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New Thermally Stable Hydroperoxo- and Peroxo-Copper Complexes

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In this report, we describe new peroxo- and hydroperoxo-dicopper(II) complexes having considerably enhanced solution and solid-state thermal stability.[1-3] Hydroperoxo-copper species have come to light as important intermediates in the 4 $e^-/4\ H^+$ reduction of O_2 (to water) mediated by the trinuclear copper ion cluster in the oxidase laccase (or ascorbate oxidase).[7] The ability to generate and characterize structural and functional model compounds is an important aspect in developing structural, spectroscopic, and reactivity correlations and, ultimately, in deducing enzyme mechanism. Having thermally stable species aids the process of characterization and comparison to proteins. Also, Cu_2O_2 (e.g. peroxo-dicopper(II)) complexes derived from Cu(I) and O_2 occur in hemocyanin (O_2-carrier)[8] and tyrosinase (*o*-phenol monooxygenase),[9] and Cu_n-OOH ($n = 1, 2$) species are implicated as important intermediates in dopamine β-hydroxylase,[10] galactose oxidase[11] (2 e^- reduction of O_2 to H_2O_2) and cyctochrome *c* oxidase[12] (4 $e^-/4\ H^+$ reduction to water). In addition, peroxo compounds are of potential interest as reagents for organic oxidations, fuel cell O_2-reduction catalysts, and practical O_2-carriers.[13]

The new peroxo and hydroperoxo complexes are derived from complexes with an unsymmetrical dinucleating ligand UN-OH,[14] an analogue of XYL-OH, from which peroxo complexes $[Cu_2(XYL\text{-}O^-)(O_2)]^+$ (**1**)[15] and $[Cu_2(XYL\text{-}O^-)(O_2H)]^{2+}$ (**2**)[16] were previously generated only in CH_2Cl_2 at −80 °C. Here, dicopper(I) precursors $[Cu_2(UN\text{-}O^-)]^+$ (**4**)[17a] and $[Cu_2(UN\text{-}OH)]^{2+}$ (**5**)[17b] were synthesized by reduction of $[Cu_2(UN\text{-}O^-)(OH)]^{2+}$ (**3**)[14] (Scheme I). Phenoxo-bridged complex **4** (Figure 1)[18] exhibits basically the same connectivity and trigonal pyramidal Cu(I) coordination (equatorial phenoxo O and pyridine N's with axial N1 or N4) seen in $[Cu_2(XYL\text{-}O^-)]^+$.[15a] However, there are differences pertaining to the relationship of the two Cu(I) ions with respect to one another, and we speculate that these variations, along with the unsymmetrical coordination environment in UN-O⁻, may be important in stabilizing resulting copper-peroxo complexes (vide infra). More detailed structural comparisons of **4** and $[Cu_2(XYL\text{-}O^-)]^+$ will be made in a future full report.

$[Cu_2(UN\text{-}O^-)]^+$ (**4**) reacts reversibly with O_2 at −80 °C in CH_2Cl_2 ($Cu/O_2 = 2.1$, average of 2 trials), giving an intensely purple solution of $[Cu_2(UN\text{-}O^-)(O_2)]^+$ (**6**) with LMCT absorption maxima at 392 ($\epsilon = 3400$), 510 ($\epsilon = 5400$), and 642 ($\epsilon = 2700$) nm (supplementary material), similar to $[Cu_2(XYL\text{-}O^-)(O_2)]^+$.[15] The protonated dicopper(I) complex $[Cu_2(UN\text{-}OH)]^{2+}$ (**5**) reacts with O_2 ($Cu/O_2 = 1.9$) to give the hydroperoxo-dicopper(II) species $[Cu_2(UN\text{-}O^-)(O_2H)]^{2+}$ (**7**), with λ_{max} 395 ($\epsilon = 7000$) and

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(1) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219-327. (b) Tyeklár, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241-248. (c) Karlin, K. D.; Tyeklár, Z.; Zuberbühler, A. D. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1992, in press.

(2) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3-68.

(3) Thus far, most Cu_n-O_2 or Cu_n-O_2H ($n = 1, 2$) species have had to be characterized as solution species at low temperature (e.g. −80 °C).[1,2] Kitajima[4] and Thompson[5] have characterized Cu_n-O_2 complexes isolable as solids. In the former case,[4] an important μ-η^2:η^2 peroxo-dicopper(II) complex was characterized by X-ray crystallography. We have also been able to isolate a solid (stable only at −80 °C) with a *trans*-μ-1,2-peroxo coordination.[1b,c,6]

(4) (a) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8975-8976. (b) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664-5671. (c) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277-1291.

