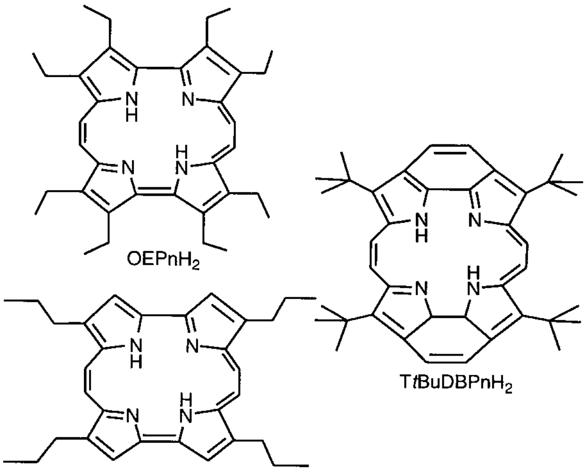
X-Ray Photoelectron Spectroscopy of Porphycenes: Charge Asymmetry Across Low-Barrier Hydrogen Bonds**

Abhik Ghosh,* John Moulder, Martin Bröring, and Emanuel Vogel

Low-barrier hydrogen bonds (LBHBs), also known as short, strong hydrogen bonds (SSHBs), appear to be ubiquitous in both organic chemistry and biology.[1] They are found in many common organic compounds such as carboxylate–carboxylic acid complexes[2] and β-diketones.[3] Gerlt and Gassman[4] have invoked LBHBs to rationalize the stabilization of various enol intermediates in enzymatic hydrogen abstraction from carboxylic acids. They proposed a bonding scenario in which the hydrogen atom resides midway between the enolic oxygen atom and the conjugate base of the active site catalyst. Cleland and Kreevoy[5] extended the same argument to cover enolate-type intermediates in enzyme-catalyzed reactions. They noted that these enzymes all exhibit unusually short heteroatom–heteroatom distances, which is a diagnostic feature of LBHBs. They further suggested that the bonding energy associated with the formation of an LBHB may be as high as 40–85 kJ mol^{-1} and that LBHBs are essentially covalent. Frey et al.[6] found evidence, in the form of a strongly deshielded proton in ^{1}H NMR spectra, of an aspartate–histidinium LBHB in the catalytic triad of serine proteases. Other researches have doubted[2] or disputed[7] the importance of LBHBs in enzyme catalysis, with the result that a lively debate has surrounded this topic.[8]

On the basis of our involvement with porphyrin chemistry[9, 10] and X-ray photoelectron spectroscopy (XPS),[11] it occurred to us that XPS[12] may furnish unique insights into the LBHBs found in porphyrin analogues, such as porphyrin isomers, corroles, and related macrocycles. The activation energy for NH tautomerism in free-base porphyrins is about 12 kcal mol^{-1}[13] and the central protons appear delocalized in the ^{1}H NMR spectra at room temperature. The maximally symmetric free-base porphyrin tetraphenylporphyrin (TPPH$_2$) reveals the presence of a single *trans* tautomer on cooling the NMR sample.[14] In contrast, XPS, which gives a practically instantaneous picture of the molecules, reveals two well-resolved ionization potentials (IPs), separated by 2.0–2.1 eV, of the nitrogen core when measured from above room temperature down to liquid-nitrogen temperature. The higher IPs are those of the protonated nitrogen atoms.[11c] An interesting feature of this result is that this difference in IPs ($\Delta I_{\text{N-1s}}$), which may be regarded as a difference of about 200 kJ mol^{-1} (of electronic charge) in the electrostatic potential between the protonated and unprotonated nitrogen atoms, is about 3–4 times the activation energy for proton transfer. Thus, there is a substantial asymmetry in the charge distribution between the donor and acceptor atoms even for moderately low-barrier hydrogen bonds. This result provided the motivation for an XPS study of the exceptionally low-barrier hydrogens bonds found in various porphyrin-type molecules.

The porphycenes (Scheme 1) are of interest in this regard. The N-H$\cdots$N hydrogen bonds in porphycene are exceptionally strong[15] and the barrier to tautomerism is so low that ^{1}H and ^{13}C NMR spectra remain unchanged down to 165 K.[16–18] A density functