

- [8] M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* **2001**, 342, 265–271.
- [9] G. S. Duesberg, J. Muster, V. Krstic, M. Burghard, S. Roth, *Appl. Phys. A* **1998**, 67, 117–119.
- [10] a) P. Collins, R. Ferrier, *Polysaccharides: Their Chemistry*, Wiley, Chichester, **1995**, pp. 478–523; b) J. Lehmann, *Carbohydrates: Structure and Biology*, Thieme, Stuttgart, **1998**, pp. 98–103; c) D. B. Thompson, *Carbohydr. Polym.* **2000**, 43, 223–239.
- [11] For an excellent review on supramolecular fullerene chemistry, see: F. Diederich, M. Gómez-López, *Chem. Soc. Rev.* **1999**, 28, 263–277.
- [12] a) T. Anderson, K. Nilsson, M. Sundahl, G. Westman, O. Wennerström, *J. Chem. Soc. Chem. Commun.* **1992**, 604–606; b) W. Kutner, P. Boulas, K. M. Kadish, *J. Electrochem. Soc.* **1992**, 139, 243C; c) M. Sundahl, T. Andersson, K. Nilsson, O. Wennerström, G. Westman, *Synth. Met.* **1993**, 56, 3252–3257; d) D. D. Zhang, Q. Liang, J. W. Chen, M. K. Li, S. S. Wu, *Supramol. Chem.* **1993**, 3, 235–238; e) Á. Buvári-Barcza, T. Braun, L. Barcza, *Supramol. Chem.* **1994**, 4, 131–135; f) Z.-i. Yoshida, H. Takekuma, S.-i. Takekuma, Y. Matsubara, *Angew. Chem.* **1994**, 106, 1658–1660; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1597–1599; g) D. D. Zhang, J. W. Chen, Y. Ying, R. F. Cai, X. L. Shen, S. H. Wu, *J. Inclusion Phenom.* **1993**, 16, 245–253; h) Y. Liu, L. F. Wang, D. D. Zhang, *Chin. Sci. Bull.* **1995**, 40, 1759–1760; i) C. Y. Jin, D. D. Zhang, T. Oguma, S. X. Qian, *J. Inclusion Phenom.* **1996**, 24, 301–310; j) T. Furuishi, T. Endo, H. Nagase, H. Ueda, T. Nagai, *Chem. Pharm. Bull.* **1998**, 46, 1658–1659; k) Á. Buvári-Barcza, J. Rohonczy, N. Rozlosnik, T. Gilányi, B. Szabó, G. Lovas, T. Braun, L. Barcza, *J. Chem. Soc. Perkin Trans. 2* **2001**, 191–196.
- [13] See *Chem. Rev.* **1998**, 98, 1741–2076 for a special issue on cyclodextrins.
- [14] a) W. Hinrichs, G. Buettner, M. Steifa, C. Betzel, V. Zabel, B. Pfannmueller, W. Saenger, *Science* **1987**, 238, 205–208; b) R. C. Teitelbaum, S. L. Ruby, T. J. Marks, *J. Am. Chem. Soc.* **1978**, 100, 3215–3217; c) R. E. Rundle, *J. Am. Chem. Soc.* **1947**, 69, 1769–1772, and references therein.
- [15] The inner diameters that have been reported (by electron diffraction studies on crystalline amylose complexes or so-called V-amylose) are 4.5, 6.0, and up to 7–8 Å: a) Y. Yamashita, *J. Polym. Sci. Part A* **1965**, 3, 3251–3260; b) Y. Yamashita, N. Hirai, *J. Polym. Sci. Part A2* **1966**, 4, 161–171; c) Y. Yamashita, K. Monobe, *J. Polym. Sci. Part A2* **1971**, 9, 1471–1481.
- [16] Molecular dynamics (MD) simulations, based on the AMBER force field, using the solvation model for water, were achieved within MacroModel. The assembly was allowed to equilibrate over the course of a 100 ps (1.5 fs time step) MD simulation at 300 K, before providing the superstructure displayed in Figure 1b. For conformational analysis of an amylose fragment (maltoheptaose) in water, see: J. Shimada, H. Kaneko, T. Takada, S. Kitamura, K. Kajiwara, *J. Phys. Chem. B* **2000**, 104, 2136–2147.
- [17] J. Kadokawa, Y. Kaneko, H. Tagaya, K. Chiba, *Chem. Commun.* **2001**, 449–450.
- [18] It has been shown that in the amylose–iodine complex, the iodine molecules exist as polyiodide chains and are composed of I_3^- and I_5^- subunits which combine to form four dominant polyiodide chains (I_9^{3-} , I_{11}^{3-} , I_{13}^{3-} , and I_{15}^{3-}) and give different absorption spectra when complexed inside the amylose. The absorption maxima associated with these chains appear at 480–510, 610–640, 690–720, and 730–760, respectively. See: X. Yu, C. Houtman, R. H. Atalla, *Carbohydr. Res.* **1996**, 292, 129–141.
- [19] I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, R. H. Hauge, *J. Phys. Chem. B* **2001**, 105, 8297–8301.
- [20] Among the numerous enzymes that will hydrolyze starch, there is amylglucosidase, an exoamylase which attacks all the α -1,4 and α -1,6 glucosidic linkages to produce glucose. For more information about the properties of this and other glucosidases, see: T. Yamamoto, *Enzyme Chemistry and Molecular Biology of Amylases and Related Enzymes*, CRC, Boca Raton, FL, USA, **1995**, pp. 3–201. α -Amylase, which is present in human saliva, is an endoamylase that attacks the α -1,4 glucosidic linkages in starch randomly and so reduces the lengths of the glucan chains. Indeed, we have found that aqueous solutions of starch-SWNTs are stable for weeks provided you do not spit on them! Addition of saliva to these solutions leads to precipitation of the carbon nanotubes after several hours.
- [21] Just as this manuscript was about to be submitted, we learned of a simple procedure for dispersing SWNTs in aqueous solutions of the acidic polysaccharide, Gum Arabic, produced by Acacia Senegal trees. See: R. Bandyopadhyaya, E. Nativ-Roth, O. Regev, R. Yerushalmi-Rozen, *Nano Lett.* **2002**, 2, 25–28.
- [22] C. Yamamoto, T. Hayashi, Y. Okamoto, S. Ohkubo, T. Kato, *Chem. Commun.* **2001**, 925–926.
- [23] Enzymatic hydrolysis of starch-wrapped SWNTs has also been followed by carrying out light-scattering measurements recorded on a Jasco J-715 spectrophotometer with a 1-cm fluorescence cell. In this experiment, an enzyme solution (2 μ L of 10 mg mL⁻¹) was added to the starch-wrapped SWNTs in aqueous solution at a concentration of 0.5 mg mL⁻¹ (Figure 4a).
- [24] In the case of the enzymatic hydrolysis of starch, the combined intensities for the anomeric protons (H_a and H_b) of D-glucopyranose equal that for the anomeric protons (H_b) in starch. However, the glucose produced on treating the starch-wrapped SWNTs integrates for significantly more than the complexed starch. It is well known that proton signals in polymer-wrapped SWNTs are not only broadened but reduced in their intensities by this kind of complexation. See: ref. [8].

