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Novel Michael Addition Products of Bis(amino acidato)metal(II) Complexes: Synthesis, Characterization, Dye Degradation, and Oxidation Properties

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Michael addition reactions of bis(amino acidato)metal(II) complexes (metal = copper, nickel, zinc; amino acid = glycine, DL-alanine, L-alanine) with acrylonitrile have been carried out under various experimental conditions in the absence of a base, resulting in mono- and disubstituted products in high yield, including partially hydrolyzed products. A reaction mechanism for the Michael addition on the nitrogen atom of the coordinated amino acid moiety, replacing the amino hydrogen atom(s), is proposed. All of the products have been characterized by Fourier transform infrared spectroscopy, electron paramagnetic resonance spectra, and elemental and electrochemical analyses. The single-crystal structures of bis(*N*-cyanoethylglycinato)copper(II) monohydrate (**1a**), diaquabis(*N*-cyanoethylglycinato)nickel(II), aquabis(*N*,*N*-dicyanoethylglycinato)copper(II) (**2a**), and bis[(*N*-propionamido-*N*-cyanoethyl)glycinato]copper(II) dihydrate (**4a**) have been confirmed by X-ray diffraction techniques. The products **1a**, **2a**, **4a**, and bis(*N*-propionamidoglycinato)copper(II) monohydrate (**3a**) have been used as catalysts for the degradation of a phenol red dye and mild oxidation of various organic substrates in the presence of hydrogen peroxide. The monosubstituted complexes have been found to catalyze the reactions to a greater extent than the disubstituted complexes.

Introduction

Chelated amino acid complexes have been the subject of study for a long time, owing to their immense potential in the areas of catalysis and medicine. Copper−histidine as well as copper−cysteine complexes are potent stimulators of the release of leuteinizing hormone-releasing hormone from isolated hypothalamic granules.[1] The zinc−glycine complex serves as an anticalculus−antiplaque−antimalodor agent in oral compositions.[2] Various copper−amino acid complexes catalyze the emulsion polymerization of acrylonitrile in the absence of an added emulsifier.[3] Among the chelated glycine−transition metal complexes, copper−glycine has a pronounced effect. A detailed investigation has also been carried out with a nickel−glycine complex.[4] Bisglycinatocopper(II) complexes, through some of their reactions, are also known to produce aggregates, which function as thermoelectric switches.[5] Some polymer-supported copper(II) complexes are also used as chiral catalysts.[6]

Nuclear magnetic resonance and other studies have demonstrated that the protons on the α-carbon atom as well as those on the nitrogen atom of chelated amino acid complexes dissociate under alkaline conditions.[7] Amino protons of such complexes have also been shown to be labile in the absence of a base in condensation reactions.[8,9] Metal−amino acid complexes undergo aldol condensa-

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(1) Ayalla, B.; Gloria, C. *Endocrinology* **1984**, *115*, 936.
(2) Ritchey, T. W.; Weaver, J. M.; Sapone, M. *U.S. Pat.* **1984**, *4*, 339–432.
(3) Sahoo, P. K.; Dey, M.; Swain, S. K. *J. Appl. Polym. Sci.* **1999**, *74*, 2785.
(4) Swain, S. K.; Sahoo, P. K. *Ind. J. Chem. Tech.* **2000**, *7*, 259.
(5) Puzari, A.; Baruah, J. B. *React. Funct. Polym.* **2001**, *47*, 147.
(6) Valodkar, V. B.; Tembe, G. L.; Ram, R. N.; Rama, H. S. *Catal. Lett.* **2003**, *90*, 91.
(7) Ng, C. H.; Teo, S. B.; Teoh, S. G.; Fun, H. K.; Declercq, J. P. *Inorg. Chim. Acta* **2002**, *340*, 81.
(8) Teo, S. B.; Teoh, S. G.; Rogers, J. R.; Snow, M. R. *J. Chem. Soc., Chem. Commun.* **1982**, 141.
(9) Teo, S. B.; Teoh, S. G. *Inorg. Chim. Acta* **1984**, *91*, L17.

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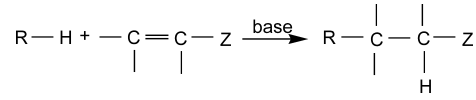
tion,[10–12] alkylation,[13,14] and Mannich aminomethylation[15–19] reactions under various experimental conditions. A series of derivatives can be obtained by the selective functionalization of the basic ligand skeleton at both carbon and nitrogen atoms.

The addition of compounds containing active hydrogen (R−H) to activated olefins (acrylonitrile, methyl acrylate, methyl methacrylate, acrolein, etc.) in the presence of bases is known as Michael reaction and involves conjugate addition:



Michael addition reactions were also carried out using amino acid Schiff base complexes[20–34] acting as a substrate containing active hydrogen, since the methylene protons of the amino acid moiety are labile under basic conditions. However, there are no reports dealing with such reactions of unprotected amino acid complexes (e.g., bis(amino acidato)metal(II) complexes), where the addition may take place on the amino group of the chelated amino acid moiety. Moreover, Michael addition reactions are generally used to prepare α-substituted amino acids and proline derivatives only after the demetalation of the product Schiff base complexes. The applications of metal-containing Michael addition products are hitherto unreported. Hence, we report, for the first-time, Michael addition reactions of bis(amino acidato)metal(II) complexes (amino acid = glycine, DL-alanine, L-alanine; metal = copper, nickel, zinc) with an activated olefin, namely, acrylonitrile, in the absence of a base, in an aqueous medium, the addition taking place on the amino group.

In the present study, some of these Michael addition products were also found to promote dye degradation (for example, phenol red, PR) and oxidation (for example, pyrocatechol, benzaldehyde, etc.) studies.

(10) (a) Ohdan, S.; Ichikawa, T.; Araki, Y.; Ishido, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1295. (b) Pasini, A.; Casella, L. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2133. (c) Brush, J. R.; Magee, R. J.; O'Connor, M. J.; Teo, S. B.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 2034. (d) Ohdan, S.; Ichikawa, T.; Araki, Y.; Ishido, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1019. (e) Ohdan, S.; Okamoto, T.; Maeda, S.; Ichikawa, T.; Araki, Y.; Ishido, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 981. (f) Ichikawa, T.; Maeda; Okamoto, T.; Araki, Y.; Ishido, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2779.

(11) (a) Ichikawa, T.; Okamoto, T.; Maeda, S.; Ohdan, S.; Araki, Y.; Ishido, Y. *Tetrahedron Lett.* **1971**, 79. (b) Aune, J. P.; Maldonado, P.; Larcheres, G.; Pierrot, M. *J. Chem. Soc., Chem. Commun.* **1970**, 1351. (c) Ichikawa, T.; Maeda, S.; Araki, Y.; Ishido, Y. *J. Am. Chem. Soc.* **1970**, *92*, 5514. (d) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133. (e) Harada, K.; Oh-hashi, J. *J. Org. Chem.* **1967**, *32*, 1103. (f) Gillard, R. D.; Harrison, P. M. *J. Chem. Soc. A* **1967**, 1657.

(12) (a) Ikutani, Y.; Okuda, T.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 582. (b) Akabori, S.; Otani, T. T.; Marshall, R.; Winitz, M.; Greenstein, J. P. *Arch. Biochem. Biophys.* **1959**, *83*, 1. (c) Benoiton, L.; Winitz, M.; Colman, R. F.; Birnbaum, S. M.; Greenstein, J. P. *J. Am. Chem. Soc.* **1959**, *81*, 1726. (d) Murakami, M.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 308. (e) Ikutani, Y.; Okuda, T.; Sato, M.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 203. (f) Sato, M.; Okawa, K.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 937.

(13) (a) Belokon, Y. N.; Bespalova, N. B.; Churkina, T. D.; Cisarova, I.; Ezernitskaya, M. G.; Harutyunyan, S. R.; Hrdina, R.; Kagan, H. B.; Kocovsky, P.; Kochetkov, K. A.; Larionov, O. V.; Lyssenko, K. A.; North, M.; Polasek, M.; Peregudov, A. S.; Prisyazhnyuk, V. V.; Vyskocil, S. *J. Am. Chem. Soc.* **2003**, *125*, 12860. (b) Ellis, T. K.; Martin, C. H.; Tsai, G. M.; Ueki, H.; Soloshonok, V. A. *J. Org. Chem.* **2003**, *68*, 6208. (c) Fu, Y.; Hammarstrom, L. G. J.; Miller, T. J.; Fronczek, F. R.; McLaughlin, M. L.; Hammer, R. P. *J. Org. Chem.* **2001**, *66*, 7118.

(14) (a) Reddy, G. S.; Smith, G. G. *Inorg. Chim. Acta* **1987**, *133*, 1. (b) Gillard, R. D.; Laurie, S. H.; Price, D. C.; Phipps, D. A.; Weick, C. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1385. (c) Nakahara, A.; Nishikawa, S.; Mitani, J. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2212.

