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A unique copper(II)-assisted transformation of acetylacetone dioxime in acetone that leads to one-dimensional, quinoxaline-bridged coordination polymers†‡

Zoi G. Lada,^{a,b} Amaia Soto Beobide,^a Aikaterini Savvidou,^c Catherine P. Raptopoulou,^c Vassilis Psycharis,*^c George A. Voyiatzis,*^a Mark M. Turnbull*^d and Spyros P. Perlepes*^{a,b}

The reactions of copper(II) carboxylate sources with acetylacetone dioxime (acacdoH₂) in Me₂CO have been studied and a novel, metal ion-assisted ligand transformation has been discovered. The reaction of $[Cu_2(diba)_4(dibaH)_2]$ and acacdoH₂ (1:1.5) in Me₂CO has provided access to the complex $[(Cu_2(diba)_4(qunx)]]_n$ (1) in low yield (25–30%), where dibaH is 3,3-dimethylbutyric acid and qunx is quinoxaline. The [Cu₂(piv)₄(pivH)₂]/acacdoH₂ (1:1.5) reaction system in warm Me₂CO, where pivH is pivalic acid, gave the analogous complex $\{[Cu_2(piv)_4(qunx)]\}_n$ (2) in moderate yield (~50%). Complexes 1 and 2 can be easily prepared by the direct 1:1 reactions between the corresponding copper(u) carboxylate starting materials and gunx in Me₂CO and MeOH, respectively. The formation of coordinated gunx in 1 and 2 is Cu^{II}-promoted (assisted) as suggested by the failure to synthesize the free gunx by a variety of reactions of acacdoH₂ and Me₂CO under aerobic conditions in the absence or even the presence of dibaH and pivH, respectively. The observed acacdoH₂ \rightarrow gunx transformation is catalytic and new in the chemistry of the dioximes of β -diketones, and a mechanism has been proposed based on well-established reactions of organic chemistry. The mechanism is based on a double Beckmann rearrangement-type transformation and the overall scheme is represented by the 1:1:1 reaction between acacdoH₂, Me₂CO and O_2 . Complexes **1** and **2** have similar molecular structures consisting of paddle-wheel { $Cu_2(\eta^1;\eta^1;\mu)-O_2CR)_4$ } units bridged by qunx ligands in a zigzag 1D chain arrangement. The geometry of the Cu^{II} ions is square pyramidal with a quinoxaline nitrogen atom occupying the apical position at each metal ion. Weak H bonds are present within the chains, the donors being qunx carbon atoms and the acceptors being coordinated carboxylate oxygen atoms. Neighbouring chains interact through C-H \cdots π interactions between diba⁻/piv⁻ methyl groups and the "pyrazine" part of gunx forming layers which are stacked along the b (1) or a (2) axis through weak van der Waals interactions. The packing of the layers is different in the two structures, due to the different nature of the carboxylate ligands. Hirshfeld surface analysis of the two structures reveals the similarity of the interchain (intralayer) interactions. The IR and Raman data of 1 and 2 are discussed in terms of the coordination mode of the carboxylate groups and permit assignments of some characteristic bands/peaks of coordinated gunx. Dc magnetic susceptibility studies in the 1.8-310 K range reveal very strong antiferromagnetic Cu^{II}...Cu^{II} exchange interactions within the carboxylatebridged Cu₂ units (J = -479 K for **1** and -532 K for **2** using the $H = -J\sum S_1 \cdot S_2$ spin Hamiltonian) and weaker antiferromagnetic interactions between the Cu₂ units via the gunx superexchange pathways, with

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^aFoundation for Research and Technology- Hellas (FORTH), Institute of Chemical Engineering Sciences (ICE-HT), Platani, P.O. Box 1414, 26504 Patras, Greece. E-mail: gvog@iceht.forth.gr; Tel: +30 2610 965253

^bDepartment of Chemistry, University of Patras, 26504 Patras, Greece. E-mail: perlepes@patreas.upatras.gr; Tel: +30 2610 996730

^c Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece. E-mail: v. psycharis@inn.demokritos.gr; Tel: +30 210 6503346 ^dCarlson School of Chemistry and Biochemistry, Clark University, Worcester, MA, USA. E-mail: MTurnbull@clarku.edu; Tel: +1-508-7937167 [†]This work is dedicated to Professor Jan Reedijk for his great contributions to inorganic chemistry over the last 45 years and on the occasion of his retirement.

‡Electronic supplementary information (ESI) available: Various structural plots (Fig. S1–S10), tables with selected interatomic distances and angles (Tables S1 and S2) and IR spectra (Fig. S11) of complexes **1** and **2**. CCDC 1503220 and 1503221. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c6dt03595g



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the latter being ~10% in strength compared to the former. A critical discussion of the $acacdoH_2 \rightarrow qunx$ transformation in **1** and **2** is provided in the light of other impressive, recently discovered Cu^{II}-assisted transformations of $acacdoH_2$, pointing out the key role of the solvent in the processes known to date.

Introduction

The term "ligand" (Latin ligare, to bind) was first proposed by Alfred Stock when lecturing in Berlin on borane and silane in 1916,¹ but it came into extensive use among English-speaking chemists in the 1950s, largely through the popularity of Jannik Bjerrum's PhD thesis.² The proper use of old ligands and the design of new ones underlie much of modern molecular inorganic chemistry. Classical coordination chemistry employed simple inorganic and organic ligands, e.g. H₂O, Cl⁻, NH₃, en, dien, py, etc., in the 1950-1970 period. However, the use of polydentate ligands with a variety of functional groups, e.g. macrocyclic ligands, crown ethers, cryptands, sepulchrates and ligands of unusual reach, which are designed to achieve specific purposes, continues to be an important research frontier in contemporary coordination chemistry.³ Theoretical concepts related to such and other specialized organic ligands are the chelate effect, the macrocyclic effect, the conformation of chelating rings, the isoelectronic and isolobal relationships and some aspects of the HSAB model.

While metal complexes are most often synthesized by the reaction of a metal precursor and a presynthesized organic ligand which is incorporated intact in the product, it is also possible to generate the ligand *in situ* from an easily available organic compound. This synthetic approach allows the reactivity of the metal ion to activate a proligand, transforming it through an *in situ* reaction, sometimes providing coordination complexes with ligands that cannot be easily prepared by conventional organic synthesis.⁴ The change from a lone pair to a bonding pair, consequent upon the formation of the coordinate bond, has effects on the other atoms or groups, which are bonded to the ligand donor atom(s). These effects are the origin of the modification of ligand reactivity that is observed in coordination complexes. Nowadays, the altered reactivity of organic ligands as a consequence of their coordination to a metal centre attracts the intense interest of inorganic chemists, because it forms the basis for the use of metal complexes as stoichiometric reagents and also as homogeneous catalysts in organic synthesis. Polarization of a substrate coordinated to a metal ion is also one of the most obvious, and best investigated, means by which the reactivity of coordinated ligands may be modified in biochemistry. Biological systems have made extensive use of these processes, and Zn^{2+} plays an important role in this function. Typical examples include the polarization of a coordinated biological ligand and its activation towards attack by a nucleophile such as H₂O or a H⁻ donor (such as NADH), or the polarization of a H₂O ligand and subsequent stabilization of a coordinated OH⁻ ion.⁵

In the last 20 years or so, we have developed an understanding of the many ways in which coordination to a metal ion may modify and control the reactivity of organic molecules bearing carbonyl (ketones and aldehydes),^{6,7} or oxime^{8,9} groups. We have observed that the reactivity at various sites in an organic ligand may be enhanced or diminished upon coordination, and that very subtle control over the organic chemistry of the ligand may be exerted.

