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Zinc(II)/Ketoxime System as a Simple and Efficient Catalyst for Hydrolysis of Organonitriles

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The hydrolysis of sterically hindered and unhindered alkyl nitriles, and also of benzyl and phenyl nitriles RCN (R = Me, CH_2Cl, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu, *p*-$MeOC_6H_4CH_2$, Ph), to carboxamides is catalyzed by a novel system of superior simplicity consisting of cheap, widely commercially available, and rather environmentally friendly compounds, that is, a ZnX_2/ketoxime combination, but it does not proceed at all with either the zinc salt or the ketoxime taken alone. The nature of the anion X^- in the zinc salt (X = NO_3, Cl, CF_3SO_3) or of the ketoxime ($Me_2C{=}NOH$, $C_4H_8C{=}NOH$, $C_5H_{10}C{=}NOH$) does not affect strongly the catalytic properties of the system, but the best results were obtained so far with a $Zn(NO_3)_2 \cdot 6H_2O$/2-propanone oxime molar ratio of 1:4; turnover numbers are typically above ca. 100 but reach as high as 1000 for *p*-$MeOC_6H_4CH_2C({=}O)NH_2$. The previously unknown structures of the two carboxamide products *n*-$BuC({=}O)NH_2$ and *p*-$MeOC_6H_4CH_2C({=}O)NH_2$ were determined by X-ray diffraction studies. The complexes $[ZnX_2(R_2C{=}NOH)_2]$ (X = Cl, R_2 = 2Me, C_4H_8, C_5H_{10}; X = NO_3, R = C_4H_8), prepared by heating the appropriate zinc salts with 2 equiv of the ketoxime in acetone and characterized by C, H, N analyses, FAB-MS, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, and also X-ray crystallography (for X = Cl, R_2 = 2Me; X = NO_3, R = C_4H_8), proved to be catalyst precursors in the conversions because the activity of these species is high only in the presence of 2 equiv of the ketoxime.

Introduction

The development of efficient methods for the formation of the C−N amide linkage is of great importance because of the high synthetic utility of amides, their industrial applications, and pharmacological interest.[1,2] Most of the known synthetic transformations leading to amides are based on the reaction between an activated carboxylic acid and an amine or ammonia.[1] An alternative preparative pathway involves hydrolysis of organonitriles. However, in the vast majority of cases, a base-catalyzed reaction leads to a carboxylate salt, because the second step of the hydrolysis (conversion of amides to carboxylic acids) is faster than the first one (conversion of nitriles to amides), and the reaction thus proceeds to the final hydration product rather than stopping at the amide stage.[1,3] Although in strong acidic solutions it can be possible to obtain amides, it is then necessary to have careful control of the temperature and of the ratio of reagents in order to avoid the formation of polymers which is promoted by the exothermic character of the hydrolysis.[4] Moreover, the final neutralization leads to an extensive salt formation with inconvenient product contamination and pollution effects.[4,5]

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(1) (a) Beckwith, A. L. J.; Zabicky, J. In *The Chemistry of Amides*; Wiley: New York, 1970; p 105. (b) Dopp, D.; Dopp, H. In *Houbel-Weyl, Methods of Organic Chemistry*; Thieme: New York, 1985; p 934. (c) Challis, B. C.; Challis, A. J. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 2, p 964.

(2) Lange, U. E. W.; Schäfer, B.; Baucke, D.; Buschmann, E.; Mack, H. *Tetrahedron Lett.* **1999**, *40*, 7067 and references therein.

(3) Brown, B. R. *The Organic Chemistry of Aliphatic Nitrogen Compounds*; Oxford University Press: Oxford, 1994.

(4) (a) Edward, J. T.; Meacock, S. C. R. *J. Chem. Soc.* **1957**, 2000. (b) Steynberg, P. J.; Denga, Z.; Steyn, R.; Bezuidenhout, B. C.; Stark, N. L. Patent WO 0026178, 2000.

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These difficulties can be overcome with the use of metal ions which can behave as extremely strong activators of RCN toward nucleophilic attack by OH^-/H_2O. This activation can result in an enhancement of the rate of hydrolysis commonly in the range 10^6-10^8 (ref 6) or even higher when involving an intramolecular attack by an hydroxide ligand,[7] and many metal-mediated processes (reviewed recently by two of us[8a]), that bring about hydration of nitriles and selective formation of metal-bound carboxamides, are known from the literature.[5,8,9] Despite that, most of the systems are not catalytic, and only a few methods are known so far to hydrate RCN under *homogeneous catalytic* conditions,[10−16] usually exhibiting a rather low activity. The most advantageous of them are based on some platinum(II) phosphinito complexes[10] and on other, less active, phosphino complexes of platinum(II) (and Pd and Ni analogues),[11,12] nonphosphinic dipalladium(II) complexes with *N*,*S*-coordinated ligands,[13a] various mononuclear Pd(II) complexes with aqua, amine, and so forth ligands,[13b] as well as some hydride phosphine complexes of low valent Ru or Ir.[5,9f] Other systems are based on Fe- or Co-containing enzymes, nitrile hydratases, which catalyze the hydration of nitriles in vivo[17,18] and, for some complexes, mimic these enzymes (although so far exhibiting a much lesser efficiency).[19] Those catalysts are rather expensive, and in addition, their preparation requires some particular skills. These drawbacks certainly restrict the application of the listed catalysts, not only in the laboratory, but also in industry, although some of them have found application therein. We now report on a system of superior simplicity for hydrolysis of aryl, benzyl, and both sterically hindered and unhindered alkyl nitriles which consists of cheap and widely commercially available compounds such as a zinc salt and a ketoxime, for example, zinc nitrate and 2-propanone oxime, and operates in air and under neutral conditions (the use of bases or acids is not required and the resulting formation of contaminating salts is thus eliminated) and without needing an excess of water thus facilitating the isolation of the product.

Results and Discussion

As a continuation of our project on metal-mediated nitrile−oxime couplings[20−23] and nitrile−nitrone cycloadditions,[24]

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(5) (a) Murahashi, S.-I.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225. (b) Murahashi, S.-I.; Naota, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1805. (c) Murahashi, S.-I.; Naota, T. *Chemtracts: Org. Chem.* **1994**, 281. (d) Murahashi, S.; Sasao, S.; Saito, E.; Naota, T. *Tetrahedron* **1993**, *49*, 8805.

(6) (a) Fairlie, D. P.; Jackson, W. G.; Skelton, B. W.; Wen, H.; White, A. H.; Wickramasinghe, W. A.; Woon, T. C.; Taube, H. *Inorg. Chem.* **1997**, *36*, 1020 and references therein. (b) Hay, R. W.; McLaren, F. M. *Transition Met. Chem. (Dordrecht, Neth.)* **1999**, *24*, 398.

(7) (a) Kim, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618. (b) Buckingham, D. A.; Morris, P.; Sargeson, A. M.; Zanella, A. *Inorg. Chem.* **1977**, *16*, 1910.

(8) For reviews see: (a) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771. (b) Kuznetsov, M. L. *Russ. Chem. Rev.*, in press. (c) Eglin, J. L. *Comments Inorg. Chem.* **2002**, *23*, 23. (d) da Rocha, Z. N.; Chiericato, G., Jr.; Tfouni, E., *Adv. Chem. Ser.* **1997**, 297. (e) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299.

(9) For recent experimental works see: (a) Cotton, F. A.; Daniels, L. M.; Donahue, J. P.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1354. (b) da Rocha, Z. N.; Ferreira, K. Q.; Silva, M.; de Oliveira, E. C.; Chiericato, G.; Tfouni, E. *Inorg. Chem.* **2001**, *40*, 5385. (c) Chin, C. S.; Chong, D.; Lee, B.; Jeong, H.; Won, G.; Do, Y.; Park, Y. J. *Organometallics* **2000**, *19*, 638. (d) Tellers, D. M.; Ritter, J. C. M.; Bergman, R. G. *Inorg. Chem.* **1999**, *38*, 4810. (e) Ruiz, J.; Cutillas, N.; Rodríguez, V.; Sampedro, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1999**, 2939. (f) Cotton, F. A.; Daniels, L. M.; Haefner, S. C.; Kuhn, F. E. *Inorg. Chim. Acta* **1999**, *287*, 159. (h) Mironov, Y. V. *Eur. J. Inorg. Chem.* **1999**, 997. (i) Nagao, H.; Ito, K.; Tsuboya, N.; Ooyama, D.; Nagao, N.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1999**, *290*, 113.

(10) (a) Parkins, A. W. *Platinum Met. Rev.* **1996**, *40*, 169. (b) Ghaffar, T.; Parkins, A. W. *J. Mol. Catal. A: Chem.* **2000**, *160*, 249. (c) Ghaffar, T.; Parkins, A. W. *Tetrahedron Lett.* **1995**, *36*, 8657. (d) Parkins, A. W.; Ghaffar, T. U.S. Patent 6,133,478, 2000. (e) Cobley, C. J.; van den Heuvel, M.; Abbadi, A.; De Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467.

(11) (a) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723. (b) Trogler, W. C.; Jensen, C. M. U.S. Patent 4,684,751, 1984.

(12) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(13) (a) McKenzie, C. J.; Robson, R. *Chem. Commun.* **1988**, 112. (b) Kaminskaia, M. V.; Kostic, N. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3677.

(14) Luo, R.-S.; Mao, X.-A.; Pan, Z.-Q.; Luo, Q.-H. *Spectrochim. Acta* **2000**, *56*, 1675.

(15) Villain, G.; Constant, G.; Gaset, A.; Kalck, P. *J. Mol. Catal.* **1980**, *7*, 355.

(16) (a) Fanelly, A. J.; Rauch, F. C. U.S. Patent 3884975, 1975; *Chem. Abstr.* **1975,** *83*, 115331. (b) Rauch, F. C.; Nachtigall, G. W. U.S. Patent 3821300, 1974; *Chem. Abstr.* **1974**, *81*, 170207. (c) Schoenbrunn, E. F. U.S. Patent 3679745, 1972; *Chem. Abstr.* **1972**, *77*, 100854.

(17) For recent reviews on nitrile hydratases see: (a) Kobayashi, M.; Shimizu, S. *Curr. Opin. Chem. Biol.* **2000**, *4*, 95. (b) Artaud, I.; Chatel, S.; Chauvin, A. S.; Bonnet, D.; Kopf, M. A.; Leduc, P. *Coord. Chem. Rev.* **1999**, *190−192*, 577. (c) Claiborne, A.; Yeh, J. I.; Mallett, T. C.; Luba, J.; Crane, E. J., III; Charrier, V.; Parsonage, D. *Biochemistry* **1999**, *38*, 15407. (d) Bianchi, D.; Bosetti, A.; Battistel, E. *Chim. Ind. (Milan)* **1999**, *81*, 1305. (e) Ramakrishna, C.; Dave, H.; Ravindranathan, M. *J. Sci. Ind. Res.* **1999**, *58*, 925. (f) Shimizu, S. *Bitamin* **1999**, *73*, 713. (g) Endo, I.; Odaka, M.; Yohda, M. *Trends Biotechnol.* **1999**, *17*, 244.

(18) For recent experimental works on nitrile hydratases: (a) Leonova, T. E.; Astaurova, O. B.; Ryabchenko, L. E.; Yanenko, A. S. *Appl. Biochem. Biotechnol.* **2000**, *88*, 231. (b) DiCosimo, R.; Hann, E. C.; Eisenberg, A.; Fager, S. K.; Perkins, N. E.; Gallagher, F. G.; Cooper, S. M.; Gavagan, J. E.; Stieglitz, B.; Hennessey, S. M. *ACS Symp. Ser.* **2000**, *767*, 114. (c) Wegman, M. A.; Heinemann, U.; Stolz, A.; van Rantwijk, F.; Sheldon, R. A. *Org. Process Res. Dev.* **2000**, *4*, 318. (d) Wang, M.-X.; Lu, G.; Ji, G.-J.; Huang, Z.-T.; Meth-Cohn, O.; Colby, J. *Tetrahedron: Asymmetry* **2000**, *11*, 1123. (e) Tauber, M. M.; Cavaco-Paulo, A.; Robra, K.-H.; Gubitz, G. M. *Appl. Environ. Microbiol.* **2000**, *66*, 1634. (f) Hann, E. C.; Eisenberg, A.; Fager, S. K.; Perkins, N. E.; Gallagher, F. G.; Cooper, S. M.; Gavagan, J. E.; Stieglitz, B.; Hennessey, S. M.; DiCosimo, R. *Bioorg. Med. Chem.* **1999**, *7*, 2239.

