# $[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]ClO_4 \cdot C_4H_{10}O$: Synthesis and Characterization of an Asymmetric Dinuclear Nickel(II) Complex Showing Unusual Coordination Behavior with Relevance to the Active Site of Urease

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*Received March 31, 1995*

The synthesis of the novel asymmetric ligand 1-[bis(2-pyridylmethyl)amino]-3-[2-(2-pyridyl)ethoxy]-2-hydroxypropane (ppepOH) is reported. The ligand is suitable to form asymmetric dinuclear complexes with various transition metal ions. As an example, the synthesis and X-ray structure analysis of the dinickel(II) complex $[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]ClO_4 \cdot C_4H_{10}O$ are described. The complex crystallizes in the monoclinic space group $P2_1/n$ with the following unit cell parameters: $a = 13.704(10)$ Å, $b = 14.849(10)$ Å, $c = 22.697(14)$ Å, $\beta = 96.80(5)°$, $Z = 4$. The nickel(II) ions are bridged by the alkoxy donor of the ligand and two benzoate anions. The hexadentate ligand leaves a free coordination site at one of the nickel(II) ions, which is occupied by a monodentate coordinated acetic acid molecule. The coordination of the neutral acetic acid molecule is selectively stabilized by a strong intramolecular hydrogen bond of the acidic proton to the $\mu$-alkoxo bridge of the dinuclear complex. The asymmetric complex was prepared in order to mimic the substrate uptake in the dinuclear active site of ureases. The magnetic and spectroscopic properties of the complex were determined and related to those of the urease enzymes.

## Introduction

Urease (urea amidohydrolase, EC 3.5.1.5) catalyzes the hydrolysis of urea. The active site of the urease from jack beans contains two nickel(II) ions per subunit. The biophysical and biochemical properties of nickel-containing ureases from plants and microbial organisms have been reviewed extensively.[1] Zerner and co-workers suggested a catalytic mechanism in which both nickel(II) ions are involved in the hydrolysis of urea in a specific manner. In the key step of the proposed mechanism, a coordinated hydroxide ion attacks the carbonyl C atom of the urea substrate which is coordinated to the opposite nickel(II) ion in the dinuclear active site.[2] The recently determined structure of the microbial urease from *Klebsiella aerogenes* provides clear evidence for a dinuclear active site in which the two nickel ions are 3.5 Å apart.[3] The hydrolysis mechanism and the proposed structure of the urease active site resemble the active centers of other hydrolytically active enzymes, namely the dizinc substructure unit of phospholipase C from *Bacillus cereus*[4] and the dinuclear active sites of the purple acid phosphatases.[5,6]

Attempting to model the structure and reactivity of such hydrolytically active dinuclear sites,[7] we have synthesized a series of asymmetric complexes. The structure of one of them, namely of the dinuclear nickel(II) complex containing the novel ligand ppepOH, will be presented in this paper preceding our comparative studies.[8]

## Experimental Section

**Preparations.** Starting materials were purchased from commercial sources and were used without further purification. Solvents were dried using standard laboratory techniques. Melting points were determined by using a Mettler melting point apparatus (FP 51) and are uncorrected. Elemental analyses were performed on a Hewlett Packard Scientific Model 185 instrument. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker WH300 and WH90 spectrometers. $^1H$ chemical shifts of the compounds are related to TMS as an internal standard for the deuterated solvent. The visible spectrum was recorded on a Shimadzu UV 3100 PC spectrophotometer using a 0.01 M solution of the compound **4** (MeOH, 1 cm optical pathway).

The asymmetric ligand ppepOH was prepared in a three-step synthesis following the reaction scheme represented in Figure 1.

