1	Dinuclear, tetranuclear and polymeric complexes in
2	copper(II) perchlorate/pyridine-2,6-diamidoxime
3	chemistry: synthetic, structural and magnetic studies†
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25 Abstract

The initial use of pyridine-2,6-diamidoxime (pdamoH₂) in metal cluster and polymer chemistry is described. Depending on the reaction conditions employed, the Cu(ClO₄)₂·6H₂O/pdamoH₂ system has provided access to the dinuclear compound [Cu2(pdamoH)2(ClO4)2(MeOH)2] (1), the chain-like polymer [Cu2(pdamoH)2]n(ClO4)2n (2) and to the tetranuclear cluster [Cu4(pdamo)2(pdamoH)2](ClO4)2 (3). Single-crystal, X-ray crystallography reveals different coordination modes for the pdamoH- ligand in each compound, providing the first evidence for the flexibility and versatility of the anionic forms of pdamoH₂. Variable-temperature magnetic susceptibility studies indicate very strong antiferromagnetic coupling in the three complexes, attributable to the double oximato bridges which link the Cu^{II} spin carriers.

48 1. Introduction

Molecular metal complexes (clusters1) and coordination polymers of paramagnetic 49 3d-metal ions continue to be a major research topic of many groups around the world because 50 of the aesthetic beauty and complexity of their structures, their exciting physical properties 51 and their potential applications. Among the diverse reasons for the interest for new clusters 52 are the search for models of metal-containing biological sites,2 and new high-spin 53 molecules3 and single-moleculemagnets.4 The intense interest in the synthesis and study of 54 55 new coordination polymers (also known as metal-organic frameworks, metal-organic coordination networks or organic-inorganic hybrid coordination polymers in the case where 56 the metal-organic connectivity is interrupted by "inorganic" bridges)5 stems from their 57 potential application in fields and areas, such as catalysis, electrical conductivity, 58 magnetism, luminescence, non-linear optics, molecular electronics, medicine, gas storage, 59 anion separation, sensing and anion exchange. The ultimate goal is the transformation of 60 some coordination polymers to functional materials. Thus, there continues to be a need for 61 62 new synthetic methods to clusters and coordination polymers.

By contrast with organic chemists who have established methods for making 63 complicated molecules and organic polymers in a systematic and controlled manner, 64 inorganic chemists have made little progress in discovering general approaches to 65 synthesizing complexes containing large or infinite numbers of metal centres. The lack of 66 control in transition-metal chemistry has led to the neologism "self-assembly".⁶ In the last 67 decade or so, several groups have been introducing elements of design into the assembly 68 process by employing rigid ligands (e.g. the cyanido ion⁷ and various tailored derivatives of 69 4,4'-bipyridine⁸) that have strong preferences for specific bonding modes and metal ions 70 with preferred coordination geometries. This "designed assembly" approach has led to many 71 beautiful clusters⁹ and coordination polymers.¹⁰ Other researchers, including our groups, 72 use much less well-behaved bridging organic ligands (some with the ability to 73 simultaneously form chelating rings) for the preparation of clusters¹¹ and polymeric metal 74 compounds.¹² The flexibility of the polydentate ligands often allows the stabilization of 75 many unpredictable structures, almost invariably incorporating further ligands, e.g., 76 77 hydroxido, oxido, alkoxido, other inorganic anions or donor solvate molecules. The so-

named "serendipitous assembly"13 in cluster chemistry and the less-designed (or "non-78 79 programmed") assembly in the chemistry of coordination polymers vastly increases the range of compounds available for study, while sometimes the unusual structures lead to 80 interesting properties. However, luck is not enough in making clusters and polymers, and 81 considerable forethought in the metal ions, ligands and reaction conditions is necessary for 82 any significant progress to be made.¹⁴ Carboxylato,¹⁵ pyridonato,¹⁶ polyalcoholato,¹⁷ 83 pyridylalcoholato¹⁸ and oximato¹⁹ ligands are frequently used in this chemistry. The 84 deprotonated oxygen atoms of these ligands are not coordinatively saturated by binding to 85 one metal centre, and therefore act as bridges leading to the build-up of larger metal clusters 86 or polymers. As the fields develop, the boundary between "designed" and "serendipitous" 87 assembly becomes not clear: examples are the interesting compounds synthesized by 88 Saalfrank's group,²⁰ the ground-state spin-switching of clusters by targeted structural 89 distortion described by Brechin's group²¹ and the switchingon of single-molecule 90 magnetism properties in triangular Mn^{III} complexes reported by Christou and co-workers.²² 91

We and others have been investigating a number of oxime-based ligands, and one broad family of these have been the 2-pyridyl oximes^{19,23} and 2,6-pyridyl dioximes²⁴ (Scheme 1).

