Reaction Intermediates

A Bis(μ-alkylperoxo)dinickel(II) Complex as a Reaction Intermediate for the Oxidation of the Methyl Groups of the Me_2-tpa Ligand to Carboxylate and Alkoxide Ligands**

*Jaeheung Cho, Hideki Furutachi, Shuhei Fujinami, and Masatatsu Suzuki**

Aliphatic C–H bond functionalization by various metal-active oxygen species M_m/O_n such as superoxo, peroxo, high-valent oxo-metal complexes, etc. is of great importance for understanding the reaction mechanisms of metalloenzymes and utilizing metal complexes as oxidation catalysts.[1–4] In some cases, aliphatic C–H bond functionalization starts from hydrogen abstraction, and the resulting alkyl radicals undergo a variety of subsequent reactions.[5–7] For example, a bis(μ-alkylperoxo)dicopper(II) complex was suggested as an intermediate in the reaction of a copper(I) complex, $[Cu(iPr_3\text{-tacn})]^+$,[8] with O_2 in the presence of 2,4-*tert*-butylphenol.[5] Very recently, an alkylperoxopalladium(II) complex was also reported which was produced from the reaction of a hydroperoxopalladium(II) complex in the presence of a copper(II) complex as a catalyst.[6] Although various transition-metal–alkylperoxo complexes are known,[9] the alkylperoxo complexes generated as reaction intermediates are limited. Previously, we found that the reaction of $[Ni_2(OH)_2(Me_3\text{-tpa})_2]^{2+}$ with H_2O_2 generates a bis(μ-oxo)dinickel(III) complex, $[Ni_2(O)_2(Me_3\text{-tpa})_2]^{2+}$, and a bis(μ-superoxo)dinickel(II) complex, $[Ni_2(O_2)_2(Me_3\text{-tpa})_2]^{2+}$.[10] The decomposition of $[Ni_2(O)_2(Me_3\text{-tpa})_2]^{2+}$ and $[Ni_2(O_2)_2(Me_3\text{-tpa})_2]^{2+}$ under O_2 caused the oxidative conversion of a methyl group of the Me_3-tpa ligand to give carboxylate and alkoxide ligands. Furthermore, the carboxylate ligand has been shown to be not derived from the autoxidation of the alkoxide ligand, and some other reaction pathways have been suggested. Herein, we report the formation, structural characterization, and reactivity of a novel bis(μ-alkylperoxo)dinickel(II) complex as a reaction intermediate in the oxidative conversion of the methyl groups of the Me_2-tpa ligand into carboxylate and alkoxide ligands; this nickel complex is the first example of a structurally characterized dinuclear transition-metal complex with bridging alkylperoxides, although a crystal structure of a main-group-metal complex with a bis(μ-alkylperoxo)Zn^{II}_2 core was reported very recently.[11]

---

[*] J. Cho, H. Furutachi, Prof. S. Fujinami, Prof. M. Suzuki
Department of Chemistry, Faculty of Science
Kanazawa University
Kakuma-machi, Kanazawa 920-1192 (Japan)
Fax: (+81) 76-264-5742
E-mail: suzuki@cacheibm.s.kanazawa-u.ac.jp

[**] Me_2-tpa = bis[(6-methyl-2-pyridyl)methyl][(2-pyridyl)methyl]amine. Financial support of this research by the Ministry of Education, Science, and Culture (Grant-in-Aid for Scientific Research to M.S.) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/ange.200353637

The reaction of a solution of the bis(μ-hydroxo)dinickel(II) complex $[Ni_2(OH)_2(Me_2\text{-tpa})_2]^{2+}$ (**1**)[12] in acetonitrile with excess hydrogen peroxide at −40 °C showed a rapid color change from sky blue to dark green. The positive ESI-TOF mass spectrum of the solution diluted with acetone at −78 °C suggested the formation of a monomeric superoxonickel(II) species,[13] $[\{Ni(O_2)(Me_2\text{-tpa})\}^+]$ (**2**; *m*/*z* 408.1078, 100 %), a bis(μ-alkylperoxo)dinickel(II) species, $[\{Ni_2(Me_1\text{-tpa-}CH_2OO)_2\}^{2+}]$ (**3**; see below), and a (μ-superoxo)(μ-alkylperoxo)dinickel(II) species, $[\{Ni_2(O_2)(Me_2\text{-tpa})(Me_1\text{-tpa-}CH_2OO)\}^{2+}]$ together with some unidentified minor species (see Supporting Information). The formation of such a monomeric superoxonickel(II) species **2** was also observed for the Me_3-tpa system in solution by ESI-TOF MS measurements, although the isolated species is a dimeric bis(μ-superoxo)Ni^{II}_2.[10] The formation of **2** implies the presence of a bis(μ-oxo)dinickel(III) species that can oxidize excess hydrogen peroxide into superoxide to generate **2**, as found for the Me_3-tpa system.[10] For the Me_3-tpa system, the superoxo species was shown to regenerate a bis(μ-oxo)dinickel(III) species by the disproportionation of the superoxo ligands, with evolution of dioxygen. The resulting bis(μ-oxo)dinickel(III) species is responsible for the abstraction of a hydrogen atom from the methyl group. The ESI-TOF mass spectrum revealed that **2** is unstable, and warming the solution at −20 °C resulted in decomposition to generate a bis(μ-alkylperoxo)dinickel(II) complex, $[Ni_2(Me_1\text{-tpa-}CH_2OO)_2]X_2$ ($X = BPh_4$ (**3**-$(BPh_4)_2$) or ClO_4 (**3**-$(ClO_4)_2$)).

The X-ray diffraction study of **3**-$(BPh_4)_2$ revealed that the complex has a $Ni_2(\mu\text{-OOR})_2$ core in which one of the methyl groups of each Me_2-tpa ligand is oxidized to a ligand-based peroxide and the resulting two peroxides link two nickel(II) ions (Figure 1). The peroxides seem to be stabilized by the formation of the six-membered chelate rings (Ni1-O1-O2-C7-C6-N2) and bridges. The O1−O2 bond length of 1.458(4) Å is in the range of those of transition-metal–alkylperoxo complexes (1.36–1.52 Å).[4,6,9] Complex **3** is a novel example of a structurally characterized reaction intermediate isolated during the oxidation reaction. The ESI-TOF mass spectrum of **3** in MeCN showed a signal at *m*/*z* 407.1008 (100 %), indicating that the dimeric structure remains intact (see Supporting Information).

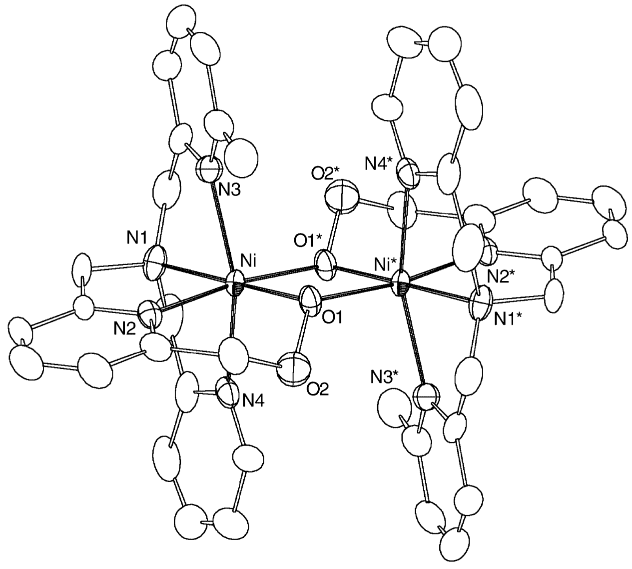
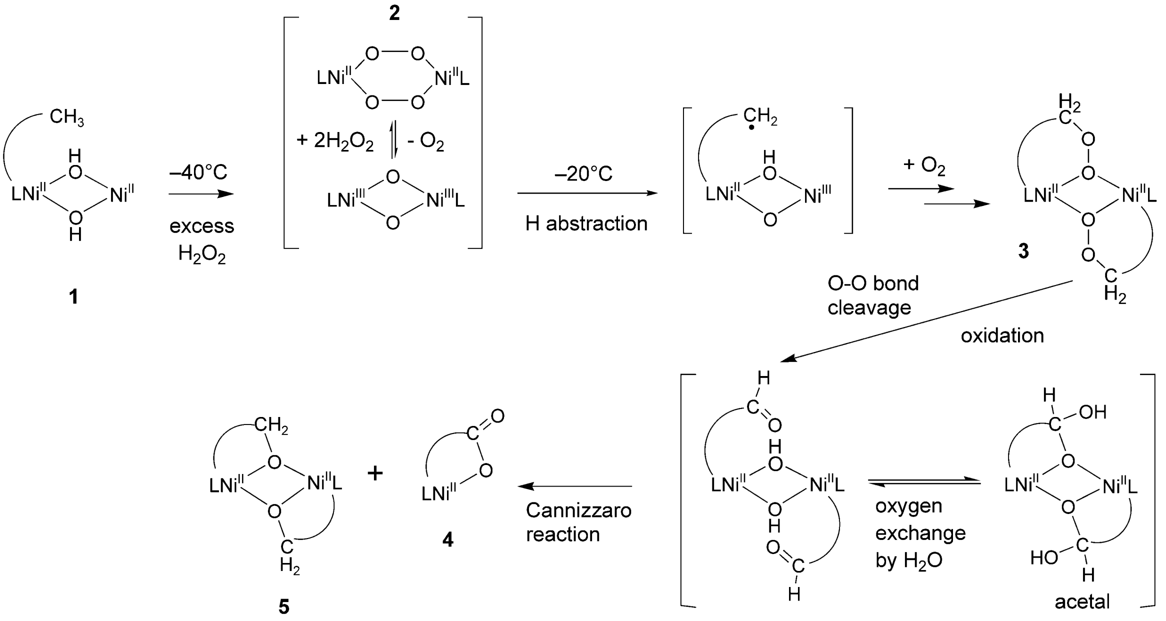


Figure 1. ORTEP diagram (50 % probability) of the $[Ni_2(Me_1\text{-tpa-}CH_2OO)_2]^{2+}$ cation in **3**-$(BPh_4)_2$. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-O1 1.993(2), Ni1-O1* 2.048(2), Ni1-N1 2.065(3), Ni1-N2 2.031(3), Ni1-N3 2.166(3), Ni1-N4 2.198(3), O1-O2 1.458(4), O1-Ni1-O1* 83.72(10), Ni1-O1-O2 108.3(2).

The oxygen source of the alkylperoxo groups in **3** was identified by isotope-labeling experiments (see Supporting Information). The ESI-TOF mass spectrum of a sample prepared by the reaction of **1** with $H_2{}^{18}O_2$ while bubbling $^{16}O_2$ through the solution revealed the formation of only ^{16}O-alkylperoxo species, whereas the reaction under N_2 (i.e. in the absence of $^{16}O_2$) gave ^{18}O-alkylperoxo species. In the latter reaction, $^{18}O_2$ may be generated by the disproportionation of the ^{18}O-superoxo species and/or the disproportionation of $H_2{}^{18}O_2$. Furthermore, only the ^{16}O-alkylperoxo species was obtained by the reaction with $H_2{}^{16}O_2$ in the presence of $H_2{}^{18}O$ under N_2. These results clearly indicate that the two oxygen atoms of the alkylperoxo ligand come from exogenous dioxygen. Although the detailed mechanism of formation of **3** is not clear at present, the reaction may involve the abstraction of a hydrogen atom from a methyl group by a bis(μ-oxo)dinickel(III) species as found for $[Ni_2(O)_2(Me_3\text{-tpa})_2]^{2+}$[10] (although not identified in this study) to generate a ligand-based radical (Me_1-tpa-$CH_2^{\bullet}$), which reacts with exogenous dioxygen to afford a peroxyl radical species (Me_1-tpa-$CH_2OO^{\bullet}$). The resulting peroxyl radical species seems to be converted into the alkylperoxo species through unidentified reaction pathway(s). Further studies are necessary for clarifying this point.