Restricting further discussion to the reactivity of coordinated oximes,^{8–10} oxime and oximato groups can bind a metal ion in various coordination modes (Scheme 1) exhibiting versatile reactivity. In contrast to many functional groups (*e.g.* amine, thiol, nitrile, carbonyl, nitrosyl, *etc.*), a coordinated oxime/oximate contains three active sites (C, N and O atoms). Many types of metal-mediated transformations are possible for the coordinated oximes/oximates, *e.g.* nucleophilic reactions, electrophilic reactions, template synthesis, Beckmann rearrangements, intramolecular redox reactions, *etc.* Retention or loss of integrity of the C=NO(H) fragment during coordination is the general characteristic used for the classification of the metal-mediated reactions of oximes.^{10c,d}

Most studies on the reactivity of coordinated oximes have been performed with ligands containing a single oxime group,¹⁰ e.g. 2-pyridyl oximes.^{8,9} With our previous experience as a background, we have embarked on a new project concerning the in-depth study of the metal ion-assisted/mediated reactions of dioximes and we started our efforts with 1,3-dioximes¹¹ which present a rather rich reactivity in organic chemistry. We selected acetylacetone dioxime (pentane-2,4dione dioxime or N,N'-dihydroxypentane-2,4-diimine), abbreviated hereafter as acacdoH₂ (Scheme 2), as the first ligand for our studies. The coordination chemistry of acacdoH₂ was practically unknown before 2014 and the only complexes that had been crystallographically characterized were the tetranuclear titanium(w) clusters [Ti₄(OⁱPr)₈(acacdo)₄] and [Ti₄O₂(OⁱPr)₈(acacdo)₂].¹² During our first reactions of acacdo H_2 and copper(II) sources, we came across an exciting report by Papaefstathiou's group which described the structures of [Cu2Cl4(acacdoH2)2] (we had also obtained this dinuclear complex) and an aesthetically beautiful $\{Cu_{16}^{II}\}$ wheel



Scheme 1 Crystallographically established coordination modes of the oxime and oximate groups; M is a metal ion and the dashed line represents a strong hydrogen bond.



with the formula $[Cu_{16}(L^1)_4(L^2)_8(L^3)_8]$ ·8H₂O.¹³ The latter comprises three different ligands, namely $(L^1)^{2-}$, $(L^2)^{2-}$ and $(L^3)^{-}$, Scheme 2, all derived from acacdoH₂; it is remarkable that the original ligand is completely absent from the complex. The $\{Cu_{2}^{II}\}\$ and $\{Cu_{16}^{II}\}\$ complexes were prepared using EtOH and EtOH/H2O as solvents, respectively. Although the transformation of acacdoH₂ to $(L^1)^{2-}$, $(L^2)^{2-}$ and $(L^3)^-$ was not anticipated, the authors were able to fully rationalize the formation of these anions. Methylene moieties (-CH₂-) attached to electron withdrawing groups can be aerially oxidized to the corresponding ketones with14 or without the presence of metal ions.^{14b} The dianion of the oxidized form of acacdoH₂, $(L^2)^{2-}$, is probably metal ion-assisted since the ¹H NMR spectra of pure acacdoH₂ in D₂O or CD₃OD remain unchanged for several months. Ketones, like $(L^2)^{2-}$, may undergo nucleophilic addition to the carbonyl C atom to form the respective hydrate (the dianion of the gem-diol form), $(L^1)^{2-}$. The electrophilic character of the carbonyl C atom is increased by coordination of the carbonyl O atom (direct polarization) or by coordination of the remote N or O atoms (induced polarization). Alternatively, acacdo H_2 may be first oxidized to H_2L^1 which upon dehydration forms the ketone form H_2L^2 . Pyrazole *N*-oxides, like $(L^3)^-$, have been previously reported to form by metal ion-assisted transformations of β -diketone dioximes.¹¹ On studying the old literature more, we found another example of a metal ion-assisted reaction of acacdoH₂. The CuCl₂·2H₂O/acacdoH₂ reaction system in MeOH/H₂O (1:20 v/v) under heating leads to $Cu^{II} \rightarrow Cu^{I}$ reduction and gives the polymeric complex ${[Cu_2^I Cl_2(L^4)]}_n$, where L^4 is the 3,5-dimethylisoxazole ligand.¹⁵ The authors proposed that the formation of L⁴ occurs through H₂NOH elimination and Cu^{II} reduction, associated with, or followed by, ring closure. Since the presence of Ln^{III} ions (Ln = Nd, Gd, Er) in the reaction mixtures has been essential for the isolation of the hexadecanuclear cluster (although the Ln^{III} ion does not appear in the final product) and given the interesting acacdoH₂ \rightarrow L⁴ transformation promoted only by copper, we started our efforts using exclusively copper(II) and were pleased to discover a new Cu^{II}-assisted transformation of acacdoH₂ to coordinated quinoxaline (qunx, Scheme 2) in acetone. Details of this transformation and the resulting 1D, carboxylate and qunx-containing copper(II) coordination polymers are described in this work.

Experimental section

Materials and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. The ligands acetylacetone dioxime (acacdoH₂) and guinoxaline (qunx) are commercially available. The copper(II) starting materials $[Cu_2(piv)_4(pivH)_2]^{16}$ and $[Cu_2(diba)_4(dibaH)_2]^{17}$ where pivH is pivalic acid and dibaH is 3,3-dimethylbutyric acid (tert-butylacetic acid) were synthesized as described in the literature. Elemental analyses (C, H, N) were performed by the University of Patras microanalytical service. FT-IR spectra (4000-400 cm⁻¹) were recorded using a Perkin Elmer 16PC FT-IR spectrometer with samples prepared as KBr pellets. The backscattering Raman spectra were obtained using the T-64000 model of Jobin Yvon (Horiba group) excited with a Cobolt Fandango[™] ISO, operating at 515 nm. The laser intensity on the samples was 0.4 mW. Dispersion and detection of the Raman phonons are done by using a 600-groove per nm grating and a 2D CCD detector (liquid nitrogen-cooled at 140 K), respectively. The spectrometer was calibrated using the standard 1001 cm⁻¹ Raman peak position of polystyrene. Electronic absorption spectra (both in solution and in the solid state) were recorded with a Perkin Elmer Lambda 950 UV/VIS spectrophotometer in the 250-800 nm range. Variable-temperature, solid state magnetic susceptibility data were collected using a Quantum Design MPMS-XL SQUID magnetometer on samples of finely ground crystals of the complexes, which were loaded into gelatin capsules, in the 1.8-310 K range. Magnetization data were collected as a function of field from 0 to 50 kOe at 1.8 K. The moment for the pivalate compound 2 (vide infra) approached saturation at 50 kOe with a moment of 55 emu mol^{-1} suggesting that the only contributions to the moment at that temperature arise from a trace paramagnetic impurity. The *tert*-butylacetate copper(π) complex 1 (vide infra) behaved similarly with a moment of 61 emu mol⁻¹ at 50 kOe (at 1.8 K). Magnetic susceptibility data were then collected from 1.8 to 310 K in a 1 kOe applied field. All data were corrected for the background signal of the sample mounting materials (measured independently), for the diamagnetic contributions of the constituent atoms as estimated via Pascal's constants and for the temperature-independent paramagnetism of the Cu^{II} ions. The data were fit using the Hamiltonian $H = -J\sum S_1 \cdot S_2$.