There is currently a renewed interest in the coordination chemistry of oximes, with the efforts of several groups being driven by a number of considerations.²⁵ 2-Pyridyl oximes and 2,6- pyridyl dioximes are popular molecules whose anions are versatile ligands for a variety of research objectives. Such ligands have been key "players" in several areas of single-molecule^{22,26} and singlechain magnetism. ²⁷ The activation of 2-pyridyl oximes by 3d-metal centres towards further reaction is also becoming an exciting area of research.²⁸

For many years, our groups have been engaged in the use of 2-pyridyl oximate ligands for cluster and coordination polymer synthesis. One step was the study of complexes of pao⁻ ,29 mpko⁻, 30 ppko⁻, 31 *i.e.*, with anionic ligands in which R contains no additional donor site (Scheme 1). In another step, we studied complexes with anionic ligands in which R contains a donor site, i.e., complexes of pyaoxH⁻/pyaox²⁻³² and (py)pko^{-29b}, 33 In a third step, we

recently initiated a study of the metal cluster and polymer chemistry of 2,6-diacetylpyridine 106 dioxime (dapdoH₂; Scheme 1) and reportedMn^{II}₃, (Mn^{II}₃)_n, Mn^{II}₂Mn^{III}₄, Mn^{II}₆ Mn^{III}₂, 107 Ni^{II}₂, Ni^{II}₃ and Ni^{II}₄ complexes.^{34–36} Our studies in metal/dapdoH₂ chemistry joined 108 previous literature reports^{24,37} on the employment of dapdoH⁻ and dapdo²⁻ for the 109 preparation of Mn^{II}₂ Mn^{III}₄,^{24a,b} Mn^{II}₂ Mn^{III}₆,^{24a} Gd^{III}₂ Mn^{IV},^{24c} Cu^{II}₂ Cr^{III}₂,^{37a} and 110 Fe^{II} Fe^{III}₂^{37b} clusters, as well as dinuclear Cu^{II}₂ complexes.^{37c} A natural extension of such 111 studies is the investigation of 2,6-pyridyl dioximes in which the non-donor Me groups are 112 replaced by potentially donor groups. If R is the amino group, the resulting ligand is 113 pyridine-2,6-diamidoxime or pyridine-2,6-dicarboxamide oxime (pdamoH₂; Scheme 1), 114 which belongs to the class of amidoximes. The presence of the two amine functionalities is 115 expected-due to their coordination capability, potential for deprotonation^{32,38} and hydrogen 116 bonding effects-to alter the coordination behaviour of this ligand (and hence the identity of 117 118 the resultant metal complexes) in comparison with that of the dapdoH₂ ligand.

In the present work, we report the initial use of the anionic pdamoH- and pdamo²⁻ 119 ligands in metal cluster and polymer chemistry by describing the products from the reaction 120 of Cu(ClO₄)₂·6H₂O and pdamoH₂ under various conditions. There are no literature reports 121 of anymetal clusters or coordination polymers of singly or doubly deprotonated pdamoH₂, 122 123 but its pyridyl, oxime and amino functionalities suggested a rich potential for the formation of such compounds. The use of *neutral* pdamoH₂ in metal chemistry had previously given 124 [Ni(pdamoH₂)₂](SO₄)·5H₂O and {[Cu(pdamoH₂)(m-SO₄)]·2H₂O}*n*,^{39a} while Salonen and 125 coworkers reported recently the crystal structure of the mononuclear complex 126 $[Ni(pdamoH)_2] \cdot 4H_2O^{39b}$ that contains the monoanionic form of the ligand. 127

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132 **2. Experimental**

133 Syntheses

134 [Cu2(pdamoH)2(ClO4)2(MeOH)2]·4MeOH (1·4MeOH). A colourless solution of 39 mg (0.2 mmol) of pdamoH₂ and 55 mg (0.4 mmol) of triethylamine in 15 mL of methanol 135 was mixed with a solution of 74 mg (0.2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 10 mL of methanol. 136 For about one hour the resulting dark green solution was stirred under heating at 50 C and 137 left to crystallize at room temperature in a closed vial. After four days, well formed dark 138 green cubic crystals of compound 1 were obtained in a 65% yield. Analytical data for 139 C20H40Cl2Cu2N10O18 (906.59): calcd. C 26.50, H 4.45, N 15.45; found: C 26.0, H 4.2, N 140 15.8. IR data (cm⁻¹): 3440 (m), 3353 (sb), 3310 (m), 1669 (s), 1627 (s), 1578 (s), 1410 (m), 141 1378 (w), 1137 (sh), 1091 (s), 1063 (sh), 927 (w), 819 (m), 732 (w), 681 (m), 626 (s), 543 142 143 (m), 465 (m).

