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# Metal-Promoted Nucleophilic Addition and Cyclization of Diamines with Dicyanonitrosomethanide, $[C(CN)_2(NO)]^-$

**Anthony S. R. Chesman, David R. Turner, Glen B. Deacon, and Stuart R. Batten*[a]**

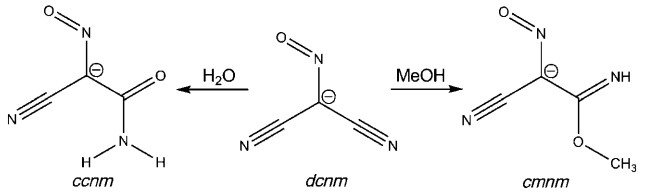
**Abstract:** The metal-promoted nucleophilic addition of diaminoalkanes to dicyanonitrosomethanide, $C(CN)_2(NO)^-$ (*dcnm*), and subsequent cyclization has been utilized in the synthesis of novel anionic species. The addition and cyclization of 1,2-diaminoethane (*en*) to both nitrile groups of *dcnm* forms the anion diimidazolinylnitrosomethanide (*dinm*), isolated in the dinuclear complex $[\{Cu(dinm)(en)\}_2en][ClO_4]_2$ (**1**). The same reaction solution yields [Cu(*cinm*)(*ainm*)] (*cinm* = cyanoimidazolinylnitrosomethanide, *ainm* = (((2-aminoethyl)amino)iminomethyl)imidazolinylnitrosomethanide) (**2**), which contains intermediates of the *dinm* species, supporting a stepwise mechanism of addition of the diamine followed by cyclization. 1,3-Diaminopropane (*pn*) added and cyclized on only one nitrile group to form a 1,4,5,6-tetrahydropyrimidine ring. This resulted in the formation of the cyanonitroso-1,4,5,6-tetrahydropyrimidinylmethanide ligand (*cnpm*) in complexes with the general formula $[M(cnpm)_2(pn)]$ (M = Cu (**3a**), Ni (**3b**), Zn (**3c**)). These reactions are contrasted to the addition of ethanolamine in the pyridine (*py*) complex $[Ni(chnm)_2(py)_2]\cdot(py)$ (**4**) (*chnm* = cyano((2-hydroxyethyl)amino)iminomethylnitrosomethanide) with no cyclization, demonstrating the higher reactivity of amines compared with alcohols. The formation of the complexes $[M(cmnm)_2(mame)]$ (M = Co (**5a**), Ni (**5b**), *cmnm* = cyano(imino(methoxy)methyl)nitrosomethanide, *mame* = 1-dimethylamino-2-methylaminoethane) indicate *mame* may be too sterically hindered to add to *dcnm* under similar reaction conditions.

**Keywords:** anions · coordination chemistry · cyclization · nucleophilic addition · reaction intermediates

## Introduction

The polynitrile anionic ligands dicyanamide, $N(CN)_2^-$ (*dca*), and tricyanomethanide, $C(CN)_3^-$ (*tcm*), have been extensively studied for their ability to form coordination polymers, some of which display magnetic interactions between neighboring metals.[1] Larger, heterofunctionalized derivatives such as dicyanonitrosomethanide, $C(CN)_2(NO)^-$ (*dcnm*),[2–6] and carbamoyldicyanomethanide, $C(CONH_2)(CN)_2^-$ (*cdm*),[7–9] have recently attracted attention as they offer potential oxygen donor groups and/or hydrogen bonding functionality that may enable the formation of heterometallic frameworks, bonding to lanthanoid ions, or hydrogen-bonded assemblies.[10] Pseudohalides and related polynitrile, -nitroso, and -nitro substituted methanides are also currently the focus of theoretical studies to understand the nature of the heavily delocalized anionic charge,[11–14] with a view for potential applications in ionic liquids.[15–17]

The *dcnm* ligand is noted for its high reactivity in the presence of transition metals and readily undergoes nucleophilic addition of water and methanol to a nitrile group (Scheme 1).[18] The water and methanol addition derivatives of *dcnm* retain their anionic character and have been shown to be of use in forming magnetically coupled pathways through N,O-bridging nitroso groups.[19,20] Analogous reac-




Scheme 1. Ions from nucleophilic addition to the dicyanonitrosomethanide anion (*dcnm*): carbamoylcyanonitrosomethanide (*ccnm*) and cyano(imino(methoxy)methyl)nitrosomethanide (*cmnm*).[25]

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tions of smaller pseudohalide species include addition to cyanate to yield pyrazole-based products.[21] Addition of nucleophiles across nitrile groups is a well-known phenomenon. For example, the metal-based hydrolytic enzymes nitrile hydratase and amidase are responsible for the metabolism of nitrile compounds in certain bacteria by the hydration of nitriles to amides.[22] Likewise, the acid catalyzed Pinner reaction involves addition to nitrile groups to give iminoethers.[23] Metal-mediated addition of dibenzylhydroxylamine to acetonitrile has also been recently reported.[24]

Addition of neutral nucleophiles to one nitrile arm of *dcnm* appears to cause deactivation of the second nitrile arm, preventing any further reactions, with examples only of monosubstituted anionic products previously reported in the literature.[18–20] There have been few attempts to extend this reactivity beyond the simple addition of water and methanol (Scheme 1).[18]

Acidic conditions have been employed in the synthesis of single or double addition products of nucleophiles, such as hydroxylamine and hydrazine, with *dcnm*. However, this method results in the protonation of the nitroso group of *dcnm* to form an oxime, yielding a neutral species with fewer coordination modes than its anionic counterpart.[26] Previous additions of amidines have bridged between both nitrile groups giving neutral pyrimidines, but require elevated reaction temperatures.[27] Double nucleophilic addition of methanol and pyrazole to the *dca* ligand has been observed.[28,29]

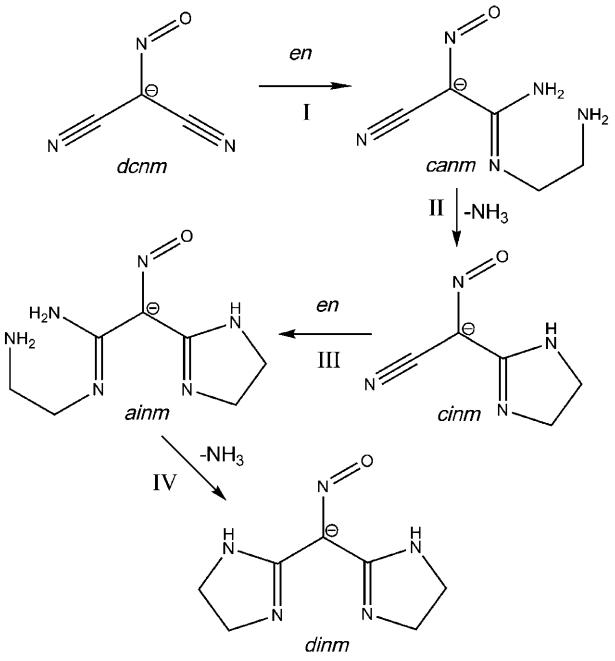
The formation of imidazoline groups through the addition and cyclization of 1,2-diaminoethane to nitriles generally proceed under relatively severe conditions and may still require a catalyst,[30] such as the presence of elemental sulphur,[31] $P_2S_5$,[32,33] or a metal catalyst.[34,35] Microwave and ultrasonic methods have also been utilized but they also require the presence of sulphur.[36–38]

Herein we report the synthesis of a new range of anionic species from the addition and cyclization of 1,2-diaminoethane and 1,3-diaminopropane across one or both of the nitrile groups of *dcnm*. These reactions form imidazoline and 1,4,5,6-tetrahydropyrimidine derivatives, respectively, with the expulsion of ammonia. We discuss the new coordination modes offered by this class of ligands and contrast the reactivity of diamines with that of ethanolamine, which does not cyclize under similar conditions, and 1-dimethylamino-2-methylaminoethane, which does not add to a nitrile group.

