Volume 32

Number 23

November 10, 1993

Inorganic Chemistry

Communications

$\mathrm{[Ni_2(OAc)_3(urea)(tmen)_2](OTf)}$ and $\mathrm{[Ni(OAc)(urea)_2(tmen)](OTf)}$, Model Complexes for the Enzyme Urease

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Received June 11, 1993

Many hydrolytic enzymes employ two metal ions to facilitate the concerted binding of substrate and addition or elimination of water.[1] The enzyme urease, which catalyzes the hydrolysis of urea to ammonium and carbamate ions, also falls into this category for it contains a pair of divalent nickel ions in each protein subunit.[2] In this case, however, X-ray structural information is not available, and attempts to define the active site geometry, including the Ni–Ni distance, have not yet afforded a unifying model. From electronic spectral and EXAFS measurements, an octahedral geometry was proposed for nickel, with nitrogen and oxygen, but not sulfur, donor ligands.[3,4] The magnetic behavior of urease was interpreted as arising either from a pair of weakly antiferromagnetically coupled Ni(II) ions, which would require a Ni–Ni separation < 4 Å,[5] or two isolated Ni(II) ions with no exchange interaction.[6] Variable-temperature MCD measurements indicated the presence of a ferromagnetically coupled dinuclear center.[7] Studies of the enzyme complexed with 2-mercaptoethanol, a strong competitive inhibitor, suggested the formation of a thiolate-bridged dinickel species, supporting the idea that the two nickel ions are in close proximity.[4,5,7]

In order to provide spectroscopic and structural analogues for the urease active site, we have prepared and characterized two urea complexes of Ni(II). One is $\mathrm{[Ni_2(OAc)_3(urea)(tmen)_2](OTf)}$ (**1**),[8] the first example of a dinuclear nickel complex with a monodentate carboxylate bridge, a feature that has recently emerged for transition metal carboxylates.[9] The other is a mononuclear analogue, $\mathrm{[Ni(OAc)(urea)_2(tmen)](OTf)}$ (**2**). Both contain coordinated urea and, as such, mimic a likely intermediate in the hydrolysis of the substrate. Complex **1**, in particular, having two Ni(II) ions and a single coordinated urea molecule, assembles several key components of the substrate-bound active site of the enzyme and represents a structural possibility not previously considered.

Compounds **1** and **2** were prepared from $\mathrm{[Ni_2(OH_2)(OAc)_4(tmen)_2]}$ (**3**), which contains a (μ-aqua)bis(μ-carboxylato)dinickel(II) core with terminal monodentate acetate anions hydrogen-bonded to the bridging water molecule.[10] When **3** was allowed to react with 1 equiv of trimethylsilyl triflate in methylene chloride solution, the green color turned to yellow-green. Subsequent addition of urea to saturation restored the original color.

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(8) Abbreviations: bpy, 2,2′-bipyridine; BIPhMe, 2,2′-bis(1-methylimidazolyl)phenylmethoxymethane; Hbimp, 2,6-bis[(bis((1-methyl-2-imidazolyl)methyl)amino)methyl]-4-methylphenol; HBPMP, 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol; $\mathrm{Me_3tacn}$, 1,4,7-trimethyl-1,4,7-triazacyclononane; $\mathrm{HBpz'_3}$, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; pz′, 3,5-diisopropylpyrazole; tmen, *N,N,N′N′*-tetramethylethylenediamine.

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Vapor diffusion of diethyl ether into the reaction mixture led first to the deposition of green blocks of **2** followed by blue-green needles of **1**. The nickel monomer was obtained in 15% yield by collecting the sample prior to the precipitation of **1**, whereas the nickel dimer was recrystallized in 55% yield after extraction into methylene chloride.[11]