(15) (a) Ng, C. H.; Lim, Y. T.; Moris, N, N.; Teoh, S. G. *Polyhedron* **2003**, *22*, 521. (b) Ng, C. H.; Chong, T. S.; Teoh, S. G.; Adams, F.; Ng., S. W. *J. Chem. Soc., Dalton Trans.* **2002**, 3361. (c) Teo, S. B.; Ng, C. H.; Teoh, S. G.; Fun, H. K. *J. Coord. Chem.* **1995**, *35*, 35. (d) Teo, S. B.; Ng, C. H.; Teoh, S. G. *Polyhedron* **1994**, *13*, 2537. (e) Balla, J.; Bernhardt, P. V.; Buglyo, P.; Comba, P.; Hambley, T. W.; Schmidlin, R.; Stebler, S.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1993**, 1143.

(16) (a) Comba, P.; Hambley, T. W.; Lawrance, G. A.; Martin, L. L.; Renold, P.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1991**, 277. (b) Teo, S. B.; Ng, C. H.; Teoh, S. G.; Fun, H. K. *J. Coord. Chem.* **1991**, *24*, 151. (c) Arulsamy, N.; Rao, C. R. K.; Zacharias, P. S. *Transition Met. Chem. (Dordrecht, Neth.)* **1991**, *16*, 606. (d) Arulsamy, N.; Srinivas, B.; Zacharias, P. S. *Transition Met. Chem. (Dordrecht, Neth.)* **1990**, *15*, 309. (e) Teo, S. B.; Ng, C. H.; Tiekink, E. R. T. *Inorg. Chim. Acta* **1989**, *163*, 129.

(17) (a) Teo, S. B.; Teoh, S. G.; Hambley, T. W.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1986**, 553. (b) Teo, S. B.; Teoh, S. G.; Snow, M. R. *Inorg. Chim. Acta* **1985**, *107*, 35. (c) Teo, S. B.; Teoh, S. G.; Snow, M. R. *Inorg. Chim. Acta* **1984**, *85*, L1. (d) Ng, C. H.; Lim, Y. T.; Moris, N, N.; Teoh, S. G. *Polyhedron* **2003**, *22*, 521.

(18) (a) Ng, C. H.; Chong, T. S.; Teoh, S. G.; Adams, F.; Ng., S. W. *J. Chem. Soc., Dalton Trans.* **2002**, 3361. (b) Teo, S. B.; Ng, C. H.; Teoh, S. G.; Fun, H. K. *J. Coord. Chem.* **1995**, *35*, 35. (c) Teo, S. B.; Ng, C. H.; Teoh, S. G. *Polyhedron* **1994**, *13*, 2537. (d) Balla, J.; Bernhardt, P. V.; Buglyo, P.; Comba, P.; Hambley, T. W.; Schmidlin, R.; Stebler, S.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1993**, 1143.

(19) (a) Comba, P.; Hambley, T. W.; Lawrance, G. A.; Martin, L. L.; Renold, P.; Varnagy, K. *J. Chem. Soc., Dalton Trans.* **1991**, 277. (b) Teo, S. B.; Ng, C. H.; Teoh, S. G.; Fun, H. K. *J. Coord. Chem.* **1991**, *24*, 151. (c) Arulsamy, N.; Rao, C. R. K.; Zacharias, P. S. *Transition Met. Chem. (Dordrecht, Neth.)* **1991**, *16*, 606. (d) Arulsamy, N.; Srinivas, B.; Zacharias, P. S. *Transition Met. Chem. (Dordrecht, Neth.)* **1990**, *15*, 309.

(20) Shono, T.; Yamashoji, Y.; Shinra, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 192.

(21) Casella, L.; Gullotti, M.; Pasini, A.; Ciani, G.; Manassero, M.; Sansoni, M.; Sironi, A. *Inorg. Chim. Acta* **1976**, *20*, L31.

(22) Casella, L.; Gullotti, M.; Pasini, A.; Psaro, R. *Synthesis* **1979**, 150.

(23) Casella, L.; Gullotti, M.; Melani, E. *J. Chem. Soc., Perkin Trans. I* **1982**, 1827.

(24) Belokon, Y. N.; Bulychev, A. G.; Ryzhov, M. G.; Vitt, S. V.; Batsanov, A. S.; Struchkov, Y. T.; Bukhmutov, V. A.; Belikov, V. M. *J. Chem. Soc., Perkin Trans. I* **1986**, 1865.

(25) Belokon, Y. N.; Bulychev, A. G.; Pavlov, V. A.; Fedorova, E. B.; Tsyryapkin, A. V.; Bukhmutov, V. A.; Belikov, V. M. *J. Chem. Soc., Perkin Trans. I* **1988**, 2075.

(26) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2172.

(27) Soloshonok, V. A.; Cai, C.; Hruby, V. J.; Meervelt, L. V.; Yamazaki, T. *J. Org. Chem.* **2000**, *65*, 6688.

(28) Cai, C.; Soloshonok, V. A.; Hruby, V. J. *J. Org. Chem.* **2001**, *66*, 1339.

(29) Soloshonok, V. A.; Ueki, H.; Tiwari, R.; Cai, C.; Hruby, V. J. *J. Org. Chem.* **2004**, *69*, 4984.

(30) Comelles, J.; Manas, M. M.; Perez, E.; Anna Roglans, A.; Sebastian, R. M.; Vallribera, A. *J. Org. Chem.* **2004**, *69*, 6834.

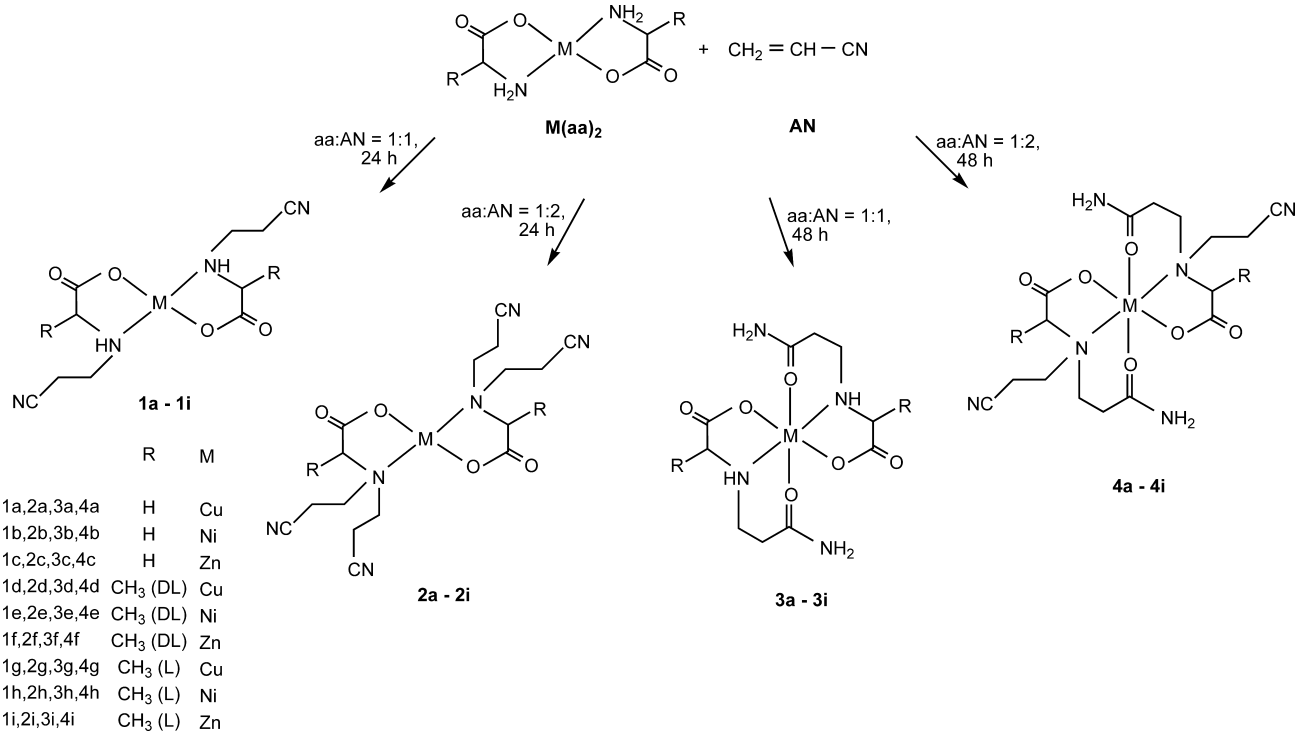
(31) Cai, C.; Yamada, T.; Tiwari, R.; Hruby, V. J.; Soloshonoka, V. A. *Tetrahedron Lett.* **2004**, *45*, 6855.