(5) (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057-4059. (b) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 8308-8309.

(6) (a) Jacobson, R. R.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690-3692. (b) Baldwin, M. J.; Ross, P. K.; Pate, J. E.; Tyeklár, Z.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8671-8679.

(7) (a) Clark, P. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 1108-1110. (b) Cole, J. L.; Ballou, D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8544-8546. (c) Cole, J. L.; Tan, G. O.; Yang, E. K.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 2243-2249. (d) Messerschmidt, A.; Huber, R. *Eur. J. Biochem.* **1990**, *187*, 341-352.

(8) (a) Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1989**, *209*, 249-279. (b) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 116-150.

(9) Wilcox, D. E.; Porras, A. G.; Hwang, Y. T.; Lerch, K.; Winkler, M. E.; Solomon, E. I. *J. Am. Chem. Soc.* **1985**, *107*, 4015-4027.

(10) (a) Brenner, M. C.; Klinman, J. P. *Biochemistry* **1989**, *28*, 4664-4670. (b) Stewart, L. C.; Klinman, J. P. *Annu. Rev. Biochem.* **1988**, *57*, 551-592.

(11) (a) Ito, N.; Phillips, S. E. V.; Stevens, C.; Ogel, Z. B.; McPherson, M. J.; Keen, J. N.; Yadav, K. D. S.; Knowles, P. F. *Nature* **1991**, *350*, 87-90. (b) Whittaker, M. M.; Whittaker, J. W. *J. Biol. Chem.* **1990**, *265*, 9610-9613.

(12) Larsen, R. W.; Pan, L.-P.; Musser, S. M.; Li, Z.; Chan, S. I. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 723-727 and references cited therein.

(13) (a) *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simándi, L. I., Ed.; Studies in Surface Science and Catalysis, Vol. 66; Elsevier Science Publishers B.V.: Amsterdam, 1991. (b) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988. (c) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989. (d) Mimoun, H. *Catal. Today* **1987**, *1*, 281-295. (e) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1. (f) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

(14) Nasir, M. S.; Karlin, K. D.; McGowty, D.; Zubieta, J. *J. Am. Chem. Soc.* **1991**, *113*, 698-700.

(15) (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668-2679. (b) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2624-2630. (c) Blackburn, N. J.; Strange, R. W.; Cruse, R. W.; Karlin, K. D. *J. Am. Chem. Soc.* **1987**, *109*, 1235-1237.

(16) Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769-6780.

(17) (a) Data for $[Cu_2(UN\text{-}O^-)]PF_6$ (**4**) are as follows. Anal. Calcd for $C_{35}H_{37}Cu_2F_6N_6OP$: C, 50.66; H, 4.46; N, 10.13. Found: C, 50.96; H, 4.61; N, 10.08. IR (Nujol): $\nu(PF_6) = 840\ cm^{-1}$. (b) Data for $[Cu_2(UN\text{-}OH)](PF_6)_2\cdot{}^1/_4Et_2O$ (**5**) are as follows. Anal. Calcd for $C_{36}H_{40.5}Cu_2F_{12}N_6O_{1.25}P_2$: C, 43.48; H, 3.62; N, 8.45. Found: C, 43.87; H, 4.05; N, 8.39. IR (Nujol): $\nu(PF_6) = 840\ cm^{-1}$.

(18) (a) X-ray-quality crystals of $[Cu_2(UN\text{-}O^-)](PF_6)\cdot CH_3CN$ (**4**) were obtained by recrystallization from CH_3CN/Et_2O. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.149$ (4) Å, $b = 13.963$ (3) Å, $c = 11.046$ (2) Å, $\alpha = 92.99$ (2), $\beta = 90.55$ (2), $\gamma = 82.12$ (2), $V = 1858$ (1) Å³, and $Z = 2$. A Rigaku AFC6S diffractometer was used in the ω-2θ scan mode to collect 6564 unique reflections, of which 3207 reflections with $I \geq 3.00\sigma(I)$ were used in the solution and refinement. The positional parameters of the copper atom were determined by direct methods. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. The structure was refined to the current residual values of $R = 0.052$ and $R_w = 0.047$ (Mo Kα, $\lambda = 0.710\ 73$ Å). (b) Supplementary material.