The First Non-Heme Iron(III) Complex with a Ligated Carboxamido Group That Exhibits Photolability of a Bound NO Ligand**

Apurba K. Patra, Raman Afshar,
Marilyn M. Olmstead, and Pradip K. Mascharak*

Dedicated to Professor Karl Wieghardt
on the occasion of his 60th birthday

Nitric oxide (NO) is the first gaseous molecule known to act as a biological messenger and it participates in several important functions including control of blood pressure, neurotransmission, and inhibition of tumor growth.^[1] The tumoricidal property of NO has raised interest in the use of organic^[1] and metal–nitrosyl complexes^[2] that release NO upon illumination as agents in photodynamic therapy (PDT).^[3] Such compounds can deliver NO to biological targets on demand and are preferred over conventional photodynamic agents such as photofrin in treating malignant tumors with hypoxic locales. In recent years, iron–nitrosyl complexes such as Na₂[Fe(CN)₅NO]^[4] and Roussin's salts^[5]

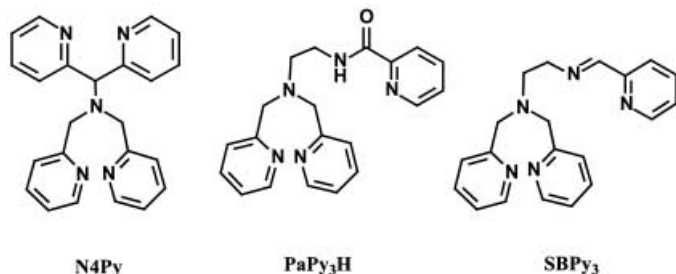
[*] Prof. Dr. P. K. Mascharak, Dr. A. K. Patra, R. Afshar
Department of Chemistry and Biochemistry
University of California
Santa Cruz, CA 95064 (USA)
Fax: (+1) 831-459-2935
E-mail: pradip@chemistry.ucsc.edu
Dr. M. M. Olmstead
Department of Chemistry
University of California
Davis, CA 95616 (USA)

[**] Financial support from the NSF (CHE-9818492) and NIH (GM 61636) is gratefully acknowledged. The Bruker SMART 1000 diffractometer was funded in part by an NSF Instrumentation Grant CHE-9808259.