(32) Ellis, T. K.; Ueki, H.; Soloshonok, V. A. *Tetrahedron Lett.* **2005**, *46*, 941.

(33) Soloshonok, V. A.; Ueki, H.; Ellis, T. K.; Yamada, T.; Ohfune, Y. *Tetrahedron Lett.* **2005**, *46*, 1107.

(34) Ellis, T. K.; Ueki, H.; Yamada, T.; Ohfune, Y.; Soloshonok, V. A. *J. Org. Chem.* **2006**, *71*, 8572.

Scheme 1. Synthesis of Michael Addition Products



Results and Discussion

Synthesis. The Michael addition products, bis(*N*-cyanoethylaminoacidato)metal(II) (**1a**−**1i**) and bis(*N,N*-dicyanoethylaminoacidato)metal(II) (**2a**−**2i**), were synthesized in good yields by treating their corresponding bis(aminoacidato)metal(II) [$M(aa)_2$] complexes (aminoacid (aa) = glycine, DL-alanine, L-alanine; metal = copper, nickel, zinc) with acrylonitrile (AN) in the molar ratio aa/AN = 1:1 and 1:2, respectively, for 24 h in the absence of a base (pH = 6.0) at room temperature. $M(aa)_2$ on treatment with AN in the molar ratio aa/AN = 1:1 for 48 h in the absence of a base yielded bis(*N*-propionamidoaminoacidato)metal(II) (**3a**−**3i**) in high yields. Here, the Michael addition of AN took place on the nitrogen of the amino acid, and subsequently, the nitrile group underwent hydrolysis to an amide group. Similarly, reactions of $M(aa)_2$ with AN in the molar ratio aa/AN = 1:2 for 48 h gave bis[(*N*-propionamido-*N*-cyanoethyl)aminoacidato]metal(II) (**4a**−**4i**) in good yields, in which the Michael addition of two AN molecules on each amino nitrogen took place, and subsequently, one of the nitrile groups partially hydrolyzed to an amide group. In all of the above reactions, the molar ratio of AN and the reaction time play an important role in the formation of the products. The products were characterized by Fourier transform infrared spectroscopy (FT-IR) and electron paramagnetic resonance (EPR) spectra as well as elemental and electrochemical analyses. The structures of the complexes bis(*N*-cyanoethylglycinato)copper(II) monohydrate (**1a**), diaquabis(*N*-cyanoethylglycinato)nickel(II) (**1b**), aquabis(*N,N*-dicyanoethylglycinato)copper(II) (**2a**), and bis[(*N*-propionamido-*N*-cyanoethyl)glycinato]copper(II) dihydrate (**4a**) were also confirmed by X-ray diffraction techniques. The synthetic routes for the preparation of the Michael addition products are shown in Scheme 1.

The formation of the products can be explained by the following mechanism (Figure 1): clearly, the nitrogen atom, upon donating its lone pair of electrons to form a covalent bond with the metal ion, acquires a positive character, whereby the N−H bond gets polarized with the electron pair shifting to the nitrogen atom, causing lability to the N−H bond. The partial negative character on the nitrogen atom enables an attack on the olefinic double bond of the acrylonitrile molecule to form the Michael addition products **1a**−**1i**. Support for this comes from an earlier observation by Teo et al.[8] wherein the authors have stated clearly that, in a condensation of formaldehyde with bis(glycinato)zinc(II), the product formation must necessarily involve

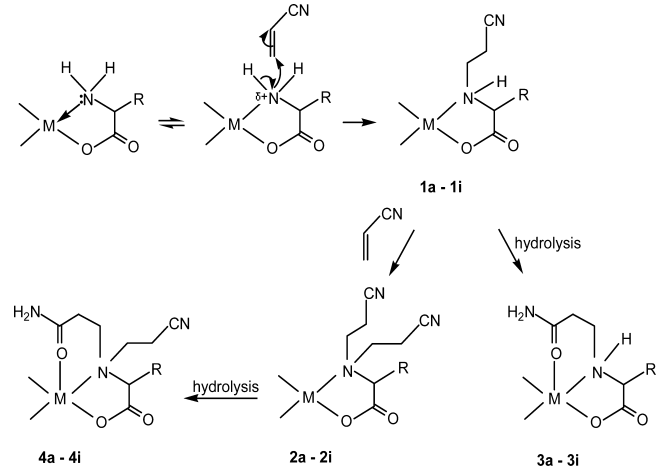


Figure 1. Proposed mechanism for the Michael addition reaction in the absence of a base.

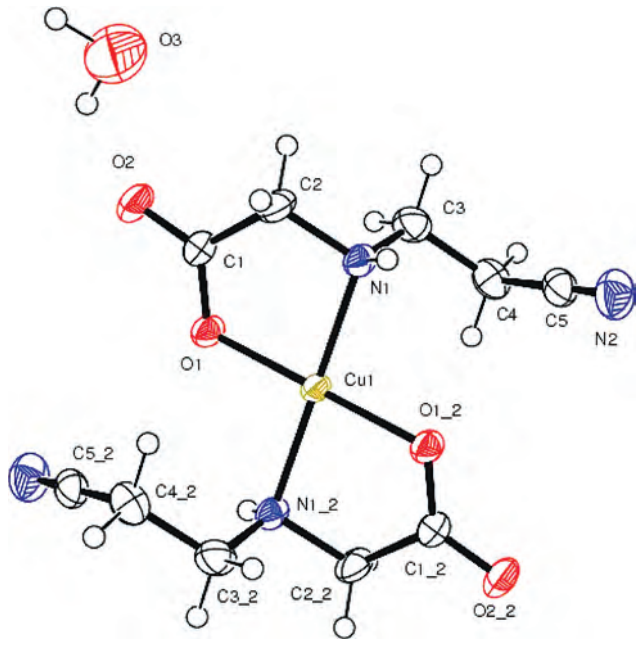


Figure 2. ORTEP representation of **1a**. Anisotropic ellipsoids are given at 50% probability. The symmetry equivalent: _2: 2 − *x*, 2 − *y*, −*z*.

the loss of protons from the nitrogen atom of the bis(glycinato)zinc(II) complex.

The products **1a**−**1i** undergo Michael addition with another molecule of acrylonitrile to give the disubstituted products **2a**−**2i**. Further, **1a**−**1i** and **2a**−**2i** undergo partial hydrolysis to form **3a**−**3i** and **4a**−**4i**. An interesting observation of these reactions is that the Michael reactions take place on the nitrogen atom of the chelated amino acids even in the absence of a base, and the products possess both nitrile and partially hydrolyzed amide groups.

It may be mentioned here that compound **3a** alone finds mention in a purely crystallographic study,[35] wherein the ligand is formed first by the reaction of glycine with acrylamide in a basic medium followed by the addition of Cu^{II} nitrate taken in a base. We have, however, prepared **3a** from a reaction of the bis(glycinato)copper(II) complex with acrylonitrile without the use of a base.

Crystal Structure Descriptions. 1a. Complex **1a** crystallizes in the triclinic system with the space group $P\bar{1}$ with half of the molecule in the asymmetric unit and one water molecule in the unit cell. An ORTEP perspective view of the complex is depicted in Figure 2. Selected bond lengths, bond angles, and hydrogen-bond distances are listed in Tables S1, S2, and S3 of the Supporting Information, respectively. The copper ion stays at the center of inversion. The amino nitrogens (N1) and carboxyl oxygens (O1) form an approximate square-planar coordination about the copper. Further, a weak coordination of cyano-nitrogens makes the geometry distorted octahedron (2.668 Å; Figure S1, Supporting Information). The molecules which are related through a-translation are linked to each other by cyanoethyl chains. Thus, the crystal is formed by one-dimensional coordinated polymeric chains running parallel to the *a* axis. The chains are further strengthened through pairs of N−H···O hydrogen-bonding interactions [2.32(2) Å, 166(2)°] between the amino nitrogen (N1) and carboxyl oxygen (O1). These chains are linked through water-mediated hydrogen bonds [2.14(4) Å, 132(5)°] and van der Waals interactions to form the three-dimensional crystalline solid.

1b. Complex **1b** crystallizes in the monoclinic system with the space group $P2_1/n$. There are two molecules in the unit cell with half of the molecule forming the asymmetric unit. An ORTEP representation of the complex is shown in Figure 3. Selected bond distances and bond angles are given in Tables S1 and S2, Supporting Information. The nickel ion stays at the center of inversion, and hence the molecule is centrosymmetric. The nickel ion is in an octahedral environment with two ligands forming approximate square-planar coordination and two water molecules forming the fifth and sixth coordination. Table S3 (Supporting Information) shows the intermolecular hydrogen-bonding scheme. The molecules are linked to each other through water-mediated O−H···O and N−H···O hydrogen bonds making a two-dimensional hydrogen-bonded network parallel to the *ac* plane (Figure S2, Supporting Information). There are C−H···N hydrogen bonds (C4−H4B···N2: 2.479 Å, 177.2°) linking these parallel networks. Thus, packing is stabilized through van der Waals and hydrogen-bonding interactions.

