Solvothermal *vs.* bench-top reactions: Control over the formation of discrete complexes and coordination polymers†

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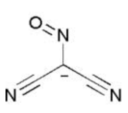
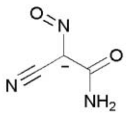
The formation of discrete complexes [M(mcoe)$_2$S$_2$] (M = Cu, Ni; S = MeOH, H$_2$O) *vs.* a nitroso-bridged ferromagnetically-coupled Cu^{II} coordination polymer [Cu(mcoe)$_2$] is influenced by the use of solvothermal reaction conditions.

The synthesis of X-ray quality crystals of coordination polymers is one of the great ongoing challenges of crystal engineering. Due to their insoluble nature, crystals are usually grown directly from the synthetic reaction mixture. As a result, solvothermal synthesis has proved to be a very useful and widely used technique for obtaining such crystals; under these conditions, organic ligands may become more soluble or be converted into different species, and the formation of kinetic species can occur.[1–4] However, few studies have directly compared the reaction products obtained from solvothermal synthesis against those obtained from conventional bench-top techniques.[5] We report here one such comparison.

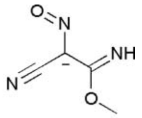
First row transition metals have been shown to promote the nucleophilic addition of water or methanol across one of the nitrile groups in dicyanonitrosomethanide (dcnm), yielding the derivative ligands cyanoacetamidoximate (cao) and methyl 2-cyano-2-(hydroxyimino)ethanimidate (mcoe), respectively. Reaction of the dcnm ligand with other nucleophiles has also been reported.[6] Only six structures have been reported containing the mcoe ligand, of which five have been discrete, mononuclear complexes.[7–11] The exception is our own [Mn$_3$(mcoe)$_6$]$^+$ cluster.[12]



dcnm

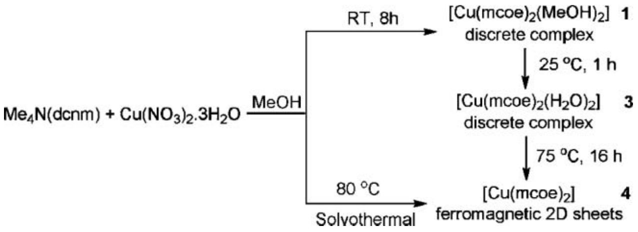


cao



mcoe

As part of our studies with the dcnm anion (for example, in [Ln(dcnm)$_6$]$^{3-}$ complexes[13]), we now report that reactions with CuX$_2$ (X = NO$_3$ or ClO$_4$) produce different products, depending upon the reaction conditions used (Scheme 1). Besides discrete complexes formed by crystallisation at room temperature, the first polymeric product of mcoe, [Cu(mcoe)$_2$], has been prepared under solvothermal conditions, and displays the unusual μ-η^1(N):η^1(O) bridging mode of the nitroso group and has magnetic properties indicative of weak ferromagnetic coupling.



Scheme 1 The product of the reaction between the dcnm ligand and Cu^{II} is dependent upon the reaction conditions, yielding both discrete and polymeric products. Single crystals of **4** can only be obtained by the bottom route.

The room temperature reaction of Me$_4$N(dcnm) with Cu(NO$_3$)$_2$·3H$_2$O in methanol yields X-ray quality single crystals of [Cu(mcoe)$_2$(MeOH)$_2$] (**1**) within a few hours.‡ The reaction of Ni(ClO$_4$) with Na(dcnm) under the same conditions yielded the isomorphous complex [Ni(mcoe)$_2$(MeOH)$_2$] (**2**) over a longer period of time. Discrete complexes **1** and **2** contain two mcoe ligands that chelate to the equatorial positions of the octahedral metal through the nitroso and imino nitrogen atoms in a transoid manner (Fig. 1). Methanol occupies the axial positions. Elemental analyses suggest the ready replacement of coordinated methanol by water after removal from the mother liquor, *vide infra*.§ The discrete complexes stack *via* hydrogen bonding interactions to form 1D chains (Fig. 2a). The shortest hydrogen bond is that from a methanol ligand to the oxygen atom of an adjacent nitroso group. The intermolecular interaction between the imino proton

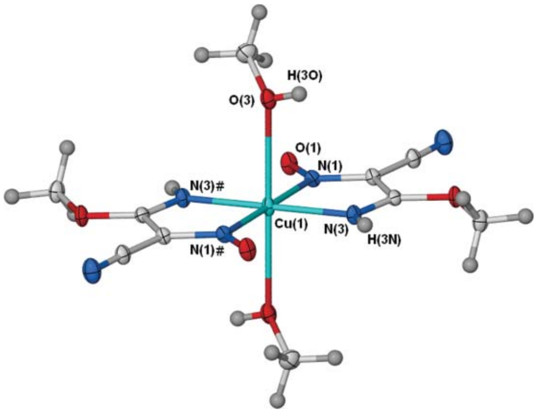


Fig. 1 Structure of the discrete molecular complex [Cu(mcoe)$_2$(MeOH)$_2$] (**1**), isomorphous with the Ni complex **2**. The ellipsoids are displayed at 50% probability. Symmetry equivalent: # = $-x$, $-y$, $1 - z$.

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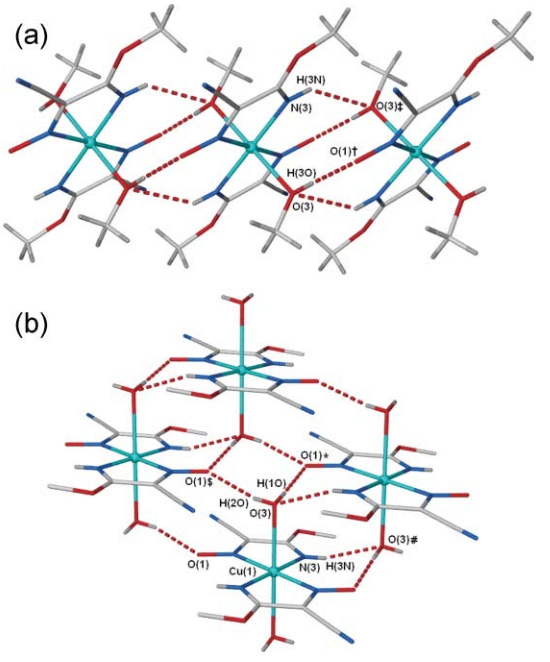

Fig. 2 Hydrogen bonded networks between complexes in the structures of (a) $[M(mcoe)_2(MeOH)_2]$ (**1** and **2**) and (b) $[Cu(mcoe)_2(H_2O)_2]$ (**3**). Symmetry equivalents: † = 1 + *x*, *y*, *z*; ‡ = 1 − *x*, −*y*, 1 − *z*; * = 1 + *x*, *y*, *z*; $ = −*x*, −*y*, −*z*; # = 1 − *x*, 1 − *y*, −*z*. Hydrogen bond distances (H···A/Å). **1**: H(3O)···O(1)† = 2.03(3), H(3N)···O(3)‡ = 2.25(2); **2**: H(3O)···O(1)† = 1.87(2), H(3N)···O(3)‡ = 2.38(2); **3**: H(1O)···O(1)* = 1.97(3), H(2O)···O(1)$ = 2.26(3), H(3N)···O(3)# = 2.23(3).

and the methanol oxygen atom is significantly longer. Overall, these interactions form an $R_2^2(7)$ motif[14] (incorporating a copper atom) between a methanol ligand of one complex and the two mcoe ligands of an adjacent complex. This single motif holds each chain together, and there are no significant intermolecular interactions between adjacent chains.

The reaction of $Cu(ClO_4)_2·6H_2O$ in methanol with Na(dcnm) in the presence of NaSCN over the course of two weeks yielded single crystals of a differently solvated product, $[Cu(mcoe)_2(H_2O)_2]$ (**3**), similar to a previously reported Ni complex.[11] Aqua-containing complex **3** is similar to complex **1**, with water in place of the axial methanol ligands (Fig. 2b).‡ The presence of water results in a change in the intermolecular interactions, although parallels can be drawn with those found in the structures of **1** and **2**. The $R_2^2(7)$ motif is again present, with the water oxygen atom and one of the associated hydrogen atoms substituting for the methanol donor/acceptor sites. This interaction forms chains analogous to those in the structures of **1** and **2**. The second proton of the aqua ligand acts as a hydrogen bond donor to an adjacent nitroso oxygen atom, resulting in a centrosymmetric $R_2^4(8)$ ring and consequently a 2D hydrogen-bonded network.

When harsher reaction conditions were employed, a very different product was formed. The solvothermal reaction of $Cu(NO_3)_2·3H_2O$ and Na(dcnm) in methanol at 80 °C for two days afforded the complex $[Cu(mcoe)_2]$ (**4**) in a reproducibly good yield. The composition and purity of the bulk sample was confirmed by microanalysis and IR spectroscopy.§ The Cu^{II} complex 'monomer' is square planar, with two ligands chelating through the nitroso nitrogen atom and the amide nitrogen atom, as seen for **1–3**.‡ The coordination sphere of the Cu^{II} is completed by axial coordination of the nitroso oxygen atoms of adjacent complexes with significant Jahn–Teller distortion (Cu–O = 2.517(3) Å), Fig. 3a. Bridging nitroso groups have been well-studied in regard to organic (mostly neutral) compounds with metals, and a variety of bridging modes are known.[15,16] However, the only mcoe structure that has previously been observed to show μ-η^1(N):η^1(O) bridging of the nitroso functionality is the discrete cluster $[Mn_3(mcoe)_6]^+$.[12] This mode of binding, in which one of the metals is also chelated by the ligand, has been referred to as five-membered ring-assisted bridging.[17] The $[Cu(mcoe)_2]$ complexes act as 4-connecting nodes in the formation of 2D (4,4) sheets (Fig. 3b). The sheets are cross-linked into a 3D network, primarily through a hydrogen bond from the imino proton to a nitrile acceptor (H···A = 2.53(4) Å). Strong hydrogen bond interactions involving the nitrile group as an acceptor are not observed in the structures of **1–3**, presumably due to the presence of either methanol or water ligands providing better acceptor groups.

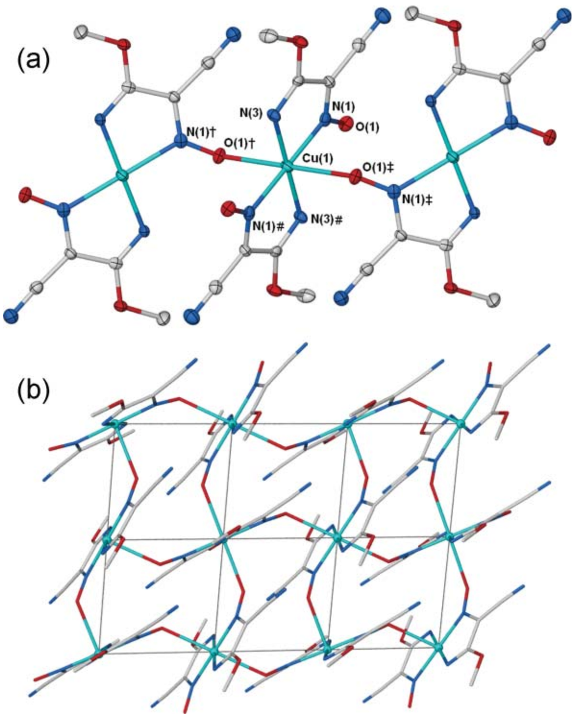

Fig. 3 (a) One $[Cu(mcoe)_2]$ unit in the structure of **4**, with two adjacent nitroso-bridged complexes shown. The ellipsoids are displayed at 50% probability. (b) The complex forms a (4,4)-sheet with each Cu^{II} N,O-bridged to four others. Hydrogen atoms are omitted for clarity. Symmetry equivalents: # = 1 − *x*, 1 − *y*, 1 − *z*; † = *x*, − *y*, *z* − ½; ‡ = 1 − *x*, *y* − ½, − *z*.

Thermal analyses were conducted on the Cu^{II} complexes to examine the potential interconversion between species. X-Ray powder diffraction of the initial bulk reaction product mixture from Me_4N(dcnm) and $Cu(NO_3)_2·3H_2O$ at room temperature showed that a mixture of **1** and **3** was present (and a trace amount of **4**), with the peaks for **1** disappearing within 1 h, confirming the elemental analysis results that suggested the ready replacement of methanol by water.§ After heating the powdered sample at 75 °C overnight, a further XRPD scan indicated the formation of **4** with some residual hydrated product **2** (see ESI†).

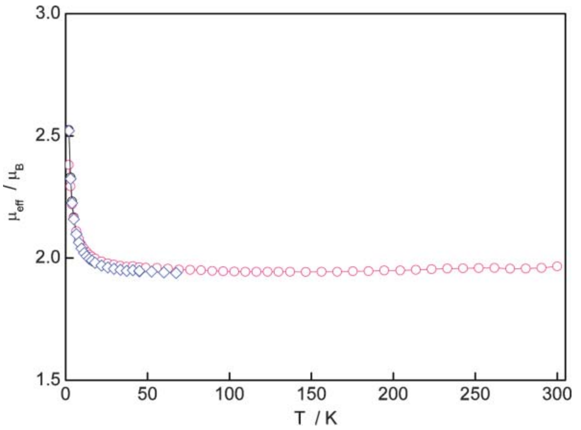

Fig. 4 Magnetic moment plot (μ_{eff} *vs.* T) of [Cu(mcoe)$_2$] (**4**). The circles are in a field of 1 T; the diamonds are in a field of 0.01 T.

The magnetic susceptibility of **4** in the temperature range 300–40 K obeys a Curie law dependence, with the corresponding μ_{eff} values of 1.9 μ_B remaining essentially independent of temperature (Fig. 4).¶ Below 40 K, a Curie–Weiss dependence was followed ($\chi_M = C/(T - \theta)$). A constant of $\theta = 0.16$ K ($C = 0.47$ cm^3 mol^{-1} K) is observed, with μ_{eff} values increasing quite rapidly, reaching 2.55 μ_B at 2 K, indicative of weak ferromagnetic coupling. Variation of the applied field, from 1 to 0.01 T in the temperature range 60–2 K, gave the same values of μ_{eff}. Thus, the rapid increase in μ_{eff} at low temperatures is not due to traces of ferromagnetic impurities but it is intrinsic to complex **4**. The reason for weak ferromagnetic coupling, occurring *via* the Cu–N–O–Cu bridging moieties, is probably because the four such bridges per Cu link adjacent {Cu^{II}(N)$_4$} planes *via* both d_{z^2} and $d_{x^2-y^2}$ pathways, thus giving orthogonal overlap that leads to ferromagnetic coupling. In the cluster complex [Mn$_3$(mcoe)$_6$]$^+$, the coupling was antiferromagnetic in nature.[12] A survey of the related oximate bridged M–O–N(=C)–M systems[18] shows that antiferromagnetic coupling is more common but that weak ferromagnetic coupling is known.[19,20]

In summary, methanolic reactions involving the dcnm$^-$ ligand with Cu^{II} salts resulted in rapid conversion of the ligand into the nucleophilic addition product mcoe$^-$. Solvated room temperature products **1–3** formed as single crystals within a matter of hours. A change in reaction conditions from room temperature to solvothermal promoted the formation of solvent-free polymeric complex **4**. Nitroso bridging between the Cu^{II} atoms in **4** allowed weak ferromagnetic coupling to occur, but without any long range ordering. Future work will explore the use of the bridging capability of mcoe in clusters and framework materials.

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Notes and references

‡ Crystallographic data (at 123 K):

[Cu(mcoe)$_2$(MeOH)$_2$] (**1**): C$_{10}$H$_{16}$CuN$_6$O$_6$, M = 379.83, dark green needle, monoclinic, $P2_1/c$, a = 5.3351(1), b = 15.8068(4), c = 9.3759(3) Å, β = 97.597(2)°, V = 783.74(4) Å^3, Z = 2, 9490 reflections collected, 1793 unique (R_{int} = 0.0472), 1720 observed ($I > 2\sigma(I)$), $R1$ = 0.0273, w$R2$ = 0.0646. CCDC 648200.

[Ni(mcoe)$_2$(MeOH)$_2$] (**2**): C$_{10}$H$_{16}$N$_6$Ni$_1$O$_6$, M = 375.00, purple needle, monoclinic, $P2_1/c$, a = 5.2198(1), b = 15.9545(3), c = 9.3351(2) Å, β = 98.222(1)°, V = 769.43(3) Å^3, Z = 2, 8666 reflections collected, 1754 unique (R_{int} = 0.0186), 1679 observed ($I > 2\sigma(I)$), $R1$ = 0.0190, w$R2$ = 0.0468. CCDC 648201.

[Cu(mcoe)$_2$(H$_2$O)$_2$] (**3**): C$_8$H$_{12}$CuN$_6$O$_6$, M = 351.78, brown plate, triclinic, P-1, a = 5.1369(10), b = 6.7710(14), c = 10.113(2) Å, α = 74.96(3), β = 83.83(3), γ = 79.17(3)°, V = 333.01(12) Å^3, Z = 1, 5983 reflections collected, 1527 unique (R_{int} = 0.0435), 1436 observed ($I > 2\sigma(I)$), $R1$ = 0.0257, w$R2$ = 0.0627. CCDC 648202.

[Cu(mcoe)$_2$] (**4**): C$_8$H$_8$Cu$_1$N$_6$O$_4$, M = 315.74, brown plate, monoclinic, $P2_1/c$, a = 11.6289(8), b = 6.7788(8), c = 7.3868(13) Å, β = 104.975(4)°, V = 562.53(13) Å^3, Z = 2, 3310 reflections collected, 1281 unique (R_{int} = 0.0602), 796 observed ($I > 2\sigma(I)$), $R1$ = 0.0467, w$R2$ = 0.0750. CCDC 648203. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707709b

§ A 5 ml methanolic solution of Cu(NO$_3$)$_2$·3H$_2$O (51 mg, 0.21 mmol) and Na(dcnm) (50 mg, 0.43 mmol) was placed in a 23 ml sealed pressure vessel and heated to 80 °C over the course of 6 h. The vessel was left at this temperature for 48 h before being cooled steadily to room temperature over a further 48 h giving **4** (46%). All other reactions were carried out on a similar scale at room temperature. **1/3**: IR (ν/cm^{-1}) 3487w, 3287m, 2220m, 1634s, 1468m, 1410m, 1308m, 1205w, 1135m, 1090w. ESI$^+$-MS: m/z = 316 [Cu(mcoe)$_2$ + H]$^+$, 338 [Cu(mcoe)$_2$ + Na]$^+$. Anal. calc. for [Cu(mcoe)$_2$(H$_2$O)$_2$] (C$_8$H$_{12}$Cu$_1$N$_6$O$_6$): C, 27.31; H, 3.43; N, 23.89. Found: C, 27.47; H, 3.46; N, 23.78%. **2**: IR (ν/cm^{-1}): 3334s, 2957m, 2219m, 1646s, 1459m, 1425m, 1395s, 1284m, 1199m, 1123m. ESI$^+$-MS: m/z = 311 [Ni(mcoe)$_2$ + H]$^+$, 333 [Ni(mcoe)$_2$ + Na]$^+$. Anal. calc. for [Ni(mcoe)$_2$(H$_2$O)$_2$] (C$_8$H$_{12}$Ni$_1$N$_6$O$_6$): C, 27.69; H, 3.48; N, 24.22. Found: C, 27.54; H, 3.55; N, 23.64%. **4**: IR (ν/cm^{-1}): 3491w, 3332s, 2208m, 1624s, 1463w, 1420m, 1374s, 1342m, 1307m, 1204s, 1180w, 1124s. Anal. calc. for [Cu(mcoe)$_2$] (C$_8$H$_8$Cu$_1$N$_6$O$_4$): C, 30.43; H, 2.55; N, 26.62. Found: C, 30.48; H, 2.57; N, 26.46%.

¶ Variable temperature magnetic susceptibilities were obtained on a powdered ~20 mg sample using a Quantum Design MPMS5 Squid magnetometer in a field of 1 T.[12]

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