[Cu2(pdamoH)2]n(ClO4)2n·2nMeCN (2·2MeCN). A colourless solution of 39 mg 144 (0.2 mmol) of pdamoH2 in 10 mL of methanol wasmixed with a solution of 74mg (0.2 mmol) 145 ofCu(ClO₄)₂·6H₂O in 20 mL of acetonitrile and stirred under heating at 50 C for 30 min. 146 147 Upon layering the resulting dark green solution with diethyl ether, well-formed dark green 148 crystals of compound 2 were obtained in three days in a 55% yield. Analytical data for C18H22Cl2Cu2N12O12 (796.44): calcd. C 27.14, H 2.78, N 21.10; found: C 27.3, H 2.5, N 149 21.0. IR data (cm⁻¹): 3435 (m), 3339 (sb), 3150 (mb), 1659 (s), 1631 (s), 1576 (s), 1559 (m), 150 1411 (w), 1348 (w), 1108 (vs), 919 (w), 812 (m), 730 (w), 625 (s), 545 (m), 461 (m). 151

[Cu4(pdamo)2(pdamoH)2](ClO4)2·2.5H2O (3·2.5H2O). A colourless solution of 78
mg (0.4 mmol) of pdamoH2 and 46 mg (0.8 mmol) of sodium methoxide in 15 mL of
methanol was mixed with a solution of 296 mg (0.8 mmol) of Cu(ClO4)2·6H2O in 10 mL
of methanol and stirred under heating at 50 C for one hour. Slow evaporation at room
temperature gave well-formed dark green crystals of compound 3 in 1–2 days in a 75% yield.
Analytical data for C₂₈H₃₅Cl₂Cu₄N₂₀O_{18.5} (1273.79): calcd. C 26.42, H 2.77, N 22.01;
found: C 26.8, H 2.6, N 22.2. IR data (cm⁻¹): 3425 (mb), 3307 (sb), 3150 (mb), 1631 (vs),

159 1582 (s), 1558 (m), 1490 (w), 1407 (w), 1300 (vw), 1121 (sh), 1089 (vs), 1052 (s), 1020 (m),

 $160 \qquad 810 \ ({\rm w}), \ 737 \ ({\rm w}), \ 681 \ ({\rm vw}), \ 636 \ ({\rm vw}), \ 625 \ ({\rm m}), \ 536 \ ({\rm vw}), \ 467 \ ({\rm vw}).$

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162 X-Ray structure determination

Prismatic crystals were selected and mounted on a MAR345 diffractometer with an 163 164 image plate detector (1 and 2)/Enraf-Nonius CAD4 four-circle diffractometer (3). Wavelength 0.71073 Å was used for 1-3. Lorentz-polarization (for 1-3) and absorption (for 165 1 and 3) corrections were made. The structures were solved by direct methods using the 166 SHELXS computer program⁴⁰ and refined by full-matrix least-squares method with 167 SHELX97⁴¹ The function minimized was $\sum w ||F_0|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0672P)^2]$ 168 $(+0.3349P]^{-1}$ for **1**, w = $[\sigma^{2}(I) + (0.1246P)^{2} + 0.2506P]^{-1}$ for **2**, w = $[\sigma^{2}(I) + (0.1304P)^{2}]^{-1}$ 169 for **3** and $P = (|F_0|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-Ray 170 Crystallography.⁴² The non-hydrogen atoms were refined anisotropically, whereas 171 hydrogen atoms were treated by a mixture of restrained and constrained refinement. 172

For compound 1·4MeOH, the hydrogen atoms of the hydroxyl group of the tree MeOH molecules have been localized by difference Fourier maps and refined by fixing the bond lengths and angles. Other 17 hydrogen atoms were placed at calculated positions and refined using a riding model; the isotropic temperature factors have been restrained to a value 1.2 times that of the corresponding atom which are linked. The bond lengths of the perchlorate molecule were fixed.

For compound $2 \cdot 2$ MeCN and $3 \cdot 2.5$ H₂O, all the hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 time that of the corresponding atom which are linked.

182 Itmust be emphasized that, in the above mentioned compounds, the hydrogen atoms 183 of solvent molecules could not be calculated. Details of the data collection and refinement 184 and bond parameters are summarized in Table 1.

185 CCDC-770935 (for 1), 770937 (for 2) and 770936 (for 3) contain the supplementary
186 crystallographic data for this paper.[†]

188 Physical measurements

Magnetic susceptibility measurements were carried out on polycrystalline samples with a Quantum Design susceptometer working in the range 2–300 K under magnetic fields of 0.3 T. Diamagnetic corrections were estimated from Pascal Tables. Infrared spectra ($4000-400 \text{ cm}^{-1}$) were recorded from KBr pellets.

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196 **3. Results and discussion**

197 Synthetic aspects

198 The formation of 1–3 can be represented by eqn (1)–(3).
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$$2Cu(ClO_4)_2 \cdot 6H_2O + 2pdamoH_2 + 2Et_3N + 2MeOH$$

200 $[Cu_2 (pdamoH)_2 (ClO_4)_2 (MeOH)_2] + 2(Et_3NH)ClO_4 + 12H_2O$ (1)
201
202 $2n Cu(ClO_4)_2 \cdot 6H_2O + 2n pdamoH_2 \xrightarrow{MeCN;MeOH}$
203 $[Cu_2 (pdamoH)_2]_n (ClO_4)_{2n} + 2n HClO_4 + 12n H_2O$ (2)
204

$$4Cu(ClO_4)_2 \cdot 6H_2O + 4pdamoH_2 + 6NaOME \xrightarrow{MeOH}$$

206
$$[Cu_4 (pdamo)_2 (pdamoH)_2]_n (ClO_4)_2 + 6NaClO_4 + 24H_2O$$
 (3)