2a. Complex **2a** crystallizes in the monoclinic system with the space group $P2_1/n$, and there are four molecules in the unit cell. An ORTEP perspective view of the complex is shown in Figure 4. Selected bond lengths and bond angles are listed in Tables S1 and S2 (Supporting Information). The copper ion is pentacoordinated with the two ligands forming approximate square-planar coordination, and the water molecule forms a fifth coordination. The four ligand atoms O1, O2, N1, and N2 form nearly an ideal plane. The copper atom is 0.1827(9) Å (0.0009) in the mean plane formed by O1, O2, N1, and N2. Table S3 (Supporting Information) shows the intermolecular hydrogen-bonding scheme in the crystal lattice. The molecules are linked to each other through water-mediated hydrogen bonds to form a one-dimensional network running parallel to the *b* axis (Figure S3, Supporting Information). These one-dimensional chains pack in the crystal lattice through van der Waals and C−H···N hydrogen-bonding (C2−H2B···N3: 2.543 Å, 161.12°; C10−H10B···N6: 2.477 Å, 161.07°) interactions.

3a. Complex **3a** crystallizes in the monoclinic system with the space group *C*2/*c*. The unit cell parameters $a = 18.57$ Å, $b = 5.47$ Å, $c = 16.10$ Å, $\alpha = 90°$, $\beta = 115.41°$, and $\gamma = 90°$ and volume = 1477 Å^3 are in good agreement with the reported values[35] and thus confirm the Michael reaction of chelated glycine with acrylonitrile.

4a. Complex **4a**crystallizes in the monoclinic system with the space group $P2_1/c$ with half of the molecule in the asymmetric unit. There are two molecules in the unit cell. An ORTEP perspective view of the complex is depicted in Figure 5. Selected bond distances and bond angles are given in Tables S1 and S2 (Supporting Information). The copper ion stays at the center of inversion. The geometry around the metal ion is

(35) Lim, M. C.; Chen, W.; Ali, H. M. *Transition Met. Chem. (Dordrecht, Neth.)* **1994**, *19*, 409.

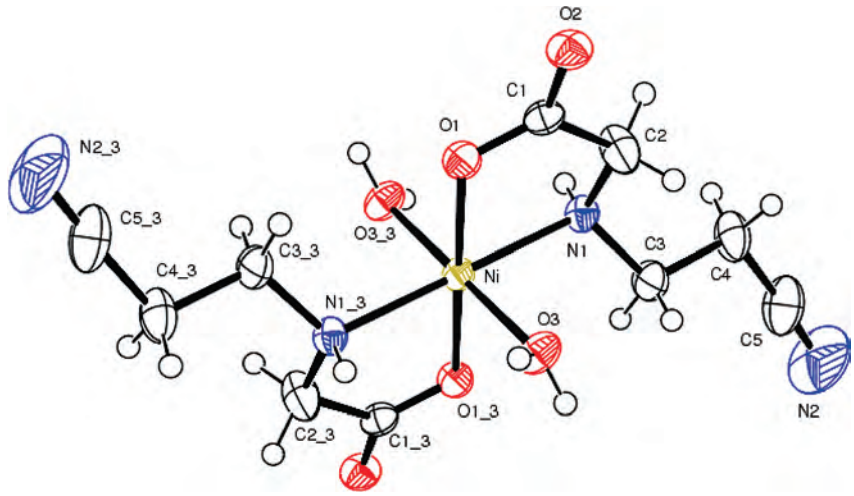


Figure 3. ORTEP representation of **1b**. Anisotropic ellipsoids are given at 50% probability. The symmetry equivalent: _3: $-x$, $-y$, $-z$.

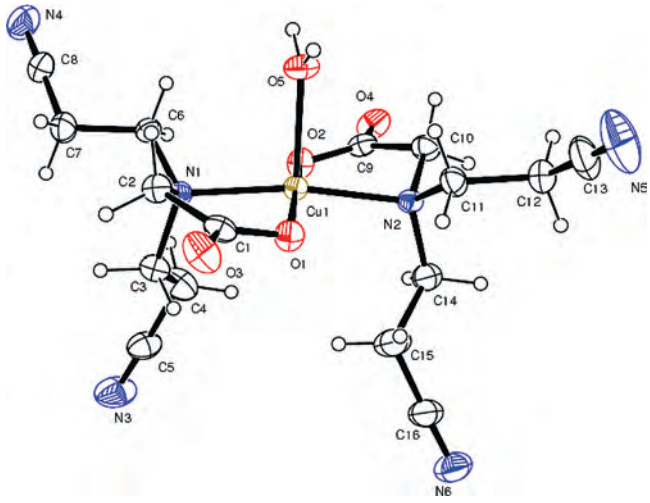


Figure 4. ORTEP representation of **2a**. Atoms are represented with 50% probability ellipsoids.

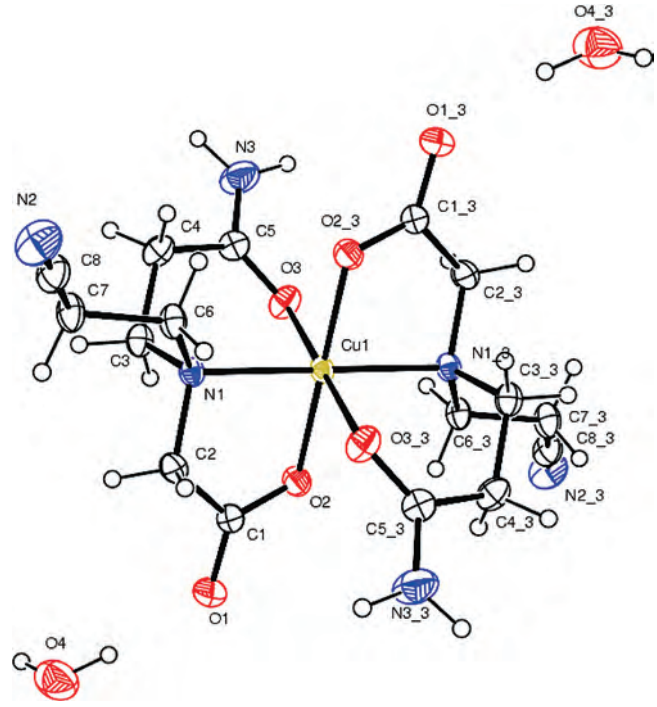


Figure 5. ORTEP representation of **4a**. Anisotropic ellipsoids are given at 40% probability. The symmetry equivalent: _3: $2 - x$, $-y$, $2 - z$.

elongated-octahedral with a carboxyethyl bite angle of 83.88° and an amide moiety bite angle of 90.94°. Table S3 (Supporting Information) shows intermolecular O−H···O and N−H···O hydrogen bonding. The O−H···O (including water-mediated hydrogen bonds) and N−H···O interactions form a three-dimensional network of hydrogen bonds linking the molecules (Figure S4, Supporting Information).

The bond lengths and bond angles around the metal ions in all of the above complexes are comparable to those reported previously.[11b,18c,36,37]

Spectroscopic and Electrochemical Characterization. The IR spectra of complexes **1a**−**1i** exhibit a sharp band in the frequency region 3180−3274 cm^{-1}, indicating the presence of a NH group.[38] The C≡N stretching is observed at ∼2250 cm^{-1} for complexes **1a**−**2i** and **4a**−**4i**. The absence of peaks in the frequency region 3000−3300 cm^{-1} for complexes **2a**−**2i** indicates that both of the protons of the amino group of the chelated amino acids take part in the reaction. Complexes **3a**−**3i** exhibit superimposed absorptions of amide NH_2 and chelated amino acid NH at ∼3200 cm^{-1}. The amide CO stretching is observed at ∼1670 cm^{-1} for complexes **3a**−**3i** and **4a**−**4i**. The amide NH asymmetric and symmetric stretching frequencies are observed at ∼3250 and ∼3180 cm^{-1}, respectively, for the complexes **4a**−**4i**. All of the complexes exhibit bands at ∼1600 and ∼1400 cm^{-1} and in the frequency range 3331−3547 cm^{-1} due to coordinated carboxylate asymmetric, symmetric, and OH stretching (water molecules, except for **2f**, **2g**, and **4i**), respectively. All DL- and L-alaninato complexes of metal(II) are found to undergo the Michael reaction with acrylonitrile to give the same product, showing thereby that there is no role for chirality in these reactions.

Furthermore, microanalytical data support the postulated formulas of these complexes.

(36) Freeman, H. C.; Snow, M. R.; Nitta, I.; Tomita, K. *Acta Crystallogr.* **1964**, *17*, 1463.
(37) Freeman, H. C.; Guss, J. M. *Acta Crystallogr. Sect. B* **1968**, *24*, 113.
(38) Comba, P.; Curtis, N. F.; Lawrence, G. A.; O'Leary, M. A.; Skelton, B. W.; White, A. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2145.

Table 1. Cyclic Voltammetry Data for the Copper and Nickel Complexes

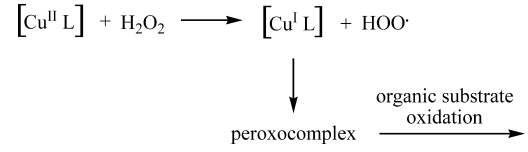
	reduction [M(II) ⇌ M(I)]	oxidation [M(II) ⇌ M(III)]			
complexes	E_{pc}/V	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	ΔE/mV
1b, **1e**, **1h**	−0.57	0.65	0.46	0.56	190
2b, **2e**, **2h**	−0.66	0.75	0.32	0.54	430
3b, **3e**, **3h**	−0.57	0.66	0.42	0.54	240
4b, **4e**, **4h**	−0.65	0.74	0.31	0.53	430
1a, **1d**, **1g**	−0.31				
2a, **2d**, **2g**	−0.49				
3a, **3d**, **3g**	−0.32				
4a, **4d**, **4g**	−0.47				

The EPR spectra of all of the copper complexes show g_{II}, $g_{\perp}$, and A_{II} values at ∼2.20, ∼2.02, and ∼170 G, respectively. The values of g_{II} ($> g_{\perp}$) are characteristic of axial copper(II) complexes in elongated-octahedral or square-pyramidal stereochemistries, that is, all copper(II) geometries associated with a $d_{x^2-y^2}$ ground state.[39] Figure S5 (Supporting Information) shows the EPR spectra of products **1a**, **2a**, **3a**, and **4a**.

The cyclic voltammograms of the mono- and disubstituted copper and nickel complexes show irreversible M^{II}/M^{I} reduction at ∼−0.31, ∼−0.47, −0.57, and ∼−0.65 V, respectively (Table 1). The electrochemical data indicate that the monosubstituted complexes undergo reduction at a lesser negative potential than that of the disubstituted complexes. The relatively high reduction potentials for the redox process of the disubstituted complexes arise due to the presence of rigid and sterically hindered disubstitution in the ligands. All of the nickel complexes show a single redox wave in the potential range 0 to +1.0 V (Figure S6, Supporting Information). The Ni^{II}/Ni^{III} oxidation process for the complexes is quasireversible in nature, as is evident from the criteria; namely, (i) the $E_{1/2}$ values are independent of scan rate, (ii) E_p increases with increasing scan rate and is always greater than 60 mV, and (iii) i_{pc}/i_{pa} are not the same at different scan rates.

Catalytic Activities. Degradation of Phenol Red Dye. The Michael addition products bis(N-cyanoethylglycinato)-copper(II) monohydrate (**1a**), aquabis(N,N-dicyanoethylglycinato)copper(II) (**2a**), bis(N-propionamidoglycinato)-copper(II) monohydrate (**3a**), and bis[(N-propionamido-N-cyanoethyl)glycinato]copper(II) dihydrate (**4a**) are used as catalysts for the degradation of PR dye (also known as phenolsulfonphthalein) in the presence of hydrogen peroxide (H_2O_2). Spectrophotometric measurements revealed that no absorbance change was observed at 430 nm when H_2O_2 was mixed with PR dye. However, upon the addition of the complexes, the absorbance at 430 nm was found to decrease. Linear relationships are obtained by plotting $2 + \log A$ versus time (A = absorbance), which shows that the reactions follow first-order kinetics. The rate of a reaction is calculated from the slope of the straight line. The rates of the degradation of PR using **1a**, **2a**, **3a**, and **4a** are found to be 3.1×10^{-3}, 11.4×10^{-4}, 2.5×10^{-3}, and 9.2×10^{-4} M s^{-1}, respectively, at fixed concentrations of H_2O_2 (0.01 M), complexes (0.001 M), and dye (6.0×10^{-5} M) (Figure S7, Supporting Information). The rate values reveal that the monosubstituted complexes **1a** and **3a** are relatively more effective than the disubstituted complexes **2a** and **4a**. This may be due to the monosubstitution of the copper complexes **1a** and **3a** (aa/AN = 1:1), which produce the highly active hydroxyl radicals at a higher rate than the disubstituted copper complexes **2a** and **4a** (aa/AN = 1:2). Thus, the number and nature of the substituents on glycine ligands of the copper complexes play an important role. The reaction mechanism involves the formation of a highly active hydroxyl radical, which is formed by the interaction of the complexes with H_2O_2. The hydroxyl radical attacks PR, forming a PR radical adduct which gets decomposed, resulting in the formation of the final oxidation products, namely, CO_2, sulfate, and water.[40]

Oxidation of Organic Substrates. Complexes **1a**, **2a**, **3a**, and **4a** were used as catalysts for the oxidation of pyrocatechol, benzaldehyde, *p*-methoxy benzaldehyde, *p*-nitro benzaldehyde, and benzyl alcohol to *o*-quinone, benzoic acid, *p*-methoxy benzoic acid, *p*-nitro benzoic acid, and benzaldehyde, respectively, in the presence of H_2O_2. That these complexes were effective catalysts was established by the fact that, in the absence of these complexes, H_2O_2 alone effected these oxidations at a much slower rate. These catalysts also converted benzylamine to benzaldehyde. The results obtained for the oxidation of organic substrates are given in Table 2. The percentage yields and time taken for the conversion of oxidation products reveal that complexes **1a** and **3a** are relatively more effective catalysts when compared to **2a** and **4a**. This may be due to the monosubstituted copper complexes (**1a** and **3a**) producing active peroxo complexes by interacting with H_2O_2 at a higher rate than the disubstituted copper complexes (**2a** and **4a**). The oxidation reactions follow the mechanism given below as reported previously.[41]



The catecholase mimetic activities of the copper complexes **1a**, **2a**, **3a**, and **4a** were carried out using pyrocatechol as a model substrate. The course of the reaction was followed spectrophotometrically for nearly 45 min at regular time intervals of 5 min. The slopes were determined by the method of initial rates by monitoring the growth of the 390 nm band of the product *o*-quinone.

Linear relationships for initial rate and the complex concentrations obtained for the copper complexes show a first-order dependence on the complex concentration for the

(39) (a) Bonomo, R. P.; Maccarrone, G.; Rizzarelli, E.; Vidali, M. *Inorg. Chem.* **1987**, *26*, 2893. (b) Duff, J. C. *J. Chem. Soc.* **1941**, 547.

(40) (a) Supriya, S.; Raghavan, A.; Vijayaraghavan, V. R.; Chinnakali, K.; Fun, H. K.; Subramanian, J. *Polyhedron* **2007**, *26*, 3217. (b) Ozawa, T.; Hanaki, A. *J. Chem. Soc., Chem. Commun.* **1991**, 330. (c) Lachheb, H.; Puzenat, E.; Houas, A.; Ksibi, M.; Elaloui, E.; Guillard, C.; Herrmann, J. M. *Appl. Catal., B* **2002**, *39*, 75. (d) Guillard, C.; Lachheb, H.; Houas, A.; Ksibi, M.; Elaloui, E.; Herrmann, J. M. *J. Photochem. Photobio., A* **2003**, *158*, 27.

(41) Sharma, S.; Barooah, N.; Baruah, J. B. *J. Mol. Catal. A* **2005**, *229*, 171.

Table 2. Results of **1a**, **2a**, **3a**, and **4a** Catalyzed Oxidation Reactions

	time (h)					yield (%)			
substrate	**1a**	**2a**	**3a**	**4a**	product	**1a**	**2a**	**3a**	**4a**
C_6H_5CHO	1.5	2	1.6	2.1	C_6H_5COOH	98	95	97	94
p-MeO−C_6H_4CHO	1.5	2.1	1.7	2.2	*p*-MeO−C_6H_4COOH	97	94	98	95
p-NO_2−C_6H_4CHO	2	2.6	2.1	2.7	*p*-NO_2−C_6H_4COOH	97	95	97	93
$C_6H_5CH_2OH$	7	8	7.2	8.2	C_6H_5CHO	83	80	80	78
$C_6H_5CH_2NH_2$	6	6.7	6.2	6.9	C_6H_5CHO	90	86	87	85

