Cluster Compounds

The First μ_6-Peroxide Transition-Metal Complex: $[Ni_8(L)_{12}(O_2)]^{2+}$**

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There continues to be significant attention given to the structural characterization of metal peroxide complexes.[1] The coordination modes observed in such complexes range from peroxide coordination to a single metal center to peroxide acting as a bridging ligand between two, three, four, or six metal ions. Simple μ-peroxo complexes are common; iron, cobalt, and copper dimers are the most prevalent, with recent attention concentrated on Fe–peroxo–Cu complexes as models of the active site of cytochrome c oxidase (Figure 1 a).[2] μ_3-Peroxo-coordination is rare, but has been proposed as part of the laccase active site.[3,4] Molecular species with a μ_4-coordination mode are restricted to a handful of examples, with copper, iron, tungsten, antimony, and molybdenum complexes (Figure 1 b).[5–13] In addition, there are two reports of a potential μ_6-coordination mode in $[Ba_6(L)_{10}(H_2O)_n(O_2)]$ complexes ($n = 2$ or 4), where the peroxide ion in a $[Ba_4\mu_4\text{-}(O_2)]$ moiety bridges two further barium ions in a μ-η^2:η^2 fashion.[14,15] As far as we can determine, however, there are no molecular examples of peroxide acting in the μ_6-$(\eta^1)_3$ binding mode shown in Figure 1 c. This mode of binding is significant insofar as it would complete the family of possible symmetrical μ_n-$(\eta^1)_{n/2}$ peroxide binding modes in molecular complexes.

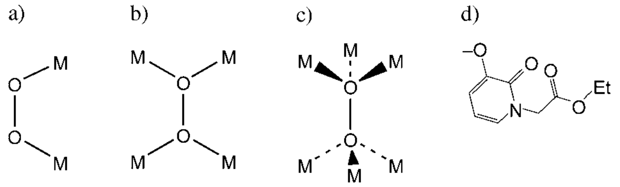

Figure 1. Peroxo binding modes: a) μ-(η^1), b) μ_4-$(\eta^1)_2$, c) μ_6-$(\eta^1)_3$, d) N-substituted 3-hydroxy-2-pyridinonate (**L**) used in this study.

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Lately we have been investigating the preparation and reactions of metal complexes that employ N-substituted 3-hydroxy-2-pyridinones (**L**-H, Figure 1 d) as ligands.[16] Hydroxypyridinones have been used extensively as ligands designed to sequester metals.[17] Also, the closely related 2-hydroxypyridine ligands have been used to synthesize metal complexes, including Ni_8 and Mn_{12} clusters.[18,19] During our study with **L** we noted the formation of an unusual peroxide-containing Ni_8 complex **1**. This complex is synthesized at room temperature from the addition of an ethanolic solution of **L**-H (2 equiv) to an ethanolic solution of $Ni(NO_3)_2 \cdot n\,H_2O$ followed by addition of aqueous H_2O_2. Addition of triethylamine (2 equiv) generates a pale green precipitate of $[Ni_8(\mathbf{L})_{12}(O_2)](NO_3)_2$ (**1**) in approximately 80 % yield. Compound **1** can be crystallized from dimethylformamide solution by vapor diffusion of diethyl ether.

Compound **1** is air-stable and was characterized by elemental analysis, UV/Vis spectroscopy, Raman spectroscopy, ES-mass spectrometry (see Supporting Information),[20] and single-crystal X-ray diffraction.[21–23] In addition to a satisfactory elemental analysis, the peroxide content of **1** could be determined iodometrically,[20] giving a peroxide content of 1.15 % (calcd: 1.10 %), and electrospray (ES) mass spectrometry shows a series of peaks with a maximum intensity at m/z 1427.1 consistent with $[Ni_8(\mathbf{L})_{12}(O_2)]^{2+}$; the isotopic distribution pattern matches that which is calculated for this elemental composition (Figure 2). Repeating the synthesis with $H_2{}^{18}O_2$ affords the same product, which gives an ES mass spectrum containing a similar pattern of peaks now centered around m/z 1429.1. This pattern is consistent with the analogous $[Ni_8(\mathbf{L})_{12}({}^{18}O_2)]^{2+}$ ion.