**(a) 1-Amino-3-[2-(2-pyridyl)ethoxy]-2-hydroxypropane (1).** A 4.0 g sample of NaH (0.166 mol) was suspended in dry THF (80 mL). 2-(2-Pyridyl)ethanol (20.0 g, 0.162 mol) was added dropwise to the cooled suspension. Afterward, 45.0 g of epichlorohydrine (0.48 mol) was added to the ice-cold solution. The solution was warmed slowly to room temperature and finally refluxed for 2 h. The solvent and the excess of epichlorohydrine were removed under reduced pressure. The residue was treated cautiously with 2−3 mL of MeOH and taken up with 40 mL of water. The suspension was extracted with $CHCl_3$, and the combined organic extracts were dried over $CaCl_2$. The solvent was

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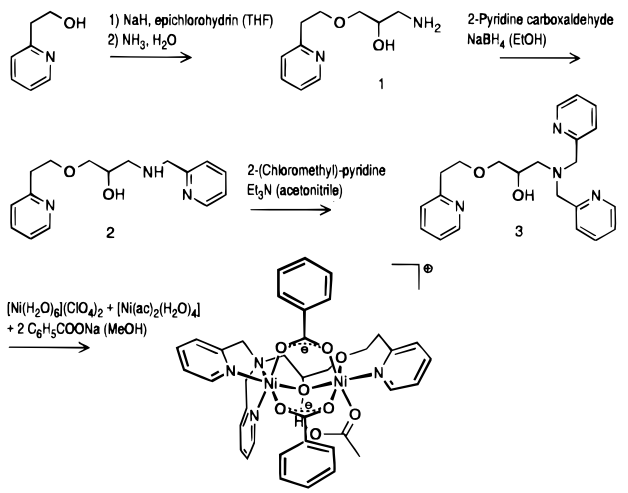


**Figure 1.** Reaction scheme for the synthesis of the $[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]^+$ cation using the asymmetric, dinucleating ligand ppepOH (**3**).

vacuum-evaporated, and the residue was distilled under reduced pressure (bp 100 °C, 0.1 Torr). The yellow oil was poured into 40 mL of concentrated ammonia immediately after the distillation. The solution was stirred overnight, and the solvent was removed with an rotary evaporator. Distillation under reduced pressure afforded **1** as a yellow, highly viscous oil (fraction at bp 85−115 °C, 0.1 Torr). Yield: 5.22 g (26.6 mmol, 16.4%). Anal. Calcd for $C_{10}H_{16}N_2O_2$ (**1**): C, 61.22; H, 8.16; N, 14.28. Found: C, 62.67; H, 8.26; N, 13.74. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 8.53−8.50 (m, 1H), 7.64−7.56 (m, 1H), 7.21−7.10 (m, 2H), 3.87 (m, 2H), 3.71 (m, 1H), 3.48 (m, 2H), 3.06 (m, 2H), 2.70 (m, 2H).

**(b) 1-[(2-Pyridylmethyl)amino]-3-[2-(2-pyridyl)ethoxy]-2-hydroxypropane (2).** A 3.06 g sample of **1** (15.6 mmol) was dissolved in 20 mL of EtOH. At room temperature, 1.84 g of pyridine-2-carbaldehyde (17.1 mmol) was added to the reaction vessel. The solution was heated to 50 °C and stirred for 20 min. The resulting Schiff's base was reduced with $NaBH_4$, and the reaction product was purified according to the published procedure.[7a] Yield: 3.35 g (11.7 mmol, 74.7%). Anal. Calcd for $C_{16}H_{20}N_3O_2$ (**2**): C, 66.90; H, 7.32; N, 14.63. Found: C, 65.59; H, 7.06; N, 13.87. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 8.53−8.49 (m, 2H), 7.67−7.52 (m, 2H), 7.19−7.07 (m, 4H), 3.92 (s, 2H), 3.87 (m, 2H), 3.56−3.43 (m, 3H), 3.05 (m, 2H), 2.70 (m, 2H). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ (pyridyl-A,B: 159.4, 158.8 $C_{ar}$-q, 149.2, 148.6, 136.5, 136.0, 123.3, 122.6, 121.8, 120.9 $C_{ar}$−H), 73.3, 69.9 O−$CH_2$, 68.8 HO−$C$−H, 54.6 N−$CH_2$−CHOH, 51.6 $C_{ar}$−$CH_2$−N, 37.8 $C_{ar}$−$CH_2$−$CH_2$.