Table 3. Elemental Analyses and IR and EPR Spectroscopic Data of the Michael Addition Products

	elemental analyses (%)						IR (cm^{-1})								EPR		
	calculated			found													
complex	C	H	N	C	H	N	OH	NH	amide NH (asym)	amide NH (sym)	CN	amide CO	COO^- (asym)	COO^- (sym)	$g_{\|}$	$g_\perp$	$A_{\|}$ (*G*)
1a	35.76	4.77	16.69	35.72	4.71	16.62	3547	3180			2250		1631	1362	2.21	2.02	176
1b	34.41	5.16	16.06	34.38	5.14	16.04	3331	3230			2252		1608	1401			
1c	33.77	5.06	15.76	33.70	5.10	15.70	3490	3200			2250		1623	1398			
1d	39.61	5.50	15.40	39.60	5.52	15.39	3465	3249			2255		1619	1394	2.18	2.01	169
1e	38.23	5.31	14.87	38.22	5.32	14.80	3350	3274			2247		1628	1384			
1f	37.56	5.74	14.61	37.51	5.72	14.62	3470	3220			2252		1620	1400			
1g	37.74	5.77	14.68	37.69	5.72	14.62	3430	3200			2253		1622	1403	2.20	2.02	175
1h	38.23	5.31	14.87	38.22	5.32	14.80	3390	3210			2250		1627	1390			
1i	37.56	5.74	14.61	37.51	5.72	14.61	3468	3180			2249		1623	1389			
2a	43.48	4.98	19.02	43.40	4.89	18.98	3380				2250		1631	1374	2.21	2.01	176
2b	42.23	5.28	18.47	42.18	5.29	18.42	3398				2252		1610	1398			
2c	41.61	5.20	18.21	41.52	5.12	18.23	3410				2249		1621	1382			
2d	44.30	5.74	17.23	44.29	5.75	17.24	3430				2251		1615	1384	2.19	2.02	168
2e	44.75	5.80	17.40	44.70	5.71	17.42	3389				2250		1620	1390			
2f	47.64	5.29	18.53	47.69	5.21	18.51					2253		1618	1401			
2g	47.84	5.32	18.60	47.79	5.33	18.59					2250		1623	1389	2.20	2.02	162
2h	44.75	5.80	17.40	44.70	5.85	17.35	3380				2248		1612	1397			
2i	44.14	5.72	17.16	44.12	5.71	17.12	3396				2250		1617	1408			
3a	32.30	5.38	15.07	32.29	5.29	15.06	3345	3212				1672	1616	1385	2.21	2.01	176
3b	32.72	5.45	15.27	32.74	5.46	15.19	3339	3207				1669	1612	1390			
3c	32.14	5.36	15.00	32.15	5.29	14.91	3354	3203				1670	1620	1376			
3d	36.08	6.01	14.02	36.16	6.09	13.96	3351	3209				1672	1627	1390	2.20	2.02	172
3e	36.48	6.08	14.19	36.41	6.14	14.20	3352	3206				1678	1629	1379			
3f	34.34	6.20	13.35	34.34	6.11	13.36	3340	3209				1666	1618	1388			
3g	36.04	6.01	14.02	35.96	5.99	13.98	3349	3214				1660	1613	1376	2.21	2.01	176
3h	34.89	6.30	13.57	34.86	6.26	13.59	3353	3217				1678	1626	1379			
3i	35.88	5.98	13.95	35.86	5.99	13.95	3351	3211				1671	1617	1386			
4a	38.75	5.65	16.95	38.70	5.61	16.90	3376		3257	3176	2250	1672	1627	1382	2.22	2.01	176
4b	39.13	5.71	17.12	39.11	5.76	17.16	3389		3262	3178	2252	1668	1630	1390			
4c	38.60	5.63	16.89	38.61	5.60	16.82	3401		3256	3172	2247	1665	1624	1389			
4d	41.26	6.11	16.04	41.26	6.08	16.12	3392		3257	3180	2252	1678	1636	1378	2.21	2.02	174
4e	43.14	5.99	16.78	43.09	5.99	16.77	3387		3262	3172	2251	1672	1630	1392			
4f	42.57	5.91	16.56	42.58	5.91	16.60	3375		3269	3179	2249	1673	1633	1388			
4g	39.89	6.28	15.51	39.86	6.23	15.53	3398		3270	3189	2248	1679	1634	1382	2.21	2.01	174
4h	43.14	5.99	16.78	43.16	5.95	16.77	3379		3252	3271	2250	1669	1628	1379			
4i	44.14	5.72	17.16	44.21	5.67	17.23			3269	3280	2252	1672	1637	1382			

systems. The rate constants for copper complexes **1a**, **2a**, **3a**, and **4a** were found to be 1.2×10^{-2}, 3.9×10^{-3}, 0.8×10^{-2}, and 2.8×10^{-3} min^{-1}, respectively. The kinetic plot of $\log(A_\infty/A_\infty - A_t)$ versus time for the catalysts are shown in Figure S8 (Supporting Information). It is observed that complexes **1a** and **3a** show higher reactivity when compared to **2a** and **4a**, as in the case of the oxidation reactions discussed earlier.

Experimental Section

Materials and Instrumentation. All chemicals were used as received without further purification. Bis(amino acidato)metal(II) complexes, $M(aa)_2$ (amino acid (aa) = glycine, DL-alanine, L-alanine; metal (M) = copper, nickel, zinc), were prepared as reported in the literature.[42–45] Infrared spectra were recorded on a Thermo mattson Satellite FT-IR spectrophotometer as KBr discs. Elemental analyses were performed on a Perkin-Elmer CHNS 2400 elemental analyzer. EPR spectra were recorded on a Varion E-112 spectrometer using a 1:1 water−methanol mixture at 77 K. Cyclic voltammetric measurements were performed on a CHI 400A electrochemical analyzer using a three-electrode cell consisting of a glassy carbon electrode as a working electrode, platinum wire as an auxiliary electrode, and a saturated calomel as a reference electrode. The experiments were carried out on 0.001 M solutions of the complexes under nitrogen using sodium perchlorate (0.1 M) as the supporting electrolyte. Gas chromatographic (GC) analyses were performed on a Nucon 5765 gas chromatograph. The kinetic

(42) Delf, B. W.; Gillard, R. D.; Brien, P. O. *J. Chem. Soc., Dalton Trans.* **1979**, 1301.

(43) Sen, D. N.; Mizushima, S. I.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1955**, *77*, 211.

(44) Ibarra, C.; Soto, R.; Adan, L.; Cecinti, A.; Bunei, S. *Inorg. Chim. Acta* **1972**, *6*, 601.

(45) Segnini, D.; Curran, C.; Quagliano, J. V. *Spectrochim. Acta* **1960**, *16*, 540.

Table 4. Crystal Data and Structure Refinement for **1a**, **2a**, **3a**, and **4a**

coordination compound	1a	1b	2a	4a
empirical formula	C_{10} H_{16} Cu N_4 O_5	C_{10} H_{18} N_4 Ni O_6	$C_{16}H_{22}CuN_6O_5$	C_{16} H_{28} Cu N_6 O_8
fw	335.81	348.99	441.94	495.98
temp/K	293(2)	293(2)	293(2)	293(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
unit cell dimensions	a = 5.415(5)	a = 5.4812(2)	a = 11.3743(4)	a = 8.5659(3)
	b = 7.186(5)	b = 22.7449(8)	b = 11.0249(4)	b = 11.5298(5)
	c = 8.806(5)	c = 6.4258(2)	c = 16.2837(5)	c = 10.9835(4)
	α = 97.129(5)	α = 90	α = 90	α = 90
	β = 100.281(5)	β = 110.672(2)	β = 109.1240(10)	β = 99.0850(10)
	γ = 97.274(5)	γ = 90	γ = 90	γ = 90
volume/Å^3	330.6(4)	749.52(4)	1929.29(11)	1071.16(7)
Z	1	2	4	2
calcd density/Mg/m^3	1.686	1.546	1.521	1.538
abs coeff/mm^{-1}	1.677	1.326	1.173	1.075
F(000)	173	364	916	518
cryst color, morphology	blue, plate	pale blue, plate	blue, needle	blue, plate
cryst size/mm	0.30 × 0.25 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
θ range for data collection/deg	2.89−23.69	3.51−32.06	2.64−29.19	2.58−37.16
limiting indices	−6 6, −8 8, −9 9	−8 8, −33 32, −5 9	−10 15, −15 15, −22 17	−6 13, −18 16, −17 17
reflns collected	6174	10385	22812	14942
independent reflns	987	2583	5207	4449 [R(int) = 0.0473]
data/restraints/parameters	987/1/111	2583/2/109	5207/3/261	4449/3/158
goodness-of-fit on F^2	1.064	1.046	1.041	1.058
final R indices [$I>2\sigma(I)$]	R1 = 0.0208, wR2 = 0.0528	R1 = 0.0312, wR2 = 0.0700	R1 = 0.0396, wR2 = 0.0979	R1 = 0.0327, wR2 = 0.0967
R indices (all data)	R1 = 0.0216, wR2 = 0.0533	R1 = 0.0429, wR2 = 0.0737	R1 = 0.0729, wR2 = 0.1108	R1 = 0.0427, wR2 = 0.1015
largest diff. peak and hole/e Å^{-3}	0.391, −0.294	0.344, −0.305	0.471, −0.299	0.416, −0.452

measurements were recorded on a Shimadzu UV-160A spectrophotometer.