207 The nature of the solvent and base, as well as the crystallization method affect the product identity. Complexes 1 and 3 can be prepared only in MeOH in the presence of 208 209 different bases. Et3N singly deprotonates the pdamoH2 ligand leading to the dinuclear complex 1, whereas double deprotonation of the half amount of the dioxime ligand is 210 211 achieved through the use of the stronger MeO- base leading to the tetranuclear cluster 3. An excess of the base (base : $pdamoH_2 = 2 : 1$ in both cases) is necessary for the isolation of 212 clean products. Somewhat to our surprise, complex **3** is prepared only in the presence of an 213 excess of Cu^{II}, because otherwise the product is contaminated with variable amounts of 1. 214 There are probably several solution species in equilibrium and it is likely that factors such 215 as pH, relative solubilities, lattice energy, crystallization kinetics and nature of the cation of 216 the base, amongst others, determine the identity of the isolated product. The 1D complex 2 217 can be isolated from the 1 : 1 Cu(ClO₄)₂ ·6H₂O/pdamoH₂ reaction mixture in MeCN or 218 MeOH in the absence of base; addition of base causes rapid precipitation of non-crystalline 219 220 solids. Addition of Et₂O into the reaction solution improves the yield, but it is not necessary 221 for the precipitation of the complex under the concentration employed.

222 Description of structures

Selected interatomic distances and angles for the three complexes are listed in Tables 224 2 and 3. The three compounds contain the planar $\{Cu(m-ON)_2Cu\}^{2+}$ subunit. The donor 225 atoms at the axial/apical coordination sites determine the final nuclearity or dimensionality 226 (1, dinuclear; 2, polymeric; 3, tetranuclear) of the products.

The coordination modes found for the anionic forms of pdamoH₂ ligand in compounds
1–3 are plotted in Scheme 2, following the rules of Harris notation.⁴³

229 Complex 1 crystallizes in the triclinic space group $P\overline{1}$. Its structure consists of 230 dinuclear [Cu2(pdamoH)2(ClO4)2(MeOH)2] molecules (Fig. 1) and solvate MeOH molecules. There is a crystallographic inversion centre at the midpoint of the $Cu^{II} \cdots Cu^{II}$ 231 axis. The Cu^{II} atoms are doubly bridged by the deprotonated diatomic oximate groups of 232 two 2.1011100 pdamoH⁻ ligands (Scheme 2). Each ligand chelates one Cu^{II} atom forming 233 two five-membered CuNCCN chelating rings, while its deprotonated oximate oxygen atom 234 235 is terminally bound to the other metal center. The neutral oxime oxygen atom and both amino groups of pdamoH⁻ remain uncoordinated. A terminal MeOH molecule and a monodentate 236 perchlorate group complete an elongated octahedral (4+2) coordination at each metal; these 237 two ligands define the Jahn–Teller axis of the Cu^{II} atom $[Cu(1) - O(6) = 2.699(4)\text{\AA}, Cu(1) - O(6) = 2.699(4) + O$ 238 O(7) = 2.630(3) Å]. 239

The equatorial bond angles deviate from the ideal 90° value due to the restrictions imposed from the chelating rings, with the N(1)–Cu(1)–N(3) and N(3)–Cu(1)–N(4) angles being $80.40(8)^{\circ}$ and $77.69(8)^{\circ}$, respectively. The torsion Cu(1)N(1)O(1)Cu(1') angle is 0° and the dinuclear unit is fully planar.

The oxygen atoms of the neutral oxime groups, coordinated and lattice MeOH molecules and the perchlorato ligands, as well as the nitrogen atoms of the uncoordinated amino groups are involved in a set of intra- and intermolecular hydrogen bonds that contribute to the stabilization of the dinuclear molecules and create a 3D network. Each coordinated MeOH molecule is intramolecularly hydrogen-bonded to an uncoordinated perchlorate oxygen atom, the $O(7) \cdots O(4^{\circ})$ distance being 2.946 Å. Atom O(9) from a lattice MeOH molecule acts as acceptor in two hydrogen bonds; the donors for these hydrogen bonds are an amino group $[O(9) \cdots N(2') = 2.961 \text{ Å}]$ and a neutral oxime group [O(9) \cdots O(2) = 2.699 Å].