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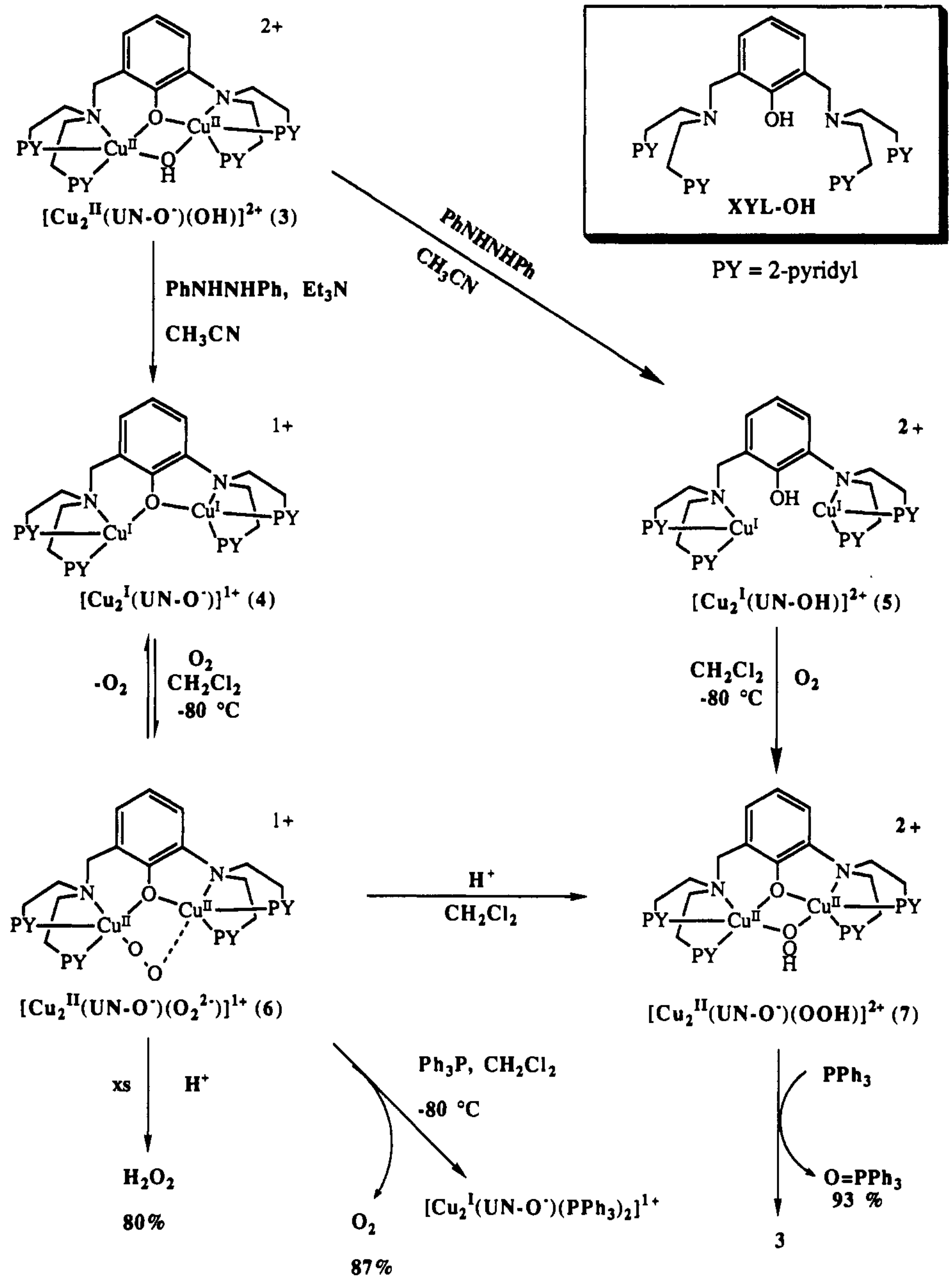
Scheme I



650 (ϵ = 660) nm; this can also be generated by direct protonation (HBF_4) of **6**, as shown in a UV–vis titration which possesses an isosbestic point at ~450 nm (supplementary material). The UV–vis spectroscopic and structural properties (vide infra) of **7** also compare closely with the related ligand complex $[Cu_2(XYL\text{-}O^-)(O_2H)]^{2+}$ (**2**),[16] suggesting they have very similar structures. $[Cu_2(UN\text{-}O^-)(O_2)]^+$ (**6**) contains a basic peroxo group as seen by its protonation to give H_2O_2 and reaction of PPh_3 liberating O_2.[19] By contrast, **7** converts PPh_3 to $O{=}PPh_3$, consistent with its hydroperoxo formulation (Scheme I).