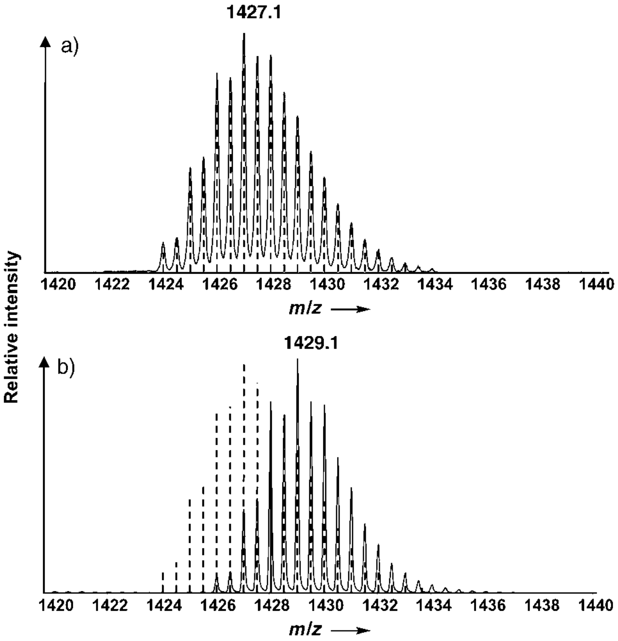

Figure 2. ES-MS analysis of a) **1** and b) $[Ni_8(\mathbf{L})_{12}({}^{18}O_2)](NO_3)_2$. Calculated isotopic distribution patterns for $[Ni_8(\mathbf{L})_{12}({}^{16}O_2)]^{2+}$ are shown as broken vertical lines. In each panel, the y-axis has been normalized to the base peak in the ion cluster.

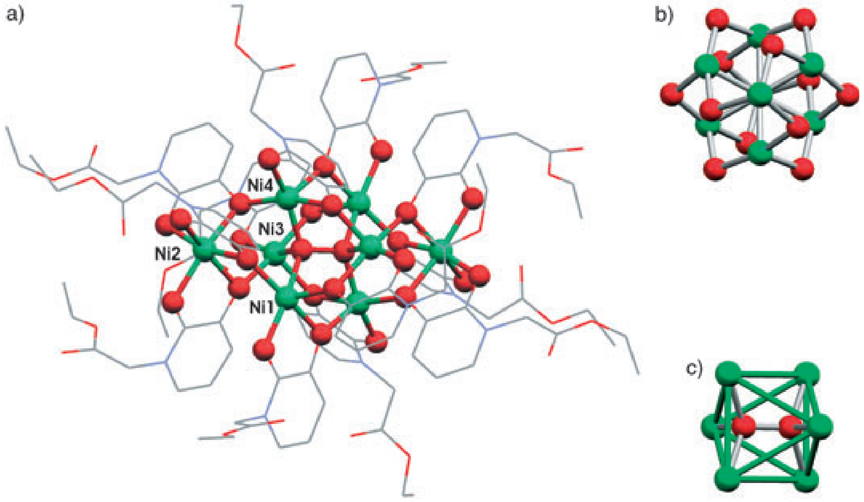

Figure 3. a) Solid-state structure of $[Ni_8(\mathbf{L})_{12}(O_2)]^{2+}$ (hydrogen atoms are omitted for clarity),[20] b) view of the Ni_8 unit along the peroxide O–O bond showing bridging oxygen atoms only, c) $Ni_6(O_2)$ core; red O, green Ni.

The structure of **1** was determined by single-crystal X-ray diffraction (Figure 3).[20,21] The Ni_8 cage is sited on a crystallographic center of symmetry and consists of a central $Ni_6(O_2)$ core with near-D_{3d} local symmetry, where the six nickel ions form the apices of an octahedron (see Figure 3; Ni···Ni separations in core, minimum = 3.234(2), maximum = 3.330(2), average = 3.291(2) Å). These separations indicate that there are no significant Ni···Ni interactions within the cage. The octahedron is end-capped by two six-coordinate nickel ions, giving an overall bicapped-octahedral arrangement of nickel ions. The eight nickel ions are held together by bridging oxygen atoms from twelve **L** ligands. The two capping nickel ions can be viewed as two $Ni(\mathbf{L})_3$ units, and the Ni_6 core as an $Ni_6(O_2)(\mathbf{L})_6$ unit.