(19) (a) Chin, J. *Acc. Chem. Res.* **1991**, *24*, 145. (b) Tyler, L. A.; Noveron, J. C.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **2000**, *39*, 357. (c) Chatel, S.; Rat, M.; Dijols, S.; Leduc, P.; Tuchagues, J. P.; Mansuy, D.; Artaud, I. *J. Inorg. Biochem.* **2000**, *80*, 239. (d) Kung, I.; Schweitzer, D.; Shearer, J.; Taylor, W. D.; Jackson, H. L.; Lovell, S.; Kovacs, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 8299. (e) Heinrich, L.; Li, Y.; Vaissermann, J.; Chottard, G.; Chottard, J.-C. *Angew. Chem., Int. Ed.* **1999**, *38*, 3526.

(20) Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu.; Michelin, R. A. *Inorg. Chem.* **2001**, *40*, 1134.

(21) (a) Kukushkin, V. Yu.; Pakhomova, T. B.; Bokach, N. A.; Wagner, G.; Kuznetsov, M. L.; Galanski, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2000**, *39*, 216. (b) Kukushkin, V. Yu.; Pakhomova, T. B.; Kukushkin, Yu. N.; Herrmann, R.; Wagner, G.; Pombeiro, A. J. L. *Inorg. Chem.* **1998**, *37*, 6511. (c) Kuznetsov, M. L.; Bokach, N. A.; Kukushkin, V. Yu.; Pakkanen, T.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 4683.

(22) Wagner, G.; Pombeiro, A. J. L.; Bokach, N. A.; Kukushkin, V. Y. *J. Chem. Soc., Dalton Trans.* **1999**, 4083.

(23) (a) Kukushkin, V. Y.; Ilichev, I. V.; Wagner, G.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1999**, 3047. (b) Kukushkin, V. Yu.; Ilichev, I. V.; Zhdanova, M. A.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 1567.

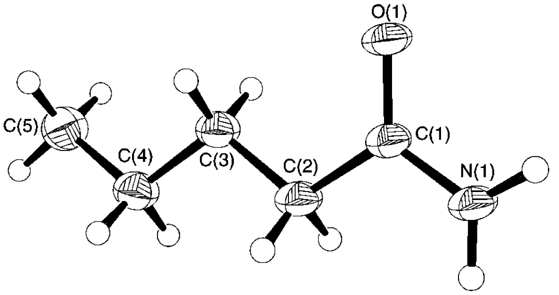

Figure 1. ORTEP view of the molecular structure of n-BuC(=O)NH_2 with atomic numbering. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): O(1)−C(1) 1.239(2), N(1)−C(1) 1.329(2), C(2)−C(1) 1.512(2), O(1)−C(1)−N(1) 121.83(12), N(1)−C(1)−C(2) 116.31(10).

we have recently found[25] that a Co(II)/ketoxime system *promotes* a facile conversion of an alkyl nitrile, RCN, to the appropriate amidine, RC(=NH)NH_2, and carboxylic acid, RC(=O)OH. Moreover, when the nitrile was diluted with water, giving a molar ratio of 5:1, the reaction went in another direction giving carboxamides, although in a non-catalytic way.[26] Inspired with this observed metal-promoted reaction, we attempted to extend it to some other metals in order to find an environmentally acceptable catalyst, derived from simple components, for generation of amides. We now report a catalytic system for the hydrolysis, under mild conditions, of organonitriles to carboxamides, based on a Zn(II)/ketoxime combination.

Description of the Catalytic System and Products Formed. The hydrolysis of sterically hindered and unhindered alkyl nitriles, and also of benzyl and phenyl nitriles RCN (R = Me, CH_2Cl, Et, n-Pr, i-Pr, n-Bu, t-Bu, p-$MeOC_6H_4CH_2$, Ph), is catalyzed by the $Zn(NO_3)_2 \cdot 6H_2O$ (0.7 mol % relative to the nitrile)/2-propanone oxime (2.8 mol %) system but does not proceed at all with either the zinc compound or the ketoxime taken alone. The obtained carboxamides were identified by comparison of their melting points, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectra with those of the commercially available carboxamides. Moreover, the previously unknown structures of the two carboxamides n-BuC(=O)NH_2 and p-$MeOC_6H_4CH_2C$(=O)NH_2 were determined by X-ray diffraction studies (Figures 1 and 2). In the carboxamides, the CH_2C(=O)NH_2 fragments are almost planar, and the C=O and C−N bond lengths and O−C−N bond angle within these moieties are in good agreement with those for other reported carboxamide structures.[27] The molecules in the crystal are held by hydrogen bonding between the complementary carbonyl and amido groups.

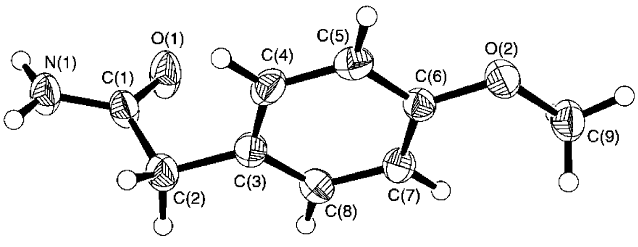

Figure 2. ORTEP view of the molecular structure of p-$MeOC_6H_4CH_2C$(=O)NH_2 with atomic numbering. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)−O(1) 1.237(2), N(1)−C(1) 1.319(3), C(1)−C(2) 1.514(3), C(6)−O(2) 1.373(2), O(2)−C(9) 1.429(3), N(1)−C(1)−O(1) 122.3(2), N(1)−C(1)−C(2) 117.0(2), C(6)−O(2)−C(9) 117.1(2).