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

have been studied extensively as prospective NO-releasing agents in PDT.

Although a survey of the coordination chemistry of NO clearly reveals its preference for Fe^{II} centers, the binding of NO to Fe^{III} centers has been reported in a few heme^[6] and non-heme^[7, 8] species. Recently, we reported the low-spin Fe^{III} complex [Fe(PaPy₃)(CH₃CN)][ClO₄]₂ (**1**) which binds to a



variety of ligands, through replacement of the solvent (acetonitrile) molecule.^[9] Herein, we report that **1** readily reacts with NO to afford [Fe(PaPy₃)(NO)][ClO₄]₂ (**2**) and that **2** rapidly loses NO upon exposure to light in solvents such as CH₃CN (thus re-forming **1**). Binding of NO at the non-heme Fe^{III} center in **1** is completely reversible and the bound NO is photolabile. We believe that the photolability of NO observed with **2** is related to the coordinated carboxamido nitrogen atom, which provides extra stability to the Fe^{III} center.^[10] To prove this hypothesis we have also synthesized the Fe^{III} complex of the Schiff base SBPy₃, a ligand identical to PaPy₃H except for the presence of an imine group in place of the carboxamide moiety. The low-spin Fe^{III} complex [Fe-(SBPy₃)(dmf)][ClO₄]₃ (**3**) is spontaneously reduced to the corresponding Fe^{II} species [Fe(SBPy₃)(CH₃CN)][ClO₄]₂ in CH₃CN and exhibits no affinity toward NO. The behavior of **3** in CH₃CN is similar to that of the iron complex containing the N4Py ligand, as reported by Feringa and co-workers.^[11]

When purified NO gas is passed through a solution of **1** in CH₃CN, its purple color rapidly turns red showing the formation of the NO adduct **2**. Since the bound NO in **2** is labile in CH₃CN under light, we have synthesized **2** by an alternative method. A slurry of [Fe(dmf)₆][ClO₄]₃ and PaPy₃H (1:1) in MeOH, was stirred with one equivalent of a mild base, in this case, triethylamine, at 45 °C. The mixture became homogeneous and reddish purple within 30 min. Passage of NO through this solution caused rapid precipitation of red microcrystalline **2** in good yield. The IR spectrum of **2** displays an NO stretch at 1919 cm⁻¹, which is within the range (1822–1937 cm⁻¹) expected for an {Fe–NO}⁶-type complex.^[6b, 8b] The ¹H NMR spectrum of **2** (prepared and run in the dark) clearly indicates its *S* = 0 ground state (see Supporting Information). The structure of the cation of **2** is shown in Figure 1.^[12] The Fe^{III} center is in a distorted octahedral geometry. The *tert*-amine and the three pyridine nitrogen atoms comprise the equatorial plane, with the carboxamido nitrogen atom and the NO ligand occupying the axial positions; the Fe–N–O bond is almost linear (Fe–N6–O2 = 173.1(2)°). Although the average Fe–N_{py} and Fe–N_{amine} bond lengths of **2** are similar to those in **1**, the Fe–N_{amido} bond