**(c) 1-[Bis(2-pyridylmethyl)amino]-3-[2-(2-pyridyl)ethoxy]-2-hydroxypropane (3).** A 1.05 g sample of 2-(chloromethyl)pyridine hydrochloride (6.4 mmol) was suspended in 10 mL of dry $CH_3CN$. After the suspension had been cooled to 0 °C, a cooled solution of 0.65 g of triethylamine in 5 mL of $CH_3CN$ was added. The filtrate of the suspension was directly added to a solution of 1.66 g of **2** (5.8 mmol) and 0.62 g of triethylamine in 20 mL of $CH_3CN$. The solution was stirred for 3 days at room temperature and for a further 5 h at 40°C. The volume of the solution was reduced to half of the original amount, and the cooled solution was filtered. The filtrate was mixed with a cooled saturated solution of potassium carbonate and extracted three times with 10 mL portions of $CHCl_3$. The organic extract was dried over magnesium sulfate. The solvent was removed with a rotary evaporator, and the residue was dried under high vacuum. Yield: 1.52 g (4.0 mmol, 70.8%). Anal. Calcd for $C_{22}H_{26}N_4O_2$ (**3**): C, 69.84; H, 6.80; N, 14.81. Found: C, 68.71; H, 6.38; N, 13.97. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 8.53−8.48 (m, 3H), 7.61−7.52 (m, 3H), 7.32−7.29 (m, 3H?, $CDCl_3$ 7.24), 7.22−7.07 (m, 3H), 3.95 (m, 1H), 3.92 (s, 2H), 3.89 (s, 2H), 3.83 (t, 2H), 3.44 (d, 2H), 3.03 (t, 2H), 2.73 (m, 2H). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ (pyridyl-A,B: 159.0, 158.7 $C_{ar}$-q, 148.9, 148.7, 136.2, 135.9, 123.3, 122.5, 121.2, 121.0 $C_{ar}$−H); 73.1, 70.3 O−$CH_2$, 67.9 HO−$C$−H, 60.3 $C_{ar}$−$CH_2$−N, 57.9 N−$CH_2$−CHOH, 38.2 $C_{ar}$−$CH_2$−$CH_2$.

**$[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]ClO_4\cdot C_4H_{10}O$ (4).** A 110 mg sample of $[Ni(H_2O)_6](ClO_4)_2$, 75 mg of $[Ni(CH_3COO)_2(H_2O)_4]$ (0.3 mmol each), and 84.2 mg of sodium benzoate (0.6 mmol) were dissolved in 2 mL of hot MeOH. To the resulting solution was added 113.4 mg of **4** (0.3 mmol). The solution was refluxed until the ligand had completely dissolved. The crude complex was precipitated by adding a large excess of diethyl ether to the cooled solution. Blue-green crystals suitable for X-ray crystallographic structure determination were obtained after dissolving the compound in a minimum amount of methanol followed by slow vapor diffusion of diethyl ether into the solution. Yield: 35 mg (0.036 mmol, 12%). Anal. Calcd for $Ni_2C_{42}H_{49}N_4O_{13}Cl$ (**4**): C, 51.96; H, 5.08; N, 5.77. Found: C, 51.29; H, 4.95; N, 5.87. Mp: 193 °C. Electronic spectrum (MeOH): $\lambda$ 390 nm, sh ($\epsilon \approx 25$ $M^{-1}$ $cm^{-1}$), 649 (17.5), 770 (13.2), 973 (26.8). *Caution*! Perchlorate salts are potentially explosive and should only be handled in small quantities.