The dipositive charge of the complex indicates that the central ligand is formally $O_2{}^{2-}$. The peroxo ligand is completely caged at the center of the Ni_6 core. The peroxide axis is collinear with a threefold rotation axis of the octahedron and the principal C_3 axis of D_{3d} (Figure 3). This structural arrangement is analogous to that observed in simple binary metal peroxides, such as $Zn(O_2)$ and $Cd(O_2)$, which adopt a cubic pyrites structure.[24] The structure of a simple $Ni(O_2)$ species is not known, although $Ni(S_2)$ is known to adopt the pyrites structure. Assuming that the $Ni_6(O_2)$ core is representative of the bulk structure of $Ni(O_2)$, then it is possible to view **1** as a small fragment of $Ni(O_2)$ surrounded by a shell of hydroxypyridinonate ligands.

In the $Ni_6(O_2)$ unit, each nickel ion has a distorted square-pyramidal coordination geometry, with the peroxo oxygen occupying a basal coordination site. The Ni–O(peroxo) bond lengths are 1.992(6), 1.963(8), and 2.019(6) Å. The Ni-O(peroxo)-Ni angles are 109.5(3), 112.2(3), and 109.7(3)°, and the nickel ions are in staggered conformation around the peroxide bond; adjacent Ni-O-O-Ni torsion angles range from 58.0 to 61.5°. A simple molecular orbital analysis of the σ bonding within the $Ni_6(O_2)$ unit indicates that a bonding combination of molecular orbitals can be formed between the HOMO of the peroxide and the $d_{x^2-y^2}$ orbitals of the nickel ions. The O—O bond length in the peroxide is 1.456(12) Å, which is within the range of other known peroxide bond lengths, but is at the shorter end of the expected range, possibly reflecting a nickel–peroxide interaction that is largely ionic in nature.[25]

The Raman spectrum of **1** recorded with laser excitation at 514.5 nm shows bands in the expected region of a peroxide vibration (600–1000 cm^{-1}) at 758(s), 769(w), 817(w), 854(vs), and 881(s) cm^{-1}. None of these bands, however, was sensitive to isotopic substitution of the peroxide (see Supporting Information). Below 350 nm, the UV/Vis spectrum of **1** is dominated by strong ligand-based absorption bands (see Supporting Information). Consequently, the peroxo→Ni^{II} charge-transfer band could not be located with certainty. Attempts to achieve resonance enhancement of the ν(O-O) vibration by excitation at 350.6 and 325.0 nm were unsuccessful. The solutions of **1** in methanol or ethanol changed color upon irradiation at these wavelengths, which may indicate photodecomposition. We are, therefore, unable to determine the peroxide stretching frequency.

Notwithstanding the wide use of nickel peroxides in organic synthesis, examples of nickel peroxides that have been structurally characterized are relatively rare.[26] A search of the Cambridge Structural Database suggests that **1** is the second molecular nickel peroxide complex to be structurally characterized; the previous example is a monomeric $[(t\mathrm{BuNC})_2Ni(O_2)]$ complex.[27] In addition, a bis(μ-alkylperoxo)dinickel complex was isolated and structurally characterized very recently,[28] the synthesis of which involved a related bis(μ-superoxo)dinickel(II) complex.[29] A monomeric $Ni-O_2$ adduct was also reported recently and described as Ni^{II}-superoxo species, although no single-crystal X-ray diffraction data were obtained.[30] Despite the scarcity of nickel peroxide complexes, however, recent calculations on $[L_nNi_2(O_2)]$ and $[L_nNi(O_2)]$ complexes suggest that molecular nickel peroxides should be stable.[31] Thus, the preparation and isolation of **1** in good yield is an indication of the accessibility of molecular nickel peroxide species. In contrast to most other metal peroxo species, **1** is thermally relatively stable and can be isolated and handled at room temperature. The effective encapsulation of the peroxide by the octanuclear nickel cage stabilizes the reactive species. Interestingly, an unusually high thermal stability was also reported for the tetranuclear μ_4-$(\eta^1)_2$-peroxocopper(II) complex.[5]