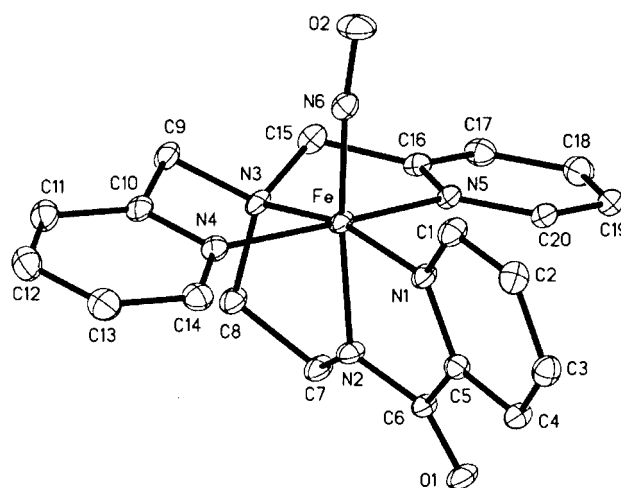


Figure 1. ORTEP diagram of [Fe(PaPy₃)(NO)]²⁺, the cation of **2**, showing the atom labeling scheme. All H atoms and the CH₃CN molecule present as solvent of crystallization have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Fe–N1 1.978(2), Fe–N2 1.9009(19), Fe–N3 1.972(2), Fe–N4 1.982(2), Fe–N5 1.983(2), Fe–N6 1.677(2), N6–O2 1.139(3); Fe–N6–O2 173.1(2), N6–Fe–N2 174.35(9), N1–Fe–N2 81.18(8), N1–Fe–N3 165.68(8), N1–Fe–N4 97.13(9), N1–Fe–N5 95.88(8), N2–Fe–N3 84.58(8), N2–Fe–N4 91.82(8), N2–Fe–N5 84.35(8), N3–Fe–N4 81.79(9), N3–Fe–N5 84.13(8), N3–Fe–N6 97.54(9), N4–Fe–N5 165.71(8), N4–Fe–N6 93.67(9), N5–Fe–N6 90.64(9).

(1.901(2) Å) is longer than that in **1** (1.826(3) Å). There is evidence of appreciable double bond character in the Fe–N(O) bond (1.677(2) Å), much like that observed in other {Fe–NO}⁶ species.^[6b, 8b]

When the red solution of **2** in CH₃CN is kept in the dark, the electronic absorption spectrum (rapid scan) does not change appreciably, even after 48 h (see Supporting Information). However, when the cuvette is exposed to light (50 W tungsten lamp), the color changes rapidly to purple (namely, the color of **1**).^[13] Clean isosbestic points are observed in successive electronic absorption spectra (Figure 2). Conversely, when NO is introduced into the cuvette, the color slowly goes back to red (the color of **2**, see Supporting Information).

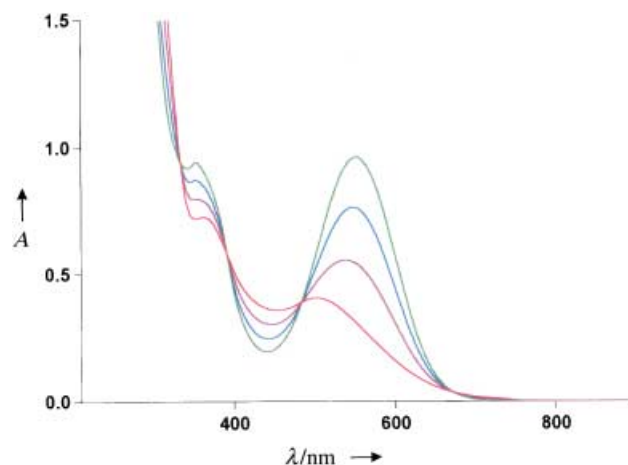


Figure 2. Conversion of [Fe(PaPy₃)(NO)][ClO₄]₂ (**2**, red trace) into [Fe(PaPy₃)(CH₃CN)][ClO₄]₂ (**1**, green trace) in CH₃CN under illumination with a 50 W tungsten lamp (*t*_{1/2} = 45 s).

The low-spin Fe^{III} complex [Fe(SBPY₃)(dmf)][ClO₄]₃ (**3**) has been isolated from the reaction of [Fe(dmf)₆][ClO₄]₃ and SBPY₃ (1:1) in MeOH. Isolation of this Fe^{III} complex is only possible from MeOH since it precipitates out from this solvent immediately on formation. When **3** is dissolved in CH₃CN or DMF, the red solution rapidly turns purple as a consequence of the spontaneous reduction of **3** to the corresponding Fe^{II} complex [Fe(SBPY₃)(solvent)][ClO₄] (see Supporting Information). As a consequence of this rapid formation, crystals of **3** suitable for structural studies were not obtained. However, analytical and spectral data clearly establish the identity of this compound. We have synthesized the purple diamagnetic Fe^{II} complex [Fe(SBPY₃)(CH₃CN)][BF₄]₂ (**4**) and characterized it by X-ray crystallography (see Supporting Information).^[14] Complex **4** exhibits a half-wave potential ($E_{1/2}$) of 1.01 V (versus the saturated calomel electrode, SCE) in CH₃CN. Clearly, the SBPY₃ ligand stabilizes the Fe^{II} center much like N4Py ($E_{1/2}$ of [Fe(N4Py)(CH₃CN)][ClO₄]₂ in CH₃CN = 1.01 V versus SCE) and hence, in both cases, one obtains the Fe^{II} complex rather easily. In the present case, complex **3** is amenable for isolation because of its low solubility in methanol.

