Novel μ_3-Coordination of Urea at a Nickel(II) Site: Structure, Reactivity and Ferromagnetic Superexchange

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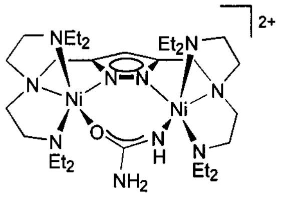
Keywords: Urea / Nickel / Coordination modes / Cooperative effects / Magnetic properties

A tetranuclear mixed-spin nickel(II) complex featuring two urea molecules in an unprecedented μ_3-κN:κN′:κO coordination mode has been structurally characterized. The two central high-spin nickel(II) ions exhibit ferromagnetic coupling ($J = +3.4$ cm^{-1}) mediated by the NH_2–C–O linkages of the bridging urea. In solution the temperature dependence of the UV/Vis optical absorption and of the magnetic moment indicate that, upon cooling, additional solvent molecules bind to the terminal low-spin metal ions and a concomitant spin change occurs. In the solid state the coordinated urea ligands can be thermally degraded to cyanate within the grip of the multimetallic nickel(II) site.

The coordination and conversion of urea at transition metal complexes,[1] in particular at dinuclear nickel(II) systems,[2−5] has received considerable attention in recent years. The main incentive for this arises from the endeavor to understand and mimic the unique properties of the natural metalloenzyme urease, which contains two cooperating nickel(II) ions within its active site, and which achieves at least a 10^{14}-fold rate enhancement for the biological hydrolysis of urea.[6][7] According to the initially proposed mechanism[8] of urease activity, the urea substrate is activated by O-coordination to one nickel(II) ion in conjunction with extensive hydrogen bonding within the active site pocket, and is attacked by a nucleophilic hydroxide bound to the adjacent second metal ion. Subsequent structural findings for both native and inhibited urease, however, together with structure-based molecular modeling of the catalytic mechanism, led to the alternative suggestion of a bridging coordination mode of both urea and hydroxide at the bimetallic core.[9] The most recent reactivity studies of urea derivatives coordinated to mononuclear metal centers have indicated that a cyanate NCO intermediate might be involved in the urease mechanism.[10] Evidently, the precise details of urea binding within the enzyme active site, as well as the key steps of its catalytic conversion, are still far from being fully understood.

This situation, therefore, stimulates the synthesis and investigation of small nickel(II) coordination compounds in order to elucidate possible coordination modes of urea − also in a more general sense − and to probe their relevance to the metal-assisted hydrolytic degradation of this fundamental and ubiquitous substrate at multimetallic sites. Whereas several dinickel(II) complexes with η^1(O)-coordinated urea have hitherto been prepared and studied,[3][4] only recently have we reported the pyrazolate-based complex **1** which represents the first structurally characterized example of a μ_2-κN:κO bridging coordination mode of (deprotonated urea at a dinickel(II) site (Scheme 1).[5]



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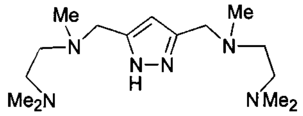
Scheme 1. Urea-bridged dinickel(II) complex **1**[5]

This system enabled a thermal decomposition of the substrate within the tight grip of the bimetallic pincer to yield a N,O-bridging cyanate, but no substantial activation towards hydrolytic degradation (tested by attempting ethanolytic cleavage to yield ethyl carbamate) could be observed. We considered the absence of any additional docking site for the alcohol nucleophile as one likely reason for the lack of hydrolytic reactivity of **1**, in accordance with the idea of a requisite activation of both the urea substrate and the nucleophile at the bimetallic core. To avoid this drawback, we have now employed a different dinucleating ligand matrix L (Scheme 2),[11] which bears fewer N-donors within the chelating side arms attached to the heterocycle, and which was thus expected to provide accessible coordination sites at both metal centers.



HL

Scheme 2. Ligand HL employed in this work[11]

Treatment of HL with two equivalents of base and [Ni(H_2O)$_6$](ClO_4)$_2$ in the presence of an excess of urea affords the red compound **2**, which is moderately soluble in polar solvents such as a mixture of methanol/acetone (1:1). Its mass spectrum shows signals corresponding to

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1434−1948/99/1111−1851 $ 17.50+.50/0

$[LNi_2(OCN_2H_3)]^+$ and $[LNi_2(OCN_2H_3)(ClO_4)]^+$, confirming the formation of a dinickel(II) complex containing deprotonated urea. The presence of the latter is further corroborated by strong IR absorptions at 1636 cm^{-1} [$\tilde{\nu}$(C=O)] as well as in the range 3100−3460 cm^{-1} [$\tilde{\nu}$(N−H)]. Small crystals of **2** could be obtained by layering a solution in methanol/acetone (1:1) with Et_2O, and an X-ray crystallographic analysis was performed (Figure 1).[12]

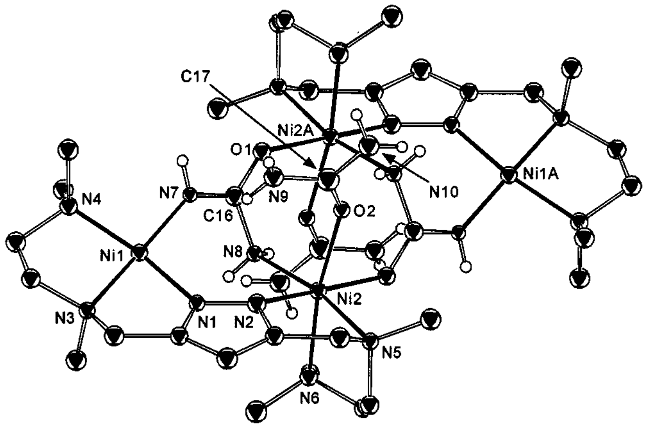
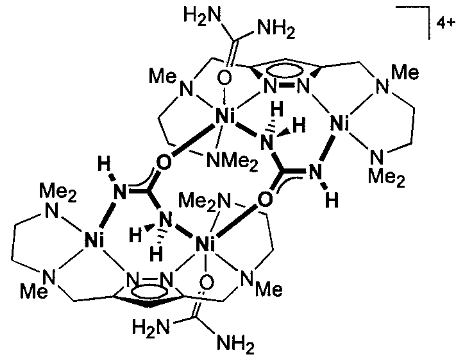


Figure 1. Molecular Structure of the cation of **2**; for clarity most of the hydrogen atoms have been omitted; selected atom distances (Å) and angles (°): Ni1−N1 1.886(3), Ni1−N3 1.897(4), Ni1−N4 1.975(3), Ni1−N7 1.897(4), Ni2−O1A 2.070(3), Ni2−O2 2.151(3), Ni2−N2 2.014(4), Ni2−N5 2.143(4), Ni2−N6 2.176(4), Ni2−N8 2.108(4), N1−N2 1.372(5), O1−C16 1.254(5), N7−C16 1.311(6), N8−C16 1.427(5), O2−C17 1.249(5), N9−C17 1.339(6), N10−C17 1.357(6), Ni1···Ni2 4.232, Ni2···Ni2A 4.349; O1−C16−N7 125.7(4), O1−C16−N8 117.8(4), N7−C16−N8 116.5(4), O2−C17−N9 123.6(5), O2−C17−N10 120.5(4), N9−C17−N10 115.9(4)

The solid-state structure of **2** reveals that pyrazolate-based bimetallic moieties containing urea as secondary bridging units have indeed been formed. Unexpectedly however, two of these moieties are found to be linked by an unprecedented μ_3-κN:κN′:κO coordination of the urea substrate. The central feature of the tetranuclear framework is an eight-membered ring system which is composed of two nickel atoms spanned by two N,O-bound urea molecules (Scheme 3), and which is situated on a crystallographic center of symmetry. The remaining deprotonated urea NH-groups are coordinated to the additional outer nickel centers.

An unambiguous distinction between the O, NH, and NH_2 donors of the μ_3-bridging, planar urea ligand (sum of angles around C16: 360.0°) is primarily based on the characteristic order of bond lengths d(C16−O1) = 1.254(4) Å, d[C16−N7(NH)] = 1.311(6) Å and d[C16−N8(NH_2)] = 1.427(5) Å, where the two C−N bonds are significantly shortened or lengthened, respectively, in comparison to the C−N bonds of purely η^1(O)-bound urea [1.339(6)/1.357(6) Å, see below]. Further corroboration stems from the assignment of the N-bound H atoms which were located in the difference fourier map and refined. Thus the sum of bond angles around the trigonal-planar amide−N7 amounts to 359.4°, while the angles around the tetrahedral amine center N8 are found in the expected range of 105−114°.



Scheme 3. Schematic structure of the cation of **2**; the central core featuring the μ_3-bridging urea is set off in bold

A further urea molecule is η^1(O)-bound to the central Ni2 and Ni2A ions, thereby completing their distorted octahedral (OC-6) coordination spheres. In contrast, the outer Ni1 and Ni1A atoms are nested in square-planar (SP-4) environments, which can be attributed to the stronger σ-donor capacity of the anionic NH(amide) donor compared to the neutral NH_2(amine) and O donor sites of the μ_3-bridging urea ligand. The predicted low-spin d^8-configuration for such SP-4 nickel(II) ions is confirmed by magnetic measurements performed on powdered samples of solid **2**, which are in accordance with the presence of a mixed-spin complex having only two paramagnetic high-spin d^8 centers per tetranuclear complex (μ_{eff} = 3.21 μ_B at 288 K per paramagnetic Ni^{II}).

Upon cooling a solution of **2** in methanol/acetone (1:1) a color change from red to greenish-blue is observed. Following this process by UV/Vis spectroscopy (Figure 2) confirms the gradual disappearance of the major optical absorption of **2** at λ_{max} = 480 nm and a slight shift and rise of the low intensity absorption bands at around 380 and 625 nm.

These changes suggest an increase in coordination number of the SP-4 nickel ions and the formation of five- or even six-coordinate metal centers caused by the additional binding of extra solvent molecules at lower temperatures. However, the absence of any isosbestic points is indicative of a more complex process which is possibly due to a sequential coordination of the solvent ligands to the two terminal metal ions in **2**, or to a concurrent break-up of the tetranuclear system into bimetallic entities. The solution magnetic moment (determined by the Evans method)[15] rises from 3.5(±0.1) μ_B at 303 K to 4.1(±0.1) μ_B at 223 K per pyrazolate-based bimetallic unit (Figure 3), where the maximum value is close to the spin-only value expected for two high-spin nickel(II) ions (the slight decrease of μ_{eff} at even lower temperatures might be due to antiferromagnetic coupling within the pyrazolate-based bimetallic units). This corroborates the assumed transformation of the low-spin

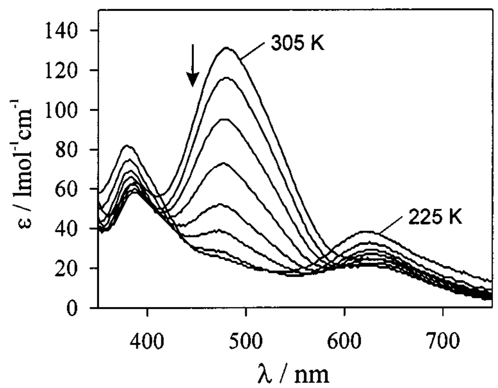


Figure 2. Temperature dependence of the UV/Vis spectrum of **2**; spectra at 225 K and in the range 245−305 K (steps of 10 K) are shown

SP-4 nickel(II) ions to five- or six-coordinate high-spin nickel(II) centers upon cooling.