Synthetic details

 ${[Cu_2(diba)_4(qunx)]}_n$ (1). Method A. A colourless slurry of acacdoH₂ (0.039 g, 0.30 mmol) in Me₂CO (2 mL) was slowly added to a pale greenish blue solution of $[Cu_2(diba)_4(dibaH)_2]$ (0.164 g, 0.20 mmol) in the same solvent (9 mL). The resulting green-blue solution was stirred for a further 20 min at room

temperature and filtered. Upon vapour diffusion of Et₂O, the colour of the reaction solution turned dark green. X-ray quality, green crystals of the product were formed in a period of 5-6 d. The crystals were collected by filtration, washed with cold Me₂CO (2 mL) and Et₂O (5 \times 2 mL), and dried in vacuo over CaCl₂. Typical yields were in the 25-30% range (based on the Cu^{II} available). Analytical data, calcd for C₃₂H₅₀Cu₂N₂O₈ (found values are in parentheses): C 53.54 (53.85), H 7.04 (7.18), N 3.90 (3.77)%. IR bands (KBr, cm⁻¹): 2962m, 2940sh, 2910w, 1614s, 1504w, 1463sh, 1410m, 1362m, 1304w, 1280w, 1238w, 1218m, 1140w, 1044m, 964m, 866m, 802w, 758m, 734m, 655m, 460w, 422w. Raman peaks (cm⁻¹): 3076w, 2957s, 2928w, 2908m, 2866sh, 1589m, 1536w, 1510w, 1446w, 1433m, 1379m, 1362s, 1296m, 1239w, 1213w, 1148w, 1048w, 1021w, 966w, 937w, 914w, 771s, 750m, 540m, 420m, 369m, 234m, 199m. Solid-state UV/VIS bands (nm): 645, 399, 335, 260. UV/VIS bands in MeOH (nm): 635wb, 321, 310, 255.

Method B. A pale greenish blue solution of [Cu₂(diba)₄(dibaH)₂] (0.164 g, 0.20 mmol) in Me₂CO (9 mL) was added to a stirred yellow solution of qunx (0.026 g, 0.20 mmol) in the same solvent (2 mL). The resulting dark green solution was stirred for a further 20 min, filtered to remove a very small quantity of a pale green solid and the filtrate was stored in a closed flask at room temperature. X-ray quality, rod-like green crystals of the product were precipitated after 2 d. The crystals were collected by filtration, washed with cold Me₂CO (1 mL) and Et₂O (2×4 mL), and dried in vacuo over CaCl₂. The yield was 45% (based on the Cu^{II} available). Analytical data calcd for C₃₂H₅₀Cu₂N₂O₈ (found values are in parentheses): C 53.54 (53.65), H 7.04 (7.40), N 3.90 (3.93)%. The finely ground crystals had IR, Raman and solid-state UV/ VIS spectra identical to those of the authentic sample prepared by method A.

 $\{[Cu_2(piv)_4(qunx)]\}_n$ (2). Method A. A colourless slurry of acacdoH₂ (0.039 g, 0.30 mmol) in Me₂CO (3 mL) was slowly added to a green solution of $[Cu_2(piv)_4(pivH)_2]$ (0.147 g, 0.20 mmol) in the same solvent (8 mL). Upon slight warming (35 °C) and vigorous stirring a bluish green solution was obtained, which was stirred for a further 10 min, filtered and layered with Et₂O (10 mL). Slow mixing gave a green solution from which were subsequently isolated dark green crystals of the product. The crystals were isolated by filtration, washed with cold Me₂CO (1 mL) and Et₂O (2×2 mL), and dried in air. Typical yields were in the 40-45% range (based on the Cu^{II} available). Analytical data, calcd for C₂₈H₄₂Cu₂N₂O₈ (found values are in parentheses): C 50.82 (52.95), H 6.41 (6.59), N 4.23 (4.09)%. IR bands (KBr, cm⁻¹): 2966sh, 2954m, 2940sh, 2918w, 1602s, 1505w, 1488m, 1454w, 1422s, 1359m, 1354m, 1224m, 1142w, 1040w, 964m, 894w, 866m, 790m, 754m, 618m, 442m, 414w. Raman peaks (cm⁻¹): 3102w, 3064w, 2985w, 2960w, 2924m, 2874w, 1589m, 1532w, 1487w, 1455w, 1422m, 1379s, 1364s, 1296m, 1213m, 1146w, 1048w, 1023w, 941w, 895w, 868w, 808s, 775s, 637w, 540m, 441m, 415w, 325w, 214s, 192s, 157w. Solid-state UV/VIS bands (nm): 652, 410, 330, 290. UV/VIS bands in Me₂CO (nm): 645wb, 315, 310, 305.

Method B. A green solution containing $[Cu_2(piv)_4(pivH)_2]$ (0.086 g, 0.10 mmol) and qunx (0.013 g, 0.10 mmol) in MeOH (20 mL) was refluxed for 2 h. No noticeable colour change occurred, but a very small quantity of a green powder was precipitated during the reflux. The green solid was removed by filtration and the filtrate was left undisturbed in a closed flask at room temperature. Dark green crystals of the product were formed over a period of 4 d. The crystals were collected by filtration, washed with cold MeOH (1 mL) and Et₂O (2 × 5 mL), and dried *in vacuo* over CaCl₂. The yield was 48% (based on the Cu^{II} available). Analytical data, calcd for C₂₈H₄₂Cu₂N₂O₈ (found values are in parentheses): C 50.82 (50.33), H 6.41 (6.64), N 4.23 (4.31)%. The finely ground crystals had IR, Raman and solid-state UV/VIS spectra identical to those of the authentic material **2** prepared by method A.

Reaction of $[Cu_2(diba)_4(dibaH)_2]$ with an excess of acacdoH₂. A colourless slurry of acacdoH₂ (0.156 g, 1.20 mmol) in Me₂CO (5 mL) was slowly added to a pale greenish-blue solution of $[Cu_2(diba)_4(dibaH)_2]$ (0.164 g, 0.20 mmol) in the same solvent (6 mL). The resulting green-blue solution was stirred for a further 20 min at room temperature. Upon vapour diffusion of Et₂O, the colour of the reaction solution became dark green. Green crystals were formed over a period of 4-5 d. The crystals were collected by filtration, washed with cold Me₂CO (1 mL) and Et₂O (1 mL), and dried in air. The green material proved to be compound 1 by IR spectroscopic comparison with the authentic material (vide supra). The yield was 35% (based on Cu^{II}). Analytical data, calcd for C₃₂H₅₀Cu₂N₂O₈ (found values are in parentheses): C 53.54 (53.03), H 7.04 (6.87), N 3.90 (4.11)%. The green filtrate from the above procedure was stirred overnight at room temperature. The resulting green solution was slowly filtered through a plug of silica gel (Davisil, Grade 634, 1.0 cm of silica gel into a porous glass funnel); after the addition of the filtrate on the funnel, the solution was allowed to stand undisturbed for 2 min and then the vacuum was turned on. This procedure was repeated and the colour of the final filtrate was yellow. Evaporation of the solvents (Me₂CO, Et₂O) in a rotary evaporator at room temperature gave a pale brown oily solid; the vacuum had to be turned off shortly after the removal of the solvents because the solid is rather volatile. The residue was treated with petroleum spirits, the resulting mixture was filtered, and the collected solid was washed with cold Et_2O (2 × 1 mL) and dried in air to give ~0.14 g (95% based on the acacdoH2 used) of a pale yellow solid. Careful IR and Raman studies of the product proved that the solid was free qunx with slight contamination by acacdoH₂. Raman peaks (cm⁻¹): 1369s, 760s, 604m, 405m.