In conclusion, we have demonstrated the preparation and characterization of a novel Ni_8–peroxide-containing cage. The assignment of the central peroxo ligand is supported by chemical analyses, X-ray crystallography, and ES mass spectrometry. The peroxide is present in an unprecedented μ_6-$(\eta^1)_3$ binding mode, thus completing the family of possible symmetrical μ_n-$(\eta^1)_{n/2}$ peroxide binding modes in molecular species. The complex can be viewed as a small fragment of solid state $Ni(O_2)$ surrounded by a shell of hydroxypyridinonate ligands.[32]

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[1] See, for example: A. G. Blackman, W. B. Tolman, *Struct. Bonding (Berlin)* **2000**, *97*, 179.

[2] E. Kim, M. E. Helton, I. M. Wasser, K. D. Karlin, S. Lu, H. W. Huang, P. Moenne-Loccoz, C. D. Incarvito, A. L. Rheingold, M. Honecker, S. Kaderli, A. D. Zuberbuhler, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3623, and references therein.

[3] U. M. Sundaram, H. H. Zhang, B. Hedman, K. O. Hodgson, E. I. Solomon, *J. Am. Chem. Soc.* **1997**, *119*, 12525.

[4] N. Hakulinen, L. L. Kiiskinen, K. Kruus, M. Saloheimo, A. Paananen, A. Koivula, J. Rouvinen, *Nat. Struct. Biol.* **2002**, *9*, 601.

[5] J. Reim, R. Werner, W. Haase, B. Krebs, *Chem. Eur. J.* **1998**, *4*, 289.

[6] F. Meyer, H. Pritzkow, *Angew. Chem.* **2000**, *112*, 2199; *Angew. Chem. Int. Ed.* **2000**, *39*, 2112.

[7] I. Shweky, L. E. Pence, G. C. Papaefthymiou, R. Sessoli, J. W. Yun, A. Bino, S. J. Lippard, *J. Am. Chem. Soc.* **1997**, *119*, 1037.

[8] R. Çelenligil-Çetin, R. J. Staples, P. Stavropoulos, *Inorg. Chem.* **2000**, *39*, 5838.

[9] W. Micklitz, S. G. Bott, J. G. Bentsen, S. J. Lippard, *J. Am. Chem. Soc.* **1989**, *111*, 372.

[10] T. Ozeki, T. Yamase, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2101.

[11] E. I. Tolis, M. Helliwell, S. Langley, J. Raftery, R. E. P. Winpenny, *Angew. Chem.* **2003**, *115*, 3934; *Angew. Chem. Int. Ed.* **2003**, *42*, 3804.

[12] R. Stomberg, L. Trysberg, I. Larking, *Acta Chem. Scand.* **1970**, *24*, 2678.

[13] O. W. Howarth, *Dalton Trans.* **2004**, 476; H. J. Breunig, T. Krüger, E. Lork, *Angew. Chem.* **1997**, *109*, 654; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 615.

[14] N. Hovnanian, J. Galloy, P. Miele, *Polyhedron* **1995**, *14*, 297.

[15] J. Auld, A. C. Jones, A. B. Leese, B. Cockayne, P. J. Wright, P. O'Brien, M. Motevalli, *J. Mater. Chem.* **1993**, *3*, 1203.

[16] E. J. Brown, A.-K. Duhme-Klair, P. H. Walton, *Dalton Trans.* **2004**, 2458.

[17] A. E. V. Gorden, J. D. Xu, K. N. Raymond, P. Durbin, *Chem. Rev.* **2003**, *103*, 4207.

