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[20] Among the numerous enzymes that will hydrolyze starch, there is amyloglucosidase, 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.

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[24] In the case of the enzymatic hydrolysis of starch, the combined intensities for the anomeric protons (H_α and H_β) of D-glucopyranose equal that for the anomeric protons (H_β) 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 $Na_2[Fe(CN)_5NO]$[4] and Roussin's salts[5]

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[*] 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)

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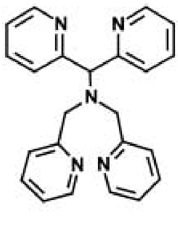
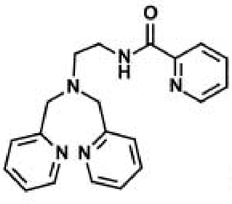
have been studied extensively as prospective NO-releasing agents in PDT.

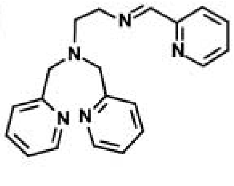
Although a survey of the coordination chemistry of NO clearly reveals its preference for $\mathrm{Fe^{II}}$ centers, the binding of NO to $\mathrm{Fe^{III}}$ centers has been reported in a few heme[6] and non-heme[7, 8] species. Recently, we reported the low-spin $\mathrm{Fe^{III}}$ complex $[\mathrm{Fe(PaPy_3)(CH_3CN)}][\mathrm{ClO_4}]_2$ (**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 $[\mathrm{Fe(PaPy_3)(NO)}][\mathrm{ClO_4}]_2$ (**2**) and that **2** rapidly loses NO upon exposure to light in solvents such as $\mathrm{CH_3CN}$ (thus re-forming **1**). Binding of NO at the non-heme $\mathrm{Fe^{III}}$ 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 $\mathrm{Fe^{III}}$ center.[10] To prove this hypothesis we have also synthesized the $\mathrm{Fe^{III}}$ complex of the Schiff base $\mathrm{SBPy_3}$, a ligand identical to $\mathrm{PaPy_3H}$ except for the presence of an imine group in place of the carboxamide moiety. The low-spin $\mathrm{Fe^{III}}$ complex $[\mathrm{Fe(SBPy_3)(dmf)}][\mathrm{ClO_4}]_3$ (**3**) is spontaneously reduced to the corresponding $\mathrm{Fe^{II}}$ species $[\mathrm{Fe(SBPy_3)(CH_3CN)}][\mathrm{ClO_4}]_2$ in $\mathrm{CH_3CN}$ and exhibits no affinity toward NO. The behavior of **3** in $\mathrm{CH_3CN}$ is similar to that of the iron complex containing the N4Py ligand, as reported by Feringa and co-workers.[11]



N4Py



PaPy₃H



SBPy₃

When purified NO gas is passed through a solution of **1** in $\mathrm{CH_3CN}$, its purple color rapidly turns red showing the formation of the NO adduct **2**. Since the bound NO in **2** is labile in $\mathrm{CH_3CN}$ under light, we have synthesized **2** by an alternative method. A slurry of $[\mathrm{Fe(dmf)_6}][\mathrm{ClO_4}]_3$ and $\mathrm{PaPy_3H}$ (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 $\mathrm{cm^{-1}}$, which is within the range (1822–1937 $\mathrm{cm^{-1}}$) expected for an $\{\mathrm{Fe-NO}\}^6$-type complex.[6b, 8b] The ^{1}H 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 $\mathrm{Fe^{III}}$ 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 $\mathrm{Fe-N_{py}}$ and $\mathrm{Fe-N_{amine}}$ bond lengths of **2** are similar to those in **1**, the $\mathrm{Fe-N_{amido}}$ bond (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 $\{\mathrm{Fe-NO}\}^6$ species.[6b, 8b]

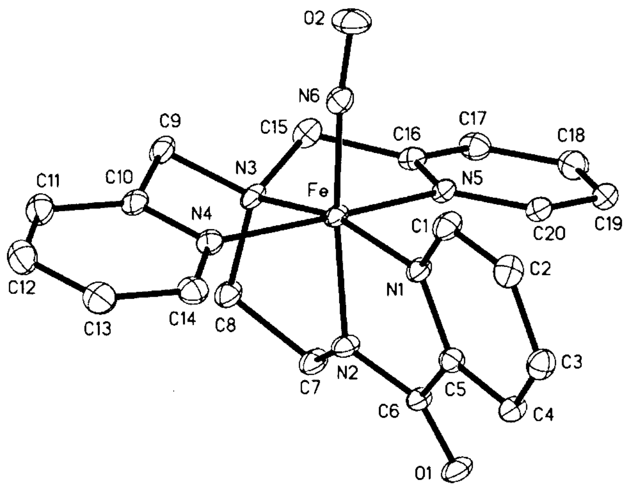


Figure 1. ORTEP diagram of $[\mathrm{Fe(PaPy_3)(NO)}]^{2+}$, the cation of **2**, showing the atom labeling scheme. All H atoms and the $\mathrm{CH_3CN}$ molecule present as solvent of crystallization have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Fe-N1 1.978(2), Fe-N2 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).

When the red solution of **2** in $\mathrm{CH_3CN}$ 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).

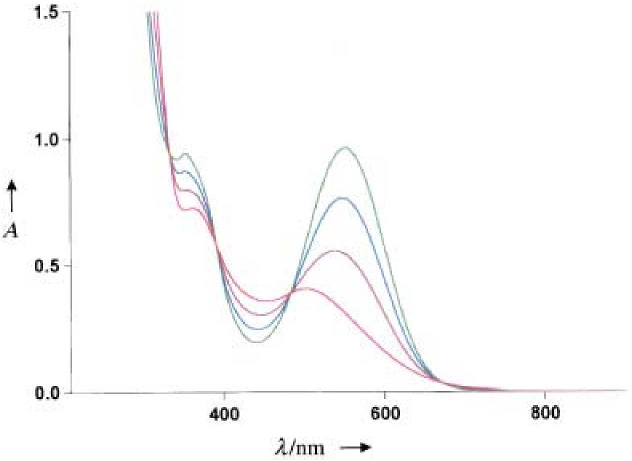


Figure 2. Conversion of $[\mathrm{Fe(PaPy_3)(NO)}](\mathrm{ClO_4})_2$ (**2**, red trace) into $[\mathrm{Fe(PaPy_3)(CH_3CN)}](\mathrm{ClO_4})_2$ (**1**, green trace) in $\mathrm{CH_3CN}$ under illumination with a 50 W tungsten lamp ($t_{1/2}=45$ s).

The low-spin Fe^{III} complex $[Fe(SBPy_3)(dmf)][ClO_4]_3$ (**3**) has been isolated from the reaction of $[Fe(dmf)_6][ClO_4]_3$ and $SBPy_3$ (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 CH_3CN or DMF, the red solution rapidly turns purple as a consequence of the spontaneous reduction of **3** to the corresponding Fe^{II} complex $[Fe(SBPy_3)(solvent)][ClO_4]$ (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 $[Fe(SBPy_3)(CH_3CN)][BF_4]_2$ (**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 CH_3CN. Clearly, the $SBPy_3$ ligand stabilizes the Fe^{II} center much like N4Py ($E_{1/2}$ of $[Fe(N4Py)(CH_3CN)][ClO_4]_2$ in $CH_3CN = 1.01$ 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 CH_3CN 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 $[Fe(N4Py)(CH_3CN)][ClO_4]_2$. 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, $[Fe(PaPy_3)(NO)][ClO_4]_2$ (**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 N_2 atmosphere.