## Results and Discussion

### Addition of Diaminoethane

As a first step in investigating possible diamine addition to nitrile groups of *dcnm*, a methanolic solution of Na(*dcnm*) and $Cu(ClO_4)_2 \cdot 6H_2O$ was reacted with diaminoethane. From the reaction mixture, crystals of $[Cu(en)_2][ClO_4]_2$ began to form immediately. These dissolved over a period of three weeks, after which brown crystals of [Cu(*cinm*)(*ainm*)]·MeOH (**2**) (*cinm* = cyanoimidazolinylnitrosomethanide, *ainm* = (((2-aminomethyl)amino)iminomethyl)imidazolinylnitrosomethanide) formed from solution (Figure 3). These were filtered from solution and over a period of two months, the reaction mixture yielded a second crop of green needle crystals. This product was determined crystallographically to be $[\{Cu(dinm)(en)\}_2(en)][ClO_4]_2$ (**1**) (*dinm* = diimidazolinylnitrosomethanide) in which the *dinm* ligand results from the addition and cyclization of 1,2-diaminoethane to both nitrile arms of the *dcnm* anion with the elimination of two equivalents of ammonia per ligand (Scheme 2). The




Scheme 2. Proposed mechanism for stepwise addition and cyclization of 1,2-diaminoethane onto nitrile groups of *dcnm* to ultimately form the *dinm* ligand.

complete conversion into imidazolinyl groups is supported by the infrared spectrum of **1** with the conspicuous absence of peaks in the 2190–2220 $cm^{-1}$ region. Peaks in this region in all other products indicate the presence of a nitrile group (see Experimental Section).

The structure of **1** contains a dicationic complex consisting of two symmetry related square pyramidal copper atoms bridged by an apically coordinated 1,2-diaminoethane ligand (Figure 1). Each metal has a *dinm* anion and a *N,N′*-chelating 1,2-diaminoethane ligand in the basal positions. The distorted square pyramidal copper atom has the *dinm* ligand chelating with a six-membered ring that is close to a right angle (N(1)–Cu(1)–N(5) = 90.6°) and the *en* ligand chelates with a N(6)–Cu(1)–N(7) angle of 81.7°. The geometry is further distorted with the angles of the axial amine nitrogen atom to equatorial nitrogen atoms in the range of 88.29° to 105.07° (Table 1). The copper atom is situated 0.29 Å above the mean plane of the basal nitrogen atoms. The nitroso group of the *dinm* anion is disordered over two positions, each orientated towards one of the imidazoline NH protons

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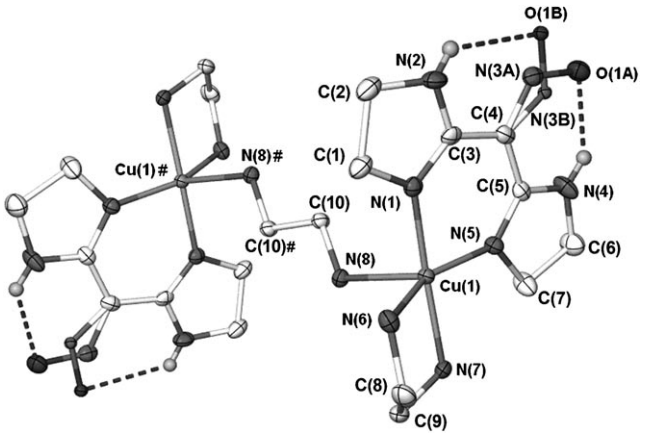



Figure 1. Structure of the dicationic complex $[\{Cu(dinm)(en)\}_2(en)]^{2+}$ in **1** showing intramolecular hydrogen bonding of the disordered nitroso group (other hydrogen atoms and perchlorate counter-anions removed for clarity). Ellipsoids are shown at 50% probability. Symmetry element used: #=1−x, −*y*, −*z*. Selected bond lengths (Å) and angles (°) for complex **1**; Cu(1)-N(1), 1.967(2); Cu(1)-N(5), 1.976(2); Cu(1)-N(6), 2.076(3); Cu(1)-N(7), 2.058(2); Cu(1)-N(8), 2.284(3); N(1)-Cu(1)-N(5), 90.61(9); N(6)-Cu(1)-N(7), 81.83(10); N(5)-Cu(1)-N(8), 104.93(10); N(1)-Cu(1)-N(8), 97.49(9); N(6)-Cu(1)-N(8), 101.40(10); N(7)-Cu(1)-N(8), 88.63.

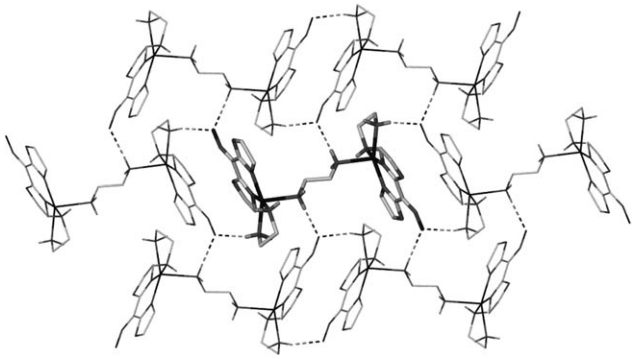


Figure 2. The 2D hydrogen bonded sheet formed by hydrogen bonding between the dinuclear molecules in the structure of **1**. CH hydrogen atoms, perchlorate anions and one of the disordered nitroso positions are omitted for clarity.

leading to the formation of a commonly observed stable, intramolecular six membered hydrogen-bond ring.[39] The nitroso group also acts as a hydrogen bond acceptor from chelating 1,2-diaminoethane ligands of two adjacent complexes and these interactions exist for both of the disordered positions (i.e., the protons are positioned approximately halfway between the two disordered components). The complexes are arranged into a 2D sheet by this hydrogen bonding (Figure 2, Table 1). The perchlorate counter-anions are well-ordered and are held in the lattice by three NH···O hydrogen bonds in addition to several much weaker CH···O interactions.

The reaction between the *dcnm* anion and 1,2-diaminoethane is interesting for several reasons. The *dinm* ligand represents, to the best of our knowledge, the first example of transition-metal-promoted nucleophilic addition to both

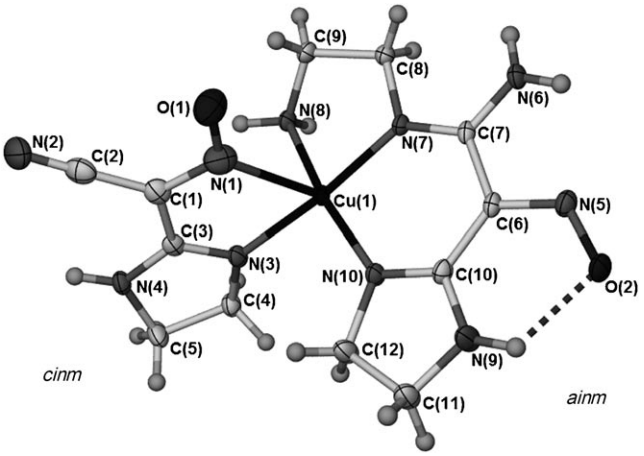



Figure 3. The crystal structure of complex **2**, [Cu(*cinm*)(*ainm*)]·MeOH, with ellipsoids shown at 50% probability (lattice methanol is omitted for clarity). Selected bond lengths (Å) and angles (°) for complex **2**: N(1)-Cu(1), 2.489(3); N(3)-Cu(1), 1.998(2); N(7)-Cu(1), 1.973(2); N(8)-Cu(1), 2.012(2); N(10)-Cu(1), 1.942(2); N(1)-Cu(1)-N(3), 73.25(9); N(1)-Cu(1)-N(7), 103.63(8); N(1)-Cu(1)-N(8), 88.36(9); N(1)-Cu(1)-N(10), 103.24(8); N(3)-Cu(1)-N(8), 91.27(8); N(7)-Cu(1)-N(8), 83.14(8); N(7)-Cu(1)-N(10), 91.84(8); N(3)-Cu(1)-N(10), 94.18(8).

Table 1. Intra/intermolecular hydrogen bond parameters in complex **1**.[a] The oxygen acceptor atom is disordered over two positions (denoted A&B).

| D−H···A[a] | D···A [Å] | H···A [Å] | D−H···A [°] |
|---|---|---|---|
| N(2)-H(1N)···O(1B) | 2.958(12) | 2.44(3) | 131(3) |
| N(4)-H(2N)···O(1A) | 2.647(4) | 2.07(3) | 132(3) |
| N(6)-H(3N)···O(1A)# | 2.898(4) | 2.08(4) | 165(3) |
| N(6)-H(3N)···O(1B)# | 2.846(12) | 2.22(4) | 132(3) |
| N(8)-H(7N)···O(1A)† | 2.945(4) | 2.11(3) | 173(3) |
| N(8)-H(7N)···O(1B)† | 3.272(11) | 2.49(3) | 154(2) |

Symmetry elements used: #=1−x, 1−*y*, −z; †=x−½, ½−y, −z.

nitrile arms of the *dcnm* anion and also the first example of room temperature alkyl amine addition under non-acid catalyzed conditions. The present result suggests a greater reactivity of amines compared with hydroxyl groups. The cyclization reaction must involve the loss of one molecule of ammonia when each 1,2-diaminoethane forms the imidazoline heterocycle.

The complex [Cu(*cinm*)(*ainm*)]·MeOH (**2**) contains two intermediates in the reaction pathway between *dcnm* and *dinm*. The *cinm* ligand is the result of the addition and cyclization of a single 1,2-diaminoethane ligand to one of the nitrile arms of *dcnm* with the second nitrile arm remaining unreacted. The *ainm* ligand is formed from the addition of a second diamine to the remaining nitrile of the *cinm* anion without cyclization. The neutral five coordinate $Cu^{II}$ complex [Cu(*cinm*)(*ainm*)] contains the *cinm* anion chelating in a bidentate fashion with the imidazoline ring coordinating in a basal position and the nitroso nitrogen atom in the Jahn–Teller distorted apical position. The coordination sphere of the square pyramidal metal is completed by the tridentate *ainm* ligand which binds in the remaining three basal positions through a nitrogen atom of the imidazoline ring and

the two nitrogen atoms of the added 1,2-diaminoethane group. The tridentate binding mode of *ainm* is similar to that observed in cobalt and copper complexes of *N*-(2-aminoethyl)imidazoline-2-carboxamide although this ligand is synthesized from the hydrolysis and ring opening of 2,2′-biimidazoline.[40] As with the *dinm* ligand in complex **1**, the *ainm* ligand contains an intramolecular hydrogen-bonded ring involving the nitroso group and the imidazoline ring. One molecule of methanol per complex resides in the lattice, disordered over two positions.

The infrared spectrum of complex **2** supports the presence of the intermediates with the peak at 2194 $cm^{-1}$ corresponding to the nitrile groups but two strong absorptions at 1631 and 1605 $cm^{-1}$ from the three different C=N bonds.

The complexes assemble into complicated hydrogen bonded sheets, primarily through NH···O interactions from amines of the uncyclized *ainm* 1,2-diaminoethane bonding to nitroso groups of neighboring complexes. These sheets also contain NH···N interactions between imidazoline rings (see the Supporting Information). The lattice methanol bridges a $NH_2$ group and a nitrile arm. Parallel sheets are linked by NH···N interactions from an imidazoline NH to a nitrile arm that forms a dimeric $R_2^2(12)$ ring, similar to a motif we have previously reported.[41]

Conceivably the reaction to form the *dinm* ligand can occur in one of two ways; a concerted mechanism in which both arms undergo the addition of *en* without cyclization, before formation of the heterocycle rings, or alternatively the complete addition and cyclization at one arm before the remaining nitrile group reacts. The observation of the intermediate ligands in the structure of **2** leads us to prefer the stepwise approach for the formation of the *dinm* anion (Scheme 2). One 1,2-diaminoethane molecule is first added to a nitrile arm before cyclizing in a second step, yielding the *cinm* intermediate (Steps I and II). A second 1,2-diaminoethane is then added, producing the *ainm* anion (Step III), before cyclizing to give the final *dinm* species (Step IV). The cyclization steps require the elimination of ammonia. We propose that the cyclization step proceeds by the intramolecular nucleophilic attack of the terminal $NH_2$ group onto the imine carbon atom which carries a slight positive partial charge.

The relatively low yield of complexes **1** and **2** may arise from the soluble products which were yet to crystallize from solution. Therefore attempts were made to determine what species may remain in the reaction solution by mass spectrometry, strongly indicating the presence of several *cinm* and *ainm* adducts and related copper complexes (see Experimental Section). One peak could be attributed to $[Cu(cinm)(ainm)+H]^+$, indicating complex **2** may not have yet completely crystallized from solution. The occurrence of *cinm* in comparison to the unobserved cyano((2-aminoethyl)aminoiminomethyl)nitrosomethanide (*canm*) ligand supports the hypothesis that ring formation may proceed relatively quickly once the diamine has added to the nitrile group. Two peaks corresponded to the presence of *dinm*, with $[Cu(en)(dinm)]^+$ conceivably a fragment of complex **1**. The absence of all peaks corresponding to *dcnm* supports that crystallization is the limiting step of the reaction, not addition within the solution.

### Addition of Diaminopropane

Following the success of adding 1,2-diaminoethane to the nitrile arms of the *dcnm* anion, similar reactions were conducted using the longer 1,3-diaminopropane molecule. The cyclization of 1,3-diaminopropane to a nitrile to form a 1,4,5,6-tetrahydropyrimidine ring has been investigated less than its imidazoline counterpart but has been achieved using $P_2S_5$[42] or lanthanoid catalysis.[35] 1,4,5,6-tetrahydropyrimidine rings have also be synthesized in a protonated form, from the addition of 1,3-diaminopropane to propionitrile, but this required severe hydrothermal conditions in an acidic environment.[43]

A single crystalline product $[Cu(cnpm)_2(pn)]$ (**3a**) (*cnpm* = cyanonitroso-1,4,5,6-tetrahydropyrimidinylmethanide, *pn* = 1,3-diaminopropane) was obtained from a methanolic solution of $[Me_4N][dcnm]$, $CuCl_2$, and an excess of 1,3-diaminopropane. Isomorphous complexes were obtained with Ni (**3b**) and Zn (**3c**). Similar to the reactions giving complexes **1** and **2**, 1,3-diaminopropane forms a heterocycle by addition and cyclization to one nitrile arm of the *dcnm* anion with the formation of a 1,4,5,6-tetrahydropyrimidinyl ring. The remaining nitrile group is unreacted, as evidenced by the infrared spectra of **3a**–**c** which retain weak peaks around 2210 $cm^{-1}$.

Complex **3** contains two *cnpm* ligands that are N,N′-chelated to the transition metal with a bidentate 1,3-diaminopropane ligand completing the coordination sphere of the octahedral metal (Figure 4). The two *cnpm* ligands form five-membered chelate rings through the nitrogen atom of the nitroso group and one of those in the tetrahydropyrimi-

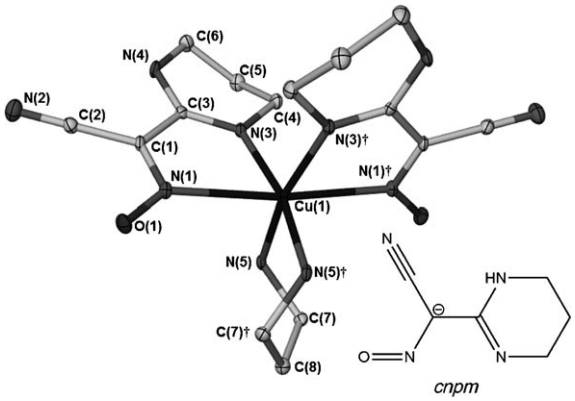



Figure 4. The discrete complex $[Cu(cnpm)_2(pn)]$ in the crystal structure of **3a** (ellipsoids are shown at 50% probability). Hydrogen atoms omitted for clarity. Symmetry element used: † = 1−x, y, $^1/_2$−z. The Ni and Zn complexes (**3b** and **3c**) are isomorphous. Selected bond lengths (Å) and angles (°) for complexes **3a**. N(1)-Cu(1), 2.474(2); N(3)-Cu(1), 2.012(2); N(5)-Cu(1), 2.035(2); N(1)-Cu(1)-N(3), 74.60(6); N(5)-M-N(5)†, 90.27(10); N(1)-M-N(1)†, 172.82(8); N(3)-M-N(3)†, 91.73(10); N(1)-M-N(3)†, 100.28(6); N(1)-M-N(5), 93.91(7); N(3)-M-N(5), 90.76(7); N(1)-M-N(5)†, 91.16(7); N(3)-M-N(5)†, 165.76(7).

dine ring, with chelating angles of 74.6°, 78.2°, and 75.5° in the complexes **3a**–**3c**, respectively. In contrast, the more flexible 1,3-diaminopropane ligand is able to accommodate nearly right-angled chelation in all cases. In the $Cu^{II}$ complex **3a**, the Jahn–Teller elongated positions are occupied by the nitroso nitrogen atoms (N(1),N(1)†) of the *cpnm* ligands, with **3b**–**3c** also showing marginally longer bonds in this position. Intermolecular hydrogen bonding is observed between discrete complexes, with the amine groups of the 1,3-diaminopropane ligands acting as hydrogen bond donors to both neighboring nitroso and nitrile groups. The nitroso group also receives an additional hydrogen bond from a nitrogen atom of the *cnpm* ring (see the Supporting Information).

Control reactions of $[Me_4N][dcnm]$ with the diamines in methanol, in the absence of any transition metal, did not yield any amine addition products and only the water addition product *ccnm* was observed by mass spectrometry (see Experimental Section). The formation of *ccnm* was presumably assisted by the hydroxide formed in situ from the reaction of amines with the residual water present in the methanol.

### Addition of Ethanolamine

The cyclization of diamines to the *dcnm* anion appears to indicate higher reactivity of amine groups compared with alcohols, considering that reactions were carried out in reaction solutions with methanol in vast excess to the amine. In an attempt to synthesize a mixed nitrogen/oxygen heterocyclic ligand, and explore the relative reactivities of $NH_2$/OH groups in the same reactant, we examined the reaction of $Ni(ClO_4)_2{\cdot}6H_2O$ and $[Me_4N][dcnm]$ with an excess of ethanolamine in a pyridine/water solution yielded the crystalline product $[Ni(chnm)_2(py)_2]{\cdot}py$ (*chnm* = cyano((2-hydroxyethyl)-amino)iminomethylnitrosomethanide) (**4**). The *chnm* anion results from the addition of ethanolamine by way of the $NH_2$ group to a single nitrile arm of the *dcnm* anion.

The centrosymmetric complex crystallizes in the space group *C*2/*c* with two *chnm* ligands N,N′-chelating in the equatorial positions of the octahedral metal center and two pyridine ligands in the axial positions (Figure 5). Support for the ethanolamine reacting through the $NH_2$ end comes from examination of the intermolecular interactions within the crystal structure. The ethanolamine derived arm of the *chnm* ligand is disordered over two positions. However, the two positions of the terminal OH groups converge so that both are in a position to donate a hydrogen bond to a nitroso oxygen atom on an adjacent complex whilst also accepting a hydrogen bond from an imine NH of the same moiety (Figure 6a). Hydrogen bonding is also observed in a ring motif between a nitrile group and the NH group from the ethanolamine-derived arm. A similar motif to this is frequently observed in heavily hydrogen bonded structures containing the related carbamoyldicyanomethanide (*cdm*) ligand.[7–9]

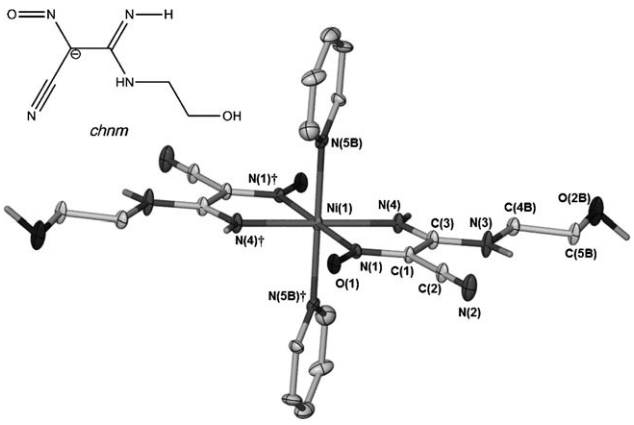



Figure 5. Structure of $[Ni(chnm)_2(py)_2]{\cdot}py$ (**4**). Ellipsoids shown at 50% probability (lattice pyridine molecules, CH protons and one of the disordered pyridine/*chnm* positions omitted for clarity). Symmetry element used: †=1−x, 1−*y*, −z. Selected bond lengths (Å) and angles (°): Ni(1)-N(1), 2.122(3); Ni(1)-N(4), 2.051(3); Ni(1)-N(5A), 2.071(11); Ni(1)-N(5B), 2.127(4); N(1)-Ni(1)-N(4), 78.20(10).

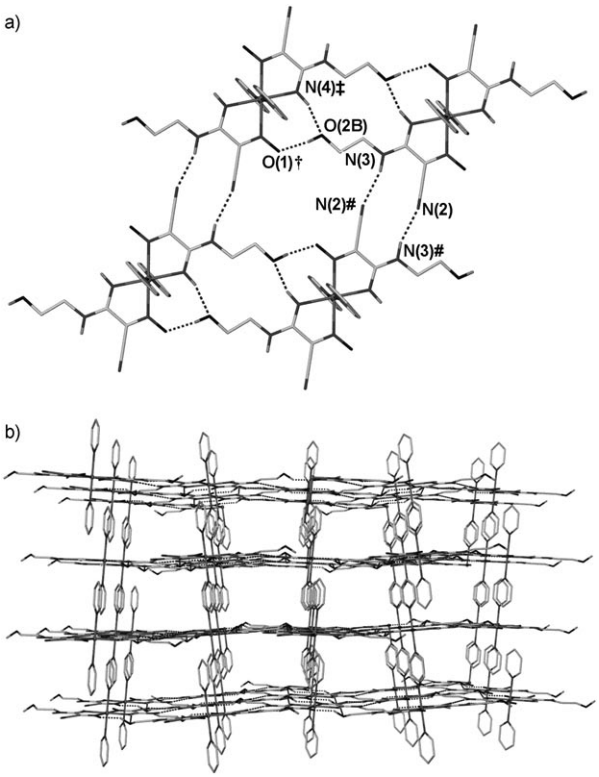



Figure 6. Hydrogen bonding in the structure of **4**. (a) Sheets propagate parallel to the *ac*-plane which (b) stack to leave channels in which lattice pyridine resides (solvent removed for clarity). Symmetry equivalents used; †=x−½, ½−y, z−½; ‡ −x, y, ½−z; #=1−x, y, ½−z. One disordered position of pyridine removed from both diagrams for clarity.

Overall the hydrogen bonding in the structure forms 2D sheets that propagate parallel to the *ac*-plane (the disordered positions of the terminal OH lie above and below the mean plane, orientated in the same direction). These sheets stack to leave channels that contain disordered pyridine

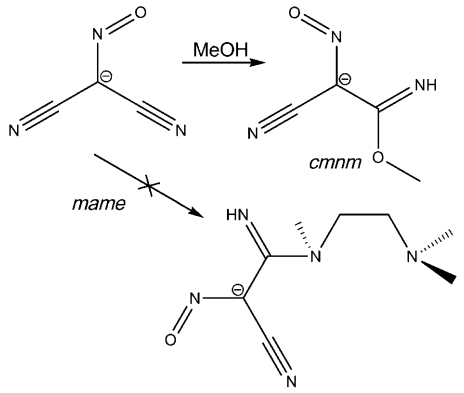
  

molecules (one per complex molecule). Isolation of the crystalline material proved problematic, as washing with methanol and ether resulted in removal of lattice and coordinated pyridines, leaving residual methanol as demonstrated by elemental analysis.

Unlike the aforementioned diamines, ethanolamine does not cyclize to form oxazoline. Such cyclizations have been observed previously for nitrile groups, but less readily, and generally requiring harsher reaction conditions, such as highly acidic or basic conditions or heating under reflux,[44] often with a metal catalyst.[45–50] The conditions employed here may not be sufficient to encourage ring closure, demonstrating the lower reactivity of ethanolamine compared to diamines.

### Attempted Addition of a Sterically Hindered Diamine

Under the same reaction conditions in which 1,3-diaminopropane cyclized, the nucleophilic attack of the sterically hindered 1-dimethylamino-2-methylaminoethane (*mame*) was not observed, with methanol preferentially added on to the nitrile group to form cyano(imino(methoxy)methyl)nitrosomethanide (*cmnm*) (Scheme 3).




Scheme 3. Preferential addition of methanol to *dcnm*, preventing the addition of *mame*.

Since *mame* cannot cyclize as the terminal amine is alkylated, it was hoped that addition of the NH group would allow for a connectivity similar to *canm*, the proposed intermediate between addition of *en* to *dcnm*, and cyclization to form *cinm* (Step I, Scheme 2).

The addition of methanol is evidenced in the crystal structures of [M(*cmnm*)$_2$(*mame*)] (M = Co (**5a**), Ni (**5b**)) which crystallize in the space groups *Cc* and *Fdd2*, respectively (Figure 7). The complexes contain octahedral metal centers with both ligands displaying a bidentate coordination mode. The $\eta^2(N,N')$ coordination mode observed is typical of *cmnm* and is widely observed in transition-metal structures containing *cmnm*.[18,19] For both complexes the hydrogen atom of the imino group participates in hydrogen bonding with an oxygen atom of the nitroso group of a neighboring complex. The *mame* coligand in **5a** is disordered over two

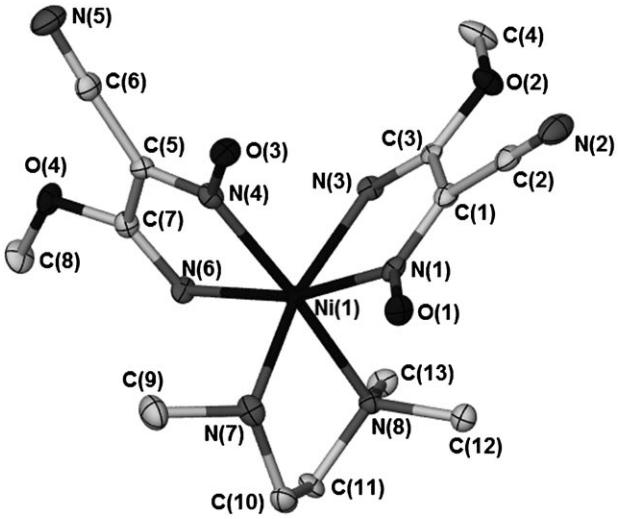



Figure 7. Structure of [Ni(*cmnm*)$_2$(*mame*)] (**5b**). Ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity. Co complex (**5a**) is isostructural. Selected bond lengths (Å) and angles (°): Ni(1)-N(1), 2.079; Ni(1)-N(3), 2.090; Ni(1)-N(4), 2.111; Ni(1)-N(6), 2.096; Ni(1)-N(7), 2.117; Ni(1)-N(8), 2.134; N(1)-Ni(1)-N(3), 78.16; N(7)-Ni(1)-N(8), 82.29.

positions. It appears *mame* is sufficiently sterically hindered to enable the excess methanol, rather than NH, to preferentially add to the nitrile group.

## Conclusions

We have detailed here, for the first time, the metal-promoted nucleophilic addition of amines across the nitrile groups of the dicyanonitrosomethanide anion, followed by cyclization in the case of diamines, with retention of the anionic character in the product. The reactions occur at room temperature and under mild conditions, and appear to be more favored than alcohol addition as they can occur across both nitriles of *dcnm*, and ethanolamine reacts only at the amine end. Steric hindrance of the amine can, however, lead to a favoring of alcohol addition. Furthermore, we have proposed a mechanism for the double addition and cyclization of diaminoethane that, unusually, is supported by a crystal structure containing two of the three intermediate species. Finally, we believe that the addition of amines to *dcnm* reported here also provides a synthetic pathway to new families of interesting and easily functionalized anions.

## Experimental Section

*Synthesis*

Laboratory reagents and solvents were used as provided. Elemental analyses (C, H, N) were performed by the Campbell Analytical Laboratory, University of Otago, New Zealand. ATR-IR spectra were recorded on a Bruker Equinox 55 series FTIR spectrometer in the range 4000–500 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Mass spectrometry was performed on a Micromass Platform 2 mass spectrometer with an electrospray source and a variable cone voltage with samples dissolved in methanol or dimethyl-

sulfoxide. Listed *m*/*z* values for metal containing species refer to the highest intensity peak of a cluster with the appropriate isotope pattern (including $^{13}C$ contributions). Proton and $^{13}C$ NMR spectra were recorded in [$D_6$]dimethylsulfoxide on a Bruker DRX 300 instrument. Na(*dcnm*) and [$Me_4N$][*dcnm*] were prepared by a metathetic reaction between Ag(*dcnm*) and the respective chloride salts in water.[51] Ag(*dcnm*) was prepared according to a literature procedure.[4] WARNING: Although no incident occurred during this work, caution must be exercised when using perchlorate metal salts at all times.

**Synthesis of [{Cu(*dinm*)(*en*)}$_2$(*en*)][$ClO_4$]$_2$ (1) and [Cu(*cinm*)(*ainm*)]·MeOH (2):** Na(*dcnm*) (50 mg, 427 μmol) was added to Cu($ClO_4$)$_2$·6$H_2O$ (79 mg, 213 μmol) dissolved in methanol (5 mL). 1,2-Diaminoethane (0.1 mL) was then added to the reaction solution. Purple needles identified by X-ray crystallography as [Cu(en)$_2$][$ClO_4$]$_2$[52] began to immediately form but redissolved over a period of three weeks, coinciding with the crystallization of **2**. This product was filtered from solution and washed with methanol. The reaction solution was left to stand for two months, after which green crystals of complex **1** formed and were characterized by X-ray crystallography. The bulk product was washed with water, resulting in the substitution of water for *en* in the analyzed complex, giving [Cu(*dinm*)(*en*)($H_2O$)][$ClO_4$] (5 mg, 6%). ATR-IR: $\tilde{\nu}$ = 3504w (N−H), 3438vw (C−H), 3343m, 3276m, 3152m, 2958m, 2889m, 1658vw, 1609s (C=N), 1553vw, 1530s, 1403m (ONC), 1368w, 1282m (N=O), 1100s ν(ClO), 1048s, 932w 875w, 750w cm$^{-1}$ (N=O); elemental analysis: calcd (%) for $C_9H_{20}Cl_1Cu_1N_7O_6$ (421.30): C 25.66, H 4.78, N 23.27; found: C 25.86, H 4.91, 23.58. [Cu(*cinm*)(*ainm*)]·MeOH (**2**): (18 mg, 20%). M.p.: 206–208°C; ATR-IR: $\tilde{\nu}$ = 3311s ν(N−H), 3214s ν(N−H), 2970s ν(C−H), 2888s, 2194m ν(C≡N), 1631s (C=N), 1605s (C=N), 1588sh, 1548w, 1509s, 1479w, 1373w, 1351w, 1317w, 1277s (N=O), 1188w, 1139s, 1064w, 1011m, 980vw cm$^{-1}$; elemental analysis: calcd (%) for $C_{12}H_{21}Cu_1N_{10}O_{3.5}$ (exchange of lattice methanol for 1.5 molecules of water per metal complex upon exposure to air) (424.91): C 33.92, H 4.98, N 32.96; found: C 34.26, H 4.92, N 32.78. Mass spectra of reaction solution: ESI-MS$^+$: 138.7 ([*cinm*$^-$+2H$^+$]$^+$, 80%), 142.9 ([2en+Na$^+$]$^+$, 65%), 160.8 ([*cinm*$^-$+H$^+$+Na$^+$]$^+$, 35%), 182.7 ([*cinm*$^-$+2Na$^+$]$^+$, 25%), 199.0 ([*ainm*$^-$+2H$^+$]$^+$, 25%), 229.8 ([Cu($ClO_4$)($H_2O$)$_2$(MeOH]$^+$, 100%), 277.1 (*ainm*$^-$+en$H_2^{2+}$+$H_2O$, 20%), 281.0 ([*cinm*$^-$+Na$^+$+H$^+$+2en]$^+$, 25%), 281.8 ([Cu(en)$_2$($ClO_4$)]$^+$, 20%), 302.9 ([Cu(*dinm*)(en)]$^+$, 20%), 359.7 ([Cu(*cinm*)$_2$+Na$^+$]$^+$, 15%), 397.9 ([Cu(*cinm*)(*ainm*)H]$^+$, 10%). ESI-MS$^-$: 98.8 ($ClO_4^-$, 100%), 410.7 ([Cu(*dinm*)(en)($H_2O$)$_6$]$^+$, 5%).

**Synthesis of [Cu(*cnpm*)$_2$(*pn*)] (3a):** To $CuCl_2$·2$H_2O$ (25 mg, 147 μmol) dissolved in methanol (2 mL) was added [$Me_4N$][*dcnm*] (50 mg, 297 μmol) in methanol (1 mL) and 1,3-diaminopropane (0.1 mL). Deep green crystals formed in seven days which were filtered from solution and washed with methanol (22 mg, 34%). M.p.: 207–210°C; ATR-IR: $\tilde{\nu}$ = 3243vw ν(N−H), 3179vw ν(N−H), 2209w ν(C≡N), 1603m ν(C=N), 1530m, 1485w, 1456w, 1414w, 1380m, 1313vw, 1252w (N=O), 1213w, 1179s, 1119vs, 1085vs, 1029s, 954s, 780w cm$^{-1}$ (N=O); ESI-MS$^-$; 69 ($C_2HN_2O^-$ (ligand degradation product), 95%), 151 (*cnpm*$^-$, 95%), 364 ([Cu(*cnpm*)$_2$−H$^+$]$^-$, 100%); elemental analysis calcd (%) for $C_{15}H_{24}Cu_1N_{10}Ni_1O_2$ (439.96): C 40.95, H 5.50, N 31.84; found: C 41.07, H 5.47, N 32.04.

**Synthesis of [Ni(*cnpm*)$_2$(*pn*)] (3b):** To $NiCl_2$ (19 mg, 147 μmol) dissolved methanol (2 mL) was added [$Me_4N$][*dcnm*] (50 mg, 297 μmol) in methanol (1 mL) and 1,3-diaminopropane (0.1 mL). Deep red crystals formed in seven days which were filtered from the reaction solution and washed with methanol (37 mg, 58%). M.p.: 281–284°C; ATR-IR: $\tilde{\nu}$ = 3321vw ν(N−H), 3270vw ν(N−H), 2933vw, 2884vw, 2211w ν(C≡N), 1625m (C=N), 1597w, 1529m, 1485w, 1457w, 1413w, 1385s (ONC), 1316w, 1215w, 1189s, 1106s, 1090s, 1072s 1033m, 951m, 789w cm$^{-1}$ (N=O); ESI-MS$^-$; 151 (*cnpm*$^-$, 70%), 359 ([Ni(*cnpm*)$_2$−H$^+$]$^-$, 100%); elemental analysis calcd (%) for $C_{15}H_{24}N_{10}Ni_1O_2$ (435.11): C 41.41, H 5.56, N 32.20; found: C 41.36, H 5.51, N 32.38.

**Synthesis of [Zn(*cnpm*)$_2$(*pn*)] (3c):** To $ZnCl_2$ (20 mg, 147 μmol) dissolved in methanol (2 mL) was added [$Me_4N$][*dcnm*] (50 mg, 297 μmol) in methanol (1 mL) and 1,3-diaminopropane (0.1 mL). Light orange crystals formed in four days which were filtered from the reaction solution and washed with methanol (41 mg, 63%). M.p.: 241–244°C; ATR-IR: $\tilde{\nu}$ = 3317m ν(N−H), 3268m ν(N−H), 3171vw, 2960vw, 2933vw, 2883w, 2885vw, 2209w (C≡N), 1623s (C=N), 1529s, 1457vw, 1441vw, 1387s (ONC), 1338vw, 1315w, 1264m (N=O), 1218m, 1189s , 1118m, 1105m, 1089m, 1073m, 1032m, 954m, 789m cm$^{-1}$ (N=O); $^1H$ NMR (300 MHz, [$D_6$]DMSO): $\delta$ = 1.42 (p, 2H; central $CH_2$, pn), 1.72 (p, 4H; $CH_2$, *cnpm*), 2.61 (t, 4H; 2$CH_2$N, pn), 3.17 ppm (m, 8H; 2$CH_2$N, *cnpm*). NH exchanged with $H_2O$ in solution; $^{13}C$ NMR (300 MHz, [$D_6$]DMSO): $\delta$ = 20.24, 31.01, 40.75, 113.29, 122.66, 152.55 ppm; elemental analysis calcd (%) for $C_{15}H_{24}N_{10}O_2Zn_1$ (441.81): C 40.78, H 5.48, N 31.70; found: C 40.97, H 5.54, N 32.14.

**Synthesis of [Ni(*chnm*)$_2$(*py*)$_2$]·*py* (4):** To Ni($ClO_4$)$_2$·6$H_2O$ (44 mg, 120 μmol) dissolved in a solution of water (2 mL) and pyridine (2 mL) was added [$Me_4N$][*dcnm*] (40 mg, 237 μmol) in pyridine (3 mL) and ethanolamine (0.1 mL). Red crystals formed in ten days, one of which was removed from solution for X-ray crystallography. The remaining crystals were filtered from the reaction solution and washed with methanol and ether (21 mg, 34%). M.p.: above 300°C; ATR-IR: $\tilde{\nu}$ = 3460m ν(O−H), 3304s ν(N−H), 3105w ν(C−H), 2949w, 2899vw, 2823vw, 2212m ν(C≡N), 1600s (C=N), 1562m, 1469vw, 1419m (ONC), 1358w, 1325m (ONC), 1270w (N=O), 1229w, 1187w, 1066m, 900vw, 842vw, 748vw cm$^{-1}$ (N=O); ESI-MS$^-$: 155.1 (*chnm*$^-$, 75%), 311.0 ([2*chnm*$^-$+H$^+$], 100%); elemental analysis calcd (%) for $C_{10.5}H_{16}N_8Ni_1O_{4.5}$ (384.98): C 32.76, H 4.19, N 29.11; found C 32.99, H 4.07, N 29.16. (The microanalytical data indicates the loss of all pyridine and a residue of half a molecule of methanol per complex).

**Synthesis of [Co(*cmnm*)$_2$(*mame*)] (5a):** [$Me_4N$][*dcnm*] (50 mg, 297 μmol) dissolved in methanol (1 mL) was added to a solution of Co($ClO_4$)$_2$·6$H_2O$ (54 mg, 148 μmol) in methanol (2 mL). To the reaction solution, 1-dimethylamino-2-methylaminoethane (0.1 mL) was added, resulting in the formation of red needle clusters overnight which were washed with methanol (33 mg, 54%). M.p.: 245–238°C; ATR-IR: $\tilde{\nu}$ = 3149w ν(N−H), 2201m ν(C≡N), 1591s (C=N), 1427w, 1398vs (ONC), 1314s (ONC), 1225vw, 1204m (COC), 1139m, 1098vs, 1067s, 1052s, 1025m, 997m, 943m ($CH_3$), 843m, 777m (N=O), 715w, 693w cm$^{-1}$; ESI-MS resulted in ligand and complex degradation; elemental analysis calcd (%) $C_{13}H_{22}Co_1N_8O_4$ (413.30) C 37.78, H 5.37, N 27.11; found: C 37.71, H 5.40, N 26.87.

**Synthesis of [Ni(*cmnm*)$_2$(*mame*)] (5b):** [$Me_4N$][*dcnm*] (50 mg, 297 μmol) dissolved in methanol (1 mL) was added to a solution of Ni($ClO_4$)$_2$·6$H_2O$ (54 mg, 148 μmol) in methanol (2 mL). To the reaction solution, 1-dimethylamino-2-methylaminoethane (0.1 mL) was added, resulting in the formation of red needle clusters overnight which were washed with methanol (14 mg, 23%). M.p.: 215–218°C; ATR-IR: $\tilde{\nu}$ = 3328vw ν(NH), 3284vw ν(NH), 2886vw, 2210m ν(C≡N), 1681w, 1608s (C=N), 1456m, 1400s (ONC), 1311m (ONC), 1201s (COC), 1114vs, 1036w, 1013w, 951m ($CH_3$), 834w, 802w, 761m cm$^{-1}$; ESI-MS resulted in ligand and complex degradation; elemental analysis calcd (%) for $C_{13}H_{22}N_8Ni_1O_4$ (413.06): C 37.80, H 5.34, N 27.13; found: C 37.92, H 5.54, N 27.36.

**Control reaction 1:** Diaminoethane (0.1 mL) was added to [$Me_4N$][*dcnm*] (50 mg, 297 μmol) dissolved in methanol (3 mL). The reaction solution was allowed to stand under ambient conditions for three weeks, after which the solvent was removed under reduced pressure. Mass spectrometry indicated quantitative conversion of *dcnm* into *ccnm*, not *cinm*, through the addition of residual water. ESI-MS$^-$: 111.7 (*ccnm*$^-$, 100%). ESI-MS$^+$: 73.9 ($Me_4N^+$, 100%).

**Control reaction 2:** Diaminopropane (0.1 mL) was added to [$Me_4N$][*dcnm*] (50 mg, 297 μmol) dissolved in methanol (3 mL). The reaction solution was allowed to stand under ambient conditions for three weeks, after which the solvent was removed under reduced pressure. Mass spectrometry indicated quantitative conversion of *dcnm* into *ccnm*, not *cnpm*, through the addition of residual water. ESI-MS$^-$: 111.9 (*ccnm*$^-$, 100%). ESI-MS$^+$: 73.8 ($Me_4N^+$, 100%).

*Crystallographic Details and Data*

Crystals were mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected on Bruker X8 Apex II CCD (**1**, **3a**, **3b**, **3c**, **4**, **5a**, **5b**) or Nonius Kappa-CCD (**2**) diffractometers, both equipped with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å). Data collection temperatures were maintained at 123 K using open flow $N_2$ cryostreams.

For data collected on the Nonius Kappa-CCD diffractometer, integration was carried out by the program DENZO-SMN and data was corrected for Lorentz-polarization effects and for absorption using the program SCALEPACK.[53] For data collected on the Bruker X8 Apex II diffractometer, integration was carried out by the program SAINT and data was corrected for Lorentz-polarization effects and for absorption using the Apex program II Suite.[54] Solutions were obtained by direct methods or Patterson synthesis using SHELXS-97[55] followed by successive refinements using full matrix least squares methods against $F^2$ using SHELXL-97.[55] The program X-Seed was used as a graphical SHELX interface.[56] Hydrogen atoms attached to carbon atoms were placed in idealized positions and refined against a riding model to the atom to which they are attached. Where possible, hydrogen atoms attached to nitrogen or oxygen atoms were located from the Fourier difference map (see individual crystal data).

CCDC 698365, CCDC 698366, CCDC 698367, CCDC 698368, CCDC 698369, CCDC 698370, CCDC 698371, CCDC 698372 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif

**Crystal data for 1.** $C_{20}H_{44}Cl_2Cu_2N_{16}O_{10}$, $M=866.69$, green block, $0.20\times0.16\times0.12$ mm$^3$, orthorhombic, space group *Pbca* (No. 61), $a=13.4785(6)$, $b=12.7531(7)$, $c=19.4085(10)$ Å, $V=3336.2(3)$ Å$^3$, $Z=4$, $\rho_{cald}=1.726$ g cm$^{-3}$, $F_{000}=1792$, 11854 reflections collected, 3818 unique ($R_{int}=0.0470$). Final $GooF=1.020$, $R1=0.0385$, $wR2=0.0816$, $R$ indices based on 2785 reflections with I > 2 sigma(I), 277 parameters, 14 restraints, $\mu=1.512$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely. The nitroso group is disordered over two positions with occupancies refined against each other (84:16). ISOR and SADI restraints were used to restrain the minor component.