[18] E. K. Brechin, W. Clegg, M. Murrie, S. Parsons, S. J. Teat, R. E. P. Winpenny, *J. Am. Chem. Soc.* **1998**, *120*, 7365.

[19] G. Aromi, A. R. Bell, M. Helliwell, J. Raftery, S. J. Teat, G. A. Timco, O. Roubeau, R. E. P. Winpenny, *Chem. Eur. J.* **2003**, *9*, 3024, and references therein.

[20] Full experimental and analytical details are available as Supporting Information.

[21] Crystal data: $C_{108}H_{120}N_{14}Ni_8O_{56}$, $M_r = 2979.86$, crystal dimensions $0.40 \times 0.18 \times 0.06$ mm^3, monoclinic, $P2_1/n$, $a = 15.0314(12)$, $b = 21.9851(17)$, $c = 19.1166(15)$ Å, $\beta = 94.453(3)°$, $V = 6298.3(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.571$ $g\,cm^{-3}$, $2\theta_{max} = 41.68°$, $T = 100(2)$ K, 8572 reflections measured, 6604 independent, $R_{int} = 0.1282$, 3920 reflections with $I = \geq 2\sigma(I)$, $\mu = 1.269$ mm^{-1}, absorption correction with SADABS[22] (v.2.03, Sheldrick),

$(0.6307 \leq T \leq 0.0277)$, 883 parameters, refinement against $|F^2|$, $R1 = 0.0560$ ($I = \geq 2\sigma(I)$), $wR2 = 0.1762$ (all data), GoF = 1.072, max shift/esd in final cycle = 0.00, largest difference peaks 0.86/ $-0.45\ e\text{Å}^{-3}$, rms peak height = $0.10\ e\text{Å}^{-3}$. Diffraction data were collected on a Bruker Smart Apex diffractometer with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using SMART.[22] Frame integration and unit-cell refinement software was carried out with the SAINT+[22] software. Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares using SHELXL-97.[23] One of the side chains of the ligand, **L**, was assumed to be disordered over two positions. All non-hydrogen atoms were refined anisotropically, except for the disordered atoms, which were refined isotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. CCDC 252525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] a) SMART Control software (v.5.625), Bruker-AXS Inc, Madison, USA; b) SAINT+ Integration software (v.6.22), Bruker-AXS Inc, Madison, USA; c) SADABS, G. M. Sheldrick, University of Göttingen, Germany.

[23] a) SHELXS-97: Program for the Solution of Crystal Structures, G. M. Sheldrick, University of Göttingen, Germany, **1997**; b) SHELXL-97: Program for the Refinement of Crystal Structures, G. M. Sheldrick, University of Göttingen, Germany, **1997**.

[24] C. W. W. Hoffman, R. C. Ropp, R. W. Mooney, *J. Chem. Soc.* **1959**, *81*, 3830.

[25] G. B. Jameson, J. A. Ibers in *Bioinorganic Chemistry* (Eds.: I. Bertini, H. B. Gray, S. J. Lippard, J. S. Valentine), University Science Books, Mill Valley, **1994**, pp. 167–252.

[26] M. V. George, K. S. Balachandran, *Chem. Rev.* **1975**, *75*, 491.

[27] M. Matsumoto, K. Nakatsu, *Acta Crystallogr. B* **1975**, *31*, 2711.

[28] J. Cho, H. Furutachi, S. Fujinami, M. Suzuki, *Angew. Chem.* **2004**, *116*, 3362; *Angew. Chem. Int. Ed.* **2004**, *43*, 3300.

[29] K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254.

[30] K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer, C. G. Riordan, *Inorg. Chem.* **2004**, *43*, 3324.

[31] G. Aullón, M. Hamidi, A Lledós, S. Alvarez, *Inorg. Chem.* **2004**, *43*, 3702.

[32] Note added in proof (January 12, 2005). The following article concerning peroxo-bridged nickel species has recently been published: M. T. Kieber-Emmons, R. Schenker, G. P. A. Yap, T. C. Bunold, C. G. Riordan, *Angew. Chem.* **2004**, *116*, 6884; *Angew. Chem. Int. Ed.* **2004**, *43*, 6716.