Reaction of CuBr₂ with an excess of acadoH₂. A brown solution of CuBr₂ (0.045 g, 0.20 mmol) in Me₂CO (10 mL) was slowly added to a colourless slurry of acadoH₂ (0.130 g, 1.00 mmol) in the same solvent (10 mL). The resulting greenish brown solution was stirred in a closed flask at room temperature for 10 min. The resulting pale green-brown solution was left undisturbed for 4–5 d, during which time a colour change to greenish yellow and precipitation of a yellow solid was observed. The microcrystalline solid was collected by

filtration, washed with cold Et_2O (2 × 1 mL) and dried in air. The yellow material proved to be the known compound $\{[CuBr_2(qunx)]\}_n$ by microanalyses and IR spectroscopic comparison with the authentic material prepared as described in the literature¹⁸ by the direct reaction of CuBr₂ and gunx. The yield was 78% (based on the Cu^{II} available). Analytical data, calcd for C₈H₆CuN₂Br₂ (found values are in parentheses): C 27.18 (27.79), H 1.71 (1.60), N 7.93 (7.45)%. The greenish yellow filtrate from the above mentioned procedure was stirred overnight at room temperature and slowly filtered through a plug of silica gel (Davisil, Grade 634, 1.0 cm of silica gel into a porous glass funnel); after the addition of the filtrate on the funnel, the solution was allowed to stand undisturbed for 2 min and then the vacuum was turned on. Evaporation of the solvent (mainly Me₂CO) in a rotary evaporator at room temperature gave a yellow solid; the vacuum had to be turned off shortly after the removal of the solvent because the solid is rather volatile. The residue was treated with petroleum spirits, the resulting mixture was filtered, and the collected solid was washed with cold Et₂O $(3 \times 1 \text{ mL})$ and dried in air to give ~0.10 g (92% based on the acacdoH₂ used) of a pale yellow solid. Careful IR and Raman studies of the product proved this to be free qunx with negligible contamination by acacdoH₂. Raman peaks (cm^{-1}): 1370s, 759s, 604m, 406m.

Single-crystal X-ray crystallography

A suitable single-crystal of 1 $(0.14 \times 0.33 \times 0.43 \text{ mm})$ was taken from the mother liquor and immediately cooled to -113 °C; a crystal of 2 ($0.04 \times 0.37 \times 0.50$ mm) was mounted in air. All the crystallisation efforts for 2 gave poorly diffracting crystals which were very thin plates. Finally, data collection was performed at room temperature. X-ray diffraction data for 1 and 2 were collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite-monochromated Cu K α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CrystalClear program package.19 The structures were solved by direct methods using SHELXS-97^{20a} and refined by full-matrix least-squares techniques on F^2 with the latest version of SHELXL (2014/7).^{20b} For 1 the H atoms were refined isotropically at positions located either from difference Fourier maps or at the calculated ones using a riding model. The structure of 2 is not centrosymmetric and it was refined as an inversion twin (the Flack parameter takes the value of 0.44). For 2 all H atoms were introduced at the calculated positions as riding on their respective bonded atoms. All non-H atoms for both complexes were refined anisotropically. Plots of the structures were drawn using the Diamond 3 program package.²¹ The packing of the complexes in the crystal structures was further investigated using the CrystalExplorer package.22

Important crystallographic data are listed in Table 1. Full details can be found in the CIF files.

Table 1	Crystallographic	data for con	npounds 1 and 2

Parameter	1	2	
Formula	C32H50Cu2N2O8	C ₂₈ H ₄₂ Cu ₂ N ₂ O ₈	
Fw	717.82	661.71	
Crystal system	Triclinic	Orthorhombic	
Space group	$P\bar{1}$	$Pna2_1$	
a/Å	9.9649(2)	21.2259(4)	
b/Å	11.0985(2)	17.2370(3)	
c/Å	17.6722(3)	9.3165(2)	
$a/^{\circ}$	71.044(1)	90.0	
$\beta/^{\circ}$	82.983(1)	90.0	
γ/°	73.748(1)	90.0	
V/Å ³	1773.56(6)	3408.64(11)	
Ζ	2	4	
$\rho_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.344	1.289	
T/K	160(2)	293(2)	
Radiation/ μ (mm ⁻¹)	Cu Kα/1.875	Cu Kα/1.908	
Reflns collected/unique (R_{int})	18 264/5724	16 260/4009	
1 ((0.0456)	(0.0629)	
Reflns with $I > 2\sigma(I)$	4789	2559	
No. of parameters	520	374	
$R_1[I > 2\sigma(I)], wR_2$ (all data)	0.0406/0.113	0.0594/0.1744	
$\operatorname{GOF}(F^2)$	1.096	1.133	
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min} (e {\rm \AA}^{-3})$	0.630/-0.573	0.544 / -0.861	
CCDC number	1503220	1503221	

Results and discussion

Synthetic comments

Our approach to activate the proligand acetylacetone dioxime for further reactivity was to treat a copper(II) starting material with acacdoH₂. Our initial efforts were with CuX_2 (X = Cl, Br), $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 6H_2O$ using alcohols or/and MeCN as solvents and various crystallization techniques. Powders were mostly obtained which could not be characterized, the only crystalline compound obtained being $[Cu_2Cl_4(acacdoH_2)]$. Then we came across the very interesting communication by Papaefstathiou's group which reported the chloro-bridged copper(II) dimer and the exciting $\{Cu_{16}^{II}\}$ wheel mentioned in Introduction; the latter contains the transformed ligands $(L^1)^{2-}$, $(L^2)^{2-}$ and $(L^3)^-$ shown in Scheme 2. This report convinced us that there was a rich reactivity of the coordinated acacdoH₂. In order to explore further reaction pathways for this ligand, we changed the nature of the metal starting materials and the solvent. Treatment of $[Cu_2(diba)_4(dibaH)_2]$ with acacdoH₂ (1:1.5) in Me₂CO at room temperature gave a green solution from which were subsequently isolated green crystals of $\{[Cu_2(diba)_4(qunx)]\}_n$ (1) in rather low yields (25–30%) upon vapour diffusion with Et_2O . The crystals were of X-ray quality and single-crystal X-ray crystallography revealed the identity of the product and the novel acacdoH₂ \rightarrow qunx transformation. We do believe that the formation of qunx in 1 (and in 2, vide infra) is Cu^{II}-promoted (or assisted). To date, we have failed to synthesize the free qunx by reactions of acacdoH2 and Me2CO (stoichiometric amount or excess) under aerobic conditions in the absence or even in the presence of dibaH. In addition, the ¹H NMR spectrum of pure acacdoH₂ in (CD₃)₂CO remains unchanged for several weeks. Since the acacdoH₂ transformations in the

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 ${\rm Cu}_{16}^{\rm II}$ wheel had been observed in the presence of several lanthanide(III) ions,¹³ we repeated the procedure described in the Experimental section (method A) by also employing ${\rm Dy}({\rm NO}_3)_3\cdot 5{\rm H}_2{\rm O}$ in a $[{\rm Cu}_2({\rm diba})_4({\rm dibaH})_2]: {\rm Dy}^{\rm III}$ reaction ratio of 2 : 1. Somewhat to our surprise, crystals of 1 (unit cell determination) were again precipitated in a somewhat lower yield (~20%). Thus, it seems that the acacdoH₂ \rightarrow qunx transformation is assisted by either Cu^{II} or a Cu^{II}–Dy^{III} combination. Dy(NO₃)_3·5H₂O/acacdoH₂ and Dy(NO₃)_3·5H₂O/acacdoH₂/dibaH reaction systems in Me₂CO have failed to date to give any characterisable solid.

Having structurally characterized compound **1**, we wondered whether this 1D coordination polymer could be prepared by the direct reaction between $[Cu_2(diba)_4(dibaH)_2]$ and qunx in Me₂CO and this turned out to be the case. The 1:1 reaction $(Cu^{II}:qunx = 2:1)$ gave crystals of **1** in a *ca.* 50% yield, eqn (1).

$$n [\operatorname{Cu}_{2}(\operatorname{diba})_{4}(\operatorname{dibaH})_{2}] + n \operatorname{qunx}$$

$$\xrightarrow{\operatorname{Me_{2}CO}} \{ [\operatorname{Cu}_{2}(\operatorname{diba})_{4}(\operatorname{qunx})] \}_{n} + 2n \operatorname{dibaH}$$

$$(1)$$

In a next step we tried to investigate the influence of the carboxylate on the transformation and product identity. The [Cu₂(piv)₄(pivH)₂] starting material led to completely analogous results with $[Cu_2(diba)_4(dibaH)_2]$. Thus, the $[Cu_2(piv)_4(pivH)_2]/acacdoH_2$ (1:1.5) reaction mixture in Me_2CO (the solvent had to be warmed to facilitate the reaction) gave a blue-green solution from which were subsequently isolated green crystals of $\{[Cu_2(piv)_4(qunx)]\}_n$ (2) in moderate yields (~50%) upon liquid diffusion with Et_2O . As in the case of 1, compound 2 can be easily prepared by the direct 1:1 reaction between $[Cu_2(piv)_4(pivH)_2]$ and qunx in a *ca.* 50% yield. The product obtained in Me₂CO repeatedly gave analytical results slightly outside the acceptable range. The preferable solvent for its preparation is MeOH. The reaction solution had to be refluxed to precipitate a minor quantity of a byproduct whose IR spectrum is similar (but not identical) to that of 2. The reactions of $acacdoH_2$ and other copper(II) carboxylate sources, e.g. $[Cu_2(O_2CMe)_4(H_2O)_2]$ and $Cu(O_2CPh)_2 \cdot xH_2O$, in Me₂CO gave green powders that we could not crystallize; however their IR spectra show the typical bands of the coordinated qunx.

The observed acacdoH₂ \rightarrow qunx transformation is new in the chemistry of 1,3-dioximes.^{11,13,15} A proposed mechanism, based on well-established reactions in organic chemistry,²³ is shown in Scheme 3. The overall reaction is illustrated in Scheme 4. The mechanism is based on a double Beckmann rearrangement-type reaction. The Cu^{II} ion ensures the correct configuration of the groups during the double Beckmann rearrangement which demands *anti* conformation of the leaving (H₂O) and migrating alkyl groups (CH₂R at the beginning and CH₃ later on).

Steps i and ii in Scheme 3 represent Beckmann rearrangements. The group that migrates is the one *anti* to the hydroxyl group.²³ Each Beckmann rearrangement is followed by a step

in which the carbocation is intercepted by an internal O atom. It is well known that the carbocation may combine with a species possessing an electron pair (a Lewis acid-base reaction). This species may be OH⁻, halide ion, or any other negative atom (as in the present case), or it may be a neutral species with an electron pair to donate, in which case, of course, the immediate product must bear a positive charge.²³ The intermediate VI, formed after two cycles of Beckmann rearrangement and carbocation interception, gives the new intermediate XI, most probably through the formation of X. The $\mathbf{X} \to \mathbf{X}\mathbf{I}$ process is a [1,3] sigmatropic migration of hydrogen.^{23,24} Several examples of thermal or photochemical rearrangements in which a hydrogen atom migrates from one end of a system of a π bond to the other have been reported, though the reaction is subject to geometrical conditions. Pericyclic mechanisms are involved, and the hydrogen atom must, in the transition state, be in contact with both ends of the chain at the same time. Furthermore, there are two geometrical pathways by which any sigmatropic rearrangement can take place. In one of the two pathways, the hydrogen moves along the top or bottom of the π system (suprafacial migration). In the other pathway, the hydrogen moves across the π system from top to bottom or vice versa (antarafacial migration). The suprafacial [1,3]-hydrogen sigmatropic rearrangement is forbidden by orbital symmetry. The antarafacial [1,3]-hydrogen sigmatropic rearrangement is allowed by orbital symmetry; however, this type of rearrangement is geometrically impossible due to the inability to maintain the overlap of the 1s atomic orbital of the migrating hydrogen atom with the necessary lobes of the terminal 2p atomic orbitals at the midpoint of the migration.^{24a} In the present case the migration is facilitated because the double bonded carbon atom to which the hydrogen atom migrates also participates in a second double bond (cumulative double bonds).²³ XI is transformed into the new intermediate XII through an electrocyclic rearrangement (such rearrangements take place by pericyclic mechanisms), which involves redistribution of π bonds and the formation of a new C–C σ bond.²³ The intermediate XII undergoes a conjugate addition by the coordinated enolate species (or simply by the free enolate ion) to give XIII; the conjugate addition (also called Michael addition) is a typical 1,4addition to the carbon-carbon double bond.23 Step viii in Scheme 3 is an oxidative aromatization of the heterocyclic ring which leads to XIV. Generally, six-membered alicyclic rings can be aromatized in a number of ways.²⁵ The reaction can also be applied to heterocyclic 5- and 6- (as in the present case) rings. Aromatization is accomplished most easily if there are already one or two (as in the case of XIII) double bonds in the ring.²³ Among other reagents that have been used are atmospheric oxygen (the case here), H2O2, MnO2, SeO2, various strong bases and chromic acid. The intermediate XIV undergoes a nucleophilic aromatic substitution and, after dehydration, the dihydroquinoxaline XV is formed. The nucleophilic aromatic substitution most probably proceeds through an S_NAr mechanism and is facilitated by the presence of the strongly activated hetero nitrogen atoms at the α and γ positions relative to the



Scheme 3 A proposed mechanism that leads to the $acacdoH_2 \rightarrow qunx$ transformation. Important steps are: (i) 1st Beckmann rearrangement; (ii) interception of the carbocation by an internal O atom; (iii) 2nd Beckmann rearrangement; (iv) interception of the carbocation by an internal O atom; (v) 1,3-hydride shift (sigmatropic rearrangement); (vi) electrocyclic reaction; (vii) conjugate addition; (viii) oxidative aromatization; (ix) nucleophilic aromatic substitution; (x) dehydration; (xi) oxidative aromatization. A coordination number of four (4) is arbitrarily assigned to the copper ion. The vacant coordination sites might be filled by solvent molecules. The dashed line represents a H bond. XH = dibaH, pivH.



Scheme 4 The overall reaction that takes place during the preparation of the 1D coordination polymers 1 and 2. RCOOH = dibaH, pivH.

leaving group.²³ Finally, qunx arises from **XV** through oxidative aromatization (*vide supra*) by H_2O_2 which has been produced in the previous step of the sequence. We want to emphasize at this point that we have not investigated the mechanism of the acacdoH₂ \rightarrow qunx transformation by solution methods (kinetics, UV/VIS, EPR, *etc.*). Due to the complicated nature of the transformation, it is doubtful if such studies will provide any reliable mechanistic information. In addition, the paramagnetic nature of copper(II) precludes the use of NMR spectroscopy which might be more useful. We do believe that the proposed mechanism is not entirely speculative and the sequences shown in Scheme 3 represent a logical mechanistic approach in which the role of Cu^{II} is to activate groups by coordination, facilitating their reactions.

The rearrangement of ketoximes to the corresponding amides, known as the Beckmann reaction or rearrangement, is a common method in organic chemistry and a topic of current interest. It accomplishes both the cleavage of a carbon–carbon bond and the formation of a carbon–nitrogen bond.²⁶ It represents a powerful method particularly for manufacturing ε -caprolactam in the chemical industry. The reaction generally requires high reaction temperatures and dehydrating media. Thus, the reaction can lead to large amounts of byproducts and precludes its application to sensitive substrates. Several catalysts, including metal ions, have been employed for this reaction. In the case of acacdoH₂, the "normal" double Beckmann rearrangement would be expected to lead to the *N*-acetylglycine methylamide product **XXII** (Scheme 5). The presence of this product as an intermediate in the acacdoH₂ \rightarrow qunx transformation could not be ruled out. Work is in progress in our laboratories to synthesize **XXII** and to investigate whether its reaction with [Cu₂(diba)₄(dibaH)₂] and [Cu₂(piv)₄(pivH)₂] in Me₂CO would give compounds **1** and **2**.

Another question that arises from our results is the following: "Is the acacdoH₂ \rightarrow qunx transformation catalytic or stoichiometric?" We have strong evidence that the reaction is catalytic.²⁷ As detailed in the Experimental section, the reaction of $[Cu_2(diba)_4(dibaH)_2]$ with a large excess of acacdoH₂ in Me₂CO at room temperature gives complex 1 and free gunx with almost no signs of contamination by acacdoH₂. After removal of the precipitated amount of 1 by filtration, the coloured filtrate was passed through silica gel in which the Cu^{II} content (from the soluble quantity of the complex) remained bound. Evaporation of the filtrate gave free qunx. The catalytic role of Cu^{II} in the transformation was also shown²⁷ by the reaction of CuBr₂, *i.e.* a non-carboxylate copper(II) source, with a large excess of acacdoH2 in Me2CO at room temperature which gave the known complex { $[CuBr_2(qunx)]$ }¹⁸ and almost pure qunx; full details are given in the Experimental section.

Description of structures

The aspects of the molecular and crystal structures of **1** and **2** are shown in Fig. 1–4 and S1–S7.[‡] Selected interatomic distances and angles are listed in Tables S1 and S2.[‡]

Compound 1 contains two crystallographically independent paddle-wheel $\{Cu_2(diba)_4\}$ units (secondary building units, SBUs), each at an inversion centre, and these dimers are linked into one-dimensional (1D) chains parallel to the [-1, 0, 1] direction through the use of qunx as a bidentate bridging ligand (Fig. S1[‡]). The asymmetric unit of the cell consists of two Cu^{II} atoms (Cu1, Cu2), four *syn,syn*-\eta¹:η¹:µ diba⁻ groups



Scheme 5 The anticipated "normal" product from the Cu^{II}-assisted double Beckmann rearrangement of acacdoH₂. Steps (i) and (ii) represent Beckmann rearrangements. A coordination number of four is arbitrarily assigned to the copper ion. The vacant coordination sites might be filled by solvent molecules. The dashed line represents a H bond. The intermediate XVII is the same as I in Scheme 3. XH = dibaH, pivH.



Fig. 1 A portion of a chain that is present in the structure of $\{[Cu_2(diba)_4(qunx)]\}_n$ (1); only two Cu₂ units are shown. The dashed green lines represent intrachain H bonds. Symmetry operations used to generate equivalent atoms: (') -x + 1, -y + 2, -z; ('') -x, -y + 2, -z + 1.



Fig. 2 The formation of a layer parallel to the (010) plane through $C(methyl)-H\cdots\pi(diazine)$ interactions in **1**; the interactions are shown with dashed orange and dashed magenta lines.



Fig. 3 A portion of a chain that is present in the structure of $\{[Cu_2(piv)_4(qunx)]\}_n$ (2); only two Cu₂ units are shown. The dashed green lines represent intrachain H bonds. Symmetry operations used to generate equivalent atoms: (') -x + 3/2, y + 1/2, z + 1/2; ('') -x + 3/2, y - 1/2, z - 1/2.



Fig. 4 The stacking of two successive layers along the *a* axis in the crystal structure of **2**. Thick red and thin blue lines are used for the representation of the chains in the bottom and top layers, respectively; the successive bottom and top layers are extended parallel to the [0, -1, 1] and [0, 1, 1] crystallographic directions, respectively.

and one qunx ligand and thus the complex is best formulated as $\{[Cu_2(diba)_4(qunx)]\}_n$. The Cu^{II}...Cu^{II} vectors are not colinear but form a zigzag line, with Cu1...Cu2...Cu2" and Cu1' ...Cu1-Cu2 angles of 160.3(1) and 158.2(1)°, respectively. There are three distinct Cu^{II}...Cu^{II} separations along the chain which alternate in an ...ABCBABCB... pattern where (using the viewpoint of Fig. 1) A = Cu1...Cu1' = 2.609(2) Å, B = Cu1...Cu2 = 7.159(2) Å and C = Cu2...Cu2' = 2.611(1) Å. Note that the four *syn,syn* bridging *tert*-butylacetates allow the closest approach of metal centres with the Cu1...Cu1' and Cu2...Cu2' distances being typical of those found with a number of $[Cu_2(O_2CR)_4L_2]$ complexes (2.6–2.7 Å), where L is a monodentate ligand.²⁸

The geometry of Cu1 and Cu2 can be described as square pyramidal with a quinoxaline nitrogen atom occupying the apical position at each metal ion. Analysis of the shape-determining angles using the approach of Addison, Reedijk *et al.*²⁹ yields values for the trigonality index, τ , of ~0 (Cu1/Cu1') and 0.005 (Cu2/Cu2') ($\tau = 0$ and 1 for square pyramidal and trigonal bipyramidal geometry, respectively). Weak H bonds are present within the chains (intrachain H bonds). The donors are carbon atoms from the phenyl and diazine parts of qunx (C25, C28, and C31) and acceptors are the carboxylate oxygen atoms O4, O8 and O2.

Neighbouring chains communicate through C–H··· π interactions between the diba[–] methyl groups bearing C11 and C17, and the "pyrazine" part of qunx (H11C···Cg1 = 2.634 Å and H17C···Cg1 = 3.233 Å, where Cg1 is the centroid of the diazine ring) forming layers parallel to the (010) plane (Fig. 2, the stronger C11–H11C···Cg1 and the weaker C17–H17C···Cg1 interactions are indicated with dashed orange and dashed magenta lines, respectively). The distance between the neighbouring chains within these layers is 9.104 Å. The layers are stacked along the *b* axis, probably interacting through weak van der Waals interactions (Fig. S2‡). Other views of the supramolecular structure of **1** are shown in Fig. S3 and S4.‡

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The molecular structure of 2 is similar to that of 1 but the symmetry elements differ. Complex 2 crystallizes in the noncentrosymmetric space group Pna21. The asymmetric unit of the cell consists of two Cu^{II} atoms, four piv⁻ groups and one qunx ligand and thus the complex is best formulated as $\{[Cu_2(piv)_4(qunx)]\}_n$. There is one crystallographically independent dinuclear unit consisting of Cu1 and Cu2; these metal ions are bridged by four, crystallographically independent syn, $syn-\eta^1:\eta^1:\mu$ piv⁻ groups forming a paddle-wheel unit, the Cu1…Cu2 distance being 2.606(2) Å. A nitrogen atom of the bridging qunx ligand completes five-coordination at each metal ion. All this part of the structure lies close to the *n* glide plane which is normal to the *a* axis and the result of this symmetry element is the formation of polymeric chains parallel to the [0, 1, -1] direction (Fig. S5^{\ddagger}). As in the case of 1, the Cu^{II}...Cu^{II} vectors in 2 are not co-linear forming a zigzag line with Cu1···Cu2···Cu1" and Cu2···Cu1"···Cu2" of 166.5(4) and 164.2(4)°, respectively. There are two distinct Cu^{II}...Cu^{II} separations along the chain which alternate according to the sequence \dots ABAB \dots where (using the viewpoint of Fig. 3) A = Cu1...Cu2 = 2.606(2) Å and B = Cu2...Cu1'' = 7.274(2) Å. The coordination geometries of Cu1 and Cu2 are square pyramidal ($\tau = 0.023$ and 0.047, respectively). The apical site of each copper(II) square pyramid is occupied by a nitrogen atom of the bridging qunx ligand. Weak H bonds are present within the chains. The donor atoms are carbon atoms from the phenyl and azine parts of gunx (C21, C22, C25, and C28) and acceptors are the carboxylate oxygen atoms O3, O4, O7 and O8.

