1990, *29*, 510; Y. Mizobe, Y. Ishii, M. Hidai, *Coord. Chem. Rev.* **1995**, *139*, 281.

[2] For C-bonded diazoalkane late transition metal compounds, see the following: Pd complexes: S. I. Murahashi, Y. Kitani, T. Hosokawa, K. Miki, N. Kasai, *J. Chem. Soc. Chem. Commun.* **1979**, 450; Os complexes: M. A. Gallo, T. C. Jones, C. E. F. Rickard, W. R. Roper, *J. Chem. Soc. Chem. Commun.* **1979**, 450; Rh complexes: E. Deydier, M.-J. Menu, M. Dartiguenave, Y. Dartiguenave, M. Simard, A. L. Beauchamp, J. C. Brewer, H. B. Gray, *Organometallics* **1996**, *15*, 1166; M.-J. Menu, J. Desrosiers, M. Dartiguenave, Y. Dartiguenave, G. Bertrand, *Organometallics* **1987**, *6*, 1822; Ni complexes: M.-J. Menu, H. König, M. Dartiguenave, Y. Dartiguenave, H. F. Klein, *J. Am. Chem. Soc.* **1990**, *112*, 5351.

[3] a) T. Luker, R. J. Whitby, M. Webster, *J. Organomet. Chem.* **1995**, *492*, 53; b) G. A. Vaughan, G. L. Hillhouse, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 7994; c) S. Gamboratta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1983**, *22*, 2029.

[4] E. Hey, U. Müller, *Z. Naturforsch. B* **1989**, *44*, 1538; E. Hey, M. F. Lappert, J. L. Atwood, S. G. Bott, *Polyhedron* **1988**, *7*, 2083; E. Hey, F. Weller, *Chem. Ber.* **1988**, 1207.

[5] T. A. Hanna, A. M. Baranger, R. G. Bergman, *Angew. Chem.* **1996**, *108*, 693; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 653.

[6] V. Cadierno, B. Donnadieu, A. Igau, J.-P. Majoral, *Eur. J. Inorg. Chem.* **2000**, 417.

[7] U. Blaschke, G. Erker, M. Nissinen, E. Wegelius, R. Fröhlich, *Organometallics* **1999**, *18*, 1224, and references therein.

[8] V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, A.Skowronska, *Chem. Eur. J.*, in press.

[9] J. A. Davies, P. L. Watson, J. F. Liebman, A. Greeberg, *Selective Hydrocarbon Activation*, VCH, New York, **1990**; *Activation and Functionalization of Alkanes* (Ed.: C. L. Hill), Wiley, New York, **1989**; A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Hingham, MA, **1984**; W. D. Jones, F. J. Feher, *Acc. Chem. Res.* **1989**, *2*, 91; A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403; A. Sen, *Acc. Chem. Res.* **1988**, *21*, 421; R. H. Crabtree, *Chem. Rev.* **1985**, *85*, 245.

[10] K. Horchler von Locquenhien, R. Réau, G. Bertrand, *J. Chem. Soc. Chem. Commun.* **1991**, 1192.

[11] Elemental analyses gave satisfactory results, see the Experimental Section.

[12] D. J. Cardin, M. F. Lappert, C. L. Raston, *Chemistry of Organo-Zirconium and -Hafnium Compounds*, Wiley, New York, **1986**, and references therein.

[13] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**, p. 260.

[14] For Zr–N σ/π bonding, see for example C. E. Holloway, I. M. Walker, M. Melnik, *J. Organomet. Chem.* **1987**, *321*, 143; R. Fandos, M. Lanfranchi, A. Otero, M. A. Pellinghelli, M. J. Ruiz, P. Terreros, *Organometallics* **1996**, *15*, 4725; P. J. Walsh, M. J. Carney, R. G. Bergman, *J. Am. Chem. Soc.* **1984**, *106*, 2210.

[15] For other five-coordinate zirconate complexes (containing Cp_2Zr) bonded to at least one nitrogen atom, see for example V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, A. Skowronska, *Chem. Eur. J.* **2000**, *6*, 345; V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, *Organometallics* **1999**, *18*, 1882; T. Luker, R. J. Whitby, M. Webster, *J. Organomet. Chem.* **1995**, *492*, 53.