Table 1. Quantitative Parameters for the Zinc(II)/Ketoxime Catalyzed Synthesis[a] of Carboxamides RC(=O)NH_2

R	TOF,[b] mol/(mol·h)	yield, %	TON,[c] mol/mol
Me	7.7	46	77
CH_2Cl	13.1	77	131
Et	11.3	68	113
n-Pr	11.0	66	110
i-Pr	8.6	52	86
n-Bu	14.3	86	143
t-Bu	4.5	27	45
p-$MeOC_6H_4CH_2$	45.0	90	450[d]
Ph	10.8	65	108

[a] See Experimental Section for the conditions. [b] Turnover frequency [mol(carboxamide)/{mol(Zn^{2+})·hour}]. [c] Turnover number [mol(carboxamide)/mol(Zn^{2+})]. [d] Can increase to ca. 1000 by further addition of RCN/H_2O to the mother liquor separated from the carboxamide (concomitant decrease of the TOF to ca. 20).

In the catalysis, the best results were obtained so far with a $Zn(NO_3)_2 \cdot 6H_2O$/2-propanone oxime molar ratio of 1:4 (turnover numbers (TONs) typically above ca. 100, Table 1); with less oxime, for example, 1:2, the rate of reaction, TON, and yield decrease significantly. Other ketoximes, for example, C_4H_8C=NOH or $C_5H_{10}C$=NOH, can also be used with a similar efficiency. The reaction with all nitriles (with the exception of MeCN when a homogeneous system is formed) is biphasic and requires vigorous stirring and reflux. At those conditions, however, 5−9% (R = Et, n-Pr, i-Pr, n-Bu, t-Bu, p-$MeOC_6H_4CH_2$, Ph) of the corresponding carboxylic acids are formed, but those byproducts are easily removed by recrystallization. In the cases of R = Me and CH_2Cl, the amount of the acids is larger (ca. 20%).

The hydrolysis of p-$MeOC_6H_4CH_2CN$ is different from that of the other nitriles because the appropriate carboxamide, that is, p-$MeOC_6H_4CH_2C$(=O)NH_2, is insoluble in the reaction mixture. Most likely, its precipitation and removal from the reaction medium facilitate the process, and this is reflected in the highest turnover number reached (Table 1). Moreover, if p-$MeOC_6H_4CH_2C$(=O)NH_2 is filtered off after 10 h when the reaction is completed and a new portion of the nitrile/H_2O is added to the filtrate, the process goes further, and the turnover number can be increased to ca. 1000.

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(24) (a) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *J. Am. Chem. Soc.* **2000**, *122*, 3106. (b) Wagner, G.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2001**, *40*, 264. (c) Wagner, G.; Pakhomova, T. B.; Bokach, N. A.; Fraústo da Silva, J. J. R.; Vicente, J.; Pombeiro, A. J. L.; Kukushkin, V. Y. *Inorg. Chem.* **2001**, *40*, 1683.

(25) Kopylovich, M. N.; Kukushkin, V. Yu.; Guedes da Silva, M. F. C.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1569.

(26) Kopylovich, M. N.; Kukushkin, V. Yu.; Pombeiro, A. J. L. Unpublished results.

(27) (a) Zobel, D.; Luger, P.; Dreissig, W.; Koritsanszky, T. *Acta Crystallogr., Sect. B* **1992**, *48*, 837. (b) Usanmaz, A.; Adler, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 660. (c) Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; DeFrees, D. J.; Binkley, J. S.; Pople J. A. *Acta Crystallogr., Sect. B* **1980**, *36*, 2292. (d) Kalyanaraman, B.; Kispert, L. D.; Atwood J. L. *J. Cryst. Mol. Struct.* **1978**, *8*, 175. (e) Qi, G.; Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K. *Acta Crystallogr., Sect. B* **1991**, *47*, 742. (f) Ruble, J. R.; Galvão, A. *Acta Crystallogr., Sect. B* **1995**, *51*, 835.

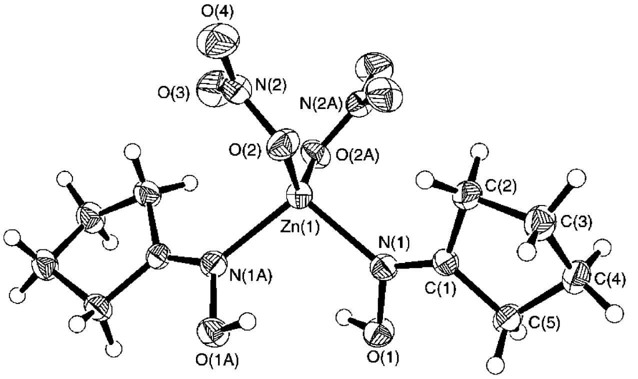

Figure 3. ORTEP view of the molecular structure of $[Zn(NO_3)_2(C_4H_8C{=}NOH)_2]$ with the atomic numbering. The thermal ellipsoids are drown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) 2.044(2), Zn(1)−O(2) 2.0387(14), Zn(1)−O(3) 2.483(2), N(1)−O(1) 1.415(2), N(1)−C(1) 1.274(2), N(2)−O(4) 1.216(2), N(2)−O(3) 1.240(2), N(2)−O(2) 1.294(2), N(1)−Zn(1)−O(3) 160.67(6), O(2)−Zn(1)−N(1) 106.41(6), C(1)−N(1)−Zn(1) 129.57(13), O(1)−N(1)−Zn(1) 118.38(11), O(4)−N(2)−O(3) 124.8(2), O(4)−N(2)−O(2) 118.8(2), O(3)−N(2)−O(2) 116.5(2).

The nature of the anion in the zinc salt does not affect strongly the catalytic properties of the Zn(II)/ketoxime systems. Thus, experiments with the hydrolysis of *p*-$MeOC_6H_4CH_2CN$ mediated by 2-propanone oxime and $Zn(NO_3)_2\cdot 6H_2O$, $ZnCl_2$, and $Zn(CF_3SO_3)_2$ gave the following turnover frequency (TOF), yield, and TON values: 45, 90, 450 for the nitrate; 37, 81, 370 for the chloride; and 33, 77, 330 for the triflate.