A solid sample of **3** is relatively stable at room temperature, whereas the ESI-TOF mass spectrum in a dry DMF/MeCN mixture showed that decomposition occurs within 1 hour at room temperature, and **3** is converted into a ligand-based carboxylato complex $[\{Ni(Me_1\text{-tpa-COO})(dmf)\}^+]$ (**4**·dmf; *m*/*z* 478.1380, 100 %) and a ligand-based alkoxo complex $[\{Ni_2(Me_1\text{-tpa-}CH_2O)_2\}^{2+}]$ (**5**; *m*/*z* 391.1125, 20 %) together with some unidentified species (see Supporting Information).[14] The carboxylato complex **4** was isolated as $[Ni(Me_1\text{-tpa-COO})(H_2O)]ClO_4$ (**4**-H_2O·ClO_4) (see Experimental Section and Supporting Information). The formation of both Me_1-tpa-COO^- and Me_1-tpa-CH_2OH was also confirmed by a ligand-recovery experiment after the decomposition of **3**-$(ClO_4)_2$·H_2O in DMF under Ar; the yields of Me_1-tpa-COO^- and Me_1-tpa-CH_2OH are approximately 62 % and 37 %, respectively (see Supporting Information). It was also found that the decomposition of **3** containing Me_1-tpa-$CH_2{}^{16}O^{16}O^-$ in the presence of $H_2{}^{18}O$ under N_2 gave a mixture of ^{16}O-^{16}O, ^{16}O-^{18}O, and ^{18}O-^{18}O carboxylato species **4** (see Supporting Information), and the same is true for the formation of the alkoxo complex **5**. Decomposition under $^{18}O_2$ in the presence of $H_2{}^{16}O$, however, gave only ^{16}O-^{16}O carboxylato species. These results indicate that there is some reactive species that reacts with water molecules during the conversion of **3** into **4** and **5**. One possible reaction pathway for the formation of Me_1-tpa-COO^- and Me_1-tpa-CH_2OH involves the following steps: (Scheme 1): 1) the peroxide

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. Possible pathway for the formation of carboxylate and alkoxide ligands.

ligand can be converted into a ligand-based aldehyde by either homolysis or heterolysis of the O–O bond, 2) the oxygen atom of the aldehyde can be exchanged through the formation of an acetal, 3) disproportionation of the aldehyde may give a carboxylate and an alkoxide through the Cannizzaro reaction and/or the aldehyde can be oxidized by an additional alkylperoxo ligand. Insertion of oxygen into the alkoxo ligand of **5** from water strongly supports the disproportionation of the aldehyde by the Cannizzaro reaction. The presence of a larger amount of the carboxylate ligand than the alkoxide ligand probably suggests that some other side reaction(s) take(s) place at the same time. As mentioned before, such oxidation of a methyl group into carboxylate has also been observed for the decomposition of $[Ni_2(O)_2(Me_3\text{-}tpa)_2]^{2+}$ and $[Ni_2(O_2)_2(Me_3\text{-}tpa)_2]^{2+}$ under O_2,[10] during which ligand-based alkylperoxo species such as **3** seem to be common intermediates for the conversion into the corresponding carboxylato complexes. Further studies into a detailed conversion mechanism are in progress.

In conclusion, we have succeeded in the isolation and structural characterization of bis(μ-alkylperoxo)dinickel(II) complex **3** derived from the reaction of the bis(μ-hydroxo)-dinickel(II) complex **1** with H_2O_2 and O_2 through the formation of the $Me_1\text{-tpa-}CH_2^{\bullet}$ and $Me_1\text{-tpa-}CH_2OO^{\bullet}$ radicals. Subsequent decomposition of **3** afforded the carboxylato complex **4** and the alkoxo complex **5**. Thus, such an alkylperoxo species seems to be a common intermediate for the oxidation of a methyl group of the supporting ligand into carboxylate and alkoxide ligands in the present type of nickel complexes.