The temperature dependence of both the UV/Vis data as well as of the solution magnetic moment (Figure 3) reveals that conversion of the greenish-blue species to the red complex **2** is still incomplete at temperatures up to 305 K. It is pivotal in the present context, that activation of a potential nucleophile by coordination to the terminal nickel(II) ions is apparently feasible in **2**; this is assumed to be required for a subsequent nucleophilic attack on either the bridging urea or on the η^1(O)-bound urea substrate at the proximate central site. Still, the activity of **2** for the ethanolysis of urea (determined by a method described previously[3d]) is low, amounting to a conversion of only 1.2 equivalents of the substrate after five days refluxing in ethanol. It appears reasonable to ascribe this to the anionic character of the deprotonated μ_3-urea ligand, which obviously prevents it from being susceptible to nucleophilic attack. On the other hand, heating of solid **2** to elevated temperatures (140 °C) causes conversion of coordinated urea to cyanate, as evidenced by the gradual appearance of the characteristic IR absorption for the ν_{asym}(NCO) stretch[5b] at 2193 cm^{-1} and a dominant mass spectrometric signal at m/z = 552 corresponding to $[\mathrm{LNi_2(NCO)(ClO_4)}]^+$. This finding again shows that urea can be thermally degraded to cyanate within the clamp of an appropriate arrangement of nickel(II) ions.[3c,5]

The magnetic properties of powdered samples of solid **2** have been studied over the temperature range 4.8−288 K, as major structural changes of the tetranuclear framework (as observed in solution) are not expected to occur in the solid state. Data for the magnetic susceptibility and μ_{eff} are depicted in Figure 4. The rise of μ_{eff} with decreasing temperature − reaching a maximum of 3.69 μ_B per pyrazolate-based dinickel(II) entity at 7.0 K − is indicative of ferromagnetic coupling between the two central OC-6 metal centers.

At even lower temperatures the magnetic moment tends to drop, which is probably due to zero-field splitting effects or additional intermolecular antiferromagnetic interactions.

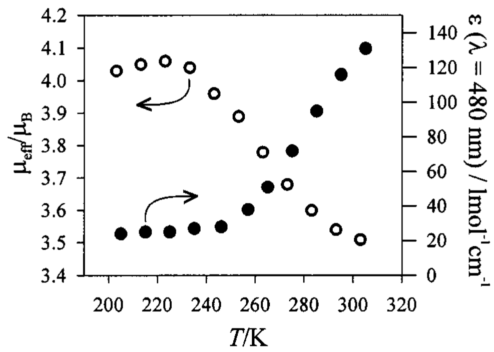


Figure 3. Temperature dependence of the molar optical absorption at 480 nm for **2** (solid circles) and of the solution magnetic moment per pyrazolate-based bimetallic fragment of **2** (open circles)

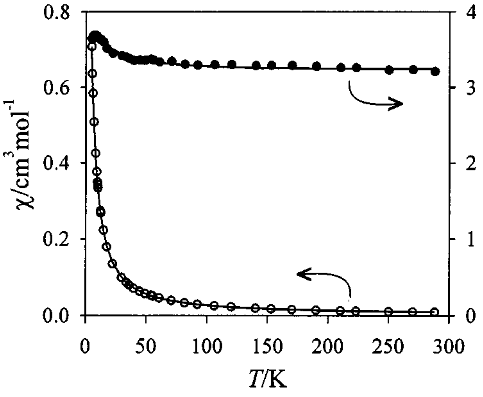


Figure 4. Temperature dependence of the molar magnetic susceptibility (open circles) and magnetic moment (solid circles) per pyrazolate-based bimetallic fragment of **2**. The solid lines represent the calculated fit (see text)

The experimental data were simulated by a modified expression based on the isotropic Heisenberg model ($\boldsymbol{H} = -2J \times \boldsymbol{S}_1 \times \boldsymbol{S}_2$ with $S_1 = S_2 = 1$) {Equation (1)} where p is the molar fraction of paramagnetic impurities and θ is a Weiss constant that was included to describe phenomenologically the decrease of $\mu_{eff}(T)$ at low temperatures.[16] The best fit parameters obtained are $g = 2.25$, $J = +3.4$ cm^{-1}, $p < 0.01$ and $\theta = -0.62$ [$R = \Sigma(\chi^{calc} - \chi^{obs})^2/\Sigma(\chi^{obs})^2 = 6.0 \times 10^{-5}$].

Considering the large separation of the two high-spin nickel(II) ions in **2** (4.349 Å), the surprising ferromagnetic exchange interaction is expected to be ligand-mediated and is evidently transmitted by a σ-bond pathway. These combined abilities of deprotonated urea to (i) mediate ferromagnetic superexchange and (ii) to bind three metal ions in a bridging fashion, make this component a promising candidate for the design of higher-dimensional coordination networks with interesting magnetic properties. Insight into the geometric requirements and the underlying mechanisms of the exchange coupling will be the subject of future studies.