Trapping and Characterization of Intermediates. Upon investigation of the hydrolysis mediated by the $Zn(NO_3)_2\cdot 6H_2O/C_4H_8C{=}NOH$ system, we observed the release of some crystals formed if the reaction mixture was cooled after 10 min. An X-ray crystallographic study allowed their identification as the complex $[Zn(NO_3)_2(C_4H_8C{=}NOH)_2]$ (see later). This compound and other similar ones, that is, $[ZnX_2(R_2C{=}NOH)_2]$ ($X = Cl$, $R_2 = 2Me$, C_4H_8, C_5H_{10}; $X = NO_3$, $R = C_4H_8$), were prepared by independent syntheses via heating the appropriate zinc salts with 2 equiv of the oxime in acetone (see Experimental Section). All these complexes gave satisfactory C, H, and N elemental analyses and expected fragmentation/isotopic patterns in the FAB mass spectra; they were also characterized by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, while $[Zn(NO_3)_2(C_4H_8C{=}NOH)_2]$ and $[ZnCl_2(Me_2C{=}NOH)_2]$ were also characterized by X-ray diffraction studies (Figures 3 and 4).

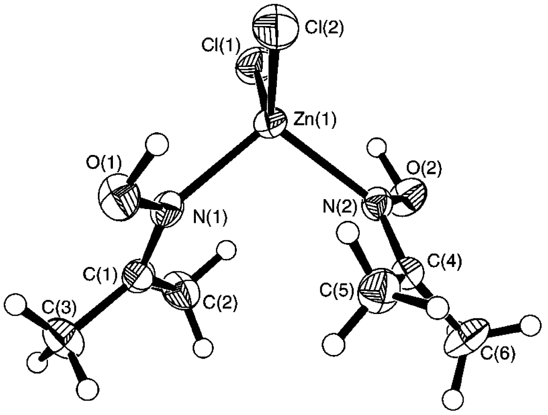

Figure 4. ORTEP view of the molecular structure of $[ZnCl_2(Me_2C{=}NOH)_2]$ with the atomic numbering. The thermal ellipsoids are drown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zn(1)−Cl(1), 2.2177(12), Zn(1)−Cl(2) 2.2291(12), Zn(1)−N(1) 2.049(4), Zn(1)−N(2) 2.054(3), N(1)−O(1) 1.407(4), C(1)−N(1) 1.282(5), N(2)−O(2) 1.408(4), C(4)−N(2) 1.279(5), N(1)−Zn(1)−Cl(1) 114.71(10), N(2)−Zn(1)−Cl(1) 101.38(10), Cl(1)−Zn(1)−Cl(2) 119.33(6), N(1)−Zn(1)−N(2) 104.64(14), O(1)−N(1)−Zn(1) 116.5(2), C(1)−N(1)−Zn(1) 130.0(3), O(2)−N(2)−Zn(1) 115.8(2), C(4)−N(2)−Zn(1) 129.3(3).

In both complexes, the main bond lengths are well-coherent with the observed values for other Zn─Cl[28] and Zn─ONO_2[29] compounds; geometric parameters of the oxime ligands agree with other oxime complexes where the ligands are bound via the oxime N atom.[30] In connection to the structures, it is worthwhile to mention the following points: (i) Despite the wealth of X-ray structures for zinc compounds containing *vic*-dioximes, the complexes characterized here are the first Zn complexes with "simple" oximes, that is, containing merely one oxime group as the only coordination site. (ii) In $[ZnCl_2(Me_2C{=}NOH)_2]$, weak intramolecular hydrogen bond interactions O(1)─H(11)···Cl(2) and O(2)─H(21)···Cl(1) (with O···Cl distances 3.193(4) and 3.234(3) Å, respectively) are stabilizing the structure. A weak interaction between O(2) and Cl(1) [O(2)···Cl(1) 3.294(3) Å] from the neighboring molecule (at equivalent position $-x$, $1 - y$, $2 - z$) can also be found (see Supporting Information for the hydrogen bonding). It is also noteworthy that the potential interest of oxime/oximato complexes for the construction of extended arrays, as has been shown previously for Pt(II)[31] and Ag(I)[32] systems, is now extended to the oxime Zn(II) compound.

We have demonstrated in separate experiments that all of the complexes $[ZnX_2(R_2C{=}NOH)_2]$ catalyze the described conversion of nitriles into carboxamides but a significant catalytic activity requires the presence of 2 equiv of the appropriate oxime; experiments with $[ZnX_2(R_2C{=}NOH)_2]$ and without added oxime showed a dramatic decrease of the

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(28) (a) Adams, H.; Bradshaw, D.; Fenton, D. E. *Eur. J. Inorg. Chem.* **2001**, 859. (b) Pfistner, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **2001**, *627*, 575. (c) Charmant, J. P. H.; Fallis, I. A.; Hunt, N. J.; Lloyd-Jones, G. C.; Murray, M.; Nowak, T. *J. Chem. Soc., Dalton Trans.* **2000**, 1723. (d) Yang, W.; Schmider, H.; Wu, Q.; Zhang, Y.-S.; Wang, S. *Inorg. Chem.* **2000**, *39*, 2397. (e) Muller, B.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **1999**, 129. (f) Alexakis, A.; Tomassini, A.; Chouillet, C.; Roland, S.; Mangeney, P.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4093.

(29) (a) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.-S.; Schroder, M. *Inorg. Chem.* **1999**, *38*, 2259. (b) Tandon, S. S.; Chander, S.; Thompson, L. K.; Bridson, J. N.; McKee, V. *Inorg. Chim. Acta* **1994**, *219*, 55. (c) Chen, H.; Olmstead, M. M.; Albright, R. L.; Devenyi, J.; Fish, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 642. (d) Kaminskaia, N. V.; Spingler, B.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 6411.

(30) For recent examples see: (a) Rosa, D. T.; Krause-Bauer, J. A.; Baldwin, M. J. *Inorg. Chem.* **2001**, *40*, 1606. (b) Cibulka, R.; Cisarova, I.; Ondracek, J.; Liska, F.; Ludvik, J. *Collect. Czech. Chem. Commun.* **2001**, *66*, 170. (c) Angeloff, A.; Daran, J.-C.; Bernadou, J.; Meunier, B. *Eur. J. Inorg. Chem.* **2000**, 1985. (d) Potocnak, I.; Heinemann, F. W.; Rausch, M.; Steinborn, D. *Acta Crystallogr., Sect. C* **1997**, *53*, 54.

(31) Kukushkin, V. Yu.; Nishioka, T.; Tudela, D.; Isobe, K.; Kinoshita, I. *Inorg. Chem.* **1997**, *36*, 6157.

(32) Aakeroey, C. B.; Beatty, A. M.; Leinen, D. S. *J. Am. Chem. Soc.* **1998**, *120*, 7383.