X-ray crystal structure analyses of **1** and **2** revealed the presence of pseudo-octahedral nickel ions and coordinated urea.[12] The cation in **1**, depicted in Figure 1, consists of two Ni(II) ions bridged by one monodentate and two bidentate acetate ligands. The second oxygen atom O(2) of the monodentate bridging carboxylate ligand is bound to Ni(1). The terminal coordination sites of the dinickel core are completed by two tmen ligands and a monodentate urea molecule coordinated through its oxygen atom O(3) to Ni(2). Several other transition metal complexes with urea or alkyl-substituted urea ligands are known.[13] In most of these structures, urea coordinates through its oxygen atom, whereas the nitrogen-bonded linkage isomer has been characterized in only a few select cases.[14] Two Ni(II) complexes with urea coordinated through its oxygen atom have been crystallographically characterized.[15] The monodentate carboxylate bridge in **1** distorts the idealized octahedral geometry for Ni(1) because of the small 61.91(8)° O(1)–Ni(1)–O(2) angle in the chelate ring. Three weak hydrogen bonds between the amino groups of the bound urea and the oxygen atoms of triflate counterions are present in the crystal lattice, with an average N···O distance of 3.00(2) Å. The Ni···Ni distance is 3.4749(6) Å.

As shown in Figure 1, the mononuclear nickel complex **2** has an N_2O_4 donor set comprised of one chelating acetate, one tmen, and two urea ligands in a Δ,*cis*-configuration.[12] The Ni–N,O distances average 2.10(3) Å, values consistent with those found for **1** and derived from EXAFS studies of urease, where a composite Ni–N,O distance of 2.06 Å was reported.[4] For **1** and **2**, the average Ni–O(urea) distance is 2.07(2) Å, and the Ni–O–C angle, 134(9)°. The bond length is typical of alkyl-substituted ureas coordinated in this manner, whereas angles ranging from ~ 120–180° are known.[13] A Ni–O distance of 2.10(2) Å was reported for a $[Ni(urea)_6]^{2+}$ complex.[15] As in complex **1**, the chelating acetate in **2** distorts the nickel coordination geometry and the urea and triflate anions form hydrogen bonds in the lattice at an average N···O separation of 2.96(4) Å.

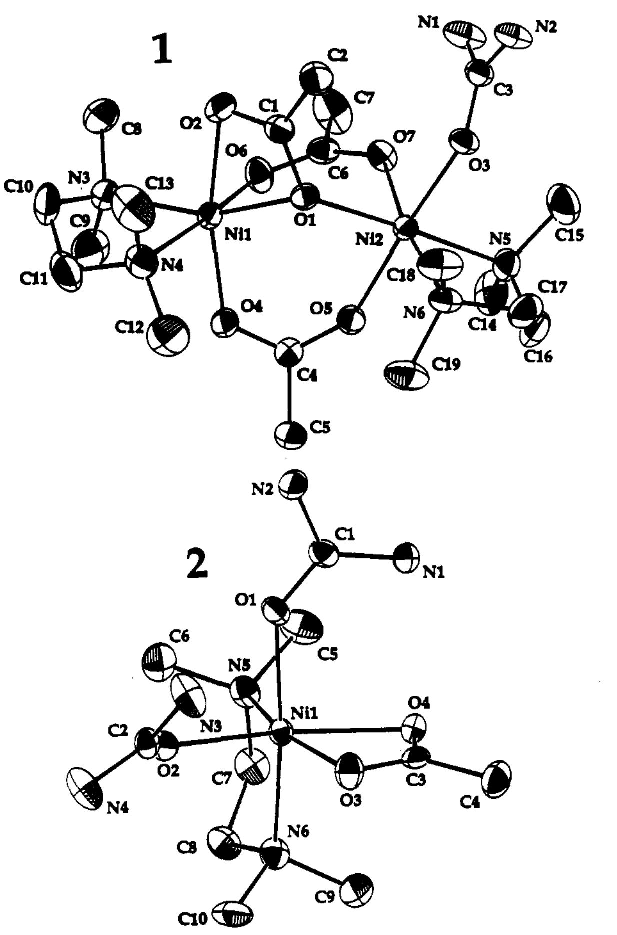

Figure 1. ORTEP drawings of the cations in $[Ni_2(OAc)_3(urea)(tmen)_2]$-(OTf) (**1**) (top) and $[Ni(OAc)(urea)_2(tmen)](OTf)$ (**2**) (bottom) showing 50% probability thermal ellipsoids and atom labels. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg) for **1** are as follows: Ni(1)···Ni(2), 3.4749(6); Ni(1)–O(1), 2.134(2); Ni(1)–O(2), 2.110(2); Ni(1)–O(4), 1.990(2); Ni(1)–O(6), 2.040(2); Ni(1)–N(3), 2.096(3); Ni(1)–N(4), 2.201(3); Ni(2)–O(1), 2.114(2); Ni(2)–O(3), 2.070(2); Ni(2)–O(5), 2.053(2); Ni(2)–O(7), 2.037(2), Ni(2)–N(5), 2.164(3); Ni(2)–N(6), 2.152(3); O(1)–Ni(1)–O(2), 61.91(8); O(1)–Ni(1)–O(4), 103.42(9); O(1)–Ni(1)–O(6), 96.23(9); O(1)–Ni(1)–N(3), 158.7(1); O(1)–Ni(1)–N(4), 92.4(1); O(2)–Ni(1)–O(4), 165.33(9); O(2)–Ni(1)–O(6), 91.9(1); O(2)–Ni(1)–N(3), 97.0(1); O(2)–Ni(1)–N(4), 92.0(1); O(4)–Ni(1)–O(6), 90.0(1); O(4)–Ni(1)–N(3), 97.6(1); O(4)–Ni(1)–N(4), 88.2(1); O(6)–Ni(1)–N(3), 87.1(1); O(6)–Ni(1)–N(4), 171.4(1); N(3)–Ni(1)–N(4), 84.7(1); O(1)–Ni(2)–O(3), 90.63(8); O(1)–Ni(2)–O(5), 90.35(8); O(1)–Ni(2)–O(7), 91.84(9); O(1)–Ni(2)–N(5), 177.4(1); O(1)–Ni(2)–N(6), 94.0(1); O(3)–Ni(2)–O(5), 175.60(9); O(3)–Ni(2)–O(7), 90.36(9); O(3)–Ni(2)–N(5), 91.6(1); O(3)–Ni(2)–N(6), 85.13(9); O(5)–Ni(2)–O(7), 93.90(9); O(5)–Ni(2)–N(5), 87.3(1); O(5)–Ni(2)–N(6), 90.5(1); O(7)–Ni(2)–N(5), 89.4(1); O(7)–Ni(2)–N(6), 172.6(1); N(5)–Ni(2)–N(6), 84.9(1). Selected distances (Å) and angles (deg) for **2** are as follows: Ni(1)–O(1), 2.097(3); Ni(1)–O(2), 2.055(3); Ni(1)–O(3), 2.095(4); Ni(1)–O(4), 2.146(3); Ni(1)–N(5), 2.093(4); Ni(1)–N(6), 2.142(4); O(1)–Ni(1)–O(2), 86.5(1); O(1)–Ni(1)–O(3), 92.5(1); O(1)–Ni(1)–O(4), 92.1(1); O(1)–Ni(1)–N(5), 90.2(2); O(1)–Ni(1)–N(6), 173.8(2); O(2)–Ni(1)–O(3), 98.4(1); O(2)–Ni(1)–O(4), 160.6(1); O(2)–Ni(1)–N(5), 97.2(1); O(2)–Ni(1)–N(6), 90.0(1); O(3)–Ni(1)–O(4), 62.3(1); O(3)–Ni(1)–N(5), 164.2(1); O(3)–Ni(1)–N(6), 93.1(2); O(4)–Ni(1)–N(5), 102.1(1); O(4)–Ni(1)–N(6), 92.8(1); N(5)–Ni(1)–N(6), 85.2(2). Numbers in parentheses are estimated standard deviations in the last digit.

The $\{M^{II}_2(O_2CR)_3\}^+$ core present in **1**, a schematic diagram of which is depicted in Figure 2, has been observed previously in manganese,[16] iron,[17] and copper chemistry.[18] Table I compares

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(11) Anal. Calcd for $Ni_2C_{20}H_{45}N_6O_{10}SF_3$ (**1**): C, 32.64; H, 6.16; N, 11.42. Found: C, 32.62; H, 6.25; N, 11.29. Electronic spectrum of **1** in methylene chloride: λ 392 nm (ε 49 cm^{-1} M^{-1}), 666 (23), 1125 (14). IR (KBr, cm^{-1}): 3456, 3407, 3345, 3273, 3219, 3017, 2981, 2908, 2846, 1669, 1620, 1556, 1468, 1426, 1347, 1291, 1247, 1166, 1027, 957, 805, 669, 638, 570, 541, 518, 496, 468, 446. Anal. Calcd for $NiC_{11}H_{27}N_6O_7SF_3$ (**2**): C, 26.26; H, 5.41; N, 16.70. Found: C, 26.49; H, 5.43; N, 16.67. Electronic spectrum of **2** in methanol: λ 391 nm (ε 24 cm^{-1} M^{-1}), 660 (12), 1080 (8). IR (KBr, cm^{-1}): 3472, 3345, 3277, 3214, 2989, 2909, 2856, 2803, 1669, 1620, 1544, 1470, 1279, 1254, 1165, 1031, 953, 805, 778, 682, 639, 611, 584, 529.

(12) Crystal data for $[Ni_2(OAc)_3(urea)(tmen)_2](OTf)$ (**1**): M_r = 736.05, triclinic, $P\bar{1}$, a = 11.509(1) Å, b = 15.2435(9) Å, c = 9.614(1) Å, α = 96.086(7)°, β = 96.473(9)°, γ = 101.655(6)°, V = 1627.0(3) Å^3, Z = 2. For 4253 unique observed reflections collected at −78 °C with $F^2 > 3\sigma(F^2)$, R = 0.033 and R_w = 0.038. Crystal data for $[Ni(OAc)(urea)_2(tmen)](OTf)$(**2**): M_r = 503.12, orthorhombic, $P2_12_12_1$, a = 11.584(2) Å, b = 22.725(1) Å, c = 7.9251(7) Å, V = 2086.3(3) Å^3, Z = 4. For 1844 unique observed reflections collected at −71 °C with $F^2 > 3\sigma(F^2)$, R = 0.031 and R_w = 0.037. The choice of enantiomer was made by comparison of the R_w values obtained following refinement of both hands.

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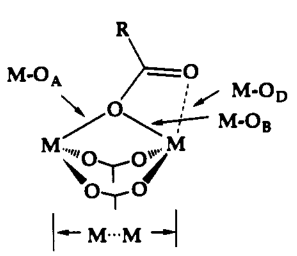

Figure 2. Structural parameters for monodentate-bridged carboxylate complexes having the $\{M^{II}_2(O_2CR)_3\}^+$ core.

Table I. Structural (Å) and Magnetic Exchange Parameters (cm^{-1}) for Monodentate-Bridged Carboxylate $\{M^{II}_2(O_2CR)_3\}^+$ Units[a]

complex[b]	M–O$_A$	M–O$_B$	M–O$_D$	M···M	J[c]
1	2.114(2)	2.134(2)	2.110(2)	3.4749(6)	–0.9
$[Mn_2(OBz)_3(pz')_2(HBpz'_3)]$[d]	2.264(8)	2.349(6)	2.235(6)	3.753(2)	*e*
$[Fe_2(O_2CH)_4(BIPhMe)_2]$[f]	2.172(2)	2.113(2)	2.787(3)	3.5736(8)	~0
$[Cu_2(OAc)_3(bpy)_2]^+$[g]	2.169(2)	1.977(2)	2.716(2)	3.392(1)	3.6

[a] Values in parentheses are estimated standard deviations in the last digits. [b] The labels of the different structural parameters are depicted in Figure 2 and are identical to those employed in ref 9. [c] The spin Hamiltonian had the form $-2JS_1 \cdot S_2$. [d] Reference 16. Pz′ is the 3,5-diisopropyl-substituted pyrazole. [e] A weak antiferromagnetic exchange interaction was reported. [f] Reference 17. [g] Reference 18.-

structural parameters of this unit among these various complexes, from which it is apparent that the three metal–oxygen bond distances for the monodentate bridging acetate ligand in **1** are almost the same, in contrast to those found for the iron and copper cases, where M–O$_D$ is significantly longer. A similar monodentate carboxylate ligand bridges the manganese and calcium sites in the protein concanavalin A.[19] In the dinuclear iron center of the R2 protein of ribonucleotide reductase, glutamate 238 shifts from a bridging to a terminal coordination mode upon oxidation of the diiron center.[20] These various modes of carboxylate coordination have been analyzed previously for a large set of coordination complexes,[9a] and the ability of polynuclear carboxylate complexes to adopt a variety of structural isomers has been termed the "carboxylate shift".[9b] Such a shift can be considered formally to have occurred in the synthesis of **1** from **3**.

The optical and IR spectroscopic properties of **1** and **2** are consistent with pseudo-octahedral coordination at nickel and oxygen-bonded urea linkage isomers, as revealed by the X-ray investigations. Absorption bands at 1125 and 1080, 666 and 660, and 392 and 391 nm for **1** and **2**, respectively, are assigned to the three spin-allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ for an octahedral d^8 ion.[21] From these values and the appropriate Tanabe–Sugano diagram may be calculated octahedral crystal field splitting parameters of 8900 and 9300 cm^{-1} and Racah parameters of approximately 810 and 770 cm^{-1} for **1** and **2**, respectively. A shoulder located at approximately 785 nm in both complexes is tentatively assigned to the spin-forbidden transition $^3A_{2g}(F) \rightarrow {}^1E_{1g}(D)$. The absorption bands of **1** and **2** may be compared with those of urease at 1060, 745, and 407 nm.[3] The IR spectra of the two molecules contain several features between 1670 and 1540 cm^{-1} arising from $\nu_{as}(CO_2^-)$ of the bridging acetate ligands and the carbonyl stretching frequency of bound urea. When urea coordinates through its nitrogen atom, the C═O stretch shifts to wavelengths greater than 1700 cm^{-1} whereas, in the O-bonded linkage isomer, the bond is weakened and $\nu_{CO} < 1700$ cm^{-1}.[13,14]

Solid-state variable-temperature magnetic susceptibility studies of **1** measured at 9 kG revealed weak antiferromagnetic coupling between the two nickel ions. The χT value decreased from 2.7 cm^3 mol^{-1} K at 300 K to 1.1 cm^3 mol^{-1} K at 2.5 K. A least-squares fit of the data to the standard isotropic exchange expression for two equivalent $S = 1$ ions based on the spin Hamiltonian $-2JS_1 \cdot S_2$ gave $J = -0.9$ cm^{-1} and $g = 2.38$.[22] The analogous $\{M^{II}_2(O_2CR)_3\}^+$ complexes, M = Fe(II) and Cu(II), are also only weakly exchange-coupled with J values on the order of a few wavenumbers (Table I). A ferromagnetic exchange interaction, however, was reported for $[Cu_2(OAc)_3(bpy)_2]^+$.[18] The magnetic properties of several other Ni(II) dimers with biomimetic ligands have been described, including **3**,[10] a (μ-hydroxo)bis(μ-carboxylato)dinickel complex $[Ni_2(OH)(OAc)_2(Me_3tacn)_2]^+$,[23] and two ($\mu$-phenoxo)bis($\mu$-carboxylato)dinickel complexes, $[Ni_2(OAc)_2(bimp)]^+$ and $[Ni_2(OAc)_2(BPMP)]^+$.[24] These complexes are all weakly antiferromagnetically exchange-coupled, the largest $|J|$ being 5 cm^{-1} in $[Ni_2(OH)(OAc)_2(Me_3tacn)_2]^+$. Although a zero-field splitting term D for the nickel ions could have been included in the analysis of the data for **1**, powder magnetic studies are a poor means of determining this parameter and, in any case, the exchange coupling constant J is relatively insensitive to its magnitude.[22,25] A g value of 2.39 for **1** is reasonable, falling near the range of 2.1–2.3 reported for octahedral Ni(II).[26] A very similar g value of 2.40 was also derived for **2**, which exhibited Curie-like behavior from 5 to 300 K with a Curie constant of 1.44 cm^3 mol^{-1} K.[27]

In conclusion, the coordination environment and optical properties of the nickel ions in **1** and **2** are consistent with those reported for urease. The complexes provide potentially useful structural, magnetic, and spectroscopic models for a likely intermediate in the catalytic mechanism.[14b,28] In particular, they might be helpful in further attempts to distinguish between binuclear or mononuclear nickel centers in the enzyme. The binding of urea to nickel in **1** and **2** should facilitate future investigations of the chemistry of this substrate, including its additional activation through coordination to the second nickel ion as well as reactions with free or bound nucleophiles.

Acknowledgment. This work was supported by the grants from the National Institutes of Health and the National Science Foundation. H.E.W. also thanks the UROP Office of M.I.T. for funding, and K.L.T. acknowledges the National Science Foundation for a predoctoral fellowship.

Supplementary Material Available: Tables of atomic positional and thermal parameters, complete listings of bond distances and angles, and plots of the variable-temperature susceptibility data and theoretical treatments described in the text for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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