

Structural characterisation of a water intercalated bis-amide tecton and copper promoted monohydration of a dinitrile

Jens K. Bjernemose,^a Christine J. McKenzie,^a Paul R. Raithby^b and Simon J. Teat^c

^a Department of Chemistry, University of Southern Denmark, Odense Campus, 5230 Odense M, Denmark. E-mail: chk@chem.sdu.dk; Fax: 45 6615 8780; Tel: 45 6550 2518

^b Department of Chemistry, University of Bath, Claverton Down, UK BA2 7AY

^c CLRC Daresbury Laboratory, Daresbury, Warrington, UK WA4 4AD

Received 2nd June 2003, Accepted 4th June 2003

First published as an Advance Article on the web 11th June 2003

Chains of H-bonded water intercalated bis-amide pairs were found in the structure of $\{[\text{Cu}(\text{cdc})_2(\text{OH}_2)]\cdot\text{H}_2\text{O}\}_\infty$ (**1**) (cdc^- = carbamoyldicyanomethanide); specific hydration of one nitrile group of the cdc^- ligands of **1** to give the previously unknown anion cyanomalonomidate (cyma^-) as a ligand in $[\text{Cu}(\text{cyma})_2]\cdot\text{H}_2\text{O}$ is possible.

An interest in carbon acids^{1,2} and coordination polymers³ prompted us to study the coordinative properties of the anion carbamoyldicyanomethanide ($(\text{NC})_2\text{CCONH}_2^-$, cdc^-). † $\text{K}(\text{cdc})$ ^{4,5} reacts with several divalent first row transition metals to give the nearly isostructural monomeric bis- cdc compounds, $[\text{M}(\text{cdc})_2(\text{OH}_2)_4]\cdot 2\text{H}_2\text{O}$, $\text{M} = \text{Mn}(\text{II})$,^{5,6} $\text{Fe}(\text{II})$,⁵ $\text{Co}(\text{II})$,^{5,7} $\text{Ni}(\text{II})$,^{5,8} $\text{Zn}(\text{II})$ ^{5,9} and related, but polymeric $\{[\text{Zn}(\text{cdc})_2(\text{HOCH}_2)_2]\cdot 4\text{CH}_3\text{OH}\}_\infty$.⁹ Furthermore, the tris ligated, polymeric $\{[\text{Eu}(\text{cdc})_3(\text{OH}_2)_3]\cdot\text{H}_2\text{O}\}_\infty$ ¹⁰ was recently reported. $\{[\text{Cu}(\text{cdc})_2(\text{OH}_2)]\cdot\text{H}_2\text{O}\}_\infty$ (**1**) ‡¹¹ (Fig. 1) like $\{[\text{Zn}(\text{cdc})_2(\text{HOCH}_2)_2]\cdot 4\text{CH}_3\text{OH}\}_\infty$ ⁹ is a 1-D coordination polymer with both cdc^- units bridging two

copper atoms of the chains in the $\mu\text{-}\kappa\text{N}:\kappa\text{N}'$ mode. The carbonyl oxygen atoms are associated to the Cu atoms of the next chain through an interaction orthogonal to the nitrile groups of the cdc^- ligands that form the backbone of the polymeric 1D chains. In turn the chains are linked by extensive H-bonding interactions. These include the bis-amide tecton $(\text{O}\cdots\text{H}-\text{N})_2$. The geometry about the Cu(II) is octahedral (tetragonally Jahn–Teller distorted) and is completed by a water ligand *trans* to the amide oxygen. An interesting feature is the intercalation of 2 molecules of water between each H bonded amide pair. One of these waters is the axial ligand of the copper atom in a chain in the adjacent plane. The other is a tightly bound lattice water. Thus the bridging $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ units furnish an ideal $\text{Cu}\cdots\text{Cu}$ separation for supporting the intercalation of water between each H bonded amide pair. We are unaware of any previous report of this particular motif and it demonstrates the way in which highly specific H bonding interactions with water might affect the topology of *e.g.* a β -sheet. The biological significance lies in mechanisms for protein folding and stabilising secondary, tertiary and quaternary structures. In $\{[\text{Zn}(\text{cdc})_2(\text{HOCH}_2)_2]\cdot 4\text{CH}_3\text{OH}\}_\infty$ ⁹ the solvent of crystallisation can furnish no hydrogen bonding between $\{[\text{Zn}(\text{cdc})_2]\}_\infty$ chains. This is because methanol unlike water only has one hydrogen atom for donation and this is used in joining the cdc^- units within one chain.

If **1** is semi-dissolved/suspended in refluxing water for 24 h it undergoes a transformation from red–brown to pale green in the two-phase reaction. The pale green product is a copper complex of the hitherto unknown anion, which we have named cyanomalonomidate ($\text{NCC}^-(\text{CONH}_2)_2$, cyma^-). † The formulation of the complex is $[\text{Cu}(\text{cyma})_2]\cdot\text{H}_2\text{O}$ (**2**) ‡¹² and the X-ray crystal structure of **2** is shown in Fig. 2. The coordination geometry around the copper ion is square planar but **2** can also be considered a coordination polymer *via* weak axial^{13,14} interactions of the copper ions to the nitrile groups of cyma^- bound to adjacent copper ions (2.7632(17)Å). The geometry favours an interpretation in which the copper–nitrile interaction is due to a trigonal nitrogen atom coordination rather than a metal– π bond ($\text{Cu}-\text{N}(4)-\text{C}(4)$ angle of 116°). A similar degree of delocalisation in the nitrile groups of cdc^- and cyma^- in **1** and **2** is evident from the similarity in the $\text{C}-\text{C}\equiv\text{N}$ bonds. A non-linear coordination of the nitriles to copper in **1** was also noted.

A Cu-promoted selective monohydration of cdc^- in **1** to produce **2** has occurred as depicted by Scheme 1. The IR spectrum of **2** contrasts to that of **1** in the regions of the nitrile $\nu_{\text{C}\equiv\text{N}}$ and amide $\nu_{\text{C}=\text{O}}$. In **1**, two strong bands due to the two nitrile groups of cdc^- are present at 2246 and 2197 cm^{-1} . In the same region in the IR spectrum of **2** one band at 2181 cm^{-1} appears. Similarly the amide $\nu_{\text{C}=\text{O}}$ at 1591, $\nu_{\text{C}-\text{N}}$ at 1402 and $\delta_{\text{N}-\text{H}}$ frequencies at 1636 cm^{-1} in **1** are split into three pairs at 1568, 1547; 1488, 1446; and 1641, 1619 cm^{-1} respectively.¹⁵ As expected there is a decrease in the absorption energy of the $\text{C}=\text{O}$ bond due to the co-ordination to the copper ion. Conversely, the $\text{C}-\text{N}$ frequency is raised indicating a higher bond order. This is counterintuitive to the fact that the amide $\text{C}-\text{N}$ bond is actually lengthened in the

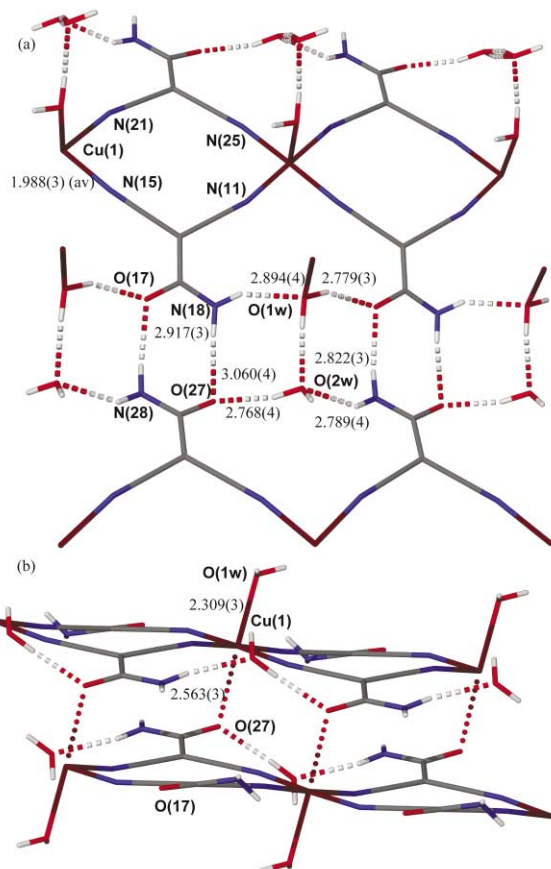


Fig. 1 The X-ray crystal structure of **1**: View along the (a) $[1\ 1\ 1]$ direction, the sheets are linked by the water intercalated bis-amide tecton chains; (b) $[0\ 1\ 1]$ direction, the intersheet bonding. Important distances (Å). H bonds are represented by broken cylindrical bonds (some distances depicted) and coordination bonds by spheres.

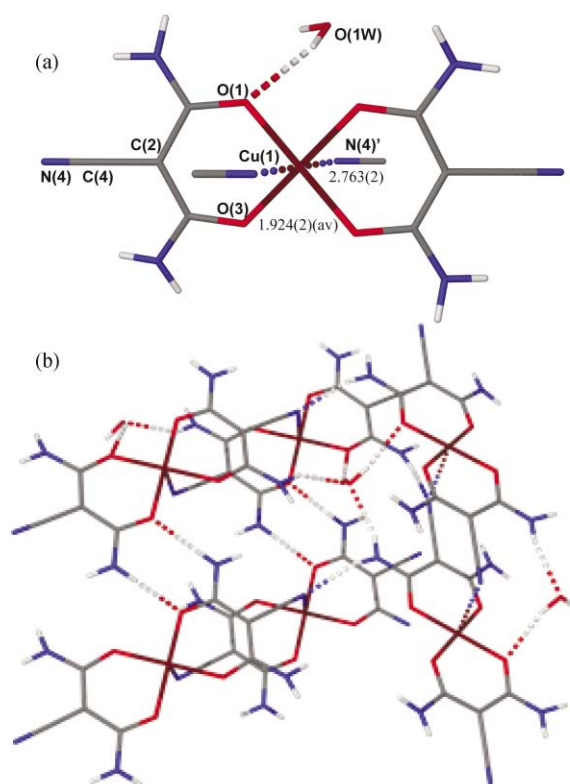
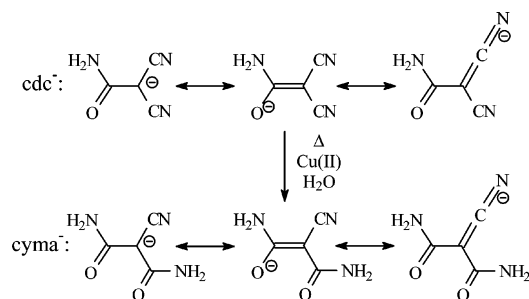


Fig. 2 The X-ray crystal structure of **2**: (a) The square planar unit, (b) view along the $[1\ 0\ \bar{1}]$ direction. Bond representations as in Fig. 1.



Scheme 1

crystal structure of **2** compared with **1**. The C–CONH₂ bond in cyma[−] of **2** is shorter than the corresponding bond in cdc[−] of **1**, consistent with an increased contribution from the enolate resonance forms due to amide O coordination.

There are at least two explanations for the selective hydration of only one of the nitrile groups of cdc[−] when **1** is heated in water. Firstly, thermodynamics. After one nitrile group is hydrated and cyma[−] is formed the insolubility of the resultant Cu(II) complex drives its precipitation. Or secondly, and in our minds more probable and significantly, is that the selectivity can be ascribed to the lowered Lewis acidity of the copper mediator in its complex with cyma[−] compared to that with cdc[−]. The structures of **1** and **2** show N₄O₂ and O₄ copper coordination respectively. Thus once the first nitrile is converted to an amide the Lewis acid centre is not sufficiently activating to promote the hydration of the second nitrile group of cdc[−]. In addition, no coordinated water is present in the structure of **2**. Metal-promoted and catalysed nitrile hydration under mild conditions are well known,¹⁶ but we believe this to be the first example leaving one of two otherwise equivalent nitriles untouched under neutral conditions. Previous examples are acid or base catalysed or take place on specifically activated non-charged substrates.¹⁷ Two mechanistic factors are important: The activation of the nitrile carbon toward nucleophilic attack by virtue of the nitrile coordination and/or the formation of a nucleophilic hydroxide at relatively low pH *via* coordination to a Lewis

acid. It is notable that thus far this reaction was observed only for the copper(II) complex of cdc[−], **1**, which shows a very different structure to the other first row complexes characterised by us and others.^{5–10} In the [M(cdc)₂(OH₂)₄] \cdot 2H₂O, M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II) complexes there is N₂O₄ coordination, while in **1** there is N₄O₂ coordination. Thus again the Lewis acidity of the metal ion may have been subtly tuned and the ligand poised more appropriately for the monohydration reaction in the case of the distinctly structurally different copper complex. This reaction opens up a synthetic pathway to the previously unknown but simple four-carbon compound, cyanomalonamide, which like its close relatives may find uses in synthetic organic chemistry.

Acknowledgements

JKB is grateful to the Oticon foundation for a grant allowing him to visit Bath. PRR acknowledges the EPSRC for allocation of beamtime at the SRS.

Notes and references

† Carbamoyldicyanomethanide = (NC)₂CCONH₂[−] = cdc[−]; cyanomalonamidate = NCC(CONH₂)₂[−] = cyma[−].
‡ Crystallographic data for **1**: C₈H₈CuN₆O₄, *M* = 315.74, triclinic, *a* = 7.2230(5), *b* = 7.4380(5), *c* = 11.5910(11) Å, *a* = 77.727(4), *β* = 80.513(4), *γ* = 74.160(6)°, *V* = 581.59(8) Å³, *T* = 293K, *P1* (no. 2), *Z* = 2, *μ*(Mo–Kα) = 1.9 mm^{−1}, 9744 reflections measured, 2661 unique (*R*_{int} = 0.042) used in all calculations. Final *wR*(*F*²) = 0.10 (all data).

Crystallographic data for **2**: C₈H₁₀CuN₆O₅, *M* = 333.76, monoclinic, *a* = 8.5923(5), *b* = 11.2749(7), *c* = 12.5768(8) Å, *β* = 106.065(2)°, *V* = 1170.83(12) Å³, *T* = 173K, *C2/c*, *Z* = 4, *μ*(0.6893 Å) = 1.9 mm^{−1}, 4025 reflections measured, 1579 unique (*R*_{int} = 0.022) used in all calculations. Final *wR*(*F*²) = 0.092 (all data). Data collected at the SRS, Daresbury.

CCDC reference numbers 207254 and 207255. See <http://www.rsc.org/suppdata/dt/b3/b306169h/> for crystallographic data in CIF or other electronic format.

- J. K. Mukhopadhyaya, S. Sklenak and Z. Rappoport, *J. Org. Chem.*, 2000, **65**, 6856.
- O. Simonsen and A. la Cour, *Acta Crystallogr., Sect. C*, 1995, **51**, 2006.
- S. R. Batten, B. F. Hoskins, B. Mourbaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1999, 2977.
- S. Trofimenko, T. L. Little and H. F. Mower, *J. Org. Chem.*, 1962, **27**, 433.
- The crystal structures of the Mn, Fe, Co, Ni and Zn complexes along with the K salt have been solved, J. K. Bjernemose, C. J. McKenzie and P. R. Raithby, unpublished.
- J. A. Schlueter, U. Geiser and J. L. Manson, *Acta Crystallogr., Sect. C*, 2003, **59**, m1.
- J. M. Shi, H. L. Yin, L. J. Sun, W. T. Yu, X. Xu and M. G. Zhao, *Chin. J. Struct. Chem.*, 2002, **21**, 178.
- J. M. Shi, S. C. Zhu, L. D. Liu, W. T. Yu, H. L. Yin and J. L. Fan, *Pol. J. Chem.*, 2001, **75**, 1591.
- J.-M. Shi, H.-L. Yin, C.-J. Wu, F.-L. Liu and W. Xu, *Polyhedron*, 2003, **22**, 493.
- J. M. Shi, W. Xu, Q. Liu, F. Liu, Z. Huang, H. Lei, W. Yu and Q. Fang, *Chem. Commun.*, 2002, 756.
- Saturated aqueous solutions of Kcdc and CuSO₄·5H₂O in stoichiometric proportions were mixed to afford reddish brown crystals of **1** in 80% yield. Elemental analysis (%CHN): Exp. 30.54, 2.59, 26.6; Calc. C₈H₈CuN₆O₄ 30.43, 2.55, 26.62.
- 1.99 g **1** was heated in 200 mL of refluxing water for 24 h, which causes **2** to precipitate as a light green powder. Yield 1.07 g (51%). Elemental analysis (%CHN): Exp. 27.10, 2.59, 23.16; Calc. C₈H₁₂CuN₆O₅ ([Cu(cy₂)]·2H₂O) 27.32, 3.44, 23.89.
- O. Angelova, G. Petrov and J. Macicek, *Acta Crystallogr., Sect. C*, 1989, **45**, 710.
- C. Tsiamaïas, A. C. Stergiu, V. Anesti, N. M. Blaton and O. M. Peeters, *Inorg. Chim. Acta*, 1998, **269**, 332.
- Assignment confirmed by deuteration.
- E. C. Constable, *Metals and Ligand Reactivity*, VCH, 1996, 65; K. L. Breno, M. D. Pluth, D. R. Tyler and R. David, *Organometallics*, 2003, **22**, 1203; C. J. McKenzie and R. Robson, *Chem. Commun.*, 1988, 112.
- P. H. Benders, *Rec. Trav. Chim. Pays-Bas*, 1973, **95**, 217; J.-P. Fleury and B. Libis, *Bull. Soc. Chim. Fr.*, 1966, 1966.