Table 2. Quantitative Parameters[a] for the Hydrolysis of p-$MeOC_6H_4CH_2CN$ Catalyzed by $[ZnCl_2(R_2C{=}NOH)_2]/R_2C{=}NOH$ and $ZnCl_2/R_2C{=}NOH$ Systems

catalytic system (molar ratio)	TOF, mol/(mol·h)	yield, %	TON, mol/mol
$ZnCl_2$/2-propanone oxime (1:4)	37.0	81	370
$[ZnCl_2(Me_2C{=}NOH)_2]$/2-propanone oxime (1:2)	36.5	76	365
$ZnCl_2/C_4H_8C{=}NOH$ (1:4)	25.6	65	256
$[ZnCl_2(C_4H_8C{=}NOH)_2]/C_4H_8C{=}NOH$ (1:2)	27.0	70	270
$ZnCl_2/C_5H_{10}C{=}NOH$ (1:4)	23.0	65	230
$[ZnCl_2(C_5H_{10}C{=}NOH)_2]/C_5H_{10}C{=}NOH$ (1:2)	24.0	67	240

[a] See footnotes *a* and *b* of Table 1.

activity (typically TON drops to about $^1/_{10}$). Representative results for $[ZnCl_2(R_2C{=}NOH)_2]$ complexes along with data for the corresponding mixtures of $ZnCl_2/R_2C{=}NOH$ are given in Table 2. Identical results, within the experimental error, were obtained for both types of systems.

The complexes of the type $[ZnX_2(\text{oxime})_2]$ are so far the only isolable intermediates (or catalyst precursors) for the conversion, and our attempts to detect other species involved in the process were not yet successful. Thus, in preparative experiments, treatment of $[ZnX_2(\text{oxime})_2]$ with an additional amount of the oxime (the complex/oxime molar ratio has ranged from 1:2 to 1:10) in acetone followed by removal of the solvent in vacuo and of the excess of the oxime by washing with diethyl ether led to recovery of the metal complexes intact. In NMR experiments, a fast exchange between $[ZnX_2(\text{oxime})_2]$ and excess of oxime, leading to only one set of signals in the temperature range from −50 to 60 °C, has been detected, and that precluded observation of other Zn-containing species by this method. In addition, attempted reaction between $[ZnX_2(\text{oxime})_2]$ and MeCN (the complex/nitrile molar ratio has ranged from 1:2 to 1:12) in $CDCl_3$ showed no interaction.

Hence, the lack of additional experimental data on intermediates involved in the catalytic system makes the interpretation of the catalysis mechanism somehow ambiguous. However, we anticipate that two principal routes for the hydrolysis are possible. In one of them, the complexes $[ZnX_2(R_2C{=}NOH)_2]$, formed in the initial stage of the reaction, might provide two neighboring coordination sites for ligation of a nitrile and water followed by the intramolecular hydration of RCN and release of the carboxamide formed. This route is coherent with one suggested in a recent theoretical study on Zn-mediated hydration of nitriles on heterogeneous catalysts.[33] However, the need for an additional 2 equiv of oxime would not be easily accounted for by this route. In the other route, a nitrile ligates to a Zn site (nitrile Zn complexes are known[34]), whereupon the ligated RCN species is attacked by the oxime, as was observed by us[20−23] and others[35] for kinetically substitutionally inert metal systems, to give a $[Zn]{-}NH{=}C(R'){-}ON{=}CR_2$ imino intermediate. Hydrolysis of the latter furnishes the carboxamide with concomitant regeneration of the Zn(II)/ketoxime catalyst upon solvolysis. In fact, the need for an additional 2 equiv of oxime to achieve the catalytic system and the previously reported results[36−38] on substitution of the OR′ moiety, by other groups, in $[M]{-}NH{=}C(R)OR'$ complexes support the latter pathway.

The facile catalytic one-pot hydrolysis of nitriles represents a viable route to carboxamides because of the simplicity and availability of the catalytic system discovered. In addition, the use of rather environmentally friendly[39] zinc systems suggests further benefits. Investigations of other metal/oxime systems in conversions of nitriles are on the way in our group.

Experimental Section

Materials and Instruments. Nitriles RCN (R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu, $ClCH_2$, p-$MeOC_6H_4CH_2$, Ph) (Aldrich), MeCN (Lab-Scan), $Me_2C{=}NOH$ (Lancaster), $C_4H_8C{=}NOH$, $C_5H_{10}C{=}NOH$ (Aldrich), $Zn(NO_3)_2{\cdot}6H_2O$ (Merck), $ZnCl_2$ (Aldrich), and $Zn(CF_3SO_3)_2$ (Fluka) were obtained from commercial sources and used as received. All instruments used were described in refs 20−24.

Synthetic Work and Characterization. Hydrolysis of Organonitriles. (a) From a Zn(II) Salt. 2-Propanone oxime (1.37 mmol) is added to a mixture of RCN (50 mmol) and undissolved $Zn(NO_3)_2{\cdot}6H_2O$ (0.33 mmol), and the system becomes homogeneous within 10 min (in the case of MeCN where the zinc salt is soluble, the homogeneous solution is immediately formed). Water (0.10 mol) is added dropwise for 1 h to the vigorously stirred reaction mixture giving a biphase system which is refluxed on continuous stirring for 10 h whereupon the reaction mixture is cooled to room temperature, the solvent is removed in vacuo at 20−25 °C to dryness, and the residue is purified by a conventional recrystallization. In the case of MeCN, in which $Zn(NO_3)_2{\cdot}6H_2O$ is soluble, addition of water gives a single solution. Quantitative parameters

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(33) Barbosa, L. A. M. M.; van Santen, R. A. *J. Mol. Catal. A: Chem.* **2001**, *166*, 101.