The solution stability of peroxo and hydroperoxo complexes **6** and **7** is considerably augmented as judged by UV–vis spectroscopy, where decomposition (i.e., loss of absorbance) occurs ~20 °C higher than observed for **1** and **2**. Whereas, we never were able to isolate **1** or **2** in a solid-state form, brown/purple $[Cu_2(UN\text{-}O^-)(O_2)]^+$ (**6**) and green $[Cu_2(UN\text{-}OH)(O_2H)]^{2+}$ (**7**) solid materials[20] could be isolated (83% and 88% yields, respectively) by low-temperature (−85 °C) precipitation from CH_2Cl_2 solution using Et_2O. The room-temperature stability of these solids is demonstrated by the ability to (1) obtain analytically pure samples,[20] (2) redissolve the solids in cold CH_2Cl_2, obtaining spectra for **6** or **7** matching those generated in situ (vide supra), (3) obtain solid-state infrared[20] and UV–vis spectra in agreement with the solution data, and (4) pump off O_2 from $[Cu_2(UN\text{-}O^-)(O_2)]^+$ (**6**) with only a modest level of decomposition (~25%); **6** can be heated in vacuo and the resulting dicopper(I) complex $[Cu_2(UN\text{-}O^-)]^+$ (**4**) redissolved in CH_2Cl_2 and oxygenated at −80 °C to regenerate **6**.

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(19) Paul, P. P.; Tyeklár, Z.; Jacobson, R. R.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 5322–5332.

(20) (a) Data for $[Cu_2(UN\text{-}O^-)(O_2)]PF_6$ (**6**) are as follows. Anal. Calcd for $C_{35}H_{37}Cu_2F_6N_6O_3P$: C, 48.78; H, 4.30; N, 9.76. Found: C, 48.53; H, 4.39; N, 9.49. IR (Nujol: $\nu(PF_6)$ = 840 cm^{-1}. (b) Data for $[Cu_2(UN\text{-}O^-)(OOH)](PF_6)_2\cdot{}^1/_2Et_2O$ (**7**) are as follows. Anal. Calcd for $C_{37}H_{43}Cu_2F_{12}N_6O_{3.5}P_2$: C, 42.53; H, 4.12; N, 8.05. Found: C, 42.38; H, 4.25; N, 8.23. IR (Nujol): $\nu(OH)$ = 3490 cm^{-1}. This contrasts with $\nu(OH)$ = 3590 cm^{-1} for **3**.[14] (c) Clear assignment of $\nu(O\text{–}O)$ for **6** and **7** was not possible, even when complexes derived from $^{16}O_2$ and $^{18}O_2$ were compared. Resonance Raman studies are in progress.

