DOI: 10.1002/anie.200903772

Dioxygen Activation

O–O Bond Activation in Heterobimetallic Peroxides: Synthesis of the Peroxide [LNi(μ,η^2:η^2-O_2)K] and its Conversion into a Bis(μ-Hydroxo) Nickel Zinc Complex**

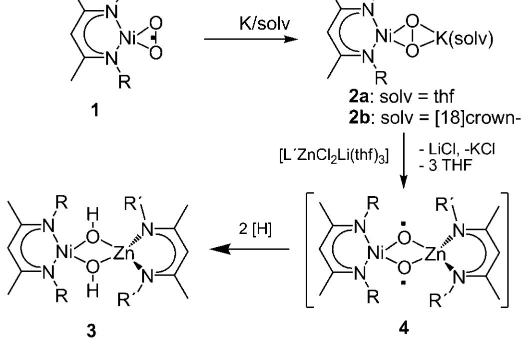
Shenglai Yao, Yun Xiong, Matthias Vogt, Hansjörg Grützmacher, Christian Herwig, Christian Limberg, and Matthias Driess**

Dedicated to Professor Karl Wieghardt

The activation of dioxygen for the subsequent oxygenation or oxidation of hydrocarbons is of importance not only in academia and industrial laboratories but also in nature. Some natural systems employ metalloenzymes containing two redox-active metal centers (e.g., tyrosinase or soluble methane monooxygenase), which cooperate in the activation process. On contact with O_2, in a first step the oxidation state of each metal atom is increased by +I and a peroxide unit is formed, which may represent the active species or just an intermediate. In a second step, the O–O bond can undergo cleavage with concomitant increase of the metal oxidation states by another unit so that M(μ-O)$_2$M cores result, which then perform the oxidation chemistry.[1] Attempts to mimic this kind of reactivity by low-molecular-weight analogues have revealed that whether or not step two occurs can depend on subtle changes of properties of the ligands, counterions, and solvents.[1a,2] Complexes with M(μ-O)$_2$M moieties (M = Cu, Fe, Ni, Co)[1–3] usually exhibit electrophilic character and can abstract hydrogen atoms from ligand substituents or exogenous sources such as solvents or added sacrificial substrates.[1–4]

Heterobimetallic species have attracted great interest because the combination of metals with different individual characteristics may lead to synergistic effects arising from asymmetry. The cyctochrome *c* oxidase, in which a Cu^I center cooperates with a (heme)Fe^{II} unit for the activation of O_2, serves as a natural example.[5] The synthesis of mixed metal complexes LM(μ-O)$_2$M′L′, however, is far more difficult than the preparation of homobimetallic analogues.[6] In the past, two strategies were pursued: 1) reaction of heterobimetallic M–M′ precursors with O_2, and 2) a two-step process in which a well-defined metal dioxygen complex is treated with a reducing metal compound. These routes have allowed for the preparation of desired heterobimetallic oxo complexes with the metal combinations Cu–Ni, Cu–Pd, Cu–Pt, Cu–Ge, Pt–Mo, Pd–Ge, and Pt–Ge.[6,7]

It is well known that NiO_2 complexes can serve as efficient oxidants in organic synthesis.[9] Furthermore, NiO_2 intermediates have been inferred as highly active species in several C–H bond transformations.[10] The consequences arising from the presence of a heterometal ion for O–O bond activation could not be explored owing to the lack of suitable precursors. Recently, some of us reported on the synthesis of the first isolable nickel(II) superoxo complex [LNi(O_2)] (**1**) (L = CH(CMeNR)$_2$, R = 2,6-iPr$_2$C$_6$H$_3$; Scheme 1),[8] which could serve as a suitable precursor for the synthesis of heterobimetallic Ni–M peroxo complexes in accordance with the synthetic strategy (2) mentioned above. Herein, we report the formation of the first heterobimetallic nickel(II) peroxo complex [LNi(μ,η^2:η^2-O_2)K] (**2**) and a metal-exchange reaction that leads to a heterobimetallic bis(μ-hydroxo) complex [LNi(μ-



Scheme 1. Synthesis of **2a, b** from **1** and their further conversion to **3** via the transient species **4**. (R = 2,6-iPr$_2$C$_6$H$_3$, R′ = 2,6-Me$_2$C$_6$H$_3$).

---

[*] Dr. C. Herwig, Prof. Dr. C. Limberg
Humboldt-Universität zu Berlin, Institut für Chemie
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
E-mail: christian.limberg@chemie.hu-berlin.de
Homepage: http://www.chemie.hu-berlin.de/aglimberg/

Dr. S. Yao, Dr. Y. Xiong, Prof. Dr. M. Driess
Technische Universität Berlin, Institute of Chemistry: Metalorganics and Inorganic Materials
Sekr. C2, Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-314-29732
E-mail: matthias.driess@tu-berlin.de
Homepage: http://www.driess.tu-berlin.de

Dipl.-Chem. M. Vogt, Prof. Dr. H. Grützmacher
Laboratorium für Anorganische Chemie
Wolfgang-Pauli-Strasse 10, ETH Hönggerberg, HCI H 131, 8093 Zürich (Switzerland)

[**] Financial support from the Cluster of Excellence "Unifying Concepts in Catalysis" (EXC 314/1, administered by the TU Berlin and funded by the Deutsche Forschungsgemeinschaft) is gratefully acknowledged. M.D. thanks the ETH Zürich for a guest professorship. L = β-diketiminate.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200903772.

OH)$_2$ZnL′] (**3**; L′ = CH(CMeNR′)$_2$, R′ = 2,6-Me$_2$C$_6$H$_3$) by unexpected O–O bond activation and hydrogen abstraction.

The electrochemical behavior of **1** suggested that the compound could serve as a suitable precursor for peroxo complexes. Cyclic voltammograms of **1** in a 0.1 M solution of NBu$_4$PF$_6$ in THF at ambient temperature show a quasi-reversible redox wave at $E^1_{1/2} = -0.98$ V (vs. [(C$_5$H$_5$)$_2$Fe]$^+$/[(C$_5$H$_5$)$_2$Fe], for details see the Supporting Information) implying that the superoxo complex may be reduced by one electron to a persistent species. In fact, the chemical reduction of **1** dissolved in THF with elemental potassium at ambient temperature leads to an immediate color change of the solutions from green to red-brown, from which the mono(thf) solvate **2a** can be isolated in the form of deep red crystals in 91 % yield (Scheme 1). As expected, the complex is diamagnetic, and its constitution is in accordance with the ^{1}H and ^{13}C NMR spectroscopic data, which revealed a highly symmetric structure with one molecule THF per K$^+$ ion (see the Supporting Information).

While crystals of **2a** were only of poor quality, single crystals of the crown ether complex **2b** suitable for X-ray diffraction study were obtained from a diethyl ether solution of **2a** in the presence of an equimolar amount of [18]crown-6 as brown-red crystals. Compound **2b** crystallizes as a centrosymmetric dimer with an inversion center between the two [K([18]c-6)]$^+$ ions (Figure 1). The most striking structural feature is the planar {Ni(μ,η^2:η^2-O$_2$)K} core, which in turn is coplanar with the six-membered C$_3$N$_2$Ni ring. Thus, the nickel(II) center is in a common square-planar coordination environment that is also found in the precursor **1**. As expected, the O–O separation of 1.468(2) Å is significantly longer than the value observed in the superoxo ligand in **1** (1.347(2) Å) but similar to the distances observed for other metal peroxo complexes (1.4–1.5 Å).[11] The peroxo character is fully supported by the IR spectrum of **2b** (and its {Ni^{18}O$_2$K} isotopologue), which exhibits a characteristic absorption band at 829 cm^{-1}, corresponding to the ^{16}O–^{16}O stretching vibration mode vs. ν(^{18}O–^{18}O) = 782 cm^{-1}.[9b] Although the potassium center is coordinated to the six oxygen atoms of the crown ether and additionally to one oxygen atom of the adjacent [18]c-6 ligand, it is also tightly coordinated to both peroxide oxygen atoms (O1, O2), with K1–O1 and K1–O2 separations of 2.695(2) and 2.734(2) Å, respectively. Remarkably, attempts to separate the K$^+$ ion from the peroxide oxygen atoms (formation of ion pairs) have been unsuccessful, and not even the powerful [2,2,2] cryptand was capable of cleaving the K–O$_2$ contact. To probe whether the K$^+$ ion can be replaced by another non-redox-active center under retention of the peroxo moiety, we performed the reaction of **2a** with the (β-diketiminato)zinc(II) chloride LiCl adduct [L′Zn(μ-Cl)$_2$Li(thf)$_3$][12] as precursor for [L′ZnCl] in THF at ambient temperature. To our surprise, the cation replacement led to the bis(μ-hydroxo) Ni^{II}(OH)$_2$Zn^{II} complex **3** instead of the expected analogous peroxo complex, which can be isolated in the form of brown crystals in 42 % yield (Scheme 1).

Compound **3** is diamagnetic and gives rise to sharp signals in the ^{1}H and ^{13}C NMR spectra in the common chemical shift range for the β-diketiminato ligands (see the Supporting Information). The bridging hydroxo protons resonate at δ = 2.01 ppm in the ^{1}H NMR spectrum, and the ν(O–H) stretching mode appears in the IR spectrum at 3660 cm^{-1}. The structure of **3** has been confirmed by single-crystal X-ray diffraction analysis (Figure 2). The compound crystallizes in the orthorhombic space group *Cmcm* and consists of two structurally distinct β-diketiminato metal subunits, a square-planar Ni^{II} unit and a tetrahedral Zn^{II} site, which are bridged by two μ-hydroxo ligands. The geometric parameters of the LNi^{II} moiety in **3** are similar to those of the dinuclear complex [LNi^{II}(μ-OH)$_2$Ni^{II}L].[8]

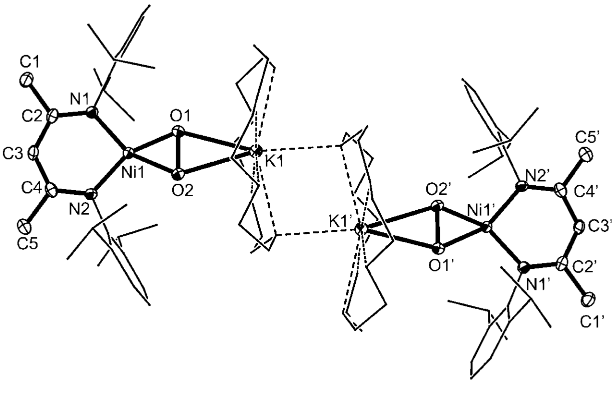


Figure 1. Molecular structure of **2b**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted. Selected interatomic distances [Å] and angles [°]: O1–O2 1.468(2), Ni1–O1 1.820(2), Ni1–O2 1.820(2), Ni1–N2 1.865(2), Ni1–N1 1.866(2), K1–O1 2.695(2), K1–O2 2.734(2), N1–C2 1.324(3), N2–C4 1.327(3), C2–C3 1.399(3), C3–C4 1.399(3), K–O(crown ether) 2.658(2)–2.923(2), K1–O′(second crown ether; smallest separation) 2.920(2), K1⋯K1′ 4.432(2); O1-Ni1-O2 47.57(6), N2-Ni1-N1 96.67(7), O1-K1-O2 31.38(4), Ni1-O1-K1 141.89(7), Ni1-O2-K1 138.98(7). Symmetry transformations used to generate equivalent atoms with (′): −*x*,−*y*,−*z*.

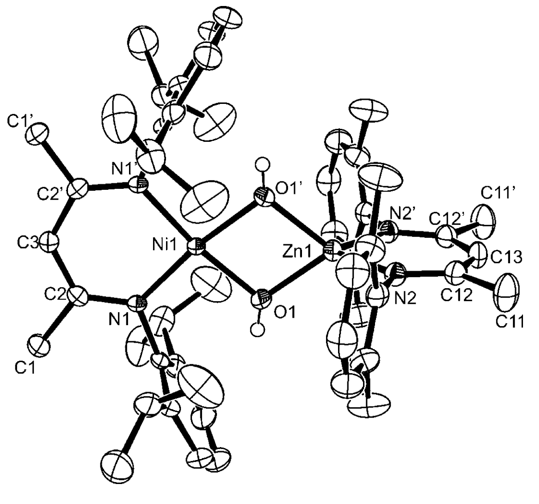


Figure 2. Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for those at oxygen atoms) are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn1–O1 1.946(3), Zn1–N2 1.972(3), Ni1–O1 1.889(2), Ni1–N1 1.893(2), N1–C2 1.328(4), C1–C2 1.498(5), N2–C12 1.323(4), C2–C3 1.397(4), C11–C12 1.509(5), C12–C13 1.397(4); O1-Zn1-O1′ 75.2(1), O1′-Ni1-O1 77.8(2), Ni1-O1-Zn1 103.5(1). Symmetry transformations used to generate equivalent atoms (′): *x*,*y*,−*z*+1/2.

The question arises as to why the peroxo moiety is stable in **2**, while replacement of K^+ by the likewise redox-innocent $L'Zn^+$ unit leads to hydrogen abstraction and thus affords **3**. To find an explanation, DFT calculations were carried out at the B3LYP/6-31G* level (see the Supporting Information). At first, geometry optimizations at the monomer **2b** based on its dimer (Figure 1) were carried out for the singlet and the triplet states of the molecule. As the experimental results clearly indicate, **2** prefers a singlet ground state, which indeed was found to be 37.2 kJ mol^{-1} lower in energy than the first triplet state. A natural bond orbital (NBO) analysis confirmed the presence of an O–O single bond in both the singlet and triplet states, and the charge distribution is consistent with an O_2^{2-} unit situated between a K^+ and a Ni^{2+} cation, with one of the positive charges on Ni being compensated by the monoanionic β-diketiminate ligand. Likewise, the results of a geometry optimization performed for **3** were in excellent agreement with the experimental results. The molecular structure was nicely reproduced for an $S=0$ situation, with the only difference that the OH bonds are slightly bent out of the O-Ni-O plane in the calculated structure. The $S=1$ state of **3** was found to be significantly higher in energy. Subsequently, the $[K([18]c\text{-}6)]^+$ subunit of **2b** was replaced by a $L'Zn^+$ moiety, and the hypothetical transient $[LNi(\mu\text{-}O_2)ZnL']$ (**4**) was subjected to a geometry optimization, again for the singlet and the triplet states. Remarkably, the electronic ground state turned out to be a triplet, which is 72.5 kJ mol^{-1} more stable than the singlet state. The coordination environment of the Ni center can be described as between square-planar and tetrahedral: the N-Ni-N and O-Ni-O planes are twisted by an angle of 31°. A second local minimum for the triplet state of **4** was found, which is only 9.1 kJ mol^{-1} higher in energy than the ground state and features the same square-planar coordination environment of the Ni center as observed in **3**. As indicated by the O–O separation and NBO analysis, there is no bond between these atoms anymore (not even for $S=0$), so that two unpaired electrons have to be accounted for. The corresponding spin density is distributed with almost equal proportions at the Ni center (40%) and the two O atoms (30% each; Figure 3).

The positive charge at the Ni center is about 20% higher than that in **2b**. The NBO analysis reveals covalent bonds between the Ni and O atoms in **4**, while they have large electrostatic contributions in **2** and **3**. On the basis of the calculations, it is thus plausible that the reactive intermediate that results from the replacement of K^+ by $L'Zn^+$ undergoes O–O scission and leads to the reactive intermediate **4.** Each of the oxo ligands of **4** exhibit strong radical character, justifying its formulation as a biradical as shown in Scheme 1. With this background it can be rationalized that H-atom abstraction, probably from exogenous sources (solvent) or supporting ligands, occurs, which finally leads to the isolation of **3**. In line with this hypothesis, employing $[D_8]$THF as solvent leads to partial formation of the O–D isotopologue of **3**, but the source of the hydroxo H atoms is not yet fully understood and deserves further investigation.

