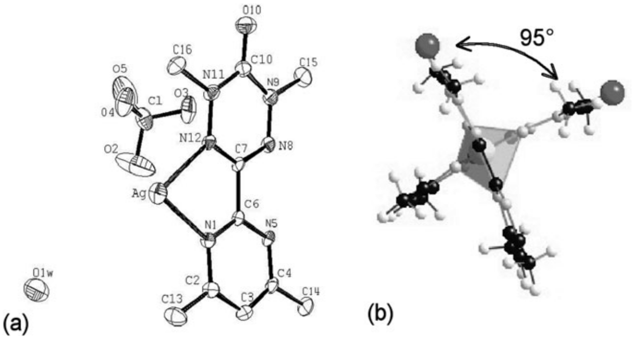


Fig. 4 (a) Molecular structure of **2**: the atoms of the asymmetric unit are shown as thermal ellipsoids at the 30% probability level. (b) View along the cationic chains of **2** illustrating the planarity of pmvd• and the tetrahedral environment of the silver ion.

oxoverdazyl-based structure where two radicals are bound through a diamagnetic ion. As such, the magnetic properties of **2** deserve particular attention.

Magnetic properties

1 is built from a d^{10} silver(I) ion and a non radical ligand. It is a diamagnetic compound. The thermal variation of the molar magnetic susceptibility χ_M of **2** shows a monotonic increase when the temperature decreases (Fig. 6). The χ_MT product decreases monotonically when the temperature decreases (insert of Fig. 6). The $\chi_M T$ value at 300 K is 0.376 emu K mol^{-1}. Its remains nearly unchanged down to 150 K and then falls smoothly to 0.226 emu K mol^{-1} at 5 K.

The $\chi_M T$ value at room temperature is very close to the theoretical value 0.375 cm^3 K mol^{-1} for one isolated spin of a radical ($S = 1/2$, $g = 2.00$). The thermal variation of the $\chi_M T$ product is characteristic of a weak but noticeable antiferromagnetic coupling between paramagnetic species. The crystal structure shows that **2** is made of well isolated chains of radicals linked by silver(I) ions. This statement is crucial since recent studies have shown both experimentally and theoretically that π-stacking can mediate very strong exchange interaction in verdazyl-based materials.[25,26] In the present case, the antiferromagnetic exchange coupling is then an intrachain one between spins 1/2 of nearest neighbours radicals S_i and S_{i+1}. The experimental magnetic susceptibility can thus be fitted with the 1D antiferromagnetic model of Bonner and Fischer:[27]

$$\chi_M = (Ng^2\mu_B^2)/(kT)(0.41058 + 0.46049x + 0.49970x^2)/(1 + 2.17368x + 2.02133x^2 + 1.90290x^3)$$

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Ag–N(12)	2.334(2)	C(7)–N(8)	1.328(3)
Ag–N(8)#1	2.284(2)	C(7)–N(12)	1.323(3)
Ag–N(5)#1	2.303(2)	N(9)–N(8)	1.353(4)
Ag–N(1)	2.269(2)	N(12)–N(11)	1.357(3)
C(6)–N(1)–Ag	118.09(19)	N(12)–C(7)–C(6)	116.3(2)
N(1)–Ag–N(12)	71.57(8)	C(7)–C(6)–N(1)	117.3(2)
N(5)#1–Ag–N(8)#1	72.06(9)	Ag–N(12)–C(7)	116.65(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1/2, -y + 1/2, z + 1/2$.

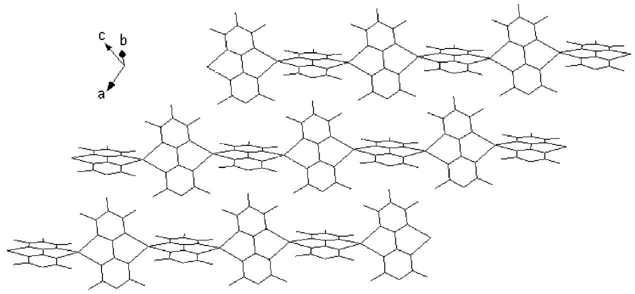


Fig. 5 Crystal packing of the cationic $Ag(pmvd^\bullet)_n^+$ chains of **2** (perchlorate ions and water molecules are omitted for clarity).

with $H = -J\,\Sigma_i\, S_i \cdot S_{i+1}$ and $x = -J/2\,kT$.

Fixing the value of g to 2.00, the best fit gives an exchange interaction constant $J = -7.5$ cm^{-1} (Fig. 6).

Because it governs the value of the overlap between the SOMOs of the radicals, the dihedral angle between the radicals is often considered as a key parameter to determine the overlap between the magnetic orbitals and therefore the sign and the value of J. Two examples taken from imino nitroxide chemistry show that strong ferromagnetic exchange interactions are found for a dihedral angle of 90° while a substantial antiferromagnetic interaction is found for an angle value close to 0°.[28] For verdazyl-based radicals, the most valuable system for comparison is the mononuclear bis(1,5-dimethyl-3-(6-methylpyridyl)-6-oxoverdazyl)copper(I) complex where a J value of -2 cm^{-1} has been found for a dihedral angle between the two radicals equal to 115.8°.[18] The decrease of the angle from 115.8° in the copper(I) complex to 95° in the silver(I) compound **2** is not followed by a decrease in the antiferromagnetic interaction. At first sight, this can appear surprising because a decrease in the overlap is expected when the dihedral angle is decreased. It means that the nature of the diamagnetic metal ion binding the two radicals, especially the energies and the diffuseness of the occupied d and vacant p orbitals, must have a strong influence on the magnitude of the exchange interaction between the radicals.[17] Previous calculations have failed to reproduce the experimental behaviour of the copper(I) bisverdazyl complexes.[19] A theoretical study based on *ab initio* calculation is under way to determine the role of the different parameters.

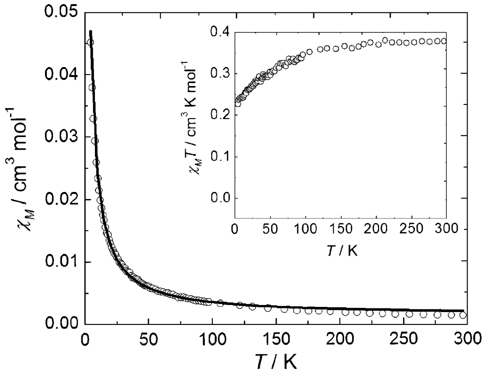


Fig. 6 Thermal variation of the molar magnetic susceptibility, χ_M and $\chi_M T$ product (inset) for **2** and best fit for χ_M (see text).

Concluding remarks

The stability under aerobic conditions of 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide (H_3pmvd) and the reduced form 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-6-oxoverdazyl (pmvd$^\bullet$) even when metal ions are present allows the use of both molecules as ligands. The reaction with silver(I) perchlorate[21] leads to single crystals of the first coordination compound with the reduced form of an oxoverdazyl radical. Thanks to the absence of electron withdrawing ligands in the coordination sphere of the metal ions, it is possible to get extended structures with both H_3pmvd and pmvd$^\bullet$ acting as bidentate bridging ligands between silver(I) ions. The comparison of these parent extended coordination compounds indicates that the Lewis basicity of the ligand is enhanced upon oxidation because of the appearance of π-accepting orbitals. When the pmvd$^\bullet$ radical is used, isolated chains of spin 1/2 coupled through the diamagnetic silver(I) are obtained. They present a uniform intrachain antiferromagnetic interaction between two successive radicals $J = -7.5\ \mathrm{cm}^{-1}$ ($H = -\Sigma_i JS_i \cdot S_{i+1}$).

As exemplified in nitronyl nitroxide,[12] the stability of the pmvd$^\bullet$ ligand and its ability to react with non-activated metal ions open new possibilities for using this versatile building block for the preparation of multifunctional molecular magnetic materials of various dimensionalities where a stronger interaction between the spin bearers allows enhancement of the critical temperatures of the systems.

Experimental

H_3pmvd and pmvd$^\bullet$ were synthesized according to literature methods.[29] All other reagents were used as received.

Synthesis and crystallization conditions

Caution! Perchlorate salts are potentially explosive and should be handled with care, at room temperature, without shocks and in small amounts.[21]

Ag(H_3pmvd)$_n{}^+$, n($ClO_4{}^-$) n(CH_3CN), 1. An ethyl acetate solution (5 mL) containing 70.8 mg of H_3pmvd (M = 236 g mol^{-1}; 0.03 mmol) is added to a solution containing 22.5 mg of silver(I) perchlorate monohydrate $Ag(ClO_4)(H_2O)$ (M = 225 g mol^{-1}; 0.01 mmol) dissolved in the minimum amount of ethyl acetate. The mixture is stirred for 30 min in the dark. Then the solution is filtered out and the yellow solid is washed twice with 2 mL of ethyl acetate to remove excess H_3pmvd ligand. The resulting solid is dissolved in a minimum of acetonitrile. Slow diffusion of gaseous ether, in the dark, allows pale yellow needle-shaped single crystals of 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide silver(I) perchlorate Ag(H_3pmvd)$_n{}^+$ n($ClO_4{}^-$)n(CH_3CN) to be obtained after four days. IR (KBr) ν_{max}/cm^{-1}:3206m (N–H), 2960w, 2923w (C–H), 1660vs (C═O), 1611s, 1542s (C═N), 1442m, 1428m (C–C), 1101s (Cl–O).§

Ag(pmvd$^\bullet$)$_n{}^+$ n($ClO_4{}^-$) n(H_2O), 2. An acetonitrile solution (5 mL) containing 45.1 mg of silver(I) perchlorate monohydrate $Ag(ClO_4)(H_2O)$ (M = 225 g mol^{-1}; 0.02 mmol) is slowly added to an acetonitrile solution (5 mL) containing 46.7 mg of pmvd$^\bullet$ (M = 233 g mol^{-1}; n = 0.02 mmol). The colour of the solution readily changes from orange to brown-red. During the 30 min stirring in the dark, a solid appears. It is redissolved by adding 5 mL of acetonitrile. Dark brown single crystals are obtained after two days by slow evaporation in the dark at room temperature.

IR (KBr) ν_{max}/cm^{-1}:2962w, 2926w (C–H), 1704vs (C═O), 1612s, 1538s (C═N), 1441m (C–C), 1095s (Cl–O).§

Physical measurements

The IR spectra were recorded on a Bio-Rad IRFT spectrometer as KBr pellets in the 4000–250 cm^{-1} region.

The magnetic susceptibility of a set of small single crystals was measured in a 0.1 T external field between 5 and 300 K on a Quantum Design MPMS5 SQUID magnetometer and corrected for temperature independent effects (1.0×10^{-3} cm^3 mol^{-1}) before fitting with the expression given in the text.

X-Ray crystallography

Crystallographic data for **1** were recorded at 250 K on a Kappa-CCD Bruker diffractometer with graphite mono-chromated MoKα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 147 reflections within the range of $3° < \theta < 17°$. The index ranges of data collection were $-11 \leq h \leq 15$, $-19 \leq k \leq 11$, $-25 \leq l \leq 24$. Intensity data were collected in the θ range 3.0–27.5°, 1904 independent reflections have $F_0{}^2 \geq 3\sigma F_0{}^2$. All the measured independent reflections were used in the analysis. The structure was solved by direct methods using SHELXS86[30] and refined with full-matrix least-squares technique on F using the CRYSTALS[31] programs. Non-hydrogen atoms were refined anisotropically (except for CH_3CN and $ClO_4{}^-$). All hydrogen atoms were set in calculated positions and isotropically refined. The values of the discrepancy indices $R1$ ($Rw2$) for all data were 0.114 (0.110), whereas those listed in Table 1 correspond to the data with $I < 3\sigma(I)$. The final Fourier–difference map showed maximum and minimum height peaks of 1.52 and −1.52 e Å^{-3}. The values of number of reflections/number of variable parameters are 196, and those of the goodness-of-fit are 1.106. The molecular structure was drawn with the program CAMERON.[32]

For **2**, a single crystal ($0.24 \times 0.06 \times 0.02$ mm^3) was mounted with Paratone-N oil (Hampton Research) coating and immediately placed in a nitrogen cold stream. X-Ray intensity data were collected at 100 K on a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Nine sets of narrow data frames (30 s per frame) were collected at different values of θ, for 4 and 5 initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω. Data were collected from $\theta = 2.41°$ up to 35.48° (99.4% coverage). The index ranges of data collection were $-16 \leq h \leq 16$, $-24 \leq k \leq 22$, $-16 \leq l \leq 18$. 38 252 reflections were collected. Data reduction was accomplished using SAINT V7.03[33] leading to 7122 independent reflections (4716 $F_0 > 4\sigma F_0$). The substantial redundancy in data allowed

---

§ Intensity: w, weak; m, medium; s, strong; vs, very strong.

a semi-empirical absorption correction (SADABS V2.10)[33] to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELXTL V6.14.[34] Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms. The highest residual electron density was 2.894 e Å^{-3}. The values of the discrepancy indices $R1$ ($Rw2$) for all data were 0.0902 (0.1469), whereas those listed in Table 1 correspond to the data with $I < 2\sigma(I)$. The final Fourier–difference map showed maximum and minimum height peaks of 2.893 and -1.396 e Å^{-3}. The values of number of reflections/number of variable parameters are 173, and the goodness-of-fit is 1.040.

Acknowledgements

Authors thank CNRS (France), Université "Pierre et Marie Curie" (France) and DFG (SPP 1137) for financial support.

References

1 (*a*) Y. Pei, M. Verdaguer, O. Kahn, J. Sletten and J.-P. Renard, *J. Am. Chem. Soc.*, 1986, **108**, 7428; (*b*) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.*, 1992, **114**, 6974; (*c*) S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701.

2 (*a*) A. Caneschi, D. Gatteschi and P. Rey, *Prog. Inorg. Chem.*, 1991, **39**, 331; (*b*) L. Bogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5817.

3 (*a*) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760; (*b*) D. Luneau and P. Rey, *Coord. Chem. Rev.*, 2005, **249**, 2591; (*c*) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 2006, **128**, 7947.

4 (*a*) H. Kumagai and K. Inoue, *Angew. Chem., Int. Ed.*, 1999, **38**, 1601; (*b*) S. Sakane, H. Kumada, S. Karasawa, N. Koga and H. Iwamura, *Inorg. Chem.*, 2000, **39**, 2891; (*c*) S. Kanewaga, S. Karasawa, M. Nakano and N. Koga, *Chem. Commun.*, 2004, 1750.

5 (*a*) A. Dei and A. Caneschi, *Inorg. Chim. Acta*, 1992, **198–200**, 813; (*b*) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331.

6 *Magnetism: Molecules to Materials*, ed. J. S. Miller and M. Drillon, vol. III, Wiley-VCH, Weinheim, 2001.

7 R. G. Hicks, M. T. Lemaire, L. K. Thompson and T. M. Barclay, *J. Am. Chem. Soc.*, 2000, **122**, 8077.

8 (*a*) T. M. Barclay, R. G. Hicks, M. T. Lemaire and L. K. Thompson, *Chem. Commun.*, 2000, 2141; (*b*) T. M. Barclay, R. G. Hicks, M. T. Lemaire and L. K. Thompson, *Inorg. Chem.*, 2003, **42**, 2261.

9 T. M. Barclay, R. G. Hicks, M. T. Lemaire and L. K. Thompson, *Inorg. Chem.*, 2001, **40**, 5581.

10 T. M. Barclay, R. G. Hicks, M. T. Lemaire, L. K. Thompson and Z. Xu, *Chem. Commun.*, 2002, 1688.

11 M. T. Lemaire, T. M. Barclay, L. K. Thompson and R. G. Hicks, *Inorg. Chim. Acta*, 2006, **359**, 2616.

12 K. Fegy, D. Luneau, T. Ohm, C. Paulsen and P. Rey, *Angew. Chem., Int. Ed.*, 1998, **37**, 1270.

13 D. J. R. Brook, S. Fornell, B. Noll, G. T. Yee and T. H. Koch, *J. Chem. Soc., Dalton Trans.*, 2000, 2019.

14 D. J. R. Brook, S. Fornell, J. E. Stevens, B. Noll, T. H. Koch and W. Eisfield, *Inorg. Chem.*, 2000, **39**, 562.

15 D. J. R. Brook, V. Lynch, B. Conklin and M. A. Fox, *J. Am. Chem. Soc.*, 1997, **119**, 5155.

16 (*a*) W. Parentheimer and R. S. Drago, *Inorg. Chem.*, 1970, **9**, 47; (*b*) A. Cogne, A. Grand, P. Rey and R. Subra, *J. Am. Chem. Soc.*, 1989, **111**, 3230; (*c*) D. Luneau, G. Risoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi and J. Laugier, *Inorg. Chem.*, 1993, **32**, 5616; (*d*) T. Yoshida, T. Suzuki, K. Kanamori and S. Kaizaki, *Inorg. Chem.*, 1999, **38**, 1059.

17 D. J. R. Brook and V. Abeyta, *J. Chem. Soc., Dalton Trans.*, 2002, 4219.

18 T. M. Barclay, R. G. Hicks, M. T. Lemaire and L. K. Thompson, *Inorg. Chem.*, 2001, **40**, 6521.

19 J. E. Stevens, D. J. R. Brook and V. W. Abeyta, *Polyhedron*, 2003, **22**, 2241.

20 G. De Munno, D. Armentano, M. Julve, F. Lloret, R. Lescouezec and J. Faus, *Inorg. Chem.*, 1999, **38**, 2234.

21 Warning: perchlorates are potentially explosive. They should be used in very small quantities and with utmost care. Every effort should be made to find appropriate substitutes for the use of perchlorate ions. In the present case, they appeared as the proper choice to combine very weak Lewis basicity and ease of crystallization.

22 H. Oshio and T. Ito, *Coord. Chem. Rev.*, 2000, **198**, 329.

23 (*a*) J. Wu, E. Bouwman, J. Reedijk, A. M. Mills and A. L. Spek, *Inorg. Chim. Acta*, 2003, **351**, 326; (*b*) A. M. Mills, J. Wu, E. Bouwman, J. Reedijk and A. L. Spek, *Acta Crystallogr., Sect. E, Struct. Rep. Online*, 2004, **E60**, 2482.

24 D. J. R. Brook, H. H. Fox, V. Lynch and M. A. Fox, *J. Phys. Chem.*, 1996, 2066.

25 J. Jornet, M. Deumal, J. Ribas-Arino, M. J. Bearpark, M. A. Robb, R. G. Hicks and J. J. Novoa, *Chem.–Eur. J.*, 2006, **12**, 3995.

26 R. G. Hicks, M. T. Lemaire, L. Ohrstrom, J. F. Richardson, L. K. Thompson and Z. Xu, *J. Am. Chem. Soc.*, 2001, **123**, 7154.

27 (*a*) G. A. J. Baker, J. L. Gammer and J. G. Willis, *J. Math. Anal. Appl.*, 1961, **3**, 405; (*b*) J. C. Bonner and M. E. Fischer, *Phys. Rev. A*, 1964, **35**, 640.

28 (*a*) H. Oshio, T. Watanabe, A. Ohto, T. Ito and U. Nagashima, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 670; (*b*) H. Oshio, A. Ohto and T. Ito, *Chem. Commun.*, 1996, 1541.

29 C. L. Barr, P. A. Chase, R. G. Hicks, M. T. Lemaire and C. L. Stevens, *J. Org. Chem.*, 1999, **64**, 8893.

30 G. M. Sheldrick, *SHELXS86*, Computer program for structure solution University of Göttingen, Germany, 1986.

31 J. R. Carruthers, P. W. Betteidge and R. I. Cooper, *CRYSTALS 11*, Chemical Crystallography Laboratory, Oxford, UK, 2001.

32 D. J. Watkin, C. K. Prout and L. J. Pearce, *CAMERON 11*, Chemical CrystallographyLaboratory, Oxford, UK, 1996.

33 APEX2 1.0-8, Bruker AXS, Madison, WI, 2003.

34 SHELXTL 6.14, Bruker AXS, Madison, WI, 2001.