**Crystal data for 2.** $C_{13}H_{22}CuN_{10}O_3$, $M=429.95$, green block, $0.15\times0.12\times0.12$ mm$^3$, triclinic, space group *P*-1 (No. 2), $a=8.2006(2)$, $b=9.5869(2)$, $c=12.0950(3)$ Å, $\alpha=74.867(2)$, $\beta=74.167(2)$, $\gamma=83.435(2)°$, $V=882.14(4)$ Å$^3$, $Z=2$, $\rho_{cald}=1.619$ g cm$^{-3}$, $F_{000}=446$, 15445 reflections collected, 4041 unique ($R_{int}=0.0224$). Final $GooF=1.065$, $R1=0.0384$, $wR2=0.0931$, $R$ indices based on 3917 reflections with I > 2 sigma(I), 289 parameters, 0 restraints, $\mu=1.278$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely. The lattice methanol molecule is disordered over two positions with occupancies refined against each other (71:29). Protons were not attached for the minor component (positioning suggests that hydrogen bonding motif remains the same regardless of the methanol orientation).

**Crystal data for 3a.** $C_{15}H_{24}CuN_{10}O_2$, $M=439.98$, green block, $0.16\times0.14\times0.11$ mm$^3$, monoclinic, space group *C*2/*c* (No. 15), $a=17.2707(35)$, $b=8.5292(17)$, $c=13.2095(26)$ Å, $\beta=111.293(30)°$, $V=1813.0(6)$ Å$^3$, $Z=4$, $\rho_{cald}=1.606$ g cm$^{-3}$, $F_{000}=916$, 12075 reflections collected, 2090 unique ($R_{int}=0.0905$). Final $GooF=1.044$, $R1=0.0333$, $wR2=0.0705$, $R$ indices based on 1774 reflections with I > 2 sigma(I), 140 parameters, 0 restraints, $\mu=1.242$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely.

**Crystal data for 3b.** $C_{15}H_{24}N_{10}NiO_2$, $M=435.15$, blue block, $0.25\times0.20\times0.15$ mm$^3$, monoclinic, space group *C*2/*c* (No. 15), $a=16.6284(4)$, $b=8.6047(2)$, $c=13.5980(3)$ Å, $\beta=110.722(2)°$, $V=1819.77(7)$ Å$^3$, $Z=4$, $\rho_{cald}=1.588$ g cm$^{-3}$, $F_{000}=912$, 8634 reflections collected, 2011 unique ($R_{int}=0.0256$). Final $GooF=1.065$, $R1=0.0243$, $wR2=0.0559$, $R$ indices based on 1943 reflections with I > 2 sigma(I), 140 parameters, 0 restraints, $\mu=1.103$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely.

**Crystal data for 3c.** $C_{15}H_{24}N_{10}O_2Zn$, $M=441.81$, colorless block, $0.20\times0.18\times0.15$ mm$^3$, monoclinic, space group *C*2/*c* (No. 15), $a=16.6880(4)$, $b=8.6165(2)$, $c=13.5581(3)$ Å, $\beta=110.917(1)°$, $V=1821.07(7)$ Å$^3$, $Z=4$, $\rho_{cald}=1.611$ g cm$^{-3}$, $F_{000}=920$, 8256 reflections collected, 2081 unique ($R_{int}=0.0170$). Final $GooF=1.053$, $R1=0.0193$, $wR2=0.0493$, $R$ indices based on 2039 reflections with I > 2 sigma(I), 140 parameters, 0 restraints, $\mu=1.386$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely.

**Crystal data for 4.** $C_{25}H_{29}N_{11}Ni_1O_4$, $M=606.30$, red block, $0.30\times0.26\times0.26$ mm$^3$, monoclinic, space group *C*2/*c* (No. 15), $a=11.927(4)$, $b=13.894(4)$, $c=19.191(4)$ Å, $\beta=98.39(3)°$, $V=3146.2(15)$ Å$^3$, $Z=1$, $\rho_{cald}=1.275$ g cm$^{-3}$, $F_{000}=1254$, $2\theta_{max}=55.0°$, 18891 reflections collected, 3600 unique ($R_{int}=0.1787$). Final $GooF=1.094$, $R1=0.0663$, $wR2=0.1760$, $R$ indices based on 2895 reflections with I > 2 sigma(I), 265 parameters, 31 restraints, $\mu=0.664$ mm$^{-1}$. The pyridyl ligands and the flexible $(CH_2)_2OH$ arms of the *chnm* ligand are disordered over two positions with the occupancies of the sites refined against each other (69:31 and 75:25, respectively). The lattice pyridine molecule is also disordered through channels in the structure and lies close to a symmetry site. Disordered pyridine groups were refined using restraints. The solvent was refined in a single position at 50% occupancy (the nitrogen atom was refined in an arbitrary position on the ring and hydrogen atoms were omitted from the model, there are signs of further disorder although this could not be modelled satisfactorily). NH and OH protons were located from the Fourier difference map and refined in these fixed positions.

**Crystal data for 5a.** $C_{13}H_{22}CoN_8O_4$, $M=413.32$, red block, $0.40\times0.15\times0.10$ mm$^3$, monoclinic, space group *Cc* (No. 9), $a=7.8570(2)$, $b=17.5546(6)$, $c=12.9440(4)$ Å, $\beta=91.672(2)°$, $V=1784.56(9)$ Å$^3$, $Z=4$, $\rho_{cald}=1.538$ g cm$^{-3}$, $F_{000}=860$, $2\theta_{max}=55.0°$, 4791 reflections collected, 2764 unique ($R_{int}=0.0325$). Final $GooF=1.123$, $R1=0.0474$, $wR2=0.0974$, $R$ indices based on 2650 reflections with I > 2 sigma(I) (refinement on $F^2$), 294 parameters, 41 restraints. $\mu=1.000$ mm$^{-1}$. The 1-dimethylamino-2-methylaminoethane ligand was disordered over two positions with occupancies refined against each other (66:34), ISOR and SADI restraints were used with both components. The proton bonded to N7B could not be located in the Fourier map. NH protons were restrained with the DFIX command. Absolute structure parameter = 0.02(3).[57]

**Crystal data for 5b.** $C_{13}H_{22}N_8NiO_4$, $M=413.10$, red block, $0.3\times0.1\times0.1$ mm$^3$, orthorhombic, space group *Fdd*2 (No. 43), $a=26.0435(6)$, $b=32.5111(6)$, $c=8.5362(2)$ Å, $V=7227.6(3)$ Å$^3$, $Z=16$, $\rho_{cald}=1.519$ g cm$^{-3}$, $F_{000}=3456$, $2\theta_{max}=54.3°$, 19109 reflections collected, 3963 unique ($R_{int}=0.0336$). Final $GooF=1.046$, $R1=0.0354$, $wR2=0.0692$, $R$ indices based on 3841 reflections with I > 2 sigma(I) (refinement on $F^2$), 252 parameters, 0 restraints, $\mu=1.111$ mm$^{-1}$. Protons attached to nitrogen were located from the Fourier difference map and allowed to refine freely. Absolute structure parameter = 0.032(12).[57]

## Acknowledgements

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