Notably, **3** does not bind NO under any conditions. Since both **1** and **3** are low-spin, the ground-state electronic configuration is not responsible for this difference. There is a difference, however, in their redox potential; the $E_{1/2}$ value for **1** in CH₃CN is 0.21 V (versus SCE). The presence of just one carboxamido nitrogen atom around the Fe^{III} center in **1** stabilizes the +3 oxidation state of iron by approximately 0.8 V relative to **3** or [Fe(N4Py)(CH₃CN)][ClO₄]₂. It appears, therefore, that a more stabilized Fe^{III} center (such as that in **1**) is required for NO binding and the photolability of the bound NO molecule (as in the NO adduct of **1**). Since the bound NO in **2** is *trans* to the carboxamido nitrogen atom, it also appears that a negatively charged donor center is another requirement for the photolability of the bound NO molecule. Reversible binding of NO has been observed at the non-heme Fe^{III} site in the microbial enzyme nitrile hydratase.^[15, 16] This Fe^{III} center is coordinated to carboxamido nitrogen atoms in the equatorial plane, and is stabilized to a great extent.^[17] Additionally, in the NO-bound "dark" form, NO is *trans* to a negatively charged cystinato sulfur donor and the enzyme releases NO upon illumination.

In conclusion, [Fe(PaPy₃)(NO)][ClO₄]₂ (**2**) is the first example of an {Fe–NO}⁶-type iron–nitrosyl species with a carboxamido nitrogen atom as a donor.^[18] It is also the first non-heme Fe^{III} species that binds NO reversibly and exhibits the photolability of a bound NO moiety under very mild conditions. Photokinetic studies of **2** and related complexes are ongoing.

Experimental Section

All reactions were carried out in an inert N₂ atmosphere.

2: A slurry of [Fe(dmf)₆][ClO₄]₃ (0.23 g, 0.29 mmol) in MeOH (10 mL) was added to a stirred solution of PaPy₃H (0.10 g, 0.29 mmol) in MeOH (10 mL), followed by the addition of triethylamine (0.03 g, 0.3 mmol) diluted in MeOH (2 mL). The reaction mixture was then stirred at 45 °C for 30 min, by which time a reddish purple solution was obtained. Purified NO gas was then introduced into the flask, and a red-colored complex

precipitated out immediately. It was then filtered, washed with anhydrous Et₂O, and dried under vacuum (0.095 g, 52 % yield). Crystals of [Fe(PaPy₃)(NO)][ClO₄]₂·CH₃CN (**2**·CH₃CN), suitable for X-ray diffraction, were grown in the dark by diffusion of Et₂O into a solution of the complex in CH₃CN. Elemental analysis calcd for C₂₂H₂₃Cl₂FeN₇O₁₀ (**2**·CH₃CN): C 39.31, H 3.45, N 14.59; found: C 39.28, H 3.51, N 14.60; FT-IR (KBr): $\tilde{\nu}$ = 3082(w), 2932(w), 2867(w), 1919(s), 1642(s), 1609(m), 1453(m), 1385(m), 1289(w), 1228(w), 1090(s), 765(m), 623(m); UV/Vis (CH₃CN, prepared in dark conditions) λ_{max} /nm (ϵ in M⁻¹cm⁻¹) = 500 (1040), 365 (1840); ¹H NMR (500 MHz, CD₃CN): δ = 8.99 (d, 1H), 8.51 (t, 1H), 8.28 (d, 1H), 8.14 (t, 2H), 8.04 (m, 1H), 7.73 (d, 2H), 7.44(t, 2H), 6.72 (d, 2H), 5.02 (dd, 4H), 3.73 (d, 2H), 3.68 (d, 2H) ppm.

