

Isolation and characterisation of a novel thermally stable octahedral bicarbonato complex of bis(2-picolyamine)copper(II): identification of rare monodentate coordination

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Received 14th January 2003, Accepted 10th February 2003

First published as an Advance Article on the web 17th February 2003

A novel bicarbonato complex, $[\text{Cu}(\text{C}_5\text{H}_4\text{NCH}_2\text{NH}_2)_2(\text{OCO}_2\text{H})_2]$ (**1**), has been synthesised under controlled pH and characterised by IR, UV-Vis spectroscopy, magnetic moment and thermal analysis; the coordination environment around the metal centre is elongated octahedral with two chelated bidentate amines in the square plane and the axial sites are occupied by two monodentate bicarbonato ligands.

A number of experiments support the hypothesis that an intramolecular proton transfer is involved in the interconversion of CO_2 and HCO_3^- during the reversible hydration of CO_2 and dehydration of HCO_3^- catalysed by human carbonic anhydrase II (HCAII).¹ Two representative mechanisms involving the different bicarbonato binding modes were proposed by Lipscomb^{2a,b} and Lindskog^{2c} respectively, to account for the proton transfer process and have generated extensive interest over the past decade. Two X-ray structures involving monodentate bicarbonato binding to different carbonic anhydrases, *i.e.* a bicarbonato-HCAII intermediate and a mutant intermediate of bicarbonato-HCAII have been determined and used to support the Lindskog structure.³ In recent progress, both coordination modes were suggested to be part of the mechanism.^{1f} In the study of model systems,⁴ bicarbonato complexes of the type $[\text{L}_n\text{M}^{\text{II}}(\text{OCO}_2\text{H})]$ ($\text{M} = \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}$) were always considered to be unstable and have not been structurally characterised to date. Structurally characterised monodentate bicarbonato complexes are rare^{5,10} and are generally prepared by nucleophilic attack of metal-coordinated hydroxide on CO_2 in non-aqueous solvents. Earlier, Yoshida *et al.* reported a chelated monomeric bicarbonato complex, $[\text{Rh}(\text{H})_2(\text{P}(\text{i-Pr})_3)_2(\text{O}_2\text{COH})]$, and Darensbourg *et al.* reported the monomeric complex $[\text{PPN}][\text{W}(\text{CO})_5(\text{OCO}_2\text{H})]$ of heavy metals.^{6,10} A chelated bicarbonato species of Co(III) was identified by Baxter *et al.*⁷ In a recent report, Mao *et al.* showed two stable isomeric complexes of the type $[\text{Cu}(\text{phen})_2(\text{O}_2\text{COH})(\text{ClO}_4)]$ and $[\text{Cu}(\text{phen})_2(\text{OCO}_2\text{H})(\text{ClO}_4)]$, which are the first examples of this type.⁸

In this work, $[\text{Cu}(\text{C}_5\text{H}_4\text{NCH}_2\text{NH}_2)_2(\text{H}_2\text{O})(\text{ClO}_4)_2]$ was used as starting material.⁹ On reaction with bicarbonato this produced an unprecedented distorted octahedral complex $[\text{Cu}(\text{C}_5\text{H}_4\text{NCH}_2\text{NH}_2)_2(\text{OCO}_2\text{H})_2]$ **1**, in which bicarbonato coordinates in a rare monodentate mode. To the best of our knowledge, this is the first example of an octahedral Cu(II) complex in which two monodentate bicarbonato groups are coordinated to a single metal centre.

Complex **1** was prepared in 38% yield by the reaction of $[\text{Cu}(\text{C}_5\text{H}_4\text{NCH}_2\text{NH}_2)_2(\text{H}_2\text{O})(\text{ClO}_4)_2]$ and NaHCO_3 in dichloromethane.†

The single crystal structure shows that **1** crystallises as a monoclinic system.‡ A perspective view of **1** with the atom numbering scheme is shown in Fig. 1 and the molecular packing diagram is shown in Fig. 2. The monomeric complex is made up of a centrosymmetric $[\text{Cu}(\text{C}_5\text{H}_4\text{NCH}_2\text{NH}_2)_2(\text{OCO}_2\text{H})_2]$ unit

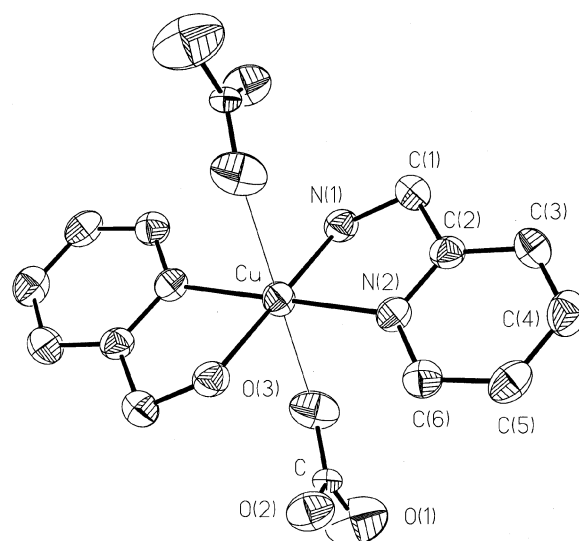


Fig. 1 Perspective view of complex **1** with atom numbering scheme.

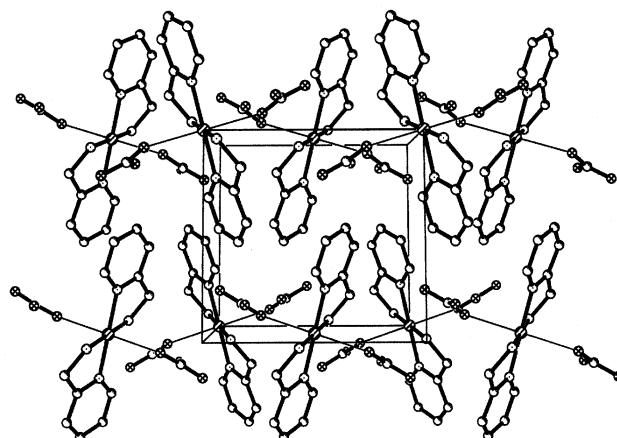


Fig. 2 Molecular packing diagram of complex **1**.

adopting a (4 + 2) surrounding. The coordination stereochemistry of the CuN_4O_2 chromophore is distorted octahedral. The basal positions are occupied by the four nitrogen atoms of the two bidentate amines and the apical positions are occupied by the oxygen atoms of the two coordinated bicarbonato groups. The four basal atoms are coplanar with $\text{N}(1)\#1-\text{Cu}-\text{N}(1)$ and $\text{N}(2)\#1-\text{Cu}-\text{N}(2)$ angles of exactly 180° , showing no deviation. The corresponding bond pairs of $\text{Cu}-\text{N}(2)$, $\text{Cu}-\text{N}(2)\#1$, $\text{Cu}-\text{N}(1)$, $\text{Cu}-\text{N}(1)\#1$ are nearly of the same length. The basal bond distances $\text{Cu}-\text{N}(1)\#1$, $\text{Cu}-\text{N}(1)$ are $1.996(3)$ Å and $\text{Cu}-\text{N}(2)\#1$, $\text{Cu}-\text{N}(2)$ are $2.023(3)$ Å respectively (see Table 1). Two identical and significantly elongated axial bond lengths $\text{Cu}-\text{O}(3)$ and $\text{Cu}-\text{O}(3)\#1$ are $2.589(1)$ Å indicate that the

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Cu–N(1)#1	1.996(3)	Cu–N(1)	1.996(3)
Cu–N(2)#1	2.023(3)	Cu–N(2)	2.023(3)
Cu–O(3)	2.589(1)	Cu–O(3)#1	2.589(1)
C–O(1)	1.217(5)	C–O(2)	1.231(5)
C–O(3)	1.236(4)		
N(1)#1–Cu–N(2)#1	81.79(14)	N(1)–Cu–N(2)#1	98.21(14)
N(1)#1–Cu–N(2)	98.21(14)	N(1)–Cu–N(2)	81.79(14)
O(1)–C–O(2)	120.4(4)	O(1)–C–O(3)	119.7(4)
O(2)–C–O(3)	119.9(3)		

#1 = $-x, -y, -z$.

HCO₃[−] group is coordinated to the Cu centre in a monodentate mode and the angle between O(3)–Cu–O(3)#1 is exactly 180°. A comparison of the bond lengths of C–O(3) [1.236(4) Å], C–O(2) [1.231(5) Å] and C–O(1) [1.217(5) Å] suggests that the hydrogen atom of HCO₃[−] is bound to the O2 atom, although it could not be located by X-ray analysis.^{8,10} There may exist a hydrogen bond between one of the NH hydrogen atoms (N(1)#1) on the coordinated 2-picolyamine and the oxygen atom (O1) on coordinated bicarbonate which has no hydrogen and the most C=O character. This hydrogen bonding is the factor stabilising the monodentate nature of the complex.

It is worth noting that there are few unidentate bicarbonate metal complexes structurally characterised by X-ray diffraction due to their tendency to afford more stable carbonate derivatives.¹¹ Furthermore, there is a scarcity of definitive infrared data on structurally characterised bicarbonate complexes.¹⁰ The infrared spectrum of **1** shows bands at 3024 and 2903 cm^{−1} which are assigned to ν(N–H). The bands at 1650, 1380, 1259 and 831 cm^{−1} are due to the coordinated bicarbonate groups. The bands near 669 and 492 cm^{−1} are due to in-plane and out-of plane deformation of the coordinated pyridine ring. All the other bands appeared at their usual positions.¹²

In methanol, the electronic spectrum of **1** showed two peaks at 203 and 269 nm which may be attributed to π–π* and n–π* transitions of the ligand to the metal respectively. The band at 373 nm is also the ligand to metal charge transfer transition. A shoulder appeared at 620 nm due to the d–d transition of the Cu(II) moiety. This type of spectrum is typical for tetragonally distorted octahedral copper(II) complexes.¹³

The complex **1** is stable up to 90 °C. The mass loss in the TGA curve in the temperature range 90–132 °C corresponds to the release of two coordinated bicarbonate groups. The release of bicarbonate ions is confirmed from the mass loss in the TGA curve. The loss of bicarbonate is also confirmed by the absence of the necessary IR spectral bands in the isolated complex with respect to the original complex. Further decomposition of the complex started at higher temperature.

The room temperature magnetic moment of **1** is found to be 1.77 μ_B which is very close to the spin-only moment for a d⁹ system.

The structural analysis clearly indicates that bicarbonate can substitute both water and perchlorate molecules in the starting complex and coordinate to the metal centre in monodentate fashion. The complex contains two coordinated bicarbonate groups and gives an insight into the structure proposed to be involved in the reversible intramolecular conversion of coordinated hydroxo-carbon dioxide to bicarbonate. So complex **1** may mimic the Lindskog-type structure and advance

the understanding of the cycle of HCAII which involves bicarbonate.

The authors are grateful to CSIR, DST, UGC and AICTE (New Delhi) for financial assistance.

Notes and references

† Preparation of [Cu(C₅H₄NCH₂NH₂)₂(OCO₂H)₂], **1**. To a 0.50 M NaHCO₃ solution, a solution of [Cu(C₅H₄NCH₂NH₂)₂(H₂O)](ClO₄)₂ (0.248 g, 0.5 mmol) was added dropwise. The precipitate formed was isolated and dissolved in 20 ml of 0.1 M NaHCO₃ in dichloromethane. The solution was filtered and allowed to stand in a sealed flask over solid P₂O₅ in a CO₂ atmosphere. After 14 days, blue block crystals suitable for X-ray diffraction were isolated. Yield: 38%. Anal. calc. for C₁₄H₁₈N₄CuO₆: C, 41.81; H, 4.48; N, 13.93; Cu, 15.80. Found: C, 42.00; H, 4.53; N, 14.00; Cu, 15.77%. IR data for coordinated bicarbonate (KBr pressed pellet)/cm^{−1}: 1650 s (ν₁), 1380 s, 1259 s (ν₂), 831 m (π); ν(N–H) 3024, 2903 cm^{−1}.

‡ Crystal data for C₁₄H₁₈N₄CuO₆: *M* = 401.86, *T* = 293(2) K, monoclinic, space group *p*2(1)/*c*, *a* = 8.632(7), *b* = 8.987(7), *c* = 9.997(11) Å, β = 99.39(7)°, *V* = 765.1(12) Å³, *Z* = 2, *D_c* = 1.744 Mg m^{−3}, μ = 2.420 mm^{−1}, *F*(000) = 414, θ range for data collection 5.19 to 49.97°, *R* indices (all data): *R*₁ = 0.0410, *wR*₂ = 0.1174, final *R* indices: *R*₁ = 0.0404, *wR*₂ = 0.1160 for [*I* > 2σ(*I*)], largest difference peak and hole 0.481 and −0.283 e Å^{−3}. CCDC reference number 201923. See <http://www.rsc.org/suppdata/dt/b3/b300548h/> for crystallographic data in CIF or other electronic format.

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