Syntheses. General Procedures for the Synthesis of Michael Addition Products. Procedure A. To a solution of $M(aa)_2$ (1 g) in 80.0 mL of water was added acrylonitrile (aa/AN = 1:1 or 1:2 molar ratio) in methanol dropwise with stirring for 24 h at room temperature.

Procedure B. To a solution of $M(aa)_2$ (1 g) in 80.0 mL water was added AN (aa/AN = 1:2 molar ratio) in methanol dropwise with stirring for 24 h at room temperature.

Procedure C. To a solution of $M(aa)_2$ (1 g) in 80.0 mL water was added AN (aa/AN = 1:1 molar ratio) in methanol dropwise with stirring for 48 h at room temperature.

Procedure D. To a solution of $M(aa)_2$ (1 g) in 80.0 mL water was added AN (aa/AN = 1:2 molar ratio) in methanol dropwise with stirring for 48 h at room temperature.

The above reaction mixtures upon concentration under reduced pressure and upon standing at room temperature yielded the corresponding Michael addition products. The products were filtered; washed with cold water and ethanol, followed by ether; and dried over calcium chloride.

Bis(*N*-cyanoethylglycinato)copper(II) Monohydrate (1a). The complex was prepared according to general procedure A, using bis(glycinato)copper(II) monohydrate {$[Cu(gly)_2]\cdot H_2O$} (1 g, 4.4 mmol) and AN (0.6 mL, 8.7 mmol) in 0.8 mL of methanol. Yield: 1.30 g (89%).

Diaquabis(*N*-cyanoethylglycinato)nickel(II) (1b). The complex was prepared according to general procedure A, using bis(glycinato)nickel(II) dihydrate {$[Ni(gly)_2]\cdot 2H_2O$} (1 g, 4.1 mmol) and AN (0.5 mL, 8.2 mmol) in 0.7 mL of methanol. Yield: 1.25 g (87%).

Diaquabis(*N*-cyanoethylglycinato)zinc(II) (1c). The complex was prepared according to general procedure A, using bis(glycinato)zinc(II) monohydrate {$[Zn(gly)_2]\cdot H_2O$} (1 g, 4.3 mmol) and AN (0.6 mL, 8.6 mmol) in 0.8 mL of methanol. Yield: 1.31 g (85%).

Bis(*N*-cyanoethyl-DL-alaninato)copper(II) Monohydrate (1d). The complex was prepared according to general procedure A, using bis(DL-alaninato)copper(II) monohydrate {$[Cu(DL\text{-}ala)_2]\cdot H_2O$} (1 g, 3.9 mmol) and AN (0.5 mL, 7.8 mmol) in 0.7 mL of methanol. Yield: 1.24 g (88%).

Bis(*N*-cyanoethyl-DL-alaninato)nickel(II) Monohydrate (1e). The complex was prepared according to general procedure A, using bis(DL-alaninato)nickel(II) trihydrate {$[Ni(DL\text{-}ala)_2]\cdot 3H_2O$} (1 g, 3.5 mmol) and AN (0.5 mL, 6.9 mmol) in 0.7 mL of methanol. Yield: 1.04 g (80%).

Diaquabis(*N*-cyanoethyl-DL-alaninato)zinc(II) (1f). The complex was prepared according to general procedure A, using bis(DL-alaninato)zinc(II) {$[Zn(DL\text{-}ala)_2]$} (1 g, 4.1 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.30 g (82%).

Bis(*N*-cyanoethyl-L-alaninato)copper(II) Dihydrate (1g). The complex was prepared according to general procedure A, using bis(L-alaninato)copper(II) {$[Cu(L\text{-}ala)_2]$} (1 g, 4.2 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.36 g (86%).

Bis(*N*-cyanoethyl-L-alaninato)nickel(II) Monohydrate (1h). The complex was prepared according to general procedure A, using bis(L-alaninato)nickel(II) trihydrate {$[Ni(L\text{-}ala)_2]\cdot 3H_2O$} (1 g, 3.5 mmol) and AN (0.5 mL, 6.9 mmol) in 0.7 mL of methanol. Yield: 1.08 g (83%).

Diaquabis(*N*-cyanoethyl-L-alaninato)zinc(II) (1i). The complex was prepared according to general procedure A, using bis(L-alaninato)zinc(II) {$[Zn(L\text{-}ala)_2]$} (1 g, 4.1 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.25 g (79%).

Aquabis(*N*,*N*-dicyanoethylglycinato)copper(II) (2a). The complex was prepared according to general procedure A, using $[Cu(gly)_2]\cdot H_2O$ (1 g, 4.4 mmol) and AN (1.2 mL, 17.4 mmol) in 1.7 mL of methanol. Yield: 1.67 g (87%).

Diaquabis(*N*,*N*-dicyanoethylglycinato)nickel(II) (2b). The complex was prepared according to general procedure B, using

$[Ni(gly)_2]\cdot 2H_2O$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.5 mmol) in 1.5 mL of methanol. Yield: 1.59 g (85%).

Diaquabis(*N*,*N*-dicyanoethylglycinato)zinc(II) (2c). The complex was prepared according to general procedure B, using $[Zn(gly)_2]\cdot H_2O$ (1 g, 4.3 mmol) and AN (1.1 mL, 17.3 mmol) in 1.5 mL of methanol. Yield: 1.66 g (83%).

Diaquabis(*N*,*N*-dicyanoethyl-DL-alaninato)copper(II) (2d). The complex was prepared according to general procedure B, using $[Cu(DL\text{-}ala)_2]\cdot H_2O$ (1 g, 3.9 mmol) and AN (1.0 mL, 15.5 mmol) in 1.4 mL of methanol. Yield: 1.60 g (85%).

Diaquabis(*N*,*N*-dicyanoethyl-DL-alaninato)nickel(II) (2e). The complex was prepared according to general procedure B, using $[Ni(DL\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.9 mL, 13.9 mmol) in 1.3 mL of methanol. Yield: 1.39 g (83%).

Bis(*N*,*N*-dicyanoethyl-DL-alaninato)zinc(II) (2f). The complex was prepared according to general procedure B, using $[Zn(DL\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.6 mmol) in 1.5 mL of methanol. Yield: 1.57 g (84%).

Bis(*N*,*N*-dicyanoethyl-L-alaninato)copper(II) (2g). The complex was prepared according to general procedure B, using $[Cu(L\text{-}ala)_2]$ (1 g, 4.2 mmol) and AN (1.1 mL, 16.7 mmol) in 1.5 mL of methanol. Yield: 1.49 g (79%).

Diaquabis(*N*,*N*-dicyanoethyl-L-alaninato)nickel(II) (2h). The complex was prepared according to general procedure B, using $[Ni(L\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.9 mL, 13.9 mmol) in 1.3 mL of methanol. Yield: 1.34 g (80%).

Diaquabis(*N*,*N*-dicyanoethyl-L-alaninato)zinc(II) (2i). The complex was prepared according to general procedure B, using $[Zn(L\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.6 mmol) in 1.5 mL of methanol. Yield: 1.68 g (83%).

Bis(*N*-propionamidoglycinato)copper(II) Monohydrate (3a). The complex was prepared according to general procedure C, using $[Cu(gly)_2]\cdot H_2O$ (1 g, 4.4 mmol) and AN (0.6 mL, 8.7 mmol) in 0.8 mL of methanol. Yield: 1.44 g (89%).

Bis(*N*-propionamidoglycinato)nickel(II) Monohydrate (3b). The complex was prepared according to general procedure C, using $[Ni(gly)_2].2H_2O$ (1 g, 4.1 mmol) and AN (0.5 mL, 8.2 mmol) in 0.7 mL of methanol. Yield: 1.30 g (86%).

Bis(*N*-propionamidoglycinato)zinc(II) Monohydrate (3c). The complex was prepared according to general procedure C, using $[Zn(gly)_2]\cdot H_2O$ (1 g, 4.3 mmol) and AN (0.6 mL, 8.6 mmol) in 0.8 mL of methanol. Yield: 1.42 g (88%).

Bis(*N*-propionamido-DL-alaninato)copper(II) Monohydrate (3d). The complex was prepared according to general procedure C, using $[Cu(DL\text{-}ala)_2]\cdot H_2O$ (1 g, 3.9 mmol) and AN (0.5 mL, 7.8 mmol) in 0.7 mL of methanol. Yield: 1.32 g (85%).

Bis(*N*-propionamido-DL-alaninato)nickel(II) Monohydrate (3e). The complex was prepared according to general procedure C, using $[Ni(DL\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.5 mL, 6.9 mmol) in 0.7 mL of methanol. Yield: 1.13 g (83%).

Bis(*N*-propionamido-DL-alaninato)zinc(II) Dihydrate (3f). The complex was prepared according to general procedure C, using $[Zn(DL\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.41 g (81%).