3: A solution of [Fe(dmf)₆][ClO₄]₃ (0.50 g, 0.63 mmol) in MeOH (20 mL) was slowly added to a solution of SBPY₃ (0.21 g, 0.63 mmol) in MeOH (10 mL) and stirred. Complex **3** rapidly precipitated from the reaction mixture as a red microcrystalline solid which was filtered, washed with anhydrous Et₂O, and dried under vacuum (0.26 g, 57 % yield). Elemental analysis calcd for C₂₄H₃₂Cl₃FeN₆O₁₄ (**3**·MeOH): C 36.45, H 4.08, N 10.63; found: C 36.31, H 4.11, N 10.73; selected IR frequencies (cm⁻¹, KBr disk): $\tilde{\nu}$ = 3425(br, m), 3072(w), 2932(w), 2791(w), 1650(m), 1602(m), 1479(w), 1437(m), 1291(m), 1090(vs), 774(s), 620(s); UV/Vis (CH₃CN) λ_{max} /nm (ϵ in M⁻¹cm⁻¹) = 545 (sh, 1500), 445 (sh, 2470), 390 (sh, 4240), 345 (5420). X-band EPR spectrum in 1:1 methanol/acetone glass (86 K): g = 2.313, 2.157, 1.933 (see Supporting Information).

4: A solution of [Fe(H₂O)₆][BF₄]₂ (0.20 g, 0.6 mmol) in MeOH (10 mL) was added to a solution of SBPY₃ (0.20 g, 0.6 mmol) in MeOH (7 mL). The deep purple solution was stirred for 1 h, at which point CH₃CN (3 mL) was added. Anhydrous Et₂O was then allowed to diffuse into this mixture at 4 °C. Magenta plates of [Fe(SBPY₃)(CH₃CN)][BF₄]₂·½Et₂O·⅓CH₃OH (**4**·½Et₂O·⅓CH₃OH) were isolated after 4 days (0.27 g, 70 % yield). Elemental analysis calcd for C₂₄H₃₀B₂F₈FeN₆O (**4**·½Et₂O·⅓CH₃OH): C 44.48, H 4.67, N 12.97; found: C 44.21, H 4.81, N 12.73; selected IR frequencies (cm⁻¹, KBr disk): $\tilde{\nu}$ = 3427(br, m), 1605(m), 1460(m), 1294(w), 1054(vs), 771(m), 523(m). UV/Vis (CH₃OH) λ_{max} /nm (ϵ in M⁻¹cm⁻¹) = 570 (4030), 395 (5690), 280 (8730), 257 (11 870); UV/Vis (CH₃CN) λ_{max} /nm (ϵ in M⁻¹cm⁻¹) = 557 (6780), 385 (10 560), 280 (10 820), 252 (16 830); ¹H NMR (500 MHz, CD₃CN): δ = 9.28 (s, 1H), 8.97 (d, 1H), 8.31 (d, 1H), 8.24 (t, 1H), 7.80 (m, 3H), 7.42 (d, 2H), 7.09 (t, 2H), 6.56 (d, 2H), 4.82 (dd, 4H), 3.82 (t, 2H), 3.18 (t, 2H) ppm.

Received: March 21, 2002 [Z18954]

- [1] a) *Methods in Nitric Oxide Research* (Eds.: M. Feelisch, J. S. Stamler), Wiley, Chichester, **1996**; b) E. Culotta, D. E. Koshland, *Science* **1992**, 258, 1862–1865.
- [2] a) P. C. Ford, J. Bourassa, K. Miranda, B. Lee, I. Lorkovic, S. Boggs, S. Kudo, L. Laverman, *Coord. Chem. Rev.* **1998**, 171, 185–202; b) M. J. Clarke, J. B. Gaul, *Struct. Bonding* **1993**, 81, 147–181.
- [3] a) R. Ackroyd, C. Kelty, N. Brown, M. Reed, *Photochem. Photobiol.* **2001**, 74, 656–669; b) R. K. Pandey, *J. Porphyrins Phthalocyanines* **2000**, 4, 368–373.
- [4] a) R. J. Singh, N. Hogg, F. Neese, J. Joseph, B. Kalyanaraman, *Photochem. Photobiol.* **1995**, 61, 325–330; b) S. Kudo, J. L. Bourassa, S. E. Boggs, Y. Sato, P. C. Ford, *Anal. Biochem.* **1997**, 247, 193–202.
- [5] a) J. Bourassa, W. DeGraff, S. Kudo, D. A. Wink, J. B. Mitchell, P. C. Ford, *J. Am. Chem. Soc.* **1997**, 119, 2853–2860; b) J. L. Bourassa, P. C. Ford, *Coord. Chem. Rev.* **2000**, 200, 887–900.
- [6] a) M. K. Ellison, W. R. Scheidt, *J. Am. Chem. Soc.* **1999**, 121, 5210–5219; b) W. R. Scheidt, Y. J. Lee, K. J. Hatano, *J. Am. Chem. Soc.* **1984**, 106, 3191–3198.
- [7] C. Hauser, T. Glaser, E. Bill, T. Weyhermuller, K. Wieghardt, *J. Am. Chem. Soc.* **2000**, 122, 4352–4364.
- [8] a) C. A. Grapperhaus, A. K. Patra, M. S. Mashuta, *Inorg. Chem.* **2002**, 41, 1039–1041; b) D. Schweitzer, J. J. Ellison, S. C. Shoner, S. Lovell, J. A. Kovacs, *J. Am. Chem. Soc.* **1998**, 120, 10996–10997.
- [9] J. M. Rowland, M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **2001**, 40, 2810–2817.
- [10] D. S. Marlin, P. K. Mascharak, *Chem. Soc. Rev.* **2000**, 29, 69–74.
- [11] a) G. Roelfes, M. Lubben, K. Chen, R. Y. N. Ho, A. Meetsma, S. Genseberger, R. M. Hermant, R. Hage, S. K. Mandal, V. G. Young, Jr., Y. Zang, H. Kooijmann, A. L. Spek, L. Que, Jr., B. L.