Complex 2.2MeCN crystallizes in the monoclinic space group $P2_1/n$. Its crystal 253 structure consists of cationic polymeric chains based on planar (Cu–O–N–Cu torsion angles 254 are lower than 1°), centro symetric dinuclear $\{Cu_2(pdamoH)_2\}^{2+}$ units (Fig. 2), perchlorate 255 counterions and solvate MeCN molecules in an 1:2:2 ratio; the latter two will not be further 256 discussed. The Cu^{II} atoms in the dinuclear unit are doubly bridged by the deprotonated 257 oximate groups of two symmetry-related pdamoH⁻ ligands. Two nitrogen atoms (one from 258 the neutral oxime group and one from the pyridyl group) and a neutral oxime oxygen atom 259 260 from a neighbouring dinuclear unit complete five-coordination at each metal centre. The coordination geometry about each metal ion is well described as square pyramidal, in which 261 the oxygen atom from the neutral oxime group occupies the apical position. 262

263 Thus, the cationic chains have a ladder-like appearance (Fig. 3) and the pdamoH⁻ 264 ligand adopts the 3.1111100 coordination mode (Scheme 2). Both neutral amino groups of the pdamoH⁻ ligand remain uncoordinated. Analysis of the shape-determining angles by 265 using the approach of Reedijk, Addison and co-workers ⁴⁴ yield a value for the trigonality 266 index, τ , of 0.26 for Cu(1) [and Cu(1')]. As expected, the axial bond [Cu(1)–O(2b) = 267 2.869(5)Å] is the longest; if we consider this weakly bonding interaction as nonbonding, 268 complex 2.2MeCN can be considered as dinuclear with a distorted square planar 269 coordination around the Cu^{II} atoms. Main hydrogen bonding in the complex involves the 270 271 amino nitrogen and neutral oxime oxygen atoms as donors, and ClO4⁻ oxygen and MeCN 272 nitrogen atoms as acceptors.

Complex 3·2.5H₂O crystallizes in the monoclinic space group C2. Its structure (Figs. 4 and 5) consists of tetranuclear $[Cu_4(pdamo)_2(pdamoH)_2]^{2+}$ cations, ClO4⁻ counterions and solvate H2O molecules. The tetranuclear cation contains two dinuclear $\{Cu_2(pdamo)(pdamoH)\}^+$ subunits (A and B, Fig. 4) linked through four oximate μ -O⁻ atoms; two of them [O(1b), O(3a)] belong to two different pdamo²⁻ ligands and the other two [O(1a), O(3b)] to the remaining pdamoH⁻ ligands. In each dinuclear subunit the Cu^{II}

atoms are doubly bridged by two deprotonated oximate groups. The subunits A and B are 279 not planar as reflected on the Cu-O-N-Cu torsion angles of 17.1°/26.5° for A and 280 23.2°/31.1° for B. The pdamo²⁻ and pdamoH⁻ ligands adopt the 3.2011100 coordination 281 mode (Scheme 2). The coordination geometry about the four Cu^{II} centers is well described 282 as square pyramidal; the apical position of each metal ion in unit A is occupied by an oximate 283 μ -O⁻ atom that belongs to unit B and vice versa. The core of the cation consists of a 284 tetrahedron of Cu^{II} atoms linked together by four μ_3 -oximate groups to form a distorted 285 ${Cu4(NO)4}^{4+}$ 'cube' (we avoid the term *cubane* since it implies the existence of only 286 monoatomic bridges between the metal ions) comprising alternate single (O) and double (N-287 O) atom edges (Fig. 5, bottom). The very strong, intramolecular pdamoH⁻ · · · pdamo²⁻ 288 289 hydrogen bonds stabilize further the linkage between the dinuclear subunits A and B (Fig. 290 5, top).

291 The donors are the neutral oxime oxygen atoms of the pdamoH⁻ ligands and the acceptors are the uncoordinated, deprotonated oximate oxygen atoms of the pdamo²⁻ 292 ligands. The O(2a) $\cdot \cdot \cdot$ O(2b) and O(4b) $\cdot \cdot \cdot$ O(4a) distances are 2.495Å and 2.436 Å, 293 respectively. Due to the short O \cdots O distances the tetranuclear cation of 3.2.5H₂O can be 294 formulated as [Cu4(pdamoHpdamo)2]^{2+.} This means that one pdamoH⁻ and its opposite 295 pdamo²⁻ group can be considered as one 4.22001111110000 trianionic polydentate ligand 296 (Scheme 3). The \geq CNO-H \cdots · ONC \leq motif is a valuable synthon in Crystal 297 Engineering.⁴⁵ The crystal structure of 3.2.5H₂O is stabilized by a hydrogen-bonding 298 299 network involving the amino groups and solvate H₂O molecules as donors, and perchlorate 300 oxygen atoms as acceptors.

Complexes 1–3 join a very small family, currently comprising three members,³⁹ of structurally characterized metal complexes with the neutral or monoanionic forms of pyridine -2, 6- diamidoxime as ligands. Two of them, namely [Ni (pdamoH₂)₂] (SO₄)·5H₂O^{39a} and [Ni (pdamoH)₂]·4H₂O^{39b} are mononuclear. The third complex, i.e.,{[Cu (pdamoH₂) (SO₄)₂]·2H₂O}n, is a coordination polymer, but the bridging ligand is the sulfato group.^{39a} In these three complexes, the pdamoH₂ and pdamoH⁻ groups behave as (Npyridyl) (N'oxime) (N''oxime/oximate)-tridentate chelating ligands. Compounds 1–3 are thus the first complexes of any metal in which the monoanionic pdamoH⁻ ligand is bridging, while **3** is the first metal complex with a formally dianionic pdamo²⁻ ligand. In addition, complex **3** is the first metal cluster containing any form of pdamoH₂ as ligand.