(34) (a) Müller, B.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **1999**, 117. (b) Batten, S. R.; Hoskins, B. F.; Robson R. *Chem. Commun.* **1991**, 445. (c) Castro, J. A.; Romero, J.; Garcia-Vazquez, J. A.; Macias, A.; Sousa, A.; Englert, U. *Polyhedron* **1993**, *12*, 1391. (d) Ohtsu, H.; Shimazaki, Y.; Odani, A.; Yamauchi, O. *Chem. Commun.* **1999**, 2393. (e) Matthews, C. J.; Clegg, W.; Heath, S. L.; Martin, N. C.; Hill, M. N. S.; Lockhart, J. C. *Inorg. Chem.* **1998**, *37*, 199. (f) Bhyrappa, P.; Krishnan, V.; Nethaji, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1901. (g) Gunter, M. J.; Jeynes, T. P.; Johnston, M. R.; Turner, P.; Chen, Z. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1945. (h) Eichhofer, A.; Fenske, D.; Fuhr, O. *Z. Anorg. Allg. Chem.* **1997**, *623*, 762. (i) Becker, B.; Radacki, K.; Wojnowski, W. *J. Organomet. Chem.* **1996**, *521*, 39. (j) Woller, E. K.; DiMagno, S. G. *J. Org. Chem.* **1997**, *62*, 1588. (k) Raubacher, F.; Weller, F. *Z. Kristallogr.* **1996**, *211*, 576. (l) Bel'sky, V. K.; Streltsova, N. R.; Bulychev, B. M.; Storozhenko, P. A.; Ivankina, L. V.; Gorbunov, A. I. *Inorg. Chim. Acta* **1989**, *164*, 211. (m) Isakov, I. V.; Zvonkova, Z. V. *Dokl. Akad. Nauk SSSR* **1962**, *145*, 801.

(35) (a) Pavlishchuk, V. V.; Kolotilov, S. V.; Addison, A. W.; Prushan, M. J.; Butcher, R. J.; Thompson, L. K. *Inorg. Chem.* **1999**, *38*, 1759. (b) Pavlishchuk, V. V.; Kolotilov, S. V.; Addison, A. W.; Prushan, M. J.; Butcher, R. J.; Thompson, L. K. *Chem. Commun.* **2002**, 468.

(36) (a) Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947. (b) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130.

(37) Raubenheimer, H. G.; Kruger, G. J.; Scott, F.; Otte, R. *Organometallics* **1987**, *6*, 1789.

(38) Pakhomova, T. B.; Kukushkin, V. Yu.; Pombeiro, A. J. L. Unpublished material.

(39) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.

of the reaction are given in Table 1. Identical procedures were followed in the case of $ZnCl_2$ or $Zn(CF_3SO_3)_2$ as the zinc salt.

(b) From a (Ketoxime)Zn(II) Complex. The procedure is similar to that described for the zinc salts, but only 2 equiv of the oxime is needed.

MeC(=O)NH$_2$, ClCH$_2$C(=O)NH$_2$, EtC(=O)NH$_2$, *n*-PrC(=O)NH$_2$, *i*-PrC(=O)NH$_2$, *n*-BuC(=O)NH$_2$, *t*-BuC(=O)NH$_2$, PhC(=O)NH$_2$, *p*-MeOC$_6$H$_4$CH$_2$C(=O)NH$_2$. Mp/(Mp lit.), 81°/(81°, p 38[40]), 119°/(119°, p 2108[40]), 80°/(80°, p 7838[40]), 116°/(115−116°, p 3218[40]), 129°/(127−129° p 1281[40]), 122°/(120−122° [41]), 156°/(154−157° p 233[40]), 130°/(130°, p 177[40]), 184°/(182−184°).[41] IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of the samples correspond to those of the commercially available carboxamides.

Preparation of (Ketoxime)Zn(II) Complexes. The ketoxime $R_2C{=}NOH$ (X = Cl, R_2 = 2Me, C_4H_8, C_5H_{10}; X = NO_3, R = C_4H_8; 4 mmol) is added to $ZnCl_2$ or $Zn(NO_3)_2{\cdot}6H_2O$ (2 mmol), whereupon acetone (10 mL) is added. The obtained slurry within ca. 1 min of stirring turns into a colorless solution which is refluxed for 8 h, the solvent is removed under vacuum to dryness at room temperature, and the residue formed is washed with three 5-mL portions of diethyl ether. Yields are 90−97%, based on Zn.

[ZnCl$_2$(Me$_2$C=NOH)$_2$]. Anal. Calcd for $C_6H_{14}N_2Cl_2O_2Zn$: C, 25.51; H, 5.00; N, 9.92. Found: C, 25.51; H, 5.33; N, 9.70. FAB$^+$-MS, *m*/*z*: 137 $[ZnMe_2CNOH + H]^+$, 172 $[ZnClMe_2CNOH]^+$, 247 $[ZnCl(Me_2CNOH)_2]^+$, 285 $[M + 4H]^+$. Mp = 105 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3580 mw, br ν(O−H), 1616 s ν(C=N), 1397 s + 1377 s $\nu_s(NO_3) + \delta_s(CH_3)$. ^1H NMR in $CDCl_3$, δ: 2.08 (s, 6*H*, 2CH$_3$), 2.10 (s, 6*H*, 2CH$_3$), 9.03 (s, br, 2*H*, 2OH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 17.6 (CH$_3$), 22.3 (CH$_3$), 164.8 (C=N).

[ZnCl$_2$(C$_4$H$_8$C=NOH)$_2$]. Anal. Calcd for $C_{10}H_{18}Cl_2N_2O_2Zn$: C, 35.90; H, 5.42; N, 8.37. Found: C, 35.98; H, 5.45; N, 8.30. FAB$^+$-MS, *m*/*z*: 299 [M − Cl], 337 $[M + 3H]^+$, 397 $[Zn_2Cl_2(Me_2CNOH)_2 - 2H]^+$, 436 $[Zn_2Cl_3(Me_2CNOH)_2 + H]^+$. Mp = 96 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3386 s ν(O−H), 2982 mw ν_{as}(C−H), 2874 mw ν_s(C−H), 1677 mw ν(C=N). ^1H NMR in $CDCl_3$, δ: 1.76 (m, 8*H*, 4CH$_2$), 2.41 (t, 4*H*, 2CH$_2$), 2.49 (t, 4*H*, 2CH$_2$), 8.97 (s, br, 2*H*, 2OH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 24.4 (CH$_2$), 25.2 (CH$_2$), 28.0 (CH$_2$), 31.1 (CH$_2$), 170.5 (C=N).