- Feringa, *Inorg. Chem.* **1999**, 38, 1929–1936; b) M. Lubben, A. Meetsma, E. C. Wilkinson, B. L. Feringa, L. Que, Jr., *Angew. Chem.* **1995**, 107, 1610–1612; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1512–1514.
- [12] Crystal data for $[\text{Fe}(\text{PaPy}_3)(\text{NO})][\text{ClO}_4]_2 \cdot \text{CH}_3\text{CN} (2 \cdot \text{CH}_3\text{CN})$: red plates, $0.48 \times 0.40 \times 0.02 \text{ mm}^3$, orthorhombic, space group *Pbca*, $a = 7.740(3)$, $b = 21.990(9)$, $c = 30.634(11) \text{ \AA}$, $V = 5214(3) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.713 \text{ Mg m}^{-3}$, $2\theta_{\text{max}} = 60^\circ$, $\mu(\text{MoK}\alpha) = 0.855 \text{ mm}^{-1}$, ω scans, $\lambda = 0.71073 \text{ \AA}$; the data were collected at 91(2) K on a Bruker SMART 1000 diffractometer; a total of 69800 reflections were measured, of which 7591 were independent ($R_{\text{int}} = 0.051$) and included in the refinement; min./max. transmission = 0.684/0.983; solution by direct methods (SHELXL-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXL-97, Sheldrick, **1997**); 380 parameters, $R1 = 0.0628$, $wR2 = 0.1270$ for all data; $R1 = 0.0476$ computed for 6082 observed data ($I > 2\sigma(I)$).
- [13] A cuvette containing a 0.4 mM solution of **2** in CH_3CN was placed 5 cm from a 50 W tungsten lamp for 30 s intervals and the absorption spectra were monitored on a Cary 50 spectrophotometer in fast-scan mode (spectra shown in Figure 2). The rate of NO release was slower ($t_{1/2} = 1.5 \text{ min}$) when a 20 W tungsten lamp was used. NO release upon illumination was also observed with solutions of **2** in DMF and water. In the solid state, **2** is very stable towards light (no observed decomposition over a period of months).
- [14] a) Crystal data for $[\text{Fe}(\text{SBPy}_3)(\text{CH}_3\text{CN})][\text{BF}_4]_2 \cdot \frac{1}{2} \text{Et}_2\text{O} \cdot \frac{2}{3} \text{CH}_3\text{OH} (4 \cdot \frac{1}{2} \text{Et}_2\text{O} \cdot \frac{2}{3} \text{CH}_3\text{OH})$: magenta-colored platelike crystals, $0.44 \times 0.29 \times 0.05 \text{ mm}^3$, monoclinic, space group *C2/c*, $a = 38.398(15)$, $b = 11.859(5)$, $c = 12.783(5) \text{ \AA}$, $\beta = 103.422(8)^\circ$, $V = 5662(4) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.520 \text{ Mg m}^{-3}$, $2\theta_{\text{max}} = 61^\circ$, $\mu(\text{MoK}\alpha) = 0.616 \text{ mm}^{-1}$, ω scans, $\lambda = 0.71073 \text{ \AA}$; the data were collected at 91(2) K on a Bruker SMART 1000 diffractometer; a total of 37587 reflections were measured, of which 8565 were independent ($R_{\text{int}} = 0.067$) and included in the refinement; min./max. transmission = 0.773/0.970; solution by direct methods (SHELXL-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXL-97, Sheldrick, **1997**); 372 parameters, $R1 = 0.1023$, $wR2 = 0.1759$ for all data; $R1 = 0.0607$ computed for 5681 observed data ($I > 2\sigma(I)$); b) CCDC-181941 (complex **2**) and CCDC-181942 (complex **4**) contain 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).
- [15] S. Nagashima, M. Nakasako, N. Dohmae, M. Tsujimura, K. Takio, M. Odaka, M. Yohda, N. Kamiya, I. Endo, *Nature Struct. Biol.* **1998**, 5, 347–351.
- [16] a) M. Odaka, K. Fujii, M. Hoshino, T. Noguchi, M. Tsujimura, S. Nagashima, N. Yohda, T. Nagamune, I. Inoue, I. Endo, *J. Am. Chem. Soc.* **1997**, 119, 3785–3791; b) T. Noguchi, M. Hoshino, M. Tsujimura, M. Odaka, I. Inoue, I. Endo, *Biochemistry*, **1996**, 35, 16777–16781.
- [17] a) P. K. Mascharak, *Coord. Chem. Rev.* **2002**, 225, 201–214; b) J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *J. Am. Chem. Soc.* **2001**, 123, 3247–3259; c) J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1998**, 37, 1138–1139.
- [18] An $[\text{Fe}(\text{NO})]^{7-}$ -type iron–nitrosyl complex with a carboxamido nitrogen atom has been reported; see: M. Ray, A. P. Golombek, M. P. Hendrich, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, A. S. Borovik, *Inorg. Chem.* **1999**, 38, 3110–3115.