2: A slurry of $[Fe(dmf)_6][ClO_4]_3$ (0.23 g, 0.29 mmol) in MeOH (10 mL) was added to a stirred solution of $PaPy_3H$ (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 Et_2O, and dried under vacuum (0.095 g, 52% yield). Crystals of $[Fe(PaPy_3)(NO)][ClO_4]_2 \cdot CH_3CN$ (**2**$\cdot CH_3CN$), suitable for X-ray diffraction, were grown in the dark by diffusion of Et_2O into a solution of the complex in CH_3CN. Elemental analysis calcd for $C_{22}H_{23}Cl_2FeN_7O_{10}$ (**2**$\cdot CH_3CN$): 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 (CH_3CN, prepared in dark conditions) λ_{max} /nm (ε in $M^{-1}cm^{-1}$) = 500 (1040), 365 (1840); ^1H NMR (500 MHz, CD_3CN): $\delta = 8.99$ (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 $[Fe(dmf)_6][ClO_4]_3$ (0.50 g, 0.63 mmol) in MeOH (20 mL) was slowly added to a solution of $SBPy_3$ (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 Et_2O, and dried under vacuum (0.26 g, 57% yield). Elemental analysis calcd for $C_{24}H_{32}Cl_3FeN_6O_{14}$ (**3**$\cdot$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 (CH_3CN) λ_{max} /nm (ε in $M^{-1}cm^{-1}$) = 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 $[Fe(H_2O)_6][BF_4]_2$ (0.20 g, 0.6 mmol) in MeOH (10 mL) was added to a solution of $SBPy_3$ (0.20 g, 0.6 mmol) in MeOH (7 mL). The deep purple solution was stirred for 1 h, at which point CH_3CN (3 mL) was added. Anhydrous Et_2O was then allowed to diffuse into this mixture at 4 °C. Magenta plates of $[Fe(SBPy_3)(CH_3CN)][BF_4]_2 \cdot \frac{1}{3}Et_2O \cdot \frac{2}{3}CH_3OH$ (**4**$\cdot \frac{1}{3}Et_2O \cdot \frac{2}{3}CH_3OH$) were isolated after 4 days (0.27 g, 70% yield). Elemental analysis calcd for $C_{24}H_{30}B_2F_8FeN_6O$ (**4**$\cdot \frac{1}{3}Et_2O \cdot \frac{2}{3}CH_3OH$): 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 (CH_3OH) λ_{max} /nm (ε in $M^{-1}cm^{-1}$) = 570 (4030), 395 (5690), 280 (8730), 257 (11870); UV/Vis (CH_3CN) λ_{max} /nm (ε in $M^{-1}cm^{-1}$) = 557 (6780), 385 (10560), 280 (10820), 252 (16830); ^1H NMR (500 MHz, CD_3CN): $\delta = 9.28$ (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.

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[12] Crystal data for [Fe(PaPy$_3$)(NO)][ClO$_4$]$_2$·CH$_3$CN (**2**·CH$_3$CN): red plates, $0.48 \times 0.40 \times 0.02$ mm^3, orthorhombic, space group *Pbca*, $a = 7.740(3)$, $b = 21.990(9)$, $c = 30.634(11)$ Å, $V = 5214(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.713$ Mg m^{-3}, $2\theta_{max} = 60°$, $\mu(Mo_{K\alpha}) = 0.855$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; 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 ($R_{int} = 0.051$) 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$_3$CN 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 ($t_{1/2} = 1.5$ 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 [Fe(SBPy$_3$)(CH$_3$CN)][BF$_4$]$_2$·⅓Et$_2$O·⅔CH$_3$OH (**4**·⅓Et$_2$O·⅔CH$_3$OH): magenta-colored platelike crystals, $0.44 \times 0.29 \times 0.05$ mm^3, monoclinic, space group *C*2/*c*, $a = 38.398(15)$, $b = 11.859(5)$, $c = 12.783(5)$ Å, $\beta = 103.422(8)°$, $V = 5662(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.520$ Mg m^{-3}, $2\theta_{max} = 61°$, $\mu(Mo_{K\alpha}) = 0.616$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; 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 ($R_{int} = 0.067$) 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).

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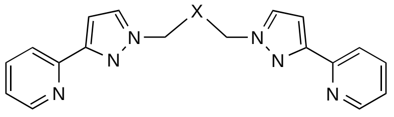
Assembly of a Truncated-Tetrahedral Chiral [M$_{12}$(μ-L)$_{18}$]$^{24+}$ Cage[**]

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

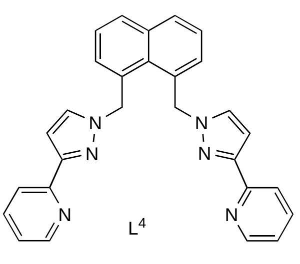
One of the most active areas of research in metallo-supramolecular chemistry at present is the assembly of polyhedral cage complexes from labile metal centers and multidentate bridging ligands.[1] Apart from the intrinsic appeal of the structures, they are of interest both for understanding the mechanisms 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$_4$L$_6$ 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$_2$L$_3$ ratio is the cube [Ni$_8$(tab)$_{12}$]$^{16+}$ (tab = 1,2,3,4-tetraaminobutane);[7] in 1997 we described a (two-dimensional) circular M$_8$L$_{12}$ 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 [Co$_4$L$_6$]$^{8+}$ cages which bind



L^1 X = 1,2-C$_6$H$_4$
L^2 X = 2,3-naphthalenediyl
L^3 X = 3,3'-biphenyl



L^4

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[*] 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

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