[ZnCl$_2$(C$_5$H$_{10}$C=NOH)$_2$]. Anal. Calcd for $C_{12}H_{22}Cl_2N_2O_2Zn$: C, 39.75; H, 6.12; N, 7.73. Found: C, 39.88; H, 6.13; N, 7.68. FAB$^+$-MS, *m*/*z*: 212 $[Zn(C_5H_{10}CNOH)Cl - 2H^+]$, 325 $[M - Cl - 2H^+]$, 365 $[M + 3H^+]$, 576 $[Zn_2(C_5H_{10}CNOH)_3Cl_3]$. Mp = 91 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3365 s, br ν(O−H), 2939 s ν_{as}(C−H), 2860 s ν_s(C−H), 1663 s ν(C=N). ^1H NMR in $CDCl_3$, δ: 1.64 (m, 12*H*, 4CH$_2$ + 2CH$_2$), 2.38 (t, 4*H*, 2CH$_2$), 2.62 (t, 4*H*, 2CH$_2$), 8.90 (s, br, 2*H*, 2OH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 25.0 (CH$_2$), 25.7 (CH$_2$), 26.5 (CH$_2$), 26.7 (CH$_2$), 32.6 (CH$_2$), 169.0 (C=N).

[Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$]. Anal. Calcd for $C_{10}H_{18}N_4O_8Zn$: C, 30.98; H, 4.68; N, 14.45. Found: C, 30.69; H, 4.85; N, 14.10. FAB$^+$-MS, *m*/*z*: 324 $[M - NO_3 - H^+]^+$. Mp = 147 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3391 s br ν(O−H), 2978 mw ν_{as}(C−H), 2874 mw ν_s(C−H), 1675 s $\nu(C{=}N) + \nu_{as}(NO_3)$, 1377 vs, br $\nu_s(NO_3) + \delta$(C−H), 825 s δ (NO$_3$). ^1H NMR in D_2O, δ: 3.58 (m, 8*H*, 4CH$_2$), 4.16 (t, 2*H*, 2CH$_2$), 4.23 (t, 2*H*, 2CH$_2$), OH were not observed. $^{13}C\{^1H\}$ NMR in D_2O, δ: 24.2 (CH$_2$), 24.9 (CH$_2$), 27.3 (CH$_2$), 30.7 (CH$_2$), 171.7 (C=N).

Table 3. Crystal Data for *n*-BuC(=O)NH$_2$ (**1**), *p*-MeOC$_6$H$_4$CH$_2$C(=O)NH$_2$ (**2**), [Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$] (**3**), and [ZnCl$_2$(Me$_2$C=NOH)$_2$] (**4**)

	1	**2**	**3**	**4**
empirical formula	$C_5H_{11}NO$	$C_9H_{11}NO_2$	$C_{10}H_{18}N_4O_8Zn$	$C_6H_{14}Cl_2N_2O_2Zn$
fw	101.15	165.19	387.65	282.46
temp, K	150(2)	150(2)	150(2)	150(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	11.0625(6)	15.9368(8)	13.8283(4)	7.10960(10)
b, Å	5.8294(3)	5.5722(2)	11.8788(4)	8.8985(2)
c, Å	9.7921(4)	9.6511(4)	9.8884(3)	10.9267(3)
α, deg	90	90	90	88.086(1)
β, deg	103.513(2)	96.096(2)	110.142(2)	71.811(1)
γ, deg	90	90	90	67.061(1)
V, Å^3	613.99(5)	852.20(6)	1524.96(8)	601.71
Z	4	4	4	2
ρ_{calcd}, g/cm^3	1.094	1.287	1.688	1.559
μ(Mo Kα), mm^{-1}	0.076	0.092	1.659	2.459
R1^a ($I \geq 2\sigma$)	0.0400	0.0493	0.0255	0.0393
wR2^b ($I \geq 2\sigma$)	0.1056	0.1199	0.0612	0.1070

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

X-ray Structure Determinations. Crystals of *n*-BuC(=O)NH$_2$ and *p*-MeOC$_6$H$_4$CH$_2$C(=O)NH$_2$ were obtained by recrystallization from acetone and methanol, respectively, while crystals of [Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$] and [ZnCl$_2$(Me$_2$C=NOH)$_2$] were grown by slow evaporation of the reaction mixtures. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) and the Collect[42] data collection program. The Denzo-Scalepack[43] program package was used for cell refinements and data reduction. The structures [Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$] and [ZnCl$_2$(Me$_2$C=NOH)$_2$] were solved by the Patterson method, and the others, by direct methods using the SHELXS-97 program.[44] An empirical absorption correction based on equivalent reflections[45] was applied to [Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$] and [ZnCl$_2$(Me$_2$C=NOH)$_2$] (T_{max}/T_{min}= 0.32258/0.26475 and 0.38090/0.34442, respectively). Structures were refined with the SHELXL-97[46] program and the WinGX graphical user interface.[47] In [Zn(NO$_3$)$_2$(C$_4$H$_8$C=NOH)$_2$], the Zn atom was positioned on a 2-fold axis. All hydrogens, except the ones in NH$_2$ and OH groups, were placed in idealized positions and constrained to ride on their parent atom. NH$_2$ and OH hydrogens were located from the difference Fourier map and were fixed or constrained to ride on their parent atom. Crystallographic data are summarized in Table 3, and selected bond lengths and angles, in the figure legends.

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(40) *The Merck Index*, 11th ed.; Merck & Co.: Rahway, NJ, 1989.

(41) Katritzky, A. R.; Pilarski, B.; Urogdi, L. *Synthesis* **1989**, 949.

(42) Data collection software: *Collect*; Nonius B. V.: Delft, The Netherlands, 1997−2000.

(43) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. *Methods in Enzymology, Vol. 276*; Macromolecular Crystallography, Part A; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997, pp 307−326.

(44) Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(45) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker Analytical X-ray Systems, Bruker AXS, Inc.: Madison, WI, 1998.

(46) Sheldrick, G. M. *SHELXL97*, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(47) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

Supporting Information Available: Tables listing crystallographic data, atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles and hydrogen bonds. X-ray crystallographic data for *n*-BuC(=O)NH_2, *p*-$MeOC_6H_4$-CH_2C(=O)NH_2, [$Zn(NO_3)_2(C_4H_8C{=}NOH)_2$], and [$ZnCl_2(Me_2C{=}NOH)_2$] in CIF format. Packing diagram of [$Zn(NO_3)_2(C_4H_8C{=}NOH)_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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