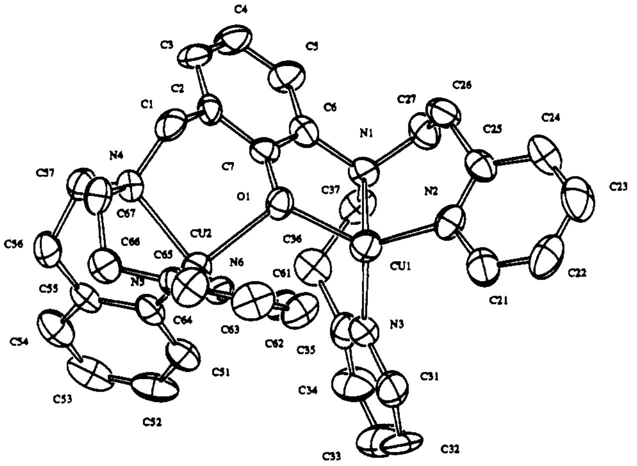

Figure 1. ORTEP diagram of the cationic portion of $Cu_2(UN\text{-}O^-)](PF_6)\cdot CH_3CN$ (4), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu1–N1, 2.207 (7); Cu1–N2, 1.993 (7); Cu1–N3, 2.017 (7); Cu1–O1, 2.023 (5); Cu2–N4, 2.174 (7); Cu2–N5, 1.968 (7); Cu2–N6, 1.977 (7); Cu2–O1, 2.156 (6); Cu1···Cu2, 3.569 (1); N1–Cu1–N2, 101.0 (3); N1–Cu1–N3, 101.4 (3); N(2)–Cu(1)–N(3), 117.9 (3); O1–Cu1–N1, 83.7 (2); O1–Cu1–N2, 120.3 (3); O1–Cu1–N3, 119.2 (3); N4–Cu2–N5, 100.6 (3); N4–Cu2–N6, 97.7 (3); N5–Cu2–N6, 137.8 (3); O1–Cu2–N4, 92.7 (2); O1–Cu2–N5, 118.4 (2); O1–Cu2–N6, 98.1 (3); Cu1–O1–Cu2, 117.3 (3).

The ability to obtain solids also facilitated probing the structures of **6** and **7** by X-ray absorption spectroscopy (supplementary material). EXAFS simulations indicate structures very similar to **1** and **2**, with Cu···Cu distances of 3.28 ± 0.07 and 2.95 ± 0.07 Å obtained for **6** and **7**, respectively.[21] The close similarity of UV–vis and EXAFS spectroscopic properties of the UN-O⁻ and XYL-O⁻ peroxo and hydroperoxo complexes suggests the structures are essentially the same, with $[Cu_2(UN\text{-}O^-)(O_2)]^+$ (**6**) possessing an unsymmetrical terminal Cu–$(O_2{}^{2-})$···Cu coordination[15b] and $[Cu_2(UN\text{-}OH)(O_2H)]^{2+}$ (**7**) with a μ-1,1-hydroperoxo coordination (Scheme I).[21] Solid-state magnetic properties appear to be consistent with these formulations, with the peroxo–dicopper(II) complexes showing moderately strong antiferromagnetic coupling;[22] magnetic moments (25 °C) are 1.2 ± 0.1 μ_B/Cu for **6** and 1.3 ± 0.1 μ_B/Cu for **7**, compared to 1.5 ± 0.1 μ_B/Cu for $[Cu_2(UN\text{-}O^-)(OH)]^{2+}$ (**3**).[14] Paramagnetically shifted ^1H NMR spectra are also in accord with these observations. Compared to the diamagnetic dicopper(I) precursor complex $[Cu_2(UN\text{-}O^-)]^+$ (**4**), **3** and **6** exhibit complicated patterns of both up and downfield shifting of ligand ^1H resonances in CD_2Cl_2 at −80 °C. We readily identified the benzylic protons by synthesizing deuterated UN-O⁻ complex analogues. The stronger magnetic coupling in peroxo compound **6** is indicated by smaller shifts in ^2H NMR spectra; i.e., δ = 3.71 ppm for $[Cu_2(UN\text{-}O^-)]^+$ (**4**), δ = 67.01 ppm for **3**, and δ = 12.68 ppm for **6**.[23]

In conclusion, the ligand modification described here has led to thermally stable complexes, allowing us to considerably expand the scope available for physical characterization and reactivity studies of interesting peroxo– or hydroperoxo–dicopper(II) compounds. We plan to further exploit this approach with these and other copper–dioxygen compounds.

Acknowledgment. We thank the National Institutes of Health (Grant GM 28962, K.D.K.; Grant NS27583, N.J.B.) for their support of this research.

Supplementary Material Available: Figures showing a UV–vis titration involving **6** and **7** and EXAFS data and analyses of **6** and **7**, text describing the crystal structure, and listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (19 pages). Ordering information is given on any current masthead page.

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[21] Previously, frozen-solution EXAFS studies of **1** and **2** revealed Cu···Cu distances of 3.31[15c] and 3.04 Å,[16] respectively.

[22] Other peroxo–dicopper(II) complexes exhibit very strong magnetic coupling. See ref 4 and: Karlin, K. D.; Tyeklár, Z.; Farooq, A.; Jacobson, R. R.; Sinn, E.; Lee, D. W.; Bradshaw, J. E.; Wilson, L. J. *Inorg. Chim. Acta* **1991**, *182*, 1–3.

[23] NMR spectroscopy can be used to evaluate magnetic interactions in dicopper(II) complexes. See ref 4b,c and: Maekawa, M.; Kitagawa, S.; Munakata, M.; Masuda, H. *Inorg. Chem.* **1989**, *28*, 1904–1909.