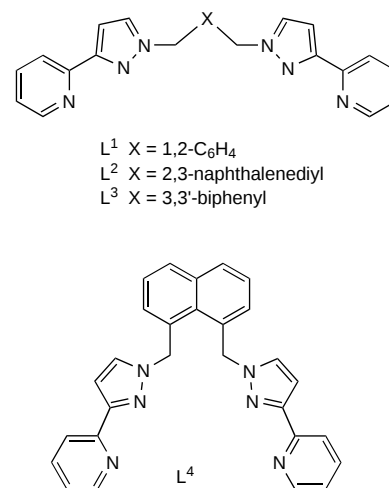
Assembly of a Truncated-Tetrahedral Chiral $[\text{M}_{12}(\mu\text{-L})_{18}]^{24+}$ Cage**

Zöe R. Bell, John C. Jeffery, Jon A. McCleverty, and Michael D. Ward*

One of the most active areas of research in metallo-supramolecular chemistry at present is the assembly of polyhedral cage complexes from labile metal centers and multidentate bridging ligands.^[1] Apart from the intrinsic appeal of the structures, they are of interest both for understanding the mechanisms of the assembly process which lead to their formation and for the host–guest chemistry associated with their large central cavities.^[1]

Tetradentate ligands with two bidentate chelating termini are commonly used in this area. When these coordinate to octahedral metal centers in the absence of any other ligands, the resulting complex must have a metal:ligand ratio of 2:3, as found in dinuclear triple helicates with three bridging ligands.^[2] The next member of this series is the M_4L_6 tetrahedron, in which a bridging ligand spans each edge of a tetrahedral array of metal ions. This type of structure has been extensively studied recently,^[3–6] and there is a well-developed host–guest chemistry based on the binding of counterions or solvent molecules in the tetrahedral cavities. The only three-dimensional cage of which we are aware with a higher nuclearity but with the same M_2L_3 ratio is the cube $[\text{Ni}_8(\text{tab})_{12}]^{16+}$ (tab = 1,2,3,4-tetraaminobutane);^[7] in 1997 we described a (two-dimensional) circular M_8L_{12} helicate with an anion encapsulated in the central cavity.^[8]

Our recent work in this area is based on ligands such as L^1 – L^3 which contain two bidentate pyrazolylpyridine units linked to an aromatic core through two methylene spacers.^[3,9] With cobalt(II) ions these ligands form $[\text{Co}_4\text{L}_6]^{8+}$ cages which bind



[*] Prof. M. D. Ward, Dr. Z. R. Bell, Dr. J. C. Jeffery, Prof. J. A. McCleverty
 School of Chemistry
 University of Bristol
 Cantock's Close, Bristol BS8 1TS (UK)
 Fax: (+44) 117-929-0509
 E-mail: mike.ward@bristol.ac.uk

[**] We thank the EPSRC for financial support.