In conclusion, we have shown that urea can simultaneously bind to three different metal ions, and that it can be thermally degraded to cyanate within such grip of a multimetallic nickel(II) site. Furthermore, urea is able to bring

$$\chi_m = (1-p)\{[Ng^2\mu_B{}^2/k(T-\theta)][2\exp(2J/kT) + 10\exp(6J/kT)]/[1 + 3\exp(2J/kT) + 5\exp(6J/kT)]\} + 2p(2Ng^2\mu_B{}^2/3kT) + 2N_\alpha \quad (1)$$

about ferromagnetic exchange coupling in the novel μ_3-κN:κN′:κO-coordination mode. These findings should offer new perspectives with respect to the use of the simple urea molecule as a building block for extended coordination networks, as well as with respect to the metal-mediated activation and transformation of this ubiquitous substrate.

Experimental Section

Caution! Although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

Complex 2: A solution of the ligand HL[11] (0.25 g, 0.84 mmol) in thf (20 mL) and MeOH (1 mL) was treated with two equivalents of *n*BuLi (2.5 M in hexane) at 0°C and stirred for 5 min. $[Ni(H_2O)_6](ClO_4)_2$ (0.62 g, 1.69 mmol) and additional MeOH (20 mL) were then added and the red solution stirred at room temperature for 1 h. After the addition of urea (0.15 g, 2.50 mmol) stirring was continued for a further 2 h. All volatile material was then removed under reduced pressure and the residue taken up in MeOH/acetone (1:1, 60 mL) and layered with Et_2O. Red crystalline material of the product **2**·2(acetone) gradually formed (0.51 g, 0.32 mmol, 77%). − IR (KBr): $\tilde{\nu}$ = 3456 (s), 3346 (s), 3115 (m), 2915 (w), 1689 (m, $C{=}O_{acetone}$), 1636 (vs), 1571(m), 1463 (s), 1096 (vs) cm^{-1}. − $C_{34}H_{76}Cl_4N_{20}Ni_4O_{20}$·2(acetone) (1577.84): calcd C 30.45, H 5.62, N 17.75; found C 30.08, H 5.63, N 17.37.

Acknowledgments

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[12] Crystallographic analysis of **2** ($C_{17}H_{38}Cl_2N_{10}Ni_2O_{10}$·acetone): *M* = 789.0, monoclinic, crystal size 0.05 × 0.04 × 0.03 mm, space group $P2_1/c$, *a* = 11.984(2), *b* = 18.535(4), *c* = 14.426(3) Å, β = 92.14(3)°, *V* = 3202(1) Å^3, *Z* = 4, ρ_{calc} = 1.637 g cm^{-3}, μ(Mo-K_α) = 1.412 mm^{-1}, *T* = 200 K, *F*(000) = 1648. The measurement was carried out on a Siemens CCD diffractometer with graphite-monochromated Mo-K_α radiation. All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-97 and refined with the SHELXL-97 program.[13] The program XPMA[14] was used for graphical handling of the data. Atomic coordinates and thermal parameters of the non-hydrogen atoms were refined in anisotropic models by full-matrix least-squares calculation based on F^2. In general the hydrogen atoms were placed at calculated positions and allowed to ride on the atoms they are attached to, except for the hydrogen atoms of the urea molecules which were located in the difference fourier map and refined. 49935 measured reflections (6220 independent), *R*1 = 0.054 and *wR*2 = 0.1071 for 3626 observed reflections [$I > 2\sigma(I)$] and 438 parameters. Largest residual electron density 0.463/-0.437 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 127485. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK {fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk}.

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[16] [16a] C. J. O′Connor, *Progr. Inorg. Chem.* **1982**, *29*, 203−283. − [16b] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**; N_α refers to the temperature-independent paramagnetism [100 × 10^{-6} cm^3/mol per nickel(II) ion]; all other parameters have their usual meaning. Experimental data have been corrected for the underlying diamagnetism.

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