Experimental Section

1-$(ClO_4)_2{\cdot}3H_2O$: nBu$_4$NOH in methanol (1M; 175 μL, 0.5 mmol) was added to a stirred mixture of $Ni(ClO_4)_2{\cdot}6H_2O$ (183 mg, 0.5 mmol) and Me_2-tpa (159 mg, 0.5 mmol) in methanol (20 mL) in a Schlenk tube under N_2. The resulting solution was allowed to stand overnight at 0 °C to afford **1** as sky blue crystals. FTIR (KBr): $\tilde{\nu} = 1604, 1577, 1484, 1457, 1353, 1105, 786, 624\ cm^{-1}$; UV/Vis (DMF): λ_{max} (ε) = 610 nm (23); ESI-TOF MS (MeCN): m/z (%): 393.1167 (100) $[\{Ni_2(OH)_2(Me_2\text{-}tpa)_2\}^{2+}]$; elemental analysis (%) calcd for $C_{40}H_{52}N_8Cl_2Ni_2O_{13}$: C 46.14, H 5.03, N 10.76; found: C 46.20, H 4.70, N 10.82. X-ray crystallographically suitable crystals were obtained by the addition of $NaBPh_4$ (see Supporting Information).

3-$(BPh_4)_2$: Aqueous H_2O_2 (30%; 550 μL, 5 mmol) was added to a rapidly stirred solution of **1** (52 mg, 0.05 mmol) in MeCN (20 mL) at −40 °C under O_2. The resulting solution was allowed to stand overnight, to which a solution of $NaBPh_4$ (68 mg, 0.2 mmol) in acetonitrile (2 mL) was added. The resulting solution was left for 1 day at −20 °C to give **3**-$(BPh_4)_2$ as brown crystals (35 mg, 48%) suitable for X-ray crystallography. FTIR (KBr): $\tilde{\nu} = 1604, 1577, 1353, 1162, 705, 613\ cm^{-1}$; UV/Vis (reflectance): $\lambda_{max} = \sim 398$ (shoulder), 545, ~630 (shoulder), 780, 1035 nm; ESI-TOF MS (DMF/MeCN): m/z (%): 407.1023 (100) $[\{Ni_2(Me_1\text{-}tpa\text{-}CH_2OO)_2\}^{2+}]$ and 480.1537 (20) $[\{Ni(Me_1\text{-}tpa\text{-}CH_2OO)\}^{+} + DMF]$; elemental analysis (%) calcd for $C_{88}H_{82}N_8O_4B_2Ni_2$: C 72.66, H 5.68, N 7.70; found: C 72.84, H 5.73, N 7.88.

4-$H_2O{\cdot}ClO_4$: An excess amount of H_2O_2 (30%; 550 μL, 5 mmol) was added to a rapidly stirred suspension of **1** (52 mg, 0.05 mmol) in EtOH at room temperature. The resulting dark green suspension was allowed to stand for 1 day, without stirring, to give a blue solution, from which blue crystals of **4** were obtained. FTIR (KBr): $\tilde{\nu} = 1635, 1606, 1577, 1457, 1444, 1392, 1284, 1103, 887, 775, 624\ cm^{-1}$; UV/Vis (DMF): λ_{max} (ε) = 570 (15), 790 (14), 942 nm (32); ESI-TOF MS (DMF/MeCN): m/z (%): 478.1376 (100) $[\{Ni(Me_1\text{-}tpa\text{-}COO)\}^{+} + DMF]$; elemental analysis (%) calcd for $C_{20}H_{21}N_4ClNiO_7$: C 45.88, H 4.04, N 10.70; found: C 45.42, H 4.03, N 10.74.

Crystal data for **3**-$(BPh_4)_2$: $C_{88}H_{82}N_8B_2Ni_2O_4$, triclinic, $P\bar{1}$, $Z = 1$, $a = 10.234(1)$, $b = 14.009(2)$, $c = 14.080(1)$ Å, $\alpha = 68.931(10)$, $\beta = 73.92(1)$, $\gamma = 84.43(1)°$, $V = 1810.0(3)$ Å^3, $\rho_{calcd} = 1.334\ g\,cm^{-3}$, $0.25 \times 0.18 \times 0.08$ mm, $T = -150\,°C$, $F_{000} = 764.00$, $\mu(Mo_{K\alpha}) = 5.80\ cm^{-1}$, Rigaku Mercury CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71070$ Å), ω scan, 14484 measured, 5723 independent reflections ($I > 3.00\sigma(I)$), 469 parameters; structure solution with direct methods[15] and successive Fourier technique.[16] All calculations were performed with the teXsan[17] crystallographic software package of the Molecular Structure Corporation. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed geometrically. They were included, but not refined against $|F|$, to yield R (Rw) = 0.0562 (0.0786); largest residual electron densities 1.44/−0.71 (GOF = 1.387). CCDC-226793 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: December 30, 2003 [Z53637]