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312 Magnetic studies

Solid state dc magnetic susceptibility measurements were performed on 313 polycrystalline samples of complexes 1-3 in the temperature range 2.0-300 K. The obtained 314 data are plotted as $\chi_M T$ vs. T in Fig. 6. The $\chi_M T$ values at room temperature for Cu₂ unit are 315 0.07, 0.28 and 0.23 cm³ Kmol⁻¹ for 1, 2 and 3, respectively. These values are much lower 316 than the expected ones for systems comprising two (1, 2) and four (3) non-interacting Cu^{II} 317 centres. The $\chi_M T$ products rapidly decrease with decreasing temperature, reaching a constant 318 value very close to zero below ~100 K. The maxima in the χ_M vs. T plots should be located 319 320 above room temperature in the three cases. The χ_M value shows a continuous decrease upon cooling and the curve shows a broad minimum at ~130 K, but below this temperature it 321 slightly increases due to the presence of a small amount of paramagnetic, possibly 322 monomeric impurity. The just described behaviour is indicative of very strong 323 antiferromagnetic interactions between the Cu^{II} centres indicating zero spin ground states. 324

Close inspection of the molecular structures of 1–3 reveals that the main exchange interaction should be through the double, diatomic oximato bridge; thus, the weak basalapical interactions can be neglected in the fitting procedures for compounds 2 and 3. On this basis, the fitting of the experimental data was performed by using the conventional analytical equation derived from the spin Hamiltonian of eqns (4) and (5) and introducing a ρ term to evaluate the monomeric paramagnetic impurities (the same g value was assumed for the monomeric impurity).

332

$$H = -J(S_1 S_2) \tag{4}$$

$$H = -J(S_1 S_2 + S_3 S_4) \tag{5}$$

for compounds 1-2 and 3 respectively.

Best fit parameters are J = -812 (6) cm⁻¹, g = 2.13 (3), $\rho = 0.4\%$ for 1, J = -446 (2) cm⁻¹ 338 ¹, g = 2.086 (8), $\rho = 1.4\%$ for 2, and J = -513(2) cm⁻¹, g = 2.124(8), $\rho = 2.0\%$ for 3.

Magnetic reports for similar systems are limited. However, the strong coupling for 1-339 3, as evidenced by the large J values, was not unexpected. A very strong antiferromagnetic 340 coupling (even diamagnetism at room temperature in some cases) has been also reported for 341 other doubly N, O oximato-bridged Cu^{II} 2 units.⁴⁶ The remarkable ability of the oximato 342 bridges to mediate strong antiferromagnetic coupling between paramagnetic centres has 343 been studied by some of us ^{46h} and others^{46f} by means of Extended-Huckel MO calculations 344 on the Cu– $(R N-O)_2$ –Cu core (R = various groups). The conclusion was that the good orbital 345 overlap in Cu-(R N-O)2-Cu "rings" favours strong magnetic coupling with a poor 346 dependence of moderate geometric distortions (mainly planarity of the bridging region) on 347 the strength of the interaction; in contrast, the electronic properties of the R-substituted 348 oximate groups and/or the ligands that complete the coordination sphere of the Cu^{II} ions 349 350 play an important role modulating the magnitude of the coupling. In this context, the reported compounds provides a nice example of the influence of these factors: the isolated and fully 351 planar compound 1 gives a classical very strong coupling evaluated as greater than -800 cm⁻ 352 ¹, whereas planar compound 2 and slightly distorted compound 3 exhibit a lower and similar 353 coupling with values around -500 cm⁻¹. This feature only can be attributed to electronic 354 differences derived of the additional coordination of O-atoms of the oximato groups to the 355 axial sites of neighbour Cu^{II} atoms. This conclusion is reinforced by the magnetic behaviour 356 of the previously reported [Cu₂(dapdoH)₂(H₂O)₂](BF₄)₂ complex⁴⁷ which consist of 357 isolated dinuclear units that can be compared with compound 1. In spite that the Cu-(R =358 N–O)2–Cu core for this dapdoH⁻ derivative is not fully planar (torsion angles of 6.0° and 359 10.3°), room temperature $\chi_M T$ value was reported as 0.09 cm³ K mol⁻¹ for dinuclear unit 360

which agree with the magnitude of the coupling found for **1** with a $\chi_M T$ room temperature value of 0.07 cm³ K mol⁻¹.

