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Isolation and characterization of the first stable bicarbonato complex in a nickel(II) system: identification of unusual monodentate coordination†

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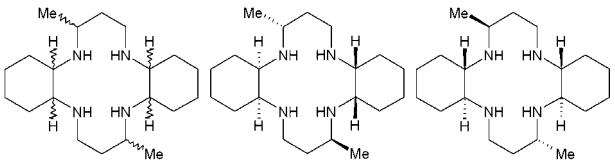
The stable monodentate Lindskog type bicarbonate nickel(II) complex and its isomer have been prepared and fully characterized.

The carbonic anhydrases are zinc containing enzymes that catalyze the reversible hydration of CO_2 and dehydration of HCO_3^-.[1] Numerous experiments suggest the hypothesis that intramolecular proton transfer is involved in the interconversion of CO_2 and HCO_3^- during the catalytic cycle for carbonic anhydrases. Lipscomb[2] and Lindskog[3] independently proposed two representative mechanisms involving different bicarbonate binding modes to account for the proton transfer process. In the Lipscomb structure, two oxygen atoms of the bicarbonate ligand coordinate to the zinc ion in a bidentate mode. On the other hand, in the Lindskog structure, one oxygen atom of the bicarbonate is bound to the metal center in a monodentate mode. Although the X-ray structures determined were used to support the monodentate mode in different carbonic anhydrases,[4] theoretical studies[5] suggested that the bidentate coordination mode contributes significantly to the catalytic activity of the enzymes. Therefore, the identification of the bicarbonate binding mode to the metal ion is significant in understanding the intramolecular proton transfer during the interconversion of CO_2 and HCO_3^- in the catalytic cycle. Earlier, bicarbonate complexes in heavy metals were reported.[6] Recently, stable monodentate and bidentate bicarbonato copper(II) and cobalt(III) complexes were isolated and structurally characterized,[7] although the bicarbonate complexes of the type $[(Ligand)_nM^{II}(O\text{-}CO_2H)]$ (M = Zn, Cu, Co, Ni) had long been considered to be unstable.[8] During our efforts to explore the stable UV–vis active model systems which enable us to directly monitor the catalytic process, we successfully prepared and structurally characterized an unprecedented stable nickel(II) bicarbonate complex $\{[Ni(\mathbf{L1})(O\text{-}CO_2H)_2]\}_n$ (**1**), and an isomeric square-planar complex $\{[Ni(\mathbf{L2})]\cdot 2HCO_3\}_n$ (**2**) from the combination of the starting material $[Ni(\mathbf{L})]\cdot 2ClO_4$ with two equivalents of sodium bicarbonate in DMF–H_2O. The ligands **L1** and **L2** are two out of the 16 possible



L **L1** **L2**

diastereoisomers of **L**.[9] To our best knowledge, the complex **1** is the first example of an octahedral nickel(II) complex in which two bicarbonate ligands are coordinated to the metal in a monodentate mode. The X-ray crystal structures of **1** and **2** were determined.§ An ORTEP drawing of the complex **1** is shown in Fig. 1. A pertinent feature of the structure is the coordination of two bicarbonate anions to the central nickel(II) ion in a monodentate fashion. This structure is stabilized by hydrogen bonds between the two sets of pre-organized N–H groups of the macrocyclic unit and bicarbonate ligands, resulting in the formation of $[Ni(\mathbf{L1})(OCO_2H)_2]$. The $[Ni(\mathbf{L1})(OCO_2H)_2]$ unit extends its structure to form the ultimate 1D supramolecule **1** through hydrogen bonding interactions between the two bicarbonate synthons. (N(1)–H(1)···O(2)#1: *d*(D···A) = 2.8724(18) Å, ∠(DHA) = 157.5°; O(3)–H(1O)···O(2)#2: *d*(D···A) = 2.6012(17) Å, ∠(DHA) = 175(3)°; symmetry transformations used to generate equivalent atoms: #1 −*x*+1,−*y*+1,−*z*+1; #2 −*x*,−*y*,−*z*+1). The *cis* fused cyclohexane rings that are *anti* with respect to the macrocyclic plane seem to be favorable for the bicarbonate anions toward the axial attack. The complex **2** contains a discrete square-planar $[Ni(\mathbf{L2})]^{2+}$ unit in which the macrocycle has two *trans* fused cyclohexane rings and two bicarbonate anions, while the nickel(II) complex with **L2** never yields coordinated bicarbonate ligands. An ORTEP drawing of the complex **2** is shown in Fig. 2. The oxygen atom of the bicarbonate anion in **2** is displaced from the central nickel(II) ion to facilitate the hydrogen bonding interactions between the pre-organized N–H groups of the macrocycle and bicarbonate anions (N(1)–H(1)···O(3): *d*(D···A) = 2.814(3) Å, ∠(DHA) = 161.8°; N(2)–H(2)···O(1)#1: *d*(D···A) = 2.834(2) Å, ∠(DHA) = 146.1°; O(2)–H(1O)···O(1)#2: *d*(D···A) = 2.651(3) Å, ∠(DHA) = 173(4)°; symmetry operations used to generate equivalent atoms: #1 −*x*+1,−*y*+1,−*z*+1; #2 −*x*,−*y*+1,−*z*+1). Similarly to **1**, the complementary bicarbonate anions in **2** interact with each other to form the ultimate 1D supramolecule. Fig. 3 shows the stick model of the hydrogen-bonded 1D structures of **1** and **2**.

The infrared spectra of **1** and **2** show bands at 3126 (**1**) and 3124 cm^{-1} (**2**) assignable to ν(N–H). The bands at 1605, 1412 cm^{-1} (**1**) and 1614, 1383 cm^{-1} (**2**) are due to the coordinated and

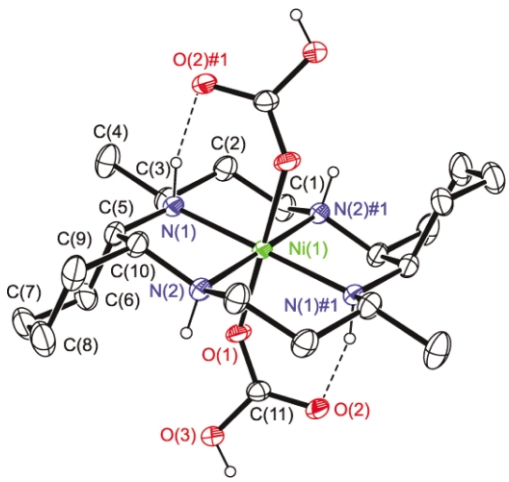


Fig. 1 Molecular structure of **1** with atom numbering scheme. Selected bond distances (Å) and angles (°): Ni(1)–N(1), 2.0975(13); Ni(1)–N(2), 2.0753(13); Ni(1)–O(1), 2.1093(11); N(2)–Ni(1)–N(2)#1, 180; N(2)–Ni(1)–N(1), 83.51(5), N(2)#1–Ni(1)–N(1), 96.49(5); N(2)–Ni(1)–O(1), 88.13(5); N(1)–Ni(1)–O(1)#1, 90.71(5); N(1)–Ni(1)–O(1), 89.29(5). Symmetry operation used to generate equivalent atoms: #1 −*x*+1, −*y*+1, −*z*+1.

† Electronic Supplementary Information (ESI) available: synthetic procedures for **L** and $[Ni(\mathbf{L})]\cdot 2ClO_4$, electronic spectra and X-ray crystallographic data for **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b405695g/

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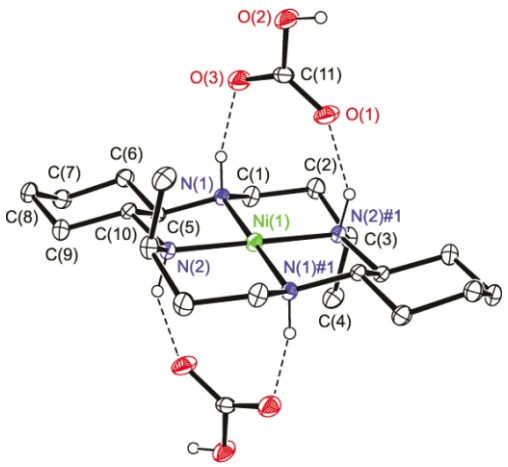

Fig. 2 Molecular structure of **2** with atom numbering scheme. Selected bond distances (Å) and angles (°): Ni(1)–N(1), 1.9643(17); Ni(1)–N(2), 1.9472(17); N(2)–Ni(1)–N(2)#1, 180; N(2)–Ni(1)–N(1), 86.06(7), N(2)#1–Ni(1)–N(1), 93.94(7). Symmetry operation used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$.

uncoordinated bicarbonate groups, respectively.[10] The solid state electronic spectrum of **1** in the visible region shows three bands at 339, 523 and 688 nm assignable to the $^3B_{1g} \rightarrow {}^3E_g{}^c$, $^3B_{1g} \rightarrow {}^3E_g{}^b$, $^3B_{1g} \rightarrow {}^3B_{2g} + {}^3B_{1g} \rightarrow {}^3A_{2g}{}^a$ transitions, which is the characteristic spectrum expected for a high-spin nickel(II) ion in a D_{4h} environment.[11] In **2** as expected for a low-spin d^8 nickel(II) ion in a square-planar environment only one band at 466 nm was observed. The infrared and electronic spectra for **1** and **2** clearly support the structures determined by the X-ray diffraction studies.

In summary, we prepared and fully characterized the stable monodentate octahedral nickel(II) bicarbonato complex **1**. In order to achieve this, we took advantage of the tetraaza macrocycle having *cis* fused cyclohexane rings that are *anti* with respect to the macrocyclic plane, and the directionality of the pre-organized N–H groups for the stabilization of bicarbonate ligands. By using an isomeric macrocyclic ligand containing *trans* fused cyclohexane rings we obtained the square-planar nickel(II) complex **2**. The bicarbonate ion in **2** shows no evidence of interaction with the nickel center. However, hydrogen bonding interactions between the pre-organized N–H groups of the macrocycle and bicarbonate anions as well as between the two bicarbonate synthons are observed in both complexes, resulting in the formation of 1D supramolecules **1** and **2**, respectively. Especially the complex **1** containing two monodentate bicarbonato groups may be used as model system for the understanding of the reversible intramolecular proton transfer during the catalytic cycle of carbonic anhydrases. The behaviour of the complex **1** in solvents of varying dielectric constant is under investigation.

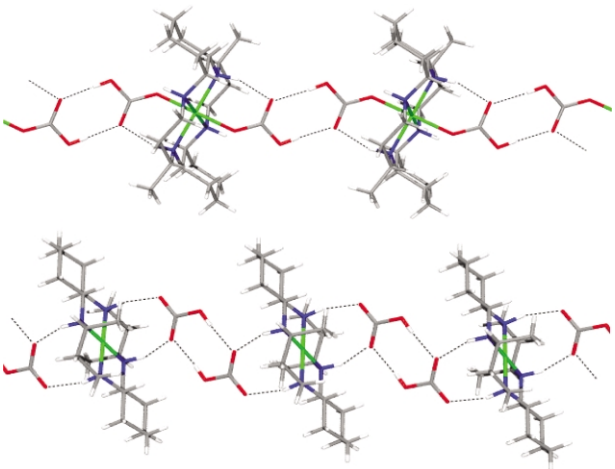

Fig. 3 1D hydrogen-bonded structures of **1** (top) and **2** (bottom).

Notes and references

§ *Crystal data for* **1**: $C_{22}H_{42}N_4NiO_6$, M_r = 517.31, triclinic, space group $P\bar{1}$, a = 7.4397(3), b = 9.2719(3), c = 10.3211 Å, α = 106.5530(18), β = 101.265(2), γ = 109.4730(18)°, V = 609.30(4) Å^3, Z = 1, d_c = 1.410 Mg m^3, μ(Mo–Kα) = 0.841 mm^{-1}, F(000) = 278, crystal size: 0.20 × 0.18 × 0.05 mm. A total of 7277 reflections were measured, 2771 reflections were unique (R_{int} = 0.0399). T = 150(1) K, 2.63° < θ < 27.50°, $-9 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 13$, R_1 = 0.0317, wR_2 = 0.0740 ($I > 2\sigma(I)$), R_1 = 0.0364, wR_2 = 0.0771 (all data), GOF = 1.060, largest difference peak and hole = 0.311 and −0.502 e Å^{-3}. *Crystal data for* **2**: $C_{22}H_{42}N_4NiO_6$, M_r = 517.31, monoclinic, space group $P2_1/n$, a = 9.3483(3), b = 9.9583(3), c = 12.8621(4) Å, β = 102.9710(16)°, V = 1166.82(6) Å^3, Z = 2, d_c = 1.472 Mg m^{-3}, μ(Mo–Kα) = 0.878 mm^{-1}, F(000) = 556, crystal size: 0.36 × 0.26 × 0.22 mm. A total of 8287 reflections were measured 2655 reflections were unique (R_{int} = 0.0348). T = 150(1) K, 3.19° < θ < 27.48°, $-12 \le h \le 11$, $-11 \le k \le 12$, $-15 \le l \le 16$, R_1 = 0.0427, wR_2 = 0.1320 ($I > 2\sigma(I)$), R_1 = 0.0475, wR_2 = 0.1360 (all data), GOF = 1.070, largest difference peak and hole = 0.457 and −0.918 e Å^{-3}. X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[12] The structures were solved and refined, using the SHELXTL\PC V5.1 package.[13] Refinement was by full-matrix least squares on F^2, using all data (negative intensities included). CCDC 236194 (**1**) and 236195 (**2**). See http://www.rsc.org/suppdata/cc/b4/b405695g/ for crystallographic data in .cif or other electronic format.

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