[16] M. Regitz, *Diazoalkanes*, Thieme, Stuttgart, **1977**; D. S. Wulfman, G. Linstrumelle, C. F. Cooper, in *The Chemistry of Diazonium and Diazo Groups, Vol. 2* (Ed.: S. Patai), Chap. 18, Wiley, New York, **1978**.

[17] See for example D. M. Roddick, J. E. Bercaw, *Chem. Ber.* **1989**, *122*, 1579; R. Choukroun, B. Douziech, F. Soleil, *J. Chem. Soc. Chem. Commun.* **1995**, 2017.

[18] G. Maas, *Top. Curr. Chem.* **1987**, *137*, 75.

[19] The NMR spectroscopic assignment have been unambiguously confirmed by 2D HMQC NMR experiments: S. Braun, H. O. Kalinowski, S. Berger, *100 and more Basic NMR Experiments*, VCH, Weinheim, **1996**.

[20] E. Negishi, J.-L. Montchamp in *Metallocenes, Synthesis, Reactivity, Applications, Vol. 1* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, p. 241; E. Negishi, *Tetrahedron* **1995**, *51*, 4255; reviews: U. Annby, S. Karlsson, *Acta Chem. Scand.* **1993**, *47*, 425; J. A. Labinger in *Comprehensive Organic Synthesis, Vol. 3* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, p. 667; E. Negishi, *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon, Oxford, **1991**, p. 1163; G. Erker, M. Aulbach, M. Mena, R. Pfaff, F. Sosna, *Chem. Scr.* **1989**, *29*, 451.

[21] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 61; G. Singh, H. Zimmer, *Organomet. Chem. Rev.* **1967**, 279.

[22] IR and NMR spectroscopies were in full agreement with the reported data: A. Baceiredo, G. Bertrand, G. Sicard, *J. Am. Chem. Soc.* **1985**, *107*, 4781.

Hybrid Coordination Polymers—Metal Oxide Compounds with Chiral Structures[**]

Li-Min Zheng, Tabatha Whitfield, Xiqu Wang, and Allan J. Jacobson[*]

Many investigations of the design and synthesis of metal–organic compounds with porous structures have been motivated by potential applications in molecule recognition, separation, and catalysis.[1–11] By using rigid, multifunctional ligands, two- or three-dimensional microporous coordination polymers have been obtained with desired pore sizes and shapes.[3–11] Other metal–organic frameworks have been reported that, though they may have other valuable properties, are not microporous because of lattice interpenetration,[12] or are unstable on removal or exchange of their guest molecules or ions. Very few examples of either framework or microporous chiral metal–organic structures have been reported.[13–17]

One strategy to enhance the stability with respect to removal of the guest species is to attach the metal–organic components to a thermally more stable inorganic backbone. Several examples of compounds of this type containing both ligated metal cation and metal oxide components are known.[18–20] These extended lattices are formed in different ways, for example, by connecting a metal oxide cluster with a coordination complex, a metal oxide cluster anion with a coordination polymer, a metal oxide lattice with an isolated coordination complex, and metal oxide lattice with a coordination polymer. All of the inorganic components in the known examples are molybdenum or vanadium oxides.[18–20]

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[*] Prof. A. J. Jacobson, Dr. L.-M. Zheng,[+] T. Whitfield, Dr. X. Wang
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1) 713-743-2787
E-mail: ajjacob@uh.edu

[+] Permanent address:
Coordination Chemistry Institute, Department of Chemistry
Nanjing University, Nanjing 210093 (P. R. China)

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We are investigating the combination of coordination polymers with metavanadate chains as a route to stable porous structures. We also have used an unsymmetrical organic ligand, 2-pyrazinecarboxylate (2-pzc)[21] to introduce chirality into the structures formed. The combination of Co(2-pzc)$^+$ and Ni(2-pzc)$^+$ with vanadate chains has led to three novel inorganic–organic hybrid compounds **1**–**3** all of which are noncentric and two of which (**1**, **2**) are chiral.

$[Co_4(2\text{-}pzc)_4(V_6O_{17})]\cdot x\,H_2O$ **1**

$[Ni_4(2\text{-}pzc)_4(V_6O_{17})]\cdot x\,H_2O$ **2**

$[(NH_4)_2Co_8(2\text{-}pzc)_8(H_2O)_2(VO_3)_{10}]\cdot x\,H_2O$ **3**

Compounds **1**–**3** were prepared by hydrothermal synthesis at 160, 180, and 130 °C, respectively. The structures were determined by single-crystal X-ray diffraction[21] and the compositions by elemental analysis.[22] Infrared spectra confirmed the presence of vanadate and coordinated pyrazinecarboxylate. Compounds **1** and **2** are isostructural enantiomers; both crystallize in the chiral space group *I*4. The local coordination geometries of the cobalt and vanadium atoms in **1** are shown in Figure 1. Aspects of the extended chiral framework of **1** are shown in Figures 2 and 3.