Bis(*N*-propionamido-L-alaninato)copper(II) Monohydrate (3g). The complex was prepared according to general procedure C, using $[Cu(L\text{-}ala)_2]$ (1 g, 4.2 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.33 g (80%).

Bis(*N*-propionamido-L-alaninato)nickel(II) Dihydrate (3h). The complex was prepared according to general procedure C, using $[Ni(L\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.5 mL, 6.9 mmol) in 0.7 mL of methanol. Yield: 1.17 g (82%).

Bis(*N*-propionamido-L-alaninato)zinc(II) Monohydrate (3i). The complex was prepared according to general procedure C, using $[Zn(L\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (0.6 mL, 8.3 mmol) in 0.8 mL of methanol. Yield: 1.33 g (80%).

Bis[(*N*-propionamido-*N*-cyanoethyl)glycinato]copper(II) Dihydrate (4a). The complex was prepared according to general procedure D, using $[Cu(gly)_2]\cdot H_2O$ (1 g, 4.4 mmol) and AN (1.2 mL, 17.4 mmol) in 1.7 mL of methanol. Yield: 1.79 g (86%).

Bis[(*N*-propionamido-*N*-cyanoethyl)glycinato]nickel(II) Dihydrate (4b). The complex was prepared according to general procedure D, using $[Ni(gly)_2]\cdot 2H_2O$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.5 mmol) in 1.5 mL of methanol. Yield: 1.68 g (83%).

Bis[(*N*-propionamido-*N*-cyanoethyl)glycinato]zinc(II) Dihydrate (4c). The complex was prepared according to general procedure D, using $[Zn(gly)_2]\cdot H_2O$ (1 g, 4.3 mmol) and AN (1.1 mL, 17.3 mmol) in 1.5 mL of methanol. Yield: 1.76 g (82%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-DL-alaninato]copper(II) Dihydrate (4d). The complex was prepared according to general procedure D, using $[Cu(DL\text{-}ala)_2]\cdot H_2O$ (1 g, 3.9 mmol) and AN (1.0 mL, 15.5 mmol) in 1.4 mL of methanol. Yield: 1.73 g (85%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-DL-alaninato]nickel(II) Monohydrate (4e). The complex was prepared according to general procedure D, using $[Ni(DL\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.9 mL, 13.9 mmol) in 1.3 mL of methanol. Yield: 1.40 g (81%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-DL-alaninato]zinc(II) Monohydrate (4f). The complex was prepared according to general procedure D, using $[Zn(DL\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.6 mmol) in 1.5 mL of methanol. Yield: 1.68 g (80%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-L-alaninato]copper(II) Trihydrate (4g). The complex was prepared according to general procedure D, using $[Cu(L\text{-}ala)_2]$ (1 g, 4.2 mmol) and AN (1.1 mL, 16.7 mmol) in 1.5 mL of methanol. Yield: 1.79 g (79%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-L-alaninato]nickel(II) Monohydrate (4h). The complex was prepared according to general procedure D, using $[Ni(L\text{-}ala)_2]\cdot 3H_2O$ (1 g, 3.5 mmol) and AN (0.9 mL, 13.9 mmol) in 1.3 mL of methanol. Yield: 1.39 g (80%).

Bis[(*N*-propionamido-*N*-cyanoethyl)-L-alaninato]zinc(II) (4i). The complex was prepared according to general procedure D, using $[Zn(L\text{-}ala)_2]$ (1 g, 4.1 mmol) and AN (1.1 mL, 16.6 mmol) in 1.5 mL of methanol. Yield: 1.58 g (78%). Elemental analyses, IR, and EPR spectroscopic data of the Michael addition products are given in Table 3.

Crystal Structure Determinations. X-ray data were collected at room temperature using a Bruker axs (kappa apex2) diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) with the ω and φ scan method. Unit cell dimensions for **1a**, **1b**, **2a**, and **4a** were refined from the setting angles of 6174, 10 385, 22 812, and 14 942 reflections in the ranges $2.89 < \theta < 23.69°$, $3.51 < \theta < 32.06°$, $2.64 < \theta < 29.19°$, and $2.58 < \theta < 37.16°$, respectively. Integration and scaling of the intensity data was accomplished using the SAINT/XPREP program.[46] The structures were solved by direct methods using SIR92 (WINGX),[47] and refinements were carried out through the full-matrix least-squares technique using SHELXL97.[48] Anisotropic displacement parameters were included for all non-hydrogen atoms. All C−H hydrogen atoms were positioned geometrically and treated as riding

(46) *SAINT, Area-Detector Integration Software*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.
(47) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(48) Sheldrick, G. M. *SHELXL97, Program for crystal structure solution and refinement*; University of Gottingen: Gottingen, Germany, 1997.

atoms, with C−H = 0.97 Å and with U_{iso}(H) values of 1.2 U_{eq}(C) for hydrogen atoms. O−H and N−H hydrogen atoms were located from difference Fourier maps and refined with distance constraints. Molecular graphics were computed using the ORTEP32 (WINGX)[49] and MERCURY[50] programs. Crystallographic data and refinement details are given in Table 4.

Catalytic Activities. Degradation of Phenol Red Dye. Complexes **1a**, **2a**, **3a**, and **4a** were used as catalysts for the degradation of PR dye in the presence of hydrogen peroxide (H_2O_2). The degradation experiments were carried out at fixed concentrations of H_2O_2 (0.01 M), complexes (0.001 M), and dye (6.0×10^{-5} M). In each degradation experiment, to a solution of 0.0034, 0.0044, 0.0037, or 0.0050 g of the catalysts **1a**, **2a**, **3a**, or **4a**, respectively, in 9.3 mL of double-distilled water was added 0.6 mL of 0.001 M dye and 0.1 mL of 0.01 M H_2O_2, and zero-time was noted. The reaction mixture was stirred continuously, and at regular time intervals, an aliquot was withdrawn and the absorbance at 430 nm recorded. The absorbance of the dye/H_2O_2 mixture remains constant for several hours in the absence of the catalyst.

Oxidation of Organic Substrates. The complexes **1a**, **2a**, **3a**, and **4a** were used as catalysts for the oxidation of pyrocatechol, benzaldehyde, *p*-methoxy benzaldehyde, *p*-nitro benzaldehyde, and benzyl alcohol to *o*-quinone, benzoic acid, *p*-methoxy benzoic acid, *p*-nitro benzoic acid, and benzaldehyde, respectively, in the presence of H_2O_2. These catalysts also converted benzylamine to benzaldehyde. Pyrocatechol oxidation experiments were carried out using a 0.1 M solution of pyrocatechol, a 0.001 M solution of the catalyst, and 0.001 M H_2O_2 in acetonitrile. The course of the reaction was followed spectrophotometrically for 45 min at regular time intervals of 5 min at 390 nm. The oxidation reactions of benzaldehyde, *p*-methoxy benzaldehyde, *p*-nitro benzaldehyde, benzyl alcohol, and benzylamine were carried out using 5 mmol of the organic substrates, 0.05 mmol of the catalysts, and 1.0 mL of H_2O_2 (30 vol %) in 5.0 mL of acetonitrile. The reactions were monitored by thin-layer chromatography or GC from time to time. After the completion of reactions, solvents were evaporated in a rotary evaporator, the catalysts were washed with water, and finally, the products were isolated by extraction with ether. The pure products were obtained by column chromatography and characterized by comparing their NMR and IR spectra with those of authentic samples.

(49) Farrugia, L. J. *J. Appl. Crystallogr* **1997**, *30*, 565.
(50) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M. K.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B* **2002**, *58*, 389.

Conclusion

A series of mono- and disubstituted Michael addition products, including partially hydrolyzed products, has been synthesized from bis(amino acidato)metal(II) complexes (metal = copper, nickel, zinc; amino acid = glycine, DL-alanine, L-alanine) and acrylonitrile in the absence of a base. Michael addition on the nitrogen atom of the coordinated amino acid moiety, replacing the amino hydrogen atom(s), is reported for the first time. A suitable reaction mechanism is also proposed. Additionally, the applications of four of these complexes were put to the test, by studying their catalytic activity on dye degradation reactions and the oxidation of organic substrates in the presence of hydrogen peroxide. The catalytic activity in all of these areas for four of these complexes is very encouraging.

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Note Added after ASAP Publication. This article was released ASAP on May 28, 2008 with Table 4 formatted incorrectly. The correct version was posted on June 30, 2008.

Supporting Information Available: Packing diagrams, EPR spectra, cyclic voltammograms, the kinetic plots for the degradation of phenol red and the oxidation of pyrocatechol to *o*-quinone, selected bond lengths, bond angles, hydrogen bonds, and crystallographic data of the structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC numbers: **1a**, 641464; **1b**, 645976; **2a**, 641463; and **4a**, 641466.

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