eliminated the Prussian blue problem by (1) using Os(CN)$_6^{4-}$ in place of Fe(CN)$_6^{4-}$ with similar results, (2) purposely making the Prussian blue complex which absorbs in the red and showing that it is not present in our absorption spectrum, and (3) proving that no enhancement occurs in the Fe(CN)$_6^{4-}$/colloidal-TiO$_2$ solution at 647.1 nm (where Prussian blue would absorb). The second problem, titanate formation during preparative TiCl$_4$ hydrolysis, can be effectively eliminated by dialysis.[7] This was confirmed by an electrochemical experiment (supplementary material) in which redox-active Fe(CN)$_6^{4-}$ (i.e., free or titanate bound) was shown to be absent from Fe(CN)$_6^{4-}$/dialyzed-colloid solutions, but present in intentionally prepared Fe(CN)$_6^{4-}$/titanate solutions.[15]

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Supplementary Material Available: One figure showing differential pulse voltammograms for Fe(CN)$_6^{4-}$/colloidal-TiO$_2$ and Fe(CN)$_6^{4-}$/titanate solutions (1 page). Ordering information is given on any current masthead page.

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[15] The source of titanate was the outer portion of a colloidal-TiO$_2$ dialysis solution. See ref 7 for related experiments.

Complexation through Nitrogen in Copper and Nickel Complexes of Substituted Ureas[†]

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Complexation of transition metals by biologically relevant ligands, such as the prevalent amide ($>N\underset{|}{C}=O$) functionality, has attracted considerable attention due to the catalytic potential of such complexes.[2-4] In principle, transition-metal ions can complex to ureas and amides via oxygen or nitrogen atoms. The oxygen lone pair is more basic than the nitrogen site. In the case of amides, the basicity difference toward protons is estimated as seven pK_a units.[5] A similar situation exists in ureas.[6] In accord with these basicity differences, complexes of ureas[7,8] or uncharged

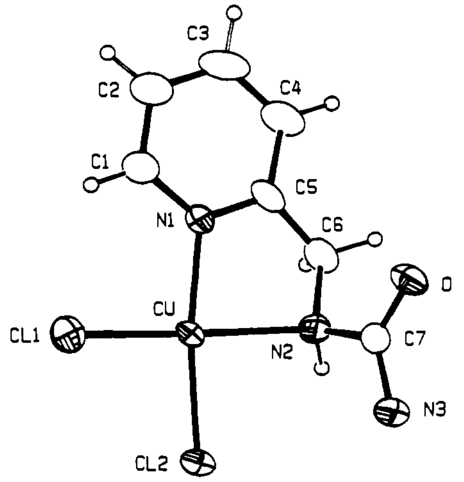

Figure 1. ORTEP drawing of the Cu(II) complex of **1a**. Selected bond lengths (Å) and angles (deg) are as follows: Cu–N1, 1.998 (9); Cu–N2, 2.127 (9); Cu–Cl1, 2.241 (3); Cu–Cl2, 2.229 (3); C7–O, 1.22 (1); C7–N2, 1.45 (2); C7–N3, 1.32 (2); C6–N2, 1.48 (2); Cl1–Cu–Cl2, 93.2 (1); Cl1–Cu–N1, 96.8 (3); Cl1–Cu–N2, 166.5 (4); Cl2–Cu–N1, 169.9 (3); Cl2–Cu–N2, 88.9 (3); N1–Cu–N2, 81.8 (3); Cu–N2–C6, 105.2 (6); Cu–N2–C7, 113.2 (7); O–C7–N2, 119 (2); O–C7–N3, 125 (1).

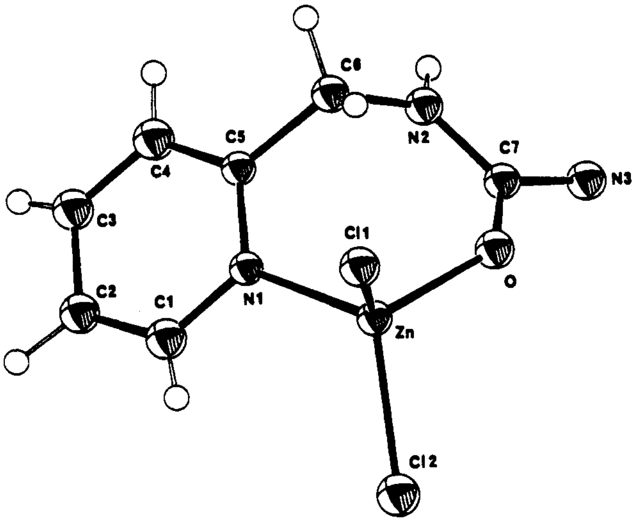

Figure 2. ORTEP drawing of the Zn(II) complex of **1a**. Selected bond lengths (Å) and angles (deg) are as follows: Zn–N1, 2.035 (4); Zn–O, 1.981 (4); Zn–Cl1, 2.234 (2); Zn–Cl2, 2.231 (2); C7–O, 1.263 (7); C7–N2, 1.359 (6); C7–N3, 1.317 (8); C6–N2, 1.449 (9); Cl1–Zn–Cl2, 110.36 (8); Cl1–Zn–N1, 112.3 (1); Cl1–Zn–O, 114.9 (1); Cl2–Zn–N1, 111.6 (1); Cl2–Zn–O, 107.7 (1); O–Zn–N1, 99.4 (2); Zn–O–C7, 135.9 (3); Zn–N1–C5, 122.7 (3); O–C7–N2, 121.9 (6); O–C7–N3, 121.2 (4).

[†] This paper is dedicated to Professor Ronald Breslow.

(1) (a) The Pennsylvania State University. (b) The University of Calgary.

(2) For a review, see: (a) Freeman, H. C. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; p 121. (b) Sigel, H., Ed. *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1973; Vol 2. (c) Ochiai, E.-I. *General Principles of Biochemistry of the Elements*; Plenum Press: New York, 1987. (d) Murzubraimov, B. *Koord. Khim.* **1985**, *11*, 158.

(3) See, for example: (a) Hay, R. W.; Morris, P. J. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1976; Vol. 5, p 173. (b) Collman, J. P.; Kimura, E. *J. Am. Chem. Soc.* **1967**, *89*, 6096. (c) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6151. (d) Buckingham, D. A.; Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726. (e) Boreham, C. J.; Buckingham, D. A.; Keene, F. R. *Inorg. Chem.* **1979**, *18*, 28. (f) Curtis, N. J.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 625. (g) Groves, J. T.; Chambers, R. R., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 630. (h) Buckingham, D. A.; Binney, G. S.; Clark, C. R.; Garnham, B.; Simpson, J. *Inorg. Chem.* **1985**, *24*, 135. (i) Nanjappan, P.; Czarnik, A. W. *J. Am. Chem. Soc.* **1987**, *109*, 1826. (j) Schepartz, A.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 1814. (k) Sutton, P. A.; Buckingham, D. A. *Acc. Chem. Res.* **1987**, *20*, 357. (l) Chin, J.; Zou, X. *J. Am. Chem. Soc.* **1984**, *106*, 3687.

(4) (a) Blakeley, R. L.; Treston, A.; Andrews, R. K.; Zerner, B. *J. Am. Chem. Soc.* **1982**, *104*, 612. (b) Andrews, R. K.; Blakeley, R. L.; Zerner, B. In *Advances in Inorganic Biochemistry*; Eichhorn, G. L., Marzilli, L. G., Eds.; Elsevier: New York, 1984; Vol. 6, p 245. (c) Andrews, R. K.; Blakeley, R. L.; Zerner, B. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH Publishers: New York, 1988; p 141.

(5) (a) Perrin, C. L.; Lollo, C. P.; Johnston, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 2749, 2754. (b) Fersht, A. R. *J. Am. Chem. Soc.* **1971**, *93*, 3504.

(6) Tetramethylurea is very similar to *N,N*-dimethylacetamide in its ability to form hydrogen bonds through the oxygen atom. Also, in both cases the protonation in fluorosulfuric acid takes place at oxygen atom: Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

(7) Urea complexes have been characterized only by IR spectroscopy as to the mode of coordination. With a few exceptions (ref 8) the data are consistent with O-coordination. There seems to be no X-ray structure of such complexes available. See, for example: (a) Murzubraimov, B.; Toktomatov, A. *Koord. Khim.* **1983**, *9*, 601. (b) Srivastava, P. C.; Aravindakshan, C. *Z. Phys. Chem.* (*Leipzig*) **1983**, *264*, 61. (c) Bailey, R. A.; Feins, I. R.; Peterson, T. R. *Can. J. Chem.* **1969**, *47*, 171. (d) Muksumova, Z. S.; Orozbaeva, N. O.; Fridman, Y. D.; Molodkin, A. K.; Rysmendeev, K. *Zh. Neorg. Khim.* **1986**, *31*, 2865. (e) Sharma, S. B.; Singh, V. P.; Singh, M. K.; Sharma, S. K. *J. Indian Chem. Soc.* **1985**, *62*, 721.

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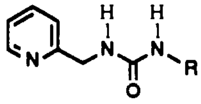
Table I. Carbonyl Stretch Frequencies in Urea Complexes of Cu(II), Ni(II), and Zn(II)

		carbonyl frequency,[a] cm^{-1}			
ligand	R	free ligand	Cu(II)	Ni(II)	Zn(II)
1a	H	1665	1714		1613
1b	Ph	1633	1736	1731	
1c	4-$NO_2C_6H_4$	1690	1742	1746	1651

[a] The IR spectra were recorded in KBr pellets.

amides[9] with transition metals show almost exclusive[8] coordination through the oxygen atom. We present here the first examples of urea complexes of nickel(II) and copper(II) ions wherein the metals coordinate via the nitrogen atom. This mode of binding is not enforced by the geometry of the ligand as shown by the structure of the analogous Zn(II) complex, which exhibits the standard mode of complexation through the oxygen atom.



1a: R = H
b: R = Ph
c: R = 4-$NO_2C_6H_4$

The complexes of Ni(II), Cu(II), and Zn(II) were prepared by mixing an excess of the metal chloride with urea-carrying pyridine ligands (**1**) in ethanol.[10] The copper and zinc complexes gave crystals suitable for X-ray analysis.[11] The ORTEP drawings of these complexes are shown in Figures 1 and 2. The copper complex has a distorted square geometry with **1a** serving as a chelating ligand. The most remarkable feature of the complex is the coordination of the copper ion via two nitrogens. Although, this mode of complexation gives a relatively strain free five-membered ring, one of the nitrogens utilized (N2) is a urea nitrogen. This nitrogen atom is pyramidalized and deconjugated from the carbonyl group.[12] The pyramidalization is clearly evident, especially since the N2 hydrogen has been located directly from the electron density map. Although the urea functionality (N2–C7–O–N3) is still planar, the N2–C7 bond is significantly longer than the N3–C7 bond, indicating the absence of amide resonance. The N2–C7 bond length is 1.45 (2), Å, very similar to the N2–C6 single-bond length of 1.48 (2) Å. For comparison, the N3–C7 bond length of 1.32 (2) Å is typical for bonds with significant double-bond character,[13] signifying resonance.

The zinc complex of **1a** shows the "expected" complexation through the oxygen atom (Figure 2). It has a slightly distorted tetrahedral geometry. The amide bonds are short (N2–C7 is 1.359 (6) Å, and N3–C7 is 1.317 (8) Å), as expected for the amide resonance. The urea moiety is planar and seems almost unperturbed.

Both modes of complexation are accessible to the same ligand binding metal ions of similar size.[14] This implies that the coordination through nitrogen is not directly enforced by the geometric limitations of the ligand. *The nitrogen of the amido group* $(>N\underset{|}{C}{=}O)$ *can, therefore, function as a coordination site.* This conclusion is supported by several other related urea complexes of copper and nickel (Table I) which were studied by IR spectroscopy.[15] Coordination through nitrogen resulting in deconjugation of the carbonyl group should lead to an increase in the carbonyl stretch frequency.[8] Such an increase is in fact observed for copper(II) and nickel(II) complexes of **1a**, **1b**, and **1c**. The carbonyl band shifts by 50–100 cm^{-1}, implying coordination through nitrogen. In contrast, coordination through oxygen lowers the stretching frequency by less than 50 cm^{-1}, as found for the Zn(II) complex of **1a** and **1c**.

Ions of transition metals catalyze hydrolysis of amides[3] and ureas.[4] Most often, the catalysis is postulated to involve activation of the metal-bound carbonyl group[3] (and stabilization of the tetrahedral intermediate formed) or activation of the metal-coordinated nucleophile.[3] In this context, the coordination through nitrogen suggests a mode of catalysis involving both the increase in electrophilicity of the carbonyl carbon (by deconjugation of the nitrogen) and assistance in departure of the amino leaving group from the tetrahedral intermediate. This last step of the reaction might in fact be rate-limiting in urea hydrolysis.

Interestingly, the nickel(II) complex of **1a** has been described[4] as the catalytic species involved in hydrolysis of **1a**. Blakeley et al. have proposed[4] that this urease mimic[16] binds the metal ion through oxygen, which activates the carbonyl group for nucleophilic attack. Although we have been unable to characterize the nickel complex of **1a**, we have found[17] that copper and nickel ions catalyze the hydrolysis of ureas **1b** and **1c** with a rate comparable to that observed by Blakeley et al.[4] On the other hand, zinc ion was a very ineffective[17] catalyst. With insufficient information about the structure of these complexes in solution, the relevance of these observations to the mechanism of catalysis is uncertain. The results *suggest*, however, that the metal ions might play an important role in the breakdown of the tetrahedral intermediate. Further studies to elucidate the structure of these complexes and probe the hydrolysis mechanism are in progress.