Keywords: nickel · oxidation · peroxides · reaction mechanisms

---

[1] J. M. Mayer, *Biomimetic Oxidations Catalyzed by Transition Metal Complexes* (Ed.: B. Meunier), Imperial College Press, London, **2000**, pp. 1–44.

[2] a) L. Que, Jr, R. Y. N. Ho, *Chem. Rev.* **1996**, *96*, 2607; b) L. Que, Jr, W. B. Tolman, *Angew. Chem.* **2002**, *114*, 1160; *Angew. Chem. Int. Ed.* **2002**, *41*, 1114; c) J.-U. Rohde, M. R. Bukowski, L. Que, Jr, *Curr. Opin. Chem. Biol.* **2003**, *7*, 674.

[3] a) E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* **2000**, *100*, 235; b) J. J. Girerd, F. Banse, A. J. Simaan, *Struct. Bonding (Berlin)* **2000**, *97*, 145.

[4] a) S. Hikichi, M. Akita, Y. Moro-oka, *Coord. Chem. Rev.* **2000**, *198*, 61; b) M. Akita, S. Hikichi, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1657.

[5] J. A. Halfen, V. G. Young, Jr, W. B. Tolman, *Inorg. Chem.* **1998**, *37*, 210.

[6] M. Kujime, S. Hikichi, M. Akita, *Chem. Lett.* **2003**, *32*, 486.

[7] K. Haas, H. Dialer, H. Piotrowski, J. Schapp, W. Beck, *Angew. Chem.* **2002**, *114*, 1969; *Angew. Chem. Int. Ed.* **2002**, *41*, 1879.

[8] iPr$_3$-tacn = 1,4,7-triisopropyl-1,4,7-triazacyclononane; Me$_2$-tpa = bis[(6-methyl-2-pyridyl)methyl][(2-pyridyl)methyl]amine; Me$_3$-tpa = tris[(6-methyl-2-pyridyl)methyl]amine.

[9] a) N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata, Y. Moro-oka, *J. Am. Chem. Soc.* **1993**, *115*, 7872; b) H. Komatsuzaki, N. Sakamoto, M. Satoh, S. Hikichi, M. Akita, Y. Moro-oka, *Inorg. Chem.* **1998**, *37*, 6554; c) S. Hikichi, H. Komatsuzaki, M. Akita, Y. Moro-oka, *J. Am. Chem. Soc.* **1998**, *120*, 4699; d) M. Bonchio, S. Calloni, F. D. Furia, G. Licini, G. Modena, S. Moro, W. A. Nugent, *J. Am. Chem. Soc.* **1997**, *119*, 6935; e) F. A. Chavez, P. K. Mascharak, *Acc. Chem. Res*, **2000**, *33*, 539; e) P. Chen, K. Fujisawa, E. I. Solomon, *J. Am. Chem. Soc.* **2000**, *122*, 10177.

[10] 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] J. Lewinski, Z. Ochal, E. Bojarski, E. Tratkiewicz, I. Justyniak, J. Lipkowski, *Angew. Chem.* **2003**, *115*, 4791; *Angew. Chem. Int. Ed.* **2003**, *42*, 4643.

[12] The crystal data and ORTEP diagram for **1** are given in the Supporting Information.

[13] Although there is a possibility of a peroxonickel(III) species as an alternative formulation, it is not clear which is correct at present.

[14] Surprisingly, it was found that the thermal decomposition of **3** was very slow in the presence of a small amount of water (> 2 days).

[15] SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[16] DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.

[17] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, **1985** & **1999**.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim