Scientific paper

Synthesis of Hetero- and Homo-multinuclear Complexes with a Tetracyanonickelate Anion: Structural Characterization \([\text{Cu(bcen)Ni(CN)}_4]_2\)

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Abstract

Two new complexes \([\text{Cu(bcen)Ni(CN)}_4]_2\) (1) and \([\text{Ni(bcen)Ni(CN)}_4]_2\) (2) where bcen is 4,7-diazadecanediamide, were synthesized by reaction of equimolar amounts of M(NO3)2 (M = Cu and Ni), bcen ligand and K2[Ni(CN)4]. Single-crystal X-ray diffraction analysis of compound 1, shows that the bcen ligand acts as a tridentate chelate, coordinating to the Cu(II) ion via the two nitrogen atoms of the amine groups and one oxygen atom of one amide group, and the other amide unit is left uncoordinated. The coordination geometry around the Cu(II) ions is five coordinate with a distorted square pyramid geometry, comprising two nitrogen atoms and one oxygen atom belonging to the bcen ligand and two nitrogen atoms of the cyano groups of two Ni(CN)42− units. The distance between the copper ion and the amide oxygen of the dangling arm of an adjacent tetranuclear species is within the expected range for an axial Cu–O bond, and hence suggests that the amide oxygen of an adjacent tetranuclear complex may weakly coordinate to the copper ion in an axial position. These contacts link the tetranuclear species into infinite chain polymers.

Keyword: Cyano bridged; Multinuclear; diamine-diamide; Crystal structure; Tetracyanonickelate

1. Introduction

In recent years a great effort has been focused on the design, synthesis and study of multinuclear transition metal complexes. These complexes not only have played an important role in the development of modern coordination chemistry, but also can be utilized as model compounds for the active sites of metalloenzymes.1,2 Among them, investigations of hetero-nuclear complexes tend to be more informative than the homo-nuclear complexes, due to interesting properties which can arise from the presence of two different metal ions.3–5

There are a variety of strategies for synthesizing homo and hetero-multinuclear complexes. A general approach is to use bridging ligands such as halides, pseudo-halides, oxalate, sulfate, etc.6–10 Self-assembly is the most efficient approach for the construction of such molecular systems.11–13 Another popular and successful approach for the preparation of multinuclear complexes with unusual and interesting properties is to employ cyano complexes (metalloligand) such as Ag(CN)2−, Ni(CN)42−, Cr(CN)63−, Pd(CN)42−, Pt(CN)42−, etc.14–17 The cyano anion is able to act either as a terminal or as a bridging ligand. Tetracyanometallic complex anions, M(CN)42− (M = Ni, Pd and Pt) can act in the bridging mode by using either one, two, three or all four cyano groups. It usually leads to formation of one-(1D), two-(2D) or three-dimensional (3D) structures.17–19

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Scheme 1. Structure of diamine-diamide complexes
Herein, we report the synthesis, spectroscopic characterization and structural aspects of two new homo and hetero-nuclear complexes derived from the metalloligand complexes Ni(CN)₄²⁻, and coordinatively unsaturated Cu(bcen)⁶⁺ and Ni(bcen)⁶⁺ complexes (bcen = 4,7-diaza-decanediamide, also known as N₂N'-bis(β-carbamoyl-ethyl)ethyldiamine) (Scheme 1).

2. Experimental

2.1. Materials and Measurements

All chemicals were of analytical reagent grade and were used without further purification. The complex K₃[Ni(CN)₄]·H₂O was prepared according to the literature procedure by mixing stoichiometric amounts of nickel(II) chloride hexahydrate (2.00 mmol, 0.521 g) in 10 mL of water. The diamine-diamide ligand 4,7-diaza-decanediamide (bcen) was prepared as previously reported from ethylenediamine and acrylamide in acetonitrile by heating the mixture under reflux. The white powder was recrystallized from CHCl₃. Infrared spectra were taken in the 400–4000 cm⁻¹ range. Elemental analyses (C, H, N) were performed by using a CHNS-O 2400II PERKIN-ELMER elemental analyzer.

2.2. X-ray Crystallography

Diffraction images were measured at 150 K on SuperNova diffractometer using Cu Kα (λ = 1.54180 Å) radiation. Data were extracted using the CrysAlis PRO package. The structures were solved by direct methods with the use of SIR92. The structures were refined on F² by full matrix least-squares techniques using the CRYSTALS program package. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C–H in the range 0.93–0.98, N–H = 0.87, O–H = 0.83 Å) and with atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Crystallographic data and refinement details for the complex are given in Table 1.

2.3. Syntheses

2.3.1 [Cu(bcen)Ni(CN)₄]₂·2CH₃OH, 1

To a solution of bcen (1.00 mmol, 0.198 g) in methanol (40 mL) was added Cu(NO₃)₂·3H₂O (1.00 mmol, 0.242 g) with stirring for 10 min. Then, to this blue solution of [Cu(bcen)]²⁺, [Ni(CN)₄]²⁻ (1.00 mmol, 0.260 g) dissolved in a minimum volume of water was added dropwise with stirring for 5 min. The precipitate that was initially obtained was filtered off and the filtrate was left aside for crystallization. Blue cube-shaped crystals suitable for X-ray diffraction appeared at the bottom of the vessel upon slow evaporation of the solvents at room temperature, and were collected by filtration, washed with methanol and dried in the air. The yield was 87%. Anal. Calc. for C₂₆H₄₄Cu₂N₁₆Ni₂O₆: C, 33.90; H, 4.81; N, 24.33. Found: C, 33.90; H, 4.81; N, 24.37. IR (KBr, cm⁻¹): C=N = 2122 and 2152. The complex 2 was synthesized in a similar manner as described for 1 by using Ni(NO₃)₂·6H₂O (1.00 mmol, 0.291 g) instead of Cu(NO₃)₂·3H₂O. The pale blue precipitate was filtered off and the filtrate left aside. Upon slow evaporation of the solvents at room temperature, a pale blue precipitate was obtained. The precipitate is insoluble in most common organic solvents such as methanol, ethanol, acetone, acetonitrile and dichloromethane and also is only very slightly soluble in water and DMF. We attempted to grow single crystals of the complex but had no success due to its insolubility. The complex was purified by washing with methanol-water (1:1 v/v) solution to remove unreacted materials from the crude solid. The yield was 71%. Anal. Calc. for C₂₆H₄₄Cu₂N₁₆Ni₂O₆: C, 33.90; H, 4.81; N, 24.37. Found: C, 30.90; H, 4.74; N, 23.88. IR (KBr, cm⁻¹): vC=Н = 2126.

Table 1. Crystallographic data of [Cu(bcen)Ni(CN)₄]₂ complex

| Compound | 1 |
|----------|---|
| Chemical formula | C₂₆H₄₄Cu₂N₁₆Ni₂O₆ |
| Formula weight | 921.25 |
| T (K) | 150 |
| Space group | Triclinic, P1 |
| Z | 1 |
| a (Å) | 9.1232(6) |
| b (Å) | 10.2600(6) |
| c (Å) | 10.4739(6) |
| α (°) | 78.683(5) |
| β (°) | 79.671(5) |
| γ (°) | 80.291(5) |
| υ(Å³) | 932.26(10) |
| F(000) | 474 |
| D_{calc} (g cm⁻³) | 1.641 |
| μ (mm⁻¹) | 2.94 |
| Measured reflections | 14724 |
| Independent reflections | 3685 |
| R_{int} | 0.023 |
| Observed reflections | 3555 |
| R[F² > 2σ(F²)] | 0.025 |
| wR(F²) (all data) | 0.069 |

ν = 1/(σ²(F²) + (0.04P)² + 0.53P), where P = (max(F²,0) + 2F²)/3

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3. Results and Discussion

3.1. Syntheses and Characterization of the Complexes

The M(bcen) complexes (M = Cu and Ni) were obtained by the in-situ reaction of metal nitrate and bcen ligand in methanol at room temperature. The M(bcen) complexes upon the addition of an equimolar ratio of Ni(CN)₄²⁻ form of complexes 1 and 2. Both complexes are stable in air and insoluble in common organic solvents and very slightly soluble in water and DMF. The insolubility of the complexes suggests that they are polymeric compounds.

Besides elemental analysis, the complexes were initially characterized by infrared spectral techniques which were useful in identifying the bonding mode (terminal or bridging) of the cyano groups in Ni(CN)₄²⁻ to the metal(II) ion. The absorption bands due to the cyano groups are the most important aspects of the infrared spectra in these types of complexes. In the IR spectrum of the free CN⁻, the cyanide stretching vibration band appears at 2077 cm⁻¹. In the IR spectrum of K₂[Ni(CN)₄] complex this band appears at 2128 cm⁻¹. In the IR spectra of 1 and 2, there are two peaks for cyano stretching vibrations arising from the presence of both bridged and non-bridged cyano groups. For 1 these are at 2126 (non-bridged) and 2172 cm⁻¹ (bridged) and for 2 they are at 2120 (non-bridged) and 2151 cm⁻¹ (bridged) (Fig. 1). The increase of cyano stretching vibration band with the formation of cyano bridge, M–N≡C–Ni (M = Cu and Ni) in the complexes in comparison with the cyano non-bridge are due to the kinematic effect, i.e. the impediment of the C–N vibration due to the attachment of the second metal unit Ni and M.

Fig. 1. The infrared spectra of complexes 1 and 2

3.2. Description of Crystal Structure the Complex, 1

The molecular structure of hetero-tetranuclear 1 is shown in Fig. 2. Selected bond lengths and angles as well as interatomic distances are summarized in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) in [Cu(bcen)Ni(CN)₄]₂ complex

| Bond/Angle | Length/° |
|------------|----------|
| CuO1       | 2.0486 (11)  |
| CuN2       | 1.9989 (14)   |
| CuN3       | 2.0417 (14)   |
| CuN5       | 1.9628 (14)   |
| CuN6a      | 2.2182 (14)   |
| N6–Cu1–N2  | 96.04 (5)      |
| N6–Cu1–N3  | 97.80 (6)      |
| N2–Cu1–N3  | 84.94 (6)      |
| N3–Cu1–N5  | 91.40 (6)      |
| O1–Cu1–N2  | 96.04 (5)      |
| N6–Cu1–N2  | 91.60 (6)      |
| N6–Cu1-N3  | 97.80 (6)      |
| N2–Cu1–N3  | 84.94 (6)      |
| N3–Cu1–N5  | 91.40 (6)      |
| O1–Cu1–N3  | 166.06 (5)     |
| N2–Cu1–N3  | 84.94 (6)      |
| O1–Cu1–N5  | 86.90 (5)      |
| N6–Cu1–N5  | 103.55 (6)     |
| Cu1–O1     | 2.0486 (11)    |
| Cu1N2      | 1.9989 (14)    |
| Cu1N3      | 2.0417 (14)    |
| Cu1N5      | 1.9628 (14)    |
| Cu1N6      | 2.2182 (14)    |
| C1–O1      | 1.2617 (19)    |
| C8–O2      | 1.2250 (20)    |
| Cu1····O2   | 2.9070 (15)    |

Complex 1 consists of discrete tetranuclear mixed metal species with two copper and two nickel centers which are connected via cyano bridging ligands.

Fig. 2. The structure of the [Cu(bcen)Ni(CN)₄]₂ complex, 1, with labelling of selected atoms. Anisotropic displacement ellipsoids exhibit 30% probability levels. Hydrogen atoms are drawn as circles with small radii.
Previous studies on the diamine-diamide ligands and copper(II) have shown complexes where the ligand is tetradentate and coordinates to the metal center through the two amine nitrogen atoms and the two amide oxygen atoms.\textsuperscript{31,32} However, in complex 1 the crystallographic analyses reveal that the bcen ligand is tridentate chelate, coordinating to the metal ion \textit{via} the two nitrogen atoms of the amine groups and the oxygen atom of one amide group, and other amide unit does not bond to that Cu atom. There have been a few studies on the formation and dissociation of the Cu(bcen)\textsuperscript{2+} complex and also on the kinetics of metal exchange complexes with the bcen ligand, and they reported that the Cu(II)–O bond to the amide is substitutionally labile.\textsuperscript{25,26,33} The X-ray characterization of complex 1 shows that the bond between Cu(II) and a labile amide oxygen of bcen ligand has broken under these experimental conditions, followed by coordination of Cu(II) to cyanide nitrogen atoms of Ni(CN)\textsubscript{4}\textsuperscript{2–} moieties.

The distance between copper ion (Cu1) and the amide oxygen of the dangling arm of an adjacent tetranuclear species (O2a, symmetry code: \(-x + 1, -y + 1, -z + 1\)) is 2.9070(15) Å which is significantly longer than the typical Cu–O covalent bond (1.98 Å), but it is slightly shorter than the sum of the van der Waals radii (2.92 Å).\textsuperscript{34} This distance is within the range of 2.2–2.9 Å, known for axial Cu–O bonds,\textsuperscript{35} and hence suggests that the amide oxygen

\begin{table}
\centering
\caption{Hydrogen bonding (Å) and angles (°) for [Cu(bcen)Ni(CN)]\textsubscript{2} complex}
\begin{tabular}{ccccccc}
\hline
D–H···A & D–H & H···A & D···A & D–H···A & Symmetry code \\
\hline
N1–H1···O1 & 0.83(3) & 2.37(3) & 3.199(3) & 173(2) & \(-x + 1, -y + 1, -z + 2\) \\
N1–H2···N7 & 0.83(3) & 2.19(3) & 3.006(3) & 168(2) & \(x, y - 1, z + 1\) \\
N2–H3···N8 & 0.89(3) & 2.25(3) & 3.023(3) & 145(2) & \(x, y - 1, z\) \\
N3–H4···O2 & 0.86(2) & 2.45(2) & 3.026(3) & 125(2) & \(x, y, z\) \\
N3–H4···O3 & 0.86(2) & 2.37(2) & 2.996(3) & 130(2) & \(-x + 2, -y + 1, -z + 1\) \\
N4–H5···O1 & 0.91(2) & 2.22(2) & 3.026(3) & 125(2) & \(-x + 2, -y + 1, -z + 1\) \\
O3–H7···N8 & 0.89(2) & 1.97(2) & 2.911(3) & 165(2) & \(-x + 2, -y + 1, -z + 1\) \\
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{The contacts between copper ion and the amide oxygen of dangling arm in adjacent tetranuclear species in complex 1.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Various hydrogen bonding interactions in complex 1 along \(ac\) plane.}
\end{figure}
of adjacent tetranuclear complex may weakly coordinate to the copper ion in an axial position. These contacts link the tetranuclear species into infinite chains along the b axis (Fig. 3).

Adjacent 1D chains are connected by C≡N(terminal)···H₂N(amide ligand) contacts to form a 2D layer structure (Fig. 4). The 2D layers are extended into 3D supramolecular networks by C≡N(terminal)···HN(amine) hydrogen bonds interactions. Full details of the hydrogen bonding are given in Table 3. Insolubility of the complex in different solvents is consistent with its polymeric nature. 27

The copper(II) centers are five-coordinate with a N₄O donor set from the bcen ligand (N₂O) and two bridging cyanides. Coordination geometry about each copper ion is essentially a square pyramid with one oxygen and two nitrogen atoms from the bcen ligand and two nitrogen atoms, one from each of two of [Ni(CN)]²⁻ units. According to the bond lengths between the copper ions and the coordinating atoms, the square base consists of the N₂O donors from the bcen ligand and the closer of the bridging cyanide nitrogen atoms (Cu–N = 1.9628(14) Å), and the apical position is occupied by the longer Cu–N from the bridging cyanide (2.2182(14) Å). The copper is displaced from the basal plane of N₂O by 0.254 Å towards the apical nitrogen atom. The Addison parameter τ value is 0.022. The τ parameter is defined as τ = (α − β)/β, where α and β are the largest angles; τ = 1 for a perfect trigonal bipyramid and τ = 0 for a regular square pyramid. 36

The Ni(II) ions are coordinated by the C atoms of four cyanide ligands in a square planar geometry. The bond distances for Ni–C and C≡N in the Ni(CN)₄²⁻ moiety are in range of 1.8553(16)–1.8767(16) Å and 1.146(2)–1.153(2) Å, respectively, which is in accordance with the reported values for similar complexes. 14–16,18,37 Although Ni–C and C≡N bond lengths can vary depending on whether they are in bridging and terminal modes, there are no significant variations. The Cu–N=C bond angles (164.64(13) and 150.09(13)°) are significantly bent, whereas the Ni–C≡N bond angles are essentially linear and range from 172.85(14) to 179.28(14)°.

The nickel core has a τ₉ index of 0.096. The τ₉ parameter is [360° − (α + β)]/141°, where α and β are the largest angles around the central metal in the complex; τ₉ = 1 for a regular tetrahedron and τ₉ = 0 for a regular square planar geometry. 38 Each [Ni(CN)]²⁻ group coordinates to two Cu(II) ions using two cis-cyanide ligands. Each Cu(bcen) unit is connected to two [Ni(CN)]²⁻ moieties through a basal plane and an apical position.

4. Conclusions

We have synthesized two multi-nuclear complexes by reaction of M(bcen)²⁺ (M = Cu and Ni) and K₂[Ni(CN)]₄. The IR spectra of the two complexes revealed the presence of both bridged and non-bridged cyano groups. The crystallographic analyses revealed that complex 1 consists of discrete tetranuclear mixed metal species with two copper and two nickel centers which are connected via cyano bridging ligands of [Ni(CN)]²⁻ moieties. The bcen tetradentate ligand in complex 1 acts as a tridentate ligand and an amide unit of the bcen was left as a dangling arm. The contact between the amide of the dangling arm and copper ion of an adjacent tetranuclear unit give rise to infinite chain polymers. Insolubility of the complex in several solvents is consistent with its polymeric nature.

5. Supplementary Material

The deposition number of the studied complex is CCDC 1547091. These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Povzetek

Z reakcijo ekvimolarnih količin M(NO₃)₂ (M = Cu in Ni), bcen liganda in K₂[Ni(CN)₄] smo sintetizirali dva nova kompleksa [Cu(bcencNi(CN)₄)]₂⁻ (1) in [Ni(bcencNi(CN)₄)]₂⁻ (2), kjer je bil 4,7-diazadekandiamid. Monokristalna analiza spojine 1 razkrije, da se bcen ligand koordinira na Cu(II) ion kot trovezni kelatni ligand preko dveh dušikovih atomov aminske skupine in enega kisikovega atoma ene amidne skupine, medtem ko druga amidna enota ni koordinirana na Cu(II) centri. Razdalja med dušikovimi atomi znotraj dveh kisikovih atomov v aksialni legi. Ta kontakt povezuje štirijedrni vzorec v neskončno verigo.