**Table 1.** Crystallographic and Refinement Data for $[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]ClO_4\cdot C_4H_{10}O$

| | |
|---|---|
| formula | $Ni_2C_{42}H_{49}N_4O_{13}Cl$ |
| MW | 970.72 |
| cryst dimens, mm | 0.18 × 0.14 × 0.18 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.710 73) |
| temp, K | 170(2) |
| space group | $P2_1/n$ |
| $a$, Å | 13.704(10) |
| $b$, Å | 14.849(10) |
| $c$, Å | 22.697(14) |
| $\beta$, deg | 96.80(5) |
| $V$, Å$^3$ | 4586 |
| $Z$ | 4 |
| $D_{calc}$, g/cm$^3$ | 1.406 |
| $\mu$, cm$^{-1}$ | 9.5 |
| trasm factor | 0.81−0.82 |
| index ranges | $-6 \le h \le 17$, $-19 \le k \le 18$, $-29 \le l \le 28$ |
| scan type | $\omega$ scan |
| $\theta$ range, deg | 2.60−27.07 |
| no. of reflcns measd | 10 288 |
| no. of reflcns used | 9882 |
| no. of variables used | 556 |
| $R$[6486, $F_o > 4\sigma(F_o)$] | $R_1{}^a = 0.0481$, $R_{2w}{}^b = 0.1230$ |
| $R$(all data) | $R_1{}^a = 0.0810$, $R_{2w}{}^b = 0.1352$ |
| GOF on $F^2$ | 0.924 |

$^a$ $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $R_{2w} = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + 0.0798P^2]$. $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

**X-ray Crystallography.** Crystal data as well as details of data collection and refinement are summarized in Table 1. A single crystal of **4** was mounted on a glass fiber and placed on a Siemens R3 diffractometer (Mo K$\alpha$, $\lambda$ = 0.710 73 Å, graphite monochromator). Cell constants and orientation matrices were determined using least-squares refinements of the angular coordinates of at least 20 accurately centered reflections. Intensity data were collected by using the $\omega$-scan technique to a maximum $2\theta$ value of 54°. As a check of crystal stability, two representative reflections were measured every 100 data points. No significant trend in their intensities was observed during the course of data acquisition. The intensity data were corrected for Lorentz and polarization factors, and an empirical absorption correction based on reflection measurements at different azimuthal angles was applied to the raw data. The structure was solvled by using the Patterson method (SHELXTL PLUS program package). Atomic scattering factors were taken from ref 9. The positions and anisotropic thermal parameters of all non-H atoms were refined against $F_o^2$ using full-matrix least-squares techniques (SHELXL-93 program[10]). Hydrogen atoms were included in calculated positions with their bonding distances and thermal parameters depending on the pivot atom.[11] The unit cell atomic coordinates of the cation of **4** and the equivalent thermal parameters are given in Table 2.

(9) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.
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(11) H−C($sp^2$): 0.95 Å, $U_H = 1.2U_{eq}$(C). H−C($sp^3$, $CH_2$ group): 0.99 Å, $U_H = 1.2U_{eq}$(C). H−C($sp^3$, $CH_3$ group): 0.98 Å, $U_H = 1.5U_{eq}$(C). H−N($sp^2$): 0.88 Å, $U_H = 1.2U_{eq}$(N). H−O($sp^3$): 0.84 Å, $U_H = 1.5U_{eq}$(O). The $U_H$ values of H atoms belonging to solvent molecules were fixed to $U_H = 0.080$ Å$^2$.

**Table 2.** Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2$ $\times$ $10^3$) for Non-Hydrogen Atoms in the Cation of **4**

| atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Ni(1) | 2942(1) | 341(1) | 1410(1) | 29(1) |
| Ni(2) | 1406(1) | 534(1) | 2468(1) | 29(1) |
| O(1) | 1875(2) | 1102(1) | 1735(1) | 29(1) |
| C(1) | 2155(2) | 2024(2) | 1801(2) | 34(1) |
| C(2) | 3270(2) | 2088(2) | 1891(2) | 33(1) |
| C(3) | 1700(3) | 2444(2) | 2313(2) | 40(1) |
| O(2) | 1829(2) | 1804(2) | 2792(1) | 37(1) |
| C(4) | 1448(3) | 2098(3) | 3322(2) | 51(1) |
| C(5) | 1710(3) | 1394(3) | 3789(2) | 56(1) |
| N(1) | 3679(2) | 1574(2) | 1417(1) | 33(1) |
| C(10) | 4742(2) | 1339(3) | 1562(2) | 38(1) |
| N(11) | 4228(2) | −71(2) | 1082(1) | 33(1) |
| C(11) | 4968(2) | 528(2) | 1204(2) | 34(1) |
| C(12) | 5883(3) | 383(3) | 1023(2) | 45(1) |
| C(13) | 6044(3) | −384(3) | 714(2) | 50(1) |
| C(14) | 5293(3) | −1000(3) | 591(2) | 47(1) |
| C(15) | 4396(3) | −814(2) | 774(2) | 38(1) |
| C(20) | 3490(3) | 2010(3) | 828(2) | 39(1) |
| N(21) | 2348(2) | 776(2) | 574(1) | 36(1) |
| C(21) | 2644(3) | 1599(3) | 432(2) | 38(1) |
| C(22) | 2231(3) | 2039(3) | −80(2) | 54(1) |
| C(23) | 1490(3) | 1615(3) | −441(2) | 62(1) |
| C(24) | 1186(3) | 776(3) | −296(2) | 57(1) |
| C(25) | 1632(3) | 370(3) | 213(2) | 45(1) |
| N(31) | 799(2) | 188(2) | 3226(1) | 36(1) |
| C(31) | 1070(3) | 570(3) | 3757(2) | 46(1) |
| C(32) | 788(4) | 187(4) | 4272(2) | 76(2) |
| C(33) | 204(4) | −566(3) | 4242(2) | 73(2) |
| C(34) | −119(3) | −925(3) | 3692(2) | 55(1) |
| C(35) | 204(3) | −538(2) | 3201(2) | 41(1) |
| O(61) | −26(2) | 986(2) | 2154(1) | 45(1) |
| O(62) | 201(2) | 972(2) | 1185(1) | 57(1) |
| C(60) | −340(3) | 988(3) | 1632(2) | 54(1) |
| C(61) | −1442(3) | 1004(4) | 1446(2) | 83(2) |
| O(41) | 3709(2) | 1(2) | 2217(1) | 36(1) |
| O(42) | 2657(2) | 39(2) | 2893(1) | 39(1) |
| C(40) | 3467(2) | −136(2) | 2724(1) | 28(1) |
| C(41) | 4215(3) | −571(2) | 3178(2) | 35(1) |
| C(42) | 3951(3) | −813(3) | 3727(2) | 47(1) |
| C(43) | 4611(4) | −1263(4) | 4131(2) | 67(1) |
| C(44) | 5524(4) | −1480(4) | 3995(2) | 88(2) |
| C(45) | 5801(3) | −1220(4) | 3452(2) | 73(2) |
| C(46) | 5143(3) | −774(3) | 3043(2) | 49(1) |
| O(51) | 2132(2) | −794(2) | 1356(1) | 36(1) |
| O(52) | 1078(2) | −645(2) | 2035(1) | 38(1) |
| C(50) | 1425(2) | −1050(2) | 1616(1) | 30(1) |
| C(51) | 942(2) | −1919(2) | 1414(1) | 31(1) |
| C(52) | 271(3) | −2325(2) | 1743(2) | 37(1) |
| C(53) | −154(3) | −3147(3) | 1563(2) | 49(1) |
| C(54) | 90(3) | −3569(3) | 1059(2) | 50(1) |
| C(55) | 739(3) | −3160(3) | 733(2) | 47(1) |
| C(56) | 1173(3) | −2343(2) | 905(2) | 39(1) |

**Magnetic Susceptibility Measurements.** Magnetic susceptibility measurements were performed on a Faraday-type magnetometer consisting of a CAHN D-200 microbalance, a Leyboldt Heraeus VNK 300 helium flux cryostat, and a Bruker BE 25 magnet connected with a Bruker B-Mn 200/60 power supply in the temperature range 7.1−277 K. Experimental susceptibility data were corrected for the underlying diamagnetism. Magnetic moments were obtained from $\mu_{eff} = 2.828(\chi T)^{1/2}$.

## Results and Discussion

**Description of the X-ray Structure.** The X-ray crystal structure of the dinuclear complex **4** shows the presence of a monodentate coordinated acetic acid molecule, which was unexpected if one considers the large excess of methanol used for the recrystallization of the compound.

In the asymmetric cation of **4** both nickel ions are bridged by the benzoate anions and additionally by the alkoxo donor function of the ligand **3**. The hexadentate ligand leaves a free coordination site at the less highly coordinated Ni(2), which is occupied by the acetic acid molecule (compare Figure 2). The assumption of a neutral acetic acid ligand simply follows from counting the electrostatic charges but may also be verified structurally. The X-ray structure analysis shows uniform C−O bond lengths for the bridging anionic benzoate ligands (average value 1.25 Å). This is consistent with a completely sp$^2$-hybridized carboxylate function with equal bond lengths due to the mesomeric structures. In contrast with this, the C−O bond lengths of the monodentate coordinated neutral acetic acid molecule differ significantly. The C−O bond length to the coordinated oxygen atom C(60)−O(61) is quite short (1.212(5) Å) while the distance to the non-coordinated oxygen atom C(60)−O(62) is rather long (1.326(5) Å). The bonding situation of the acetic acid molecule allows for assuming a double-bonded *coordinated* carbonyl group C(60)−O(61) and a C−O single bond C(60)−O(62). The sp$^3$-hybridized oxygen atom O(62) is bound to the acidic proton which forms a strong hydrogen bridge to the alkoxo function O(1) of the ligand (nonbonding distance O(62)···O(1) 2.486(5) Å). Furthermore, the bond lengths of the monodentate acetic acid molecule completely agree with the corresponding values found in the X-ray structure of [Ni(CH$_3$COOH)$_6$]$^{2+}$.[12]

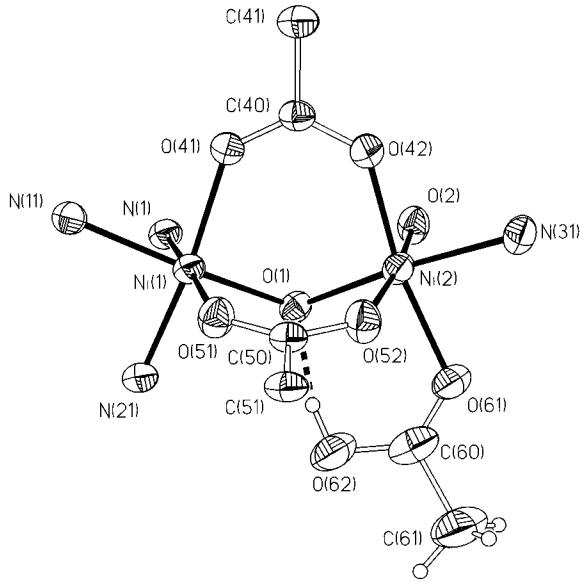


**Figure 2.** Structure of the central coordination unit of the $[Ni_2(ppepO)(C_6H_5COO)_2(CH_3COOH)]^+$ cation. The ligand C atoms and the aromatic rings of the bridging benzoate anions are omitted for clarity. Selected distances (Å) and angle (deg): Ni(1)···Ni(2), 3.387(3); O(62)···O(1), 2.486(5); Ni(1)−O(1), 2.052(3); Ni(1)−O(41), 2.064(3); Ni(1)−O(51), 2.013(3); Ni(1)−N(1), 2.089(3); Ni(1)−N(11), 2.086(3); Ni(1)−N(21), 2.077(3); Ni(2)−O(1), 2.036(2); Ni(2)−O(2), 2.082(3); Ni(2)−O(61), 2.116(3); Ni(2)−O(42), 2.005(3); Ni(2)−O(52), 2.032(3); Ni(2)−N(31), 2.063(3); O(61)−C(60), 1.212(5); O(62)−C(60), 1.326(5); O(41)−C(40), 1.251(4); O(42)−C(40), 1.244(4); O(51)−C(50), 1.252(4); O(52)−C(50), 1.266(4); Ni(1)−O(1)−Ni(2), 111.9(1).

**Electronic Absorption Properties.** The nickel ions of the dinuclear center of **4** are coordinated differently (Ni(1): 3N, 3O donor environment. Ni(2): 1N, 5O donor environment).[13] The electronic spectrum therefore displays broad and nonsymmetric absorption bands with maxima at 390, 649, and 973 nm. These bands may be assigned to the spin-allowed transitions from the $^3A_{2g}(F)$ ground state of an octahedrally coordinated d$^8$ ion to the next higher excited triplet states ($^3T_{1g}(P)$, $^3T_{1g}(F)$,

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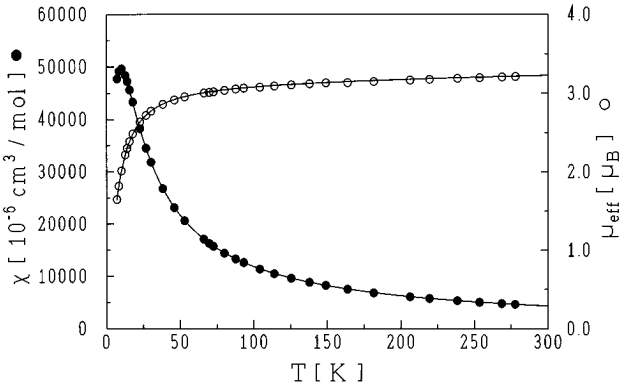


**Figure 3.** Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of complex **4**. The solid lines represent the best-fit calculated curves corresponding to eq 1 using the parameters g = 2.22(1), $J = -3.5(1)$ cm$^{-1}$, $x_p = 1.7(1)$%, and $D = 1.0(2)$ cm$^{-1}$.

and $^3T_{2g}$(F)). The weak absorption band at 770 nm may arise from spin−orbit coupling between the $^3T_{1g}$(F) and $^1E_{1g}$(D) states, which leads to a splitting of the $^3A_{2g}$(F) → $^3T_{1g}$(F) transition.[14] The electronic absorption spectrum of the jack bean enzyme displays absorption bands at 407, 745, and 1060 nm, which would suggest octahedrally coordinated nickel(II) ions within a donor environment that is particularly rich in oxygen.[15] The significant blue shift of the absorption bands of **4**, compared to the values of urease, is certainly a result of the stronger ligand field produced by the pyridine N-donors. However, the spectral properties of the enzyme might just as well indicate nickel(II) ions within a trigonal bipyramidal N,O-donor environment.[16] Biomimetic dinuclear complexes with at least one Ni(II) ion in a trigonal bipyramidal coordination sphere[17] do not only show similar band positions but even give a better correspondence between the extinction coefficents of the model compounds and the enzyme.[8]

**Magnetic Susceptibility Measurements.** The results of the magnetic susceptibility measurements on a powdered sample of **4** are consistent with a weak antiferromagnetic coupling in the dimer: The effective magnetic moment $\mu_{eff}$ per nickel changes gradually from 3.21 $\mu_B$ at 277 K to 1.64 $\mu_B$ at 7.1 K. A pronounced maximum in $\chi$ vs temperature at 10.2 K was observed (compare Figure 3). The experimental data were fitted to eq 1 on the basis of the isotropic spin-Hamiltonian $\hat{H} =$

$$\chi = (1 - x_p)\chi_{Dim} + 2\chi_{Mono} + 2N\alpha \qquad (1)$$

$-2J\hat{S}_1\cdot\hat{S}_2$ with $S_1 = S_2 = 1$ without zero-field splitting for the dimer,[18,19] where the susceptibility is expressed per nickel dimer. Here $x_p$ is the molar fraction of paramagnetic impurity, $N\alpha$ refers to the temperature-independent paramagnetism ($200 \times 10^{-6}$ cm$^3$/mol per Ni(II)), and $D$ describes the zero-field splitting of the monomeric impurities. The least-squares fit, which was of a very good quality, resulted in the following values: $g = 2.22$-(1), $J = -3.5(1)$ cm$^{-1}$, $x_p = 1.7(1)$%, and $D = 1.0(2)$ cm$^{-1}$. The obtained $J$ value is in good agreement with those observed for similar oxygen-bridged Ni(II) compounds.[20]

Asymmetric coordination of the metal ions appears to be a necessary condition for the catalytic function of dinuclear hydrolytically active enzymes since most of the well-characterized dinuclear active sites provide different coordination environments for each of the metal ions. Only very few ligand systems are suitable for modeling such asymmetric biosites.[21] The ligand ppepOH in the structure of **4** represents the first example of our endeavors to mimic, *in a predictable manner*, the differentiated functions of the metal ions in the active site of urease. One key step of a catalytic cycle comprises the selective recognition and the bonding of the substrate molecule. The bonding of the acetic acid molecule in the structure of **4** is surprising at first, since the compound was recrystallized several times from methanol and an exchange with the solvent could in fact be expected. The dinuclear center of **4** may give an answer to the question as to how, in the dinuclear active site of urease, the coordination of a neutral, weakly coordinated substrate such as urea may compete with the solvent molecules in the presence of a large excess of the protic solvent.

From a more general point of view, the ($\mu$-oxo)bis($\mu$-carboxylato)dimetal unit providing an additional free coordination site may be regarded as a receptor for those substrates which are capable of forming stable five- or six-membered rings by coordination to the metal ion and formation of the hydrogen bridge to the $\mu$-oxo bridge.

**Acknowledgment.** D.V. thanks the Graduiertenfoerderung NRW for a scholarship. We thank Thomas Johnson for carefully reviewing the manuscript.

**Supporting Information Available:** Tables listing crystal data and structure refinement details, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for the X-ray structure analysis of **4** and an ORTEP view of the cation of **4** with complete atomic labeling (16 pages). Ordering information is given on any current masthead page.

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(13) The crystal structure of the microbial urease from *Klebsiella aerogenes* shows the nickel(II) ions to be bridged by the carboxylate function of a carbamylated lysine residue. The coordination of the nickel ions is described as pseudotetrahedral (Ni(1): 2N, 2O) and trigonal bipyramidal (Ni(2): 2N, 3O); see ref 3. The low coordination numbers of both nickel ions contrast in some ways with the predictions of earlier spectroscopic and magnetochemical studies where the metal ions have been described to be five- or six-coordinated within a mixed nitrogen−oxygen donor environment: (a) Wang, S.; Lee, M. H.; Hausinger, R. P.; Clark, P. A.; Wilcox, D. E.; Scott, R. A. *Inorg. Chem.* **1994**, *33*, 1589. (b) Day, E. P.; Peterson, J.; Sendova, M. S.; Todd, M. J.; Hausinger, R. P. *Inorg. Chem.* **1993**, *32*, 634. (c) Clark, P. A.; Wilcox, D. E. *Inorg. Chem.* **1989**, *28*, 1326. (d) Clark, P. A.; Wilcox, D. E.; Scott, R. A. *Inorg. Chem.* **1990**, *29*, 579.

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(19) Theoretical expressions used to calculate magnetic susceptibility data:

$$\chi_{Dim} = \frac{N_L g^2 \mu_B{}^2}{kT} \frac{2\exp(2J/kT) + 10\exp(6J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT)}$$

$$\chi_{Mono} = \frac{2N_L g^2 \mu_B{}^2}{3kT} \frac{(2kT/D) - 2\exp(-D/kT)/(D/kT) + \exp(-D/kT)}{1 + 2\exp(-D/kT)}$$

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