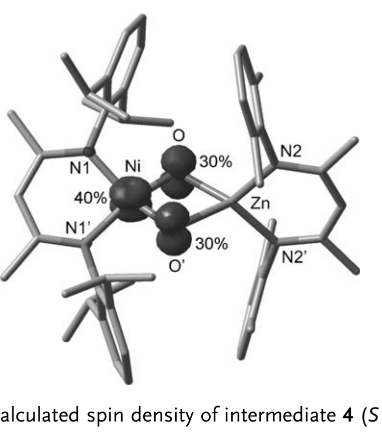


Figure 3. DFT-calculated spin density of intermediate **4** ($S=1$) Hydrogen atoms are omitted for clarity.

In summary, we have synthesized and structurally characterized the first heterobimetallic peroxo nickel potassium complexes **2a** and **2b** by one-electron reduction of the corresponding superoxo nickel complex **1** with elemental potassium in the presence of a donor solvent. The K^+ ion in the [18]c-6 solvated derivative **2b** shows a remarkably strong coordination to the peroxo moiety. Strikingly, replacement of the $[K([18]c\text{-}6)]^+$ ion in **2b** by the non-redox-active $L'Zn^+$ ion initiates O–O bond scission, Ni–O spin polarization, and subsequent H-atom abstraction to give the heterobimetallic bis(μ-hydroxo) complex **3**. The results underline the importance of subtle electronic changes for the reactivity of heterobimetallic peroxo complexes. Investigations concerning the details of the H-atom abstraction reactivity and the influences of other non-redox-active and even redox-active heterometal centers in such NiO_2M systems are in progress.

Received: July 9, 2009

Keywords: dioxygen ligands · nickel · spin polarization · triplet states

---

[1] a) L. Que, Jr., W. B. Tolman, *Angew. Chem.* **2002**, *114*, 1160; *Angew. Chem. Int. Ed.* **2002**, *41*, 1114; b) *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations* (Ed.: B. Meunier), Springer, Berlin, **2000**; c) *Biomimetic Oxidations Catalyzed by Transition Metal Complexes* (Ed.: B. Meunier), Imperial College Press, London, **2000**.

[2] L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013.

[3] Nickel and cobalt: a) S. Hikichi, M. Yoshizawa, Y. Sasakura, M. Akita, Y. More-oka, *J. Am. Chem. Soc.* **1998**, *120*, 10567; b) S. Hikichi, M. Yoshizawa, Y. Sadakura, H. Komatsuzaki, Y. Moro-oka, M. Akita, *Chem. Eur. J.* **2001**, *7*, 5011; Ni: c) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254; d) B. S. Mandimutsira, J. L. Yamarik, T. C. Brunold, W. Gu, S. P. Cramer, C. G. Riordan, *J. Am. Chem. Soc.* **2001**, *123*, 9194; e) R. Schenker, B. S. Manimutsira, C. G. Riordan, T. C. Brunold, *J. Am. Chem. Soc.* **2002**, *124*, 13842; f) S. Itoh, H. Bandoh, M. Nakagawa, S. Nagatomo, T. Kitagawa, K. D. Karlin, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 11168.

[4] For H-atom abstraction reactivity in copper and iron chemistry, compare for instance: a) T. Osako, K. Ohkubo, M. Taki, Y. Tachi, S. Fukuzumi, S. Itoh, *J. Am. Chem. Soc.* **2003**, *125*, 11027; b) J. Shearer, C. X. Zhang, L. N. Zakharov, A. L. Rheingold, K. D. Karlin, *J. Am. Chem. Soc.* **2005**, *127*, 5469; c) S. Mahapatra, J. A.

Halfen, W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 11575; d) A. P. Cole, V. Mahadevan, L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Inorg. Chem.* **2005**, *44*, 7345; e) A. J. Skulan, M. A. Hanson, H.-f. Hsu, L. Que Jr. , E. I. Solomon, *J. Am. Chem. Soc.* **2003**, *125*, 7344; f) C. Kim, Y. Dong, L. Que, Jr., *J. Am. Chem. Soc.* **1997**, *119*, 3635; g) Y. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998.

[5] a) E. Kim, E. E. Chufan, K. Kamaraj, K. D. Karlin, *Chem. Rev.* **2004**, *104*, 1077; b) J. P. Collman, R. Boulatov, C. J. Sunderland, L. Fu, *Chem. Rev.* **2004**, *104*, 561; c) R. Boulatov, *Pure Appl. Chem.* **2004**, *76*, 303.

[6] J. T. York, A. Llobet, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2007**, *129*, 7990–7999.

[7] a) N. W. Aboelella, J. T. York, A. M. Reynolds, K. Fujita, C. R. Kinsinger, C. J. Cramer, C. G. Riordan, W. B. Tolman, *Chem. Commun.* **2004**, 1716; b) J. T. York, V. G. Young, W. B. Tolman, *Inorg. Chem.* **2006**, *45*, 4191; c) P. L. Alsters, J. Boersma, G. van Koten, *Organometallics* **1993**, *12*, 1629; d) Z. T. Cygan, J. E. Bender, K. E. Litz, J. W. Kampf, M. M. Banaszak-Holl, *Organometallics* **2002**, *21*, 5373; e) K. E. Litz, M. M. Banaszak-Holl, J. W. Kampf, G. B. Carpenter, *Inorg. Chem.* **1998**, *37*, 6461.

[8] S. Yao, E. Bill, C. Milsmann, K. Wieghardt, M. Driess, *Angew. Chem.* **2008**, *120*, 7218; *Angew. Chem. Int. Ed.* **2008**, *47*, 7110.

[9] a) K. Nakagawa, R. Konake, T. Nakata, *J. Org. Chem.* **1962**, *27*, 1597; b) M. V. George, K. S. Balachandran, *Chem. Rev.* **1975**, *75*, 491; c) H. Ji, T. Wang, M. Zhang, Y. She, L. Wang, *Appl. Catal. A* **2005**, *282*, 25; d) J. M. Grill, J. W. Ogle, S. A. Miller, *J. Org. Chem.* **2006**, *71*, 9291; e) Y. Sun, B. Gaten, B. Mayers, V. Xia, *Nano Lett.* **2002**, *2*, 167; f) C. Faure, C. Delmas, M. Fouassier, *J. Power Sources* **1991**, *35*, 279.

[10] a) D. Chen, A. E. Martell, *J. Am. Chem. Soc.* **1990**, *112*, 9411; b) C. C. Cheng, J. Gulia, S. E. Rokita, C. J. Burrows, *J. Mol. Catal. A* **1996**, *113*, 379; c) G. Aullón, M. Hamidi, A Lledós, S. Alvarez, *Inorg. Chem.* **2004**, *43*, 3702; d) S. Takahashi, K. Sonogashira, N. Hagihara, *J. Chem. Soc. Jpn.* **1966**, *87*, 610; e) G. Wilke, H. Schott, P. Heimbach, *Angew. Chem.* **1967**, *79*, 62; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 92; f) S. Otsuka, A. Nakamura, Y. Tatsuno, *J. Am. Chem. Soc.* **1969**, *91*, 6994; g) E. J. Brown, A.-K. Duhme-Klair, M. I. Elliott, J. E. Thomas-Oates, P. L. Timmins, P. H. Walton, *Angew. Chem.* **2005**, *117*, 1416; *Angew. Chem. Int. Ed.* **2005**, *44*, 1392; h) J. Cho, H. Furutachi, S. Fujinami, M. Suzuki, *Angew. Chem.* **2004**, *116*, 3362; *Angew. Chem. Int. Ed.* **2004**, *43*, 3300; i) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254.

[11] a) M. H. Gubelmann, A. F. Williams, *Struct. Bonding (Berlin)* **1983**, *55*, 1; b) M. Suzuki, T. Ishiguro, M. Kozuka, K. Nakamoto, *Inorg. Chem.* **1981**, *20*, 1993.

[12] M. S. Varonka, T. H. Warren, *Inorg. Chim. Acta* **2007**, *360*, 317.