Neighbouring chains interact through C–H··· π interactions involving the piv⁻ methyl groups bearing C5 and C14 as donors and the "pyrazine" part of the coordinated qunx as acceptors forming layers parallel to the (100) plane (Fig. S6,‡ the C-H··· π interactions are indicated with dashed orange and magenta lines). The H5A…Cg1 and H14A-Cg1 distances are 2.884 and 2.867 Å, respectively, where Cg1 is the centroid of the diazine ring of qunx. The distance between the neighbouring chains within these layers is 8.196 Å. These layers are stacked along the *a* axis as shown in Fig. 4. Fig. S7[‡] shows the portions of the chains of 1 and 2 in an overlapped mode; it is clear that the chains are similar. Also similar are the layers formed in the two compounds. However, careful inspection of Fig. S2[‡] and 4 reveals that the packing of the layers, *i.e.* the overall 3D arrangement, is different in the two complexes, most probably due to the different nature of the carboxylate ligands involved (diba⁻ vs. piv⁻).

Hirshfeld surface (HS) analysis³⁰ was applied to evaluate the magnitude of interchain interactions in the crystals of **1** and **2**; data are shown in Fig. 5–8 and S8–S10.‡

A visual inspection of the d_{norm} surfaces in both 1 and 2 does not indicate any significant intermolecular interactions (Fig. 5). It should be mentioned at this point that in such an analysis, the colour scheme corresponds to the magnitude of intermolecular interactions ranging from strong (red colour) to moderate (white) to weak (blue). On the contrary, the HSs decorated with the shape index, *S*, reveal the importance of the C-H··· π interactions in both complexes (Fig. 6 and S8[‡]). These





Fig. 5 Hirshfeld surface d_{norm} maps (upper plots) and parts of the molecular structures (bottom plots) for (a) compound 1 and (b) compound 2.



Fig. 6 *S* map for **1**. Circled with white lines (a) and black lines (b) are the contact areas of HS which indicate the C11–H11C…Cg1 and C17–H17C…Cg1 interactions, respectively.



Fig. 7 Histograms summarizing the percentages of the types of atomic contacts, based on 2D fingerprint plots, for 1 and 2.

figures are the *S* property maps for the compounds and the circled regions identify complementary hollows (red) and bumps (blue) where neighbouring molecular HSs touch one another. Each C–H··· π interaction is clearly demonstrated on the *S* maps as a broad depression (of red colour and concave curvature) in the surface above the diazine ring and as a corresponding blue region of the convex curvature above the C–H donor region.

A simple way to examine the HS is by using the "fingerprint plot". The two dimensional fingerprint plot derived from the HS shows the frequency of occurrence of each combination of d_e , d_i (each such combination corresponds to some kind of interaction) in the molecular surface; d_e is the distance from



Fig. 8 $O \cdots H/H \cdots O$ (a) and $C \cdots H/H \cdots C$ (b) contributions (blue areas), along with the other kinds of contacts (gray area), into the 2D fingerprint plot for compound **1**. For the meaning of the green line, see the text.

the surface to the nearest-neighbouring atom exterior and d_i is the distance from the surface to the nearest-neighbouring atom interior. In a fingerprint plot, the observation and identification of the pairs of atoms that contribute to a specific d_e , d_i combination reveal the importance of each possible interaction type. The percentages of each type of interaction for **1** and **2** are given in Fig. 7. More than 95% of the interactions are of the H…H, O…H and C…H types in both cases. The van der Waals-type H…H interactions, which contribute ~80% in both structures, are weak and provide little stabilization. The distributions of the types of interactions are slightly different for the two complexes.

In the analysis of the 2D fingerprint plot, it is important to discuss the $d_i + d_e$ distances of the neighbouring atoms with values less than the sum of their van der Waals radii. When these values are small (i.e. the non-bonded interatomic distances are short), the intermolecular interactions should be strong.^{30d} Fig. 8 and S9[±] summarise the 2D fingerprint plots for O…H/H…O and C…H/H…C interatomic contacts in the crystals of 1 and 2, respectively. The green lines correspond to the $d_i + d_e$ distances that are equivalent to the sums of the van der Waals radii of oxygen (1.52 Å) and hydrogen (1.20 Å), Fig. 8a and S9a,[‡] and of carbon (1.70 Å) and hydrogen (1.20 Å), Fig. 8b and S9b.[‡] It is clear from Fig. 8a and S9a[‡] that a small portion of O···H interactions (the part of the fingerprint plot which overlaps with the triangular area), corresponding to ~10% of the total interactions, are effective contacts, i.e. the distances are shorter than the sum of the van der Waals radii; these H…O interactions are of the intrachain type (vide supra). The other important types of interactions, also contributing ~10% to the total interactions, consist of the interchain C-H··· π interactions; these interactions generate the characteristic distinct pattern of the pairs of "wings" for $d_{\rm e}$, $d_{\rm i} \approx$ 1.6-1.8 Å (Fig. 8b and S9b[‡] for compounds 1 and 2, respectively). Thus, the overlap of the fingerprint plot with the green area corresponds to the section that contains C···H interactions with interatomic distances shorter than the sum of the van der Waals radii of carbon and hydrogen and therefore more effective for the crystal packing. Fig. S10⁺ illustrates a combined HS d_{norm} map and the molecular representation of the neighbouring chains within the layers of compound **1**. The overall conclusion from the HS analysis is the similarity of the interchain (intralayer) interactions in the two structures.

Compounds **1** and **2** join a handful of quinoxaline-bridged polymeric copper(π) complexes;^{18,31} there are no quinoxaline-bridged carboxylate copper(π) coordination polymers and thus **1** and **2** become the first such complexes. The dinuclear complex $[Cu_2(O_2CPh)_4(qunx)_2]^{32a}$ and the polymeric compound $\{[Cu(HCO_2)_2(qunx)]\}_n^{32b}$ contain both qunx and carboxylate ligands, but the qunx group is terminal (*i.e.* monodentate). Compounds **1** and **2** are also members of a rather large family of 1D coordination polymers of the general formula $\{[Cu_2(O_2CR)_4(L-L)]\}_n$ (R various, L–L = *N,N'*-bidentate bridging ligand).^{30d,33–37}

Vibrational spectra

The Raman and IR spectra of compounds 1 and 2 are shown in Fig. 9 and S11,[‡] respectively. In the IR spectra, the strong bands at 1614 (1) and 1602 (2) cm^{-1} and the strong to medium intensity bands at 1410 (1) and 1422 (2) cm^{-1} are assigned to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ carboxylate stretching modes, respectively, the former most probably overlapping with an aromatic stretch.³⁸ The value of the spectral parameter Δ , where Δ = $\nu_{\rm as}({\rm CO}_2) - \nu_{\rm s}({\rm CO}_2)$, is less (204 cm⁻¹ in 1, 180 cm⁻¹ in 2) than the corresponding values in the "ionic" sodium salts of dibaH and pivH ($\sim 250 \text{ cm}^{-1}$), in accordance with the bidentate bridging mode of the carboxylate ligation³⁸ in the two coordination polymers. The $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ peaks in the Raman spectra appear at 1589 (1 and 2), 1433 (1), and 1422 (2) cm⁻¹, respectively. The two qunx IR bands at 604 cm⁻¹ (in plane deformation) and 405 cm^{-1} (out-of-plane deformation) are shifted to higher frequencies due to coordination, the former to 655 (1) and 618 (2) cm^{-1} , and the latter is split into 460, 422 (1) and 442, 414 (2) cm^{-1} .³⁹ The Raman spectra of both compounds are dominated by the spectral contribution of the qunx moiety. The characteristic qunx peaks at 3076 (1) and 3102, 3064 (2) cm⁻¹ are due to ν (C-H)_{qunx}, the ~1590 (1 and 2)



Fig. 9 Raman spectra of compounds $\{[Cu_2(diba)_4(qunx)]\}_n$ (**1**, bottom plot) and $\{[Cu_2(piv)_4(qunx)]\}_n$ (**2**, upper plot).

and 1379, ~1360 (1 and 2) cm⁻¹ peaks are assigned to the ring stretching vibrations of B₁ and A₁ types, respectively, while the strong peak at 808 cm⁻¹ for 2 mostly arises from a qunx breathing mode. The Raman peaks at 771 (1) and 775 (2) are tentatively attributed to a skeletal bending vibration.⁴⁰ The different nature of the diba⁻ and piv⁻ ligands is reflected in the 2990–2860 cm⁻¹ IR and Raman bands/peaks, accurate assignments of the ν_{as} (CH₃), ν_{s} (CH₃), ν_{as} (CH₂) and ν_{s} (CH₂) modes [the latter two only in the case of **1**] being difficult.⁴¹

Magnetic susceptibility studies

Magnetic susceptibility data were collected as a function of temperature from 1.8 to 310 K (Fig. 10). As anticipated from the presence of paddle-wheel {Cu₂(O₂CR)₄} units, the two compounds exhibit very strong antiferromagnetic exchange interactions with the molar magnetic susceptibility (χ) maxima occurring near or above room temperature. Both complexes show the presence of a paramagnetic impurity; this is the result of both potential chemical impurities in the sample and



Fig. 10 The temperature dependence of the magnetic susceptibility of compounds **1** (upper plot) and **2** (bottom plot). The solid lines are the best fits to the dimer model with a Curie–Weiss correction term to account for interdimer interactions.

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Table 2 Fitted magnetic exchange parameters for compounds 1 and 2

Compou	and C^a (emu K mol [–]	$^{1} \text{ Oe}^{-1}$)	$J/K^{b}(\mathbf{K})$	$\theta^{c}\left(\mathbf{K}\right)$	ρ^{d} (%)
1 2	0.78 0.78	B(1) = B(2)		-479(4) -532(4)	-48(9) -67(13)	9.5(5) 10.9(6)
^a Curie	constant	^b Magnetic	ovehence	constant	^c Weiss	constant

^d Paramagnetic impurity.

defects in the structure (broken dimers in the crystal). Given the low values of χ as a result of the strong exchange, the effects of impurities dominate the magnetic data and behavior below 100 K for both complexes.

The data were fit to the Bleaney–Bowers dimer model⁴² with a Curie–Weiss correction for interdimer interactions and a paramagnetic impurity term.⁴³ The resulting parameters are given in Table 2. The magnetic data reveal the expected strong antiferromagnetic exchange within the carboxylate dimer portions of the chains with *J* values near –500 K for both compounds. These values compare well with other reported tetra $(\eta^1:\eta^1:\mu$ -carboxylato)dicopper(II) dimers.^{44–46}

The large values for the Weiss constant (θ) suggest that there are significant antiferromagnetic interactions between the carboxylate-bridged dinuclear units *via* the quinoxaline superexchange pathways, but these values are still only ~10% of the values for the interaction within the dinuclear units. We recommend that these values should be taken as qualitative measures of the parameters. The -48(9) (1) and -67(13) (2) K values for the interdimer exchange are in good agreement with those reported in most qunx-bridged copper(π) complexes.^{18,31a}

Conclusions and perspectives

In this report, we have shown that the use of acacdoH₂ in reactions with Cu^{II} carboxylate sources in Me₂CO has led to a novel transformation of this ligand and the preparation of interesting quinoxaline- and carboxylate-bridged 1D coordination polymers which have been fully characterized. It is important to state that the originally employed ligand is not present in the reaction products. The process is catalytic and this opens the door for the catalytic synthesis of qunx and substituted qunx compounds using acacdoH2-based starting materials. Traditionally, the synthesis of quinoxalines is accomplished^{47,48} by: (a) cyclization of benzene substrates already bearing appropriate substituents, (b) cyclocondensation of benzene substrates with acyclic synthons to provide one or more of the ring atoms required to complete the pyrazine ring, (c) analogous processing of the performed pyrazine substrates, or (d) rearrangement, ring expansion/contraction, degradation, or modification of the appropriate derivatives of other heterocyclic systems. By far the most common synthetic method for quinoxalines involves the cyclocondensation of an o-phenylenediamine (or a closely related substrate) with a synthon containing an oxaly [-C(=O)-C(=O)-] or equivalent,

e.g. HC(=O)-C=N, group.48 As far as the free qunx is concerned, its synthesis is accomplished by the 1:1 reaction of o-phenylenediamine (1,2-benzenediamine) and the glyoxalsodium bisulfite adduct, OHCCHO·2NaHSO₄·H₂O (the synthon), in CH₃COOH 2 M/Na₂OCMe 4 M/H₂O (pH = 5) at 60 °C in 85% yield.^{47a} This work shows that metal-mediated reactions of 1,3-dioximes are still in their infancy. The present results also demonstrate the importance of the solvent in such reactions. The novel Cu^{II} -assisted acacdo $H_2 \rightarrow (L^1)^{2-}$, $(L^2)^{2-}$, $(L^3)^-$ transformation (Scheme 2), discovered by Papaefstathiou's group,¹³ took place in EtOH/H₂O, the H₂O being responsible for the hydration of the ketone $(L^2)^{2-}$ to the double deprotonated gem-diol $(L^1)^{2-}$. On the contrary, the acacdoH₂ \rightarrow qunx transformation takes place in Me₂CO which seems to participate actively in the (proposed) mechanism (Scheme 3), providing the extra three carbon atoms required for the transformation (Scheme 4). Investigations using other transition metal ions under similar reaction conditions are in progress; preliminary results with Ni^{II} show different and unrelated products.

We have no reasons to believe that this research area is exhausted of new results. Indeed, ongoing studies in our groups reveal that we have scratched only the surface of the area of the metal ion-assisted reactivity of dioximes, including benzil dioxime and 1,3-di(pyridine-2-yl)propane. As far as future perspectives are concerned, variation of the metal ion (e.g. use of Ni^{II}, Zn^{II}, etc.), and the R,R' groups in the RC(NOH) $CH_2C(NOH)R'$ (e.g. R = R' = Ph and $R = CH_3$, R' = Ph) family of dioximes may provide a systematic modification of products (both transformed ligands and the resulting complexes); we are currently working on these ideas and results will be reported soon. Meanwhile, we have been developing the use of solvents other than Me₂CO, e.g. MeCN and MeNO₂, in the reactions; these solvents can give strongly nucleophilic carbanions under strongly alkaline conditions, favouring the formation of unusual ligands when reacting with oxime-containing molecules in the presence of metal ions. We believe that inorganic chemists will more actively participate in the future in projects related to the many varied reactions of oximes that can take place in the presence of metal ions.

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