Acknowledgment. This research was supported in part by a grant from the NIH (GM 41489).

Supplementary Material Available: Final atomic coordinates, bond lengths, bond angles, torsional angles, and anisotropic thermal parameters for copper(II) and zinc(II) complexes of **1a** (15 pages); listing of observed and calculated structure factors for copper(II) and zinc(II) complexes of **1a** (25 pages). Ordering information is given on any current masthead page.

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(8) There is a report of urea complexes with Pt(II) and Pd(II), wherein the coordination through nitrogen is postulated on the basis of IR studies: (a) Penland, R. B.; Mizushima, S.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1957**, *79*, 1575. *N*-coordinated urea complexes of Co(III) and Rh(III) are also known: (b) Curtis, N. J.; Dixon, N. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 5347 and references therein. (c) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1988**, *150*, 81. (d) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4038. (e) Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1990**, *29*, 3139.

(9) In complexes of amides with transition metals, coordination through nitrogen is accompanied by the dissociation of the amide proton. See, for example: (a) Margerum, D. W.; Dukes, G. R. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1974; Vol. 1, p 157. (b) Margerum, D. W.; Wong, L. F.; Bossu, F. P.; Chellappa, K. L.; Czarnecki, J. J.; Kirksey, S. T., Jr.; Neubecker, T. A. In *Bioinorganic Chemistry-II*; Raymond, K. N., Ed.; American Chemical Society: Washington, DC, 1977; Vol. 162, p 281. For examples of O-coordinated complexes of amides analogous to **1**, see: (c) Bould, J.; Brisdon, B. J. *Inorg. Chim. Acta* **1976**, *19*, 159. (d) Sekizaki, M. *Acta Crystallogr.* **1973**, *B29*, 327. (e) Nonoyama, M.; Tomita, S.; Yamasaki, K. *Inorg. Chim. Acta* **1975**, *12*, 33. (f) Nonoyama, M.; Yamasaki, K. *Inorg. Chim. Acta* **1969**, *3*, 585. (g) Sekizaki, M.; Yamasaki, K. *Inorg. Chim. Acta* **1970**, *4*, 296.

(10) The details of synthesis and characterization of the complexes will be reported elsewhere.

(11) The detailed X-ray data are provided in supplementary material. The Cu(II) complex of **1a** was solved ($R_w = 0.083$) in the $P2_1/c$ space group. The unit cell contained four molecules, and its dimensions were (in Å) $a = 15.449$ (11), $b = 8.955$ (8), and $c = 7.365$ (13); $\beta = 104.3$ (1)°. The data for the Zn(II) complex of **1a** were collected at −100 °C. The structure was solved ($R_w = 0.027$) in the $P2_1/c$ space group. The unit cell contained four molecules, and its dimensions were (in Å) $a = 6.687$ (2), $b = 21.250$ (2), and $c = 7.582$ (6); $\beta = 108.96$ (2)°.

(12) Urea has planar nitrogens: Worsham, J. E., Jr.; Levy, H. A.; Peterson, S. W. *Acta Crystallogr.* **1957**, *10*, 319.

(13) C–N bond length is 1.351 (7) Å in urea (ref 12) and 1.34 Å in simple amides (Robin, M. B.; Bovey, F. A.; Basch, H. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience Publishers: New York, 1970; p 1).

(14) Ionic radii of Cu(II) and Zn(II) in tetracoordinate complexes are 0.62 and 0.60 Å: Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

(15) Due to poor solubility, the mode of complexation was studied by FTIR in KBr pellets.

(16) For other postulated urease mimics, see: refs 8b–e and (a) Buchanan, R. M.; Mashuta, M. S.; Oberhausen, K. J.; Richardson, J. F.; Li, Q.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 4497. (b) Salata, C. A.; Youinou, M.-T.; Burrows, C. J. *J. Am. Chem. Soc.* **1989**, *111*, 9278.

(17) The rate of hydrolysis of **1c** (2.22 M H_2O in EtOH, 80 °C) in the presence of an excess of metal ion was as follows: $NiCl_2$, 1.8×10^{-5} s^{-1}; $CuCl_2$, 2.5×10^{-5} s^{-1}; $ZnCl_2$, 1.4×10^{-7} s^{-1}. Without the metal salt present, the rate constant for hydrolysis of **1c** was less than 1.5×10^{-8} s^{-1}. The hydrolysis of *N*-(4-nitrophenyl)-*N*′-(3-pyridylmethyl)urea in the presence of an excess of the metal ion ($CuCl_2$ or $NiCl_2$) was slower than 8×10^{-8} s^{-1}, indicating that the chelating effect is critical for catalysis.