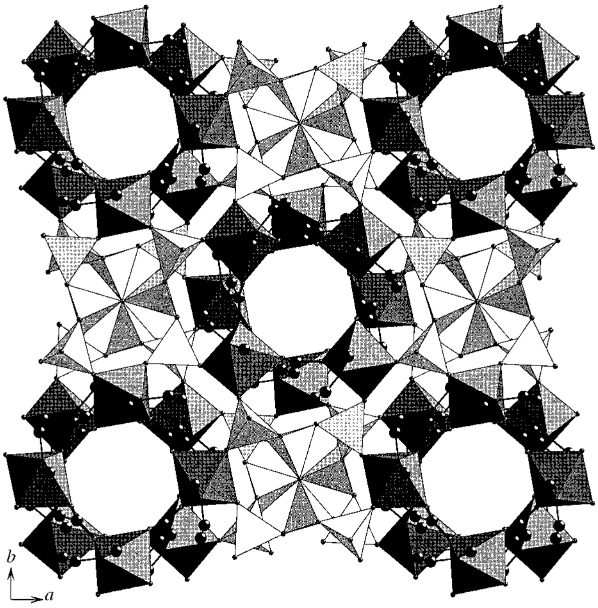

Figure 2. Polyhedral representation of the structure of **1** viewed down [001]; CoO_4N_2 octahedra: dark shaded; VO_4 tetrahedra: light shaded.

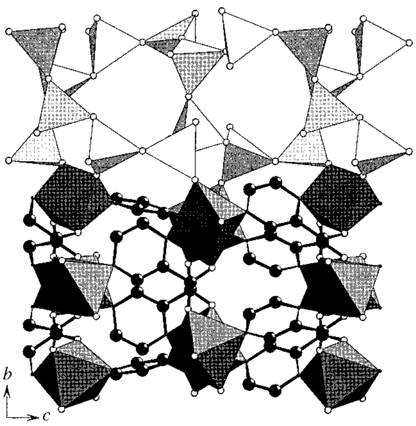

Figure 3. Polyhedral representation of the structure of **1** viewed along [100]; CoO_4N_2 octahedra: dark shaded; VO_4 tetrahedra: light shaded.

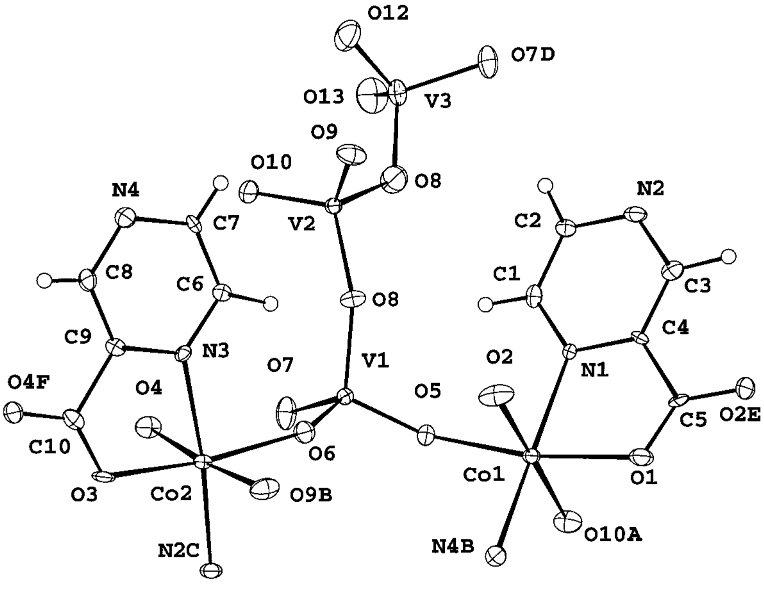

Figure 1. Coordination geometries of cobalt and vanadium in compound **1** with the atom-labeling scheme. Thermal ellipsoids are at the 50 % probability level. Selected bond lengths [Å]: Co1-O2 2.038(4), Co1-O10A 2.070(4), Co1-O1 2.093(4), Co1-O5 2.112(4), Co1-N4B 2.116(5), Co1-N1 2.141(4), Co2-O9B 2.044(4), Co2-O4 2.052(4), Co2-O3 2.100(4), Co2-O6 2.104(4), Co2-N3 2.114(4), Co2-N2C 2.122(5), V-O 1.592(5)–1.821(5).

Two crystallographically inequivalent Co atoms are present in the structure, each with a distorted octahedral coordination environment. Two nitrogen atoms from two 2-pzc ligands occupy the axial positions. The equatorial positions are filled by four oxygen atoms, two from the carboxylate groups of two 2-pzc ligands and the remaining two from the vanadate chains. The 2-pyrazinecarboxylate serves as a multidentate bridging ligand, as observed in the copper/2-pzc polymeric compounds,[23, 24] and links the Co1 and Co2 atoms into infinite helical chains. Each of the equivalent cobalt atoms are connected to each other through the 2-pzc carboxylate group from a neighboring chain. As a result, four Co/2-pzc helical chains form a chiral helical tube of composition $[\{Co_4(2\text{-}pzc)_4\}_n]$ (Figures 2 and 3). Eight oxygen atoms define the window into the tube. The $[\{Co_4(2\text{-}pzc)_4\}_n]$ tubes are stabilized by the vanadium oxide chains through corner-sharing of CoO_4N_2 octahedra with vanadium–oxygen tetrahedra.

Within the vanadium oxide chain, there are three crystallographically distinct tetrahedrally coordinated vanadium(v) atoms (Figure 1). These vanadium tetrahedra share corners with each other through oxygen atoms, forming infinite $[V_6O_{17}]_n^{4-}$ double chains along the *c* axis. The chain is bent to give perpendicularly arranged 8-rings (Figure 3). One oxygen atom is only coordinated to vanadium with a bond length significantly shorter (1.592(5) Å) than those of the other V–O bonds (1.626(4) – 1.821(5) Å). This vanadium oxide arrangement is different from the layers of corner-sharing VO_4 units that occur in $[Zn(bpy)_2]_2[V_6O_{17}]$ (bpy = 2,2′-bipyridine).[19] In **1**, each $[\{V_6O_{17}\}_n]^{4-}$ chain is connected to four $[\{Co_4(2\text{-pzc})_4\}_n]$ chains to form a three-dimensional chiral framework structure with 8-ring channels along the *c* axis (Figure 2). The frameworks of **1** and **2** are neutral. Disordered water molecules are found inside the metal – organic tubes.

Compound **3** crystallizes in the space group *Cc* and is closely related to **1** and **2**. The $[\{Co(2\text{-pzc})\}_n]$ helical tubes in **1** and **3** are comparable but **3** contains single metavanadate chains $[\{VO_3\}_n]$ instead of $[\{V_6O_{17}\}_n]$ double chains (Figure 4).

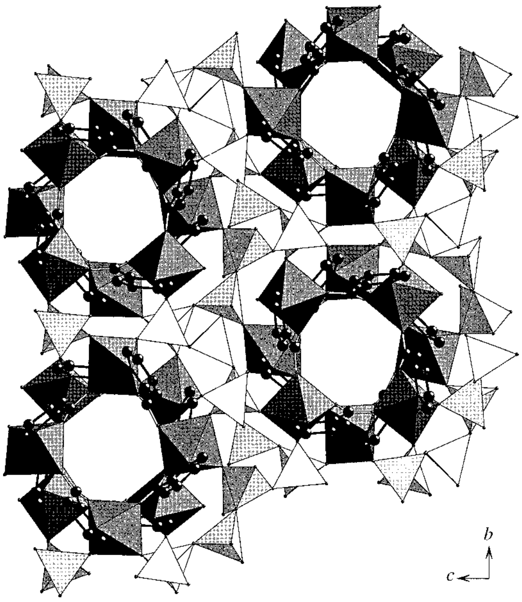

Figure 4. Polyhedral representation of the structure of **3** viewed down [100]; CoO_4N_2 octahedra: dark shaded; VO_4 tetrahedra: light shaded.

Six of the eight cobalt octahedra in **3** are corner-shared by two VO_4 tetrahedra, and two octahedra are connected to only one VO_4 tetrahedron. The octahedral environments of the two distinct Co octahedra are completed by coordinated water molecules. The framework of **3** is anionic and is charge balanced by two NH_4^+ ions. The NH_4^+ ions, together with disordered water molecules, reside in the metal – organic tubes.

Coordination of the unsymmetrical bridging ligand 2-pyrazinecarboxylate results in the formation of chiral $[\{M_4(2\text{-pzc})_4\}_n]$ or $[\{Co_8(2\text{-pzc})_8(H_2O)_2\}_n]$ helical tubes in **1** – **3**, each containing four $M(2\text{-pzc})^+$ helical chains. Unlike **1** and **2**, compound **3** is not chiral but contains equal numbers of left and right-handed helices. We note that other examples of compounds with tubelike structures have been reported.[25, 26] The formation of either **1** or **3**, containing different vanadium oxide chains but similar metal – organic components, is mainly dependent on the pH of the reaction mixture. Lower pH (≈4) promotes the formation of $[V_6O_{17}]$ double chains in **1**, whereas higher pH (≈6) favors the metavanadate chains in **3**. Reaction of **1** or **3** with NH_4VO_3 at 160 °C under hydrothermal conditions gives a higher density phase $[Co_2(2\text{-pzc})(H_2O)(VO_3)_3]$.[27]

The presence of the vanadate backbone in **1** – **3** increases significantly the thermal stability relative to metal pyrazinecarboxylate coordination polymers.[11, 24] Thermal analysis showed that **1** loses weight from 50 to 160 °C, corresponding to the removal of lattice water. A plateau region is observed from 160 to near 400 °C before the full decomposition occurs between 400 and 440 °C. The thermal decomposition behavior of **2** is very similar to that of **1** except that decomposition begins at 435 °C. For **3**, loss of lattice water, coordinated water, and the ammonium ion occurs below 300 °C, and decomposition below 500 °C. All of the thermogravimetric data agree quantitatively with the analytical compositions.

Compound **1** after dehydration at 200 °C reabsorbs water molecules on cooling in the presence of water vapor. Thermogravimetric analysis shows that the dehydration – hydration process is reversible though some hysteresis is observed. Powder X-ray diffraction confirmed the integrity of the structure after the dehydration and rehydration step.

The temperature-dependent magnetic susceptibilities of **1** – **3** were measured in a magnetic field of 0.5 T. For **1** and **3**, the effective magnetic moments (μ_{eff}) per Co at 300 K, 4.79 and 4.71 μ_B, are typical for Co^{II} compounds. Negative Weiss constants (– 10.3 K for **1**, – 13.4 K for **3**) indicate antiferromagnetic interactions. For **2**, the μ_{eff} value per molecule at 300 K is 5.88 μ_B, slightly higher than the value of 5.66 μ_B expected for four isolated Ni^{II} $S = 1$ ions. Assuming that the Ni1 – Ni1 and Ni2 – Ni2 coupling constants are the same, the data were analyzed by an exchange expression derived for a square arrangement of four $S = 1$ centers. A best fit was obtained with $g = 2.08$, $2J = -1.68\ \text{cm}^{-1}$. The small coupling constant indicates very weak antiferromagnetic interactions through the carboxylate bridges.

In conclusion, by using an unsymmetrical organic ligand, 2-pyrazinecarboxylate, three novel inorganic – organic hybrid compounds **1** – **3** have been prepared, whose framework structures contain tubes formed from four M(2-pzc) helical chains. Compounds **1** and **2** are chiral, whereas **3** contains equal numbers of left- and right-handed tubes. The pH of the syntheses determines the nature of the vanadate chains and consequently the final structure that is adopted. The thermal stabilities of **1** and **2** are among the highest of the metal – organic complexes reported. Further work is in progress to combine asymmetric ligands with other inorganic oxide networks.

Experimental Section

Syntheses were conducted hydrothermally in a Teflon-lined autoclave (23 mL).

1: $Co(NO_3)_2 \cdot 6H_2O$ (0.2918 g, 1 mmol), 2-pzcH (0.1239 g, 1 mmol), NH_4VO_3 (0.0713 g, 0.6 mmol), and H_2O (8 mL), 160 °C, 2 d, single phase, red needlelike crystals, yield about 97 % based on V.

2: $Ni(NO_3)_2 \cdot 6H_2O$ (0.1465 g, 0.5 mmol), 2-pzcH (0.0627 g, 0.5 mmol), NH_4VO_3 (0.0361 g, 0.3 mmol), and H_2O (8 mL), 180 °C, 2 d, single phase, green needlelike crystals, yield 87 % based on V.

3: $Co(NO_3)_2 \cdot 6H_2O$ (0.1437 g, 0.5 mmol), pyrazinamide (0.1134 g, 1 mmol), NH_4VO_3 (0.0589 g, 0.5 mmol), and H_2O (8 mL), 130 °C, 4 d, single phase, orange flat needles, yield 52% based on V. The hydrolysis of pyrazinamide results in a higher final pH (≈6) in the synthesis of **3** than in **1** and **2** (≈4).

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[1] C. Janiak, *Angew. Chem.* **1997**, *109*, 1499–1502; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431–1434, and references therein.

[2] G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792–795; Y.-H. Kiang, G. B. Gardner, S. Lee, Z. Xu, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1999**, *121*, 8204–8215.

[3] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 4843–4844; M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.

[4] D. M. L. Goodgame, D. A. Grachrogel, D. J. Williams, *Angew. Chem.* **1999**, *111*, 217–219; *Angew. Chem. Int. Ed.* **1999**, *38*, 153–155.

[5] F. Serpaggi, T. Luxbacher, A. K. Cheetham, *J. Solid State Chem.* **1999** *145*, 580–586.

[6] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844–1846; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725–1727; M. Kondo, T. Okubo, A. Asami, S.-I. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem.* **1999**, *111*, 190–193; *Angew. Chem. Int. Ed.* **1999**, *38*, 140–143.

[7] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[8] L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio, S. Rizzato, *Angew. Chem.* **2000**, *112*, 1566–1570; *Angew. Chem. Int. Ed.* **2000**, *39*, 1506–1510.

[9] Y. Diskin-Posner, S. Dahal, I. Goldberg, *Angew. Chem.* **2000**, *112*, 1344–1348; *Angew. Chem. Int. Ed.* **2000**, *39*, 1288–1292.

[10] L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772.

[11] Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *Solid State Sci.* **2000**, *2*, 335–341.

[12] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1588–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494, and references therein.

[13] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584–587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495.

[14] B. F. Abrahams, P. A. Jackson, R. Robson, *Angew. Chem.* **1998**, *110*, 2801–2804; *Angew. Chem. Int. Ed.* **1998**, *37*, 2656–2659.

[15] J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707–3710; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498–3501.

[16] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.

[17] C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158–5168.

[18] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798–2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684, and references therein.

[19] Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter, A. Clearfield, J. Zubieta, *Angew. Chem.* **1996**, *108*, 1067–1069; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 989–991.

[20] R. L. LaDuca, Jr., R. Finn, J. Zubieta, *Chem. Commun.* **1999**, 1669–1670; P. J. Hagrman, C. Bridges, J. E. Greedan, J. Zubieta, *J. Chem. Soc. Dalton Trans.* **1999**, 2901–2903; R. L. Laduca, Jr., C. Brodkin, R. C. Finn, J. Zubieta, *Inorg. Chem. Commun.* **2000**, *3*, 248–250; J. R. D. DeBord, Y. Zhang, R. C. Haushalter, J. Zubieta, C. J. O'Connor, *J. Solid State Chem.* **1996**, *122*, 251–258; L.-M. Zheng, J.-S. Zhao, K.-H. Lii, L.-Y. Zhang, Y. Liu, X.-Q. Xin, *J. Chem. Soc. Dalton Trans.* **1999**, 939–944; Z. Shi, L. Zhang, G. Zhu, G. Yang, J. Hua, H. Ging, S. Feng, *Chem. Mater.* **1999**, *11*, 3565–3570; X. Wang, L. Liu, A. J. Jacobson, K. Ross, **1999**, *9*, 859–861.

[21] Single-crystal data were collected at 223 K for **1** (293 K for **2**,**3**) on a Siemens Smart-CCD diffractometer. Crystal data for **1**: tetragonal, space group $I4$, $a = b = 17.6831(7)$, $c = 12.4616(7)$ Å, $V = 3896.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.250$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 31.28$ cm^{-1}. For **2**: tetragonal, space group $I4$, $a = b = 17.671(1)$, $c = 12.268(1)$ Å, $V = 3831.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.287$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 34.16$ cm^{-1}. For **3**: monoclinic, space group Cc, $a = 12.4122(11)$, $b = 24.958(2)$, $c = 24.949(2)$ Å, $\beta = 90.102(2)^\circ$, $V = 7728.6(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.195$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 29.26$ cm^{-1}. $\lambda = 0.71073$ Å, graphite monochromator, crystal dimensions: **1**, 0.3 × 0.03 × 0.03 mm; **2**, 0.3 × 0.02 × 0.02 mm; **3**, 0.35 × 0.10 × 0.02 mm; unique reflections: **1**, 4455 ($R_{int} = 0.0485$); **2**, 3930 ($R_{int} = 0.1032$); **3**, 13544 ($R_{int} = 0.0548$). Empirical absorption corrections and extinction corrections are applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares by using the SHELXTL program. All non-hydrogen atoms except the oxygen atoms (Ow) of lattice water were refined anisotropically. The disordered Ow and H atoms were refined isotropically. The H atoms attached to Ow of the lattice and coordinated water molecules or the ammonium nitrogen atom were not located. Absolute structure parameter: 0.03(2) for **1**, 0.07(3) for **2**, and 0.56(3) for **3**. $(\Delta\rho)_{max,min}$: **1**, 1.157, −0.523 e Å^{-3}; **2**, 1.075, −0.675 e Å^{-3}; **3**, 1.461, −0.663 e Å^{-3}. Final R indices ($I > 2\sigma(I)$) ($R1$, $wR2$): **1**, 0.0424, 0.0833; **2**, 0.0678, 0.1111; **3**, 0.0517, 0.1171. GOF: **1**, 1.082; **2**, 1.055; **3**, 0.993. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147014 (**1**), CCDC-147015 (**2**), and CCDC-147016 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[22] Elemental analysis: **1**: Calculated for $C_{20}H_{12}Co_4N_8O_{25}V_6 \cdot 1.6\,H_2O$ (%): C 17.99, H 1.14, N 8.39, Co 17.67, V 22.91; found: C 18.50, H 1.14, N 8.41, Co 17.26, V 21.33; **2**: Calculated for $C_{20}H_{12}Ni_4N_8O_{25}V_6 \cdot 1.6\,H_2O$ (%): C 18.00, H 1.14, N 8.40, Ni 17.61, V 22.93; found: C 17.91, H 1.27, N 8.47, Ni 17.73, V 22.41; **3**: Calculated for $C_{40}H_{36}Co_8N_{18}O_{48}V_{10} \cdot 3\,H_2O$ (%): C 18.80, H 1.57, N 9.87, Co 18.47, V 19.95; found: C 18.66, H 1.63, N 9.80, Co 19.33, V 19.87.

[23] M. A. S. Goher, N. A. Al-Salem, F. A. Mautner, K. O. Klepp, *Polyhedron* **1997**, *16*, 825–831.

[24] L.-M. Zheng, X. Wang, A. J. Jacobson, *J. Solid State Chem.* **2000**, *152*, 174–182.

[25] P. Millet, J. Y. Henry, F. Mila, J. Galy, *J. Solid State Chem.* **1999**, *147*, 676–678.

[26] G. Bonavia, R. C. Haushalter, C. J. O'Connor, C. Sangregorio, J. Zubieta, *Chem. Commun.* **1998**, 2187–2188.

[27] L.-M. Zheng, X. Wang, Y. Wang, A. J. Jacobson, unpublished results.

$[HC\{(CMe)(NAr)\}_2]Al[(NSiMe_3)_2N_2]$ ($Ar = 2,6\text{-}iPr_2C_6H_3$): The First Five-Membered AlN_4 Ring System[**]

Chunming Cui, Herbert W. Roesky,[*]
Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Pierre Braunstein

Main group heterocycles have attracted much attention from the pharmaceutical, agrochemical, and material science communities.[1] Among the varieties of ring systems, tetrazoles are of current interest. The discovery of the antiallergic, antibiotic activities and the important roles in biological systems of tetrazoles has stimulated extensive research on their chemistry in recent years.[2] In contrast, very little is

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[*] Prof. H. W. Roesky, Dipl.-Chem. C. Cui, Dr. H.-G. Schmidt,
M. Noltemeyer
Institut für Anorganische Chemie der Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-393373
E-mail: hroesky@gwdg.de

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