4. Conclusions

The use of pyridine-2,6-diamidoxime (pdamoH₂) in reactions with Cu(ClO₄)₂·6H₂O has led to the first dinuclear, cluster and polymeric complexes of any metal containing the anionic forms (pdamoH⁻, pdamo²⁻) of the ligand. The obtained products are novel in multiple ways, as described, but they also provide rare examples of Cu^{II} complexes with extremely strong antiferromagnetic coupling between the metal ions. Four different ligation modes have already been observed for pdamoH⁻ and pdamo²⁻ (Scheme 2) in only three Cu^{II} complexes, indicating the great coordination potential of this ligand systems. Our initial results described in this work suggest that reactions of pdamoH² with Cu^{II} in the presence of coligands with a strong coordination ability (e.g. carboxylates and b-diketonates) and with other paramagnetic 3d-metal ions promise to deliver many new and exciting clusters and coordination polymers.

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Compound	1.4MeOH	2.2MeCN	3.2.5H ₂ O
Formula	$C_{20}H_{40}Cl_2Cu_2$ -	$C_9H_{11}ClCuN_6O_6$	C56H69Cl4Cu8-
	$N_{10}O_{18}$		$N_{40}O_{37}$
M	906.60	398.23	2544.63
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/n$	C2
a/Å	7.880(6)	7.224(5)	22.53(1)
b/Å	11.193(6)	8.773(4)	12.073(4)
c/Å	11.412(5)	23.01(1)	17.18(2)
α (°)	68.77(4)	90	90
β(°)	74.880(3)	98.47(3)	91.90(8)
γ ^(°)	86.39(4)	90	90
$V/Å^3$	905.2(9)	1442(1)	4670(6)
Ζ	1	4	2
T/K	203(2)	293(2)	203(2)
$D_c/\mathrm{g}\mathrm{cm}^{-3}$	1.663	1.834	1.810
F(000)	466	804	2562
μ (Mo-K α)/mm ⁻¹	1.409	1.742	2.005
Measured	9970	3074	13616
reflections			
Unique reflections	5285	3074	13562
$R_{\rm int}$	0.0355	0.0454	0.0315
$\theta_{\min}/\theta_{\max}$ (°)	2.68/32.68°	2.86/32.14°	2.13/30.09°
$R(F^2)$	0.0431	0.0626	0.0648
$wR(F^2)$	0.1238	0.1893	0.1675
No. variables	247	208	677
Flack parameter			0.00(5)
$\Delta \rho_{\rm max}; \Delta \rho_{\rm min}/{ m e} { m \AA}^{-3}$	0.942/-0.508	1.005/-0.701	0.736/-1.018

Compound 1		Compound 2	
Cu(1)–O(1')	1.867(2)	Cu(1)–O(1')	1.862(3)
Cu(1) - N(1)	2.010(2)	Cu(1) - N(1)	2.012(3)
Cu(1) - N(3)	1.929(2)	Cu(1) - N(3)	1.950(3)
Cu(1)-N(4)	2.040(2)	Cu(1) - N(5)	2.070(3)
Cu(1)-O(6)	2.699(4)	Cu(1) - O(2b)	2.869(5)
Cu(1) - O(7)	2.630(3)		
N(1)-O(1)	1.341(2)	N(1)-O(1)	1.360(4)
N(4)-O(2)	1.405(3)	N(5)-O(2)	1.404(5)
O(1')-Cu(1)-N(1)	108.55(7)	O(1')-Cu(1)-N(1)	106.7(1)
O(1')-Cu(1)-N(3)	170.88(7)	O(1')-Cu(1)-N(3)	172.7(1)
O(1')-Cu(1)-N(4)	93.30(7)	O(1') - Cu(1) - N(5)	96.3(1)
N(1)-Cu(1)-N(3)	80.40(8)	N(1) - Cu(1) - N(3)	80.0(1)
N(1)-Cu(1)-N(4)	158.03(7)	N(1) - Cu(1) - N(5)	156.9(1)
N(3)-Cu(1)-N(4)	77.69(8)	N(3)-Cu(1)-N(5)	76.9(1)
Cu(1)–N(1)–O(1)	131.8(1)	Cu(1) - N(1) - O(1)	131.0(2)
Cu(1') - O(1) - N(1)	119.7(1)	Cu(1') - O(1) - N(1)	122.2(2)
Cu(1)–N(4)–O(2)	132.2(1)	Cu(1)-N(5)-O(2)	133.5(3)

Subunit A		Subunit B	
Cu(1)–O(3A)	1.892(5)	Cu(3)–O(3B)	1.857(5)
Cu(1)-N(1A)	1.950(6)	Cu(3)-N(1B)	1.936(5)
Cu(1)–N(2A)	1.985(5)	Cu(3)–N(2B)	2.024(6)
Cu(1)-N(4A)	2.003(6)	Cu(3)-N(4B)	2.036(7)
Cu(1)–O(3B)	2.476(6)	Cu(3)-O(3A)	2.609(6)
Cu(2)-O(1A)	1.870(5)	Cu(4)-O(1B)	1.905(5)
Cu(2)–N(6A)	1.936(6)	Cu(4)-N(6B)	1.950(6)
Cu(2)-N(7A)	2.005(6)	Cu(4)-N(7B)	2.008(6)
Cu(2)–N(9A)	1.960(6)	Cu(4)–N(9B)	1.987(7)
Cu(2)–O(1B)	2.631(6)	Cu(4)–O(1A)	2.518(6)
O(1A)-N(2A)	1.379(8)	O(1B)-N(2B)	1.327(8)
O(2A)-N(4A)	1.347(8)	O(2B)-N(4B)	1.355(9)
O(3A)–N(7A)	1.356(8)	O(3B)-N(7B)	1.396(8)
O(4A)-N(9A)	1.428(8)	O(4B)–N(9B)	1.437(9)
O(3A)-Cu(1)-N(1A)	169.6(2)	O(3B)-Cu(3)-N(1B)	171.1(2)
O(3A)-Cu(1)-N(2A)	106.4(2)	O(3B)-Cu(3)-N(2B)	106.0(2)
O(3A)-Cu(1)-N(4A)	96.0(2)	O(3B)-Cu(3)-N(4B)	96.6(3)
N(1A)-Cu(1)-N(2A)	78.6(2)	N(1B)-Cu(3)-N(2B)	79.6(2)
N(1A)-Cu(1)-N(4A)	78.4(2)	N(1B)-Cu(3)-N(4B)	77.5(3)
N(2A)-Cu(1)-N(4A)	157.0(2)	N(2B)-Cu(3)-N(4B)	157.1(2)
O(1A)-Cu(2)-N(6A)	173.9(2)	O(1B)-Cu(4)-N(6B)	167.9(2)
O(1A)-Cu(2)-N(7A)	106.8(3)	O(1B)-Cu(4)-N(7B)	104.8(3)
O(1A)-Cu(2)-N(9A)	96.2(3)	O(1B)-Cu(4)-N(9B)	98.0(3)
N(6A)-Cu(2)-N(7A)	79.3(2)	N(6B)-Cu(4)-N(7B)	79.0(3)
N(6A)-Cu(2)-N(9A)	77.7(2)	N(6B)-Cu(4)-N(9B)	77.8(3)
N(7A)-Cu(2)-N(9A)	156.7(2)	N(7B)-Cu(4)-N(9B)	156.8(2)
Cu(1)-O(3A)-N(7A)	120.9(4)	Cu(3)–O(3B)–N(7B)	120.0(4)
Cu(2)-O(1A)-N(2A)	129.9(4)	Cu(4)-O(1B)-N(2B)	121.5(5)
Cu(1)-N(2A)-O(1A)	130.1(4)	Cu(3) - N(2B) - O(1B)	130.6(5)
Cu(1) - N(4A) - O(2A)	128.1(5)	Cu(3) - N(4B) - O(2B)	129.0(5)
Cu(2)-N(7A)-O(3A)	130.7(4)	Cu(4) - N(7B) - O(3B)	129.2(4)
Cu(2)–N(9A)–O(4A)	126.1(4)	Cu(4)–N(9B)–O(4B)	129.3(5)

Table 3. Selected interatomic distances [Å] and angles [°] for compound **3**

564 **Figures Captions**

- 565 **Scheme 1.** Structural formulae and abbreviations of the 2-pyridyl oximes and 2,6-pyridyl dioximes discussed in the text.
- 567 Scheme 2. The crystallographically established coordination modes of pdamoH⁻ and pdamo²⁻ in 1–3, and the Harris notation⁴³ that describes these modes.
- Figure 1. Partially labeled ORTEP plot (ellipsoids at 20% probability) of complex 1·4MeOH.
 Dotted lines represent the main intramolecular hydrogen bonds.
- 571 Figure. 2. Partially labeled ORTEP plot (ellipsoids at 20% probability) of the dinuclear
- 572 ${Cu_2(pdamoH)_2}^{2+}$ unit that is present in the 1D compound 2.2MeCN; one ClO4
- 573 counterion is also shown. The oxygen atoms of the neutral oxime groups [O(2) and its
- symmetry-partner] occupy the apical sites of Cu^{II} atoms (not shown) from two neighbouring
- 575 dinuclear units. Dotted lines represent hydrogen bonds.
- Figure 3. A part of the cationic, ladder-like chain of complex 2·2MeCN; the solvate MeCN
 molecules are also shown.
- **Figure 4**. Partially labeled ORTEP plots (ellipsoid at 20% probability) for the dinuclear subunitsA(top) and B (bottom) that are present in $3 \cdot 2.5 H_2O$. The intramolecular linkages between the two subunits are not shown.
- Figure 5. View of the tetranuclear $[Cu_4(pdamo)_2(pdamoH)_2]^{2+}$ cation of $3 \cdot 2.5H_2O$ incorporating the two intramolecular pdamoH⁻ · · · pdamo²⁻ hydrogen bonds (top) and its $\{Cu_4(NO)_4\}^{4+}$ core (bottom).
- 584 Scheme 3. The 4.22001111110000 pdamoHpdamo³⁻ ligand system in $3 \cdot 2.5 H_2 O$.
- **Figure 6.** Plot of $\chi_M T$ vs. T for Cu² unit of compounds 1 (circles) 2 (squares) and 3 (solid
- diamonds). The full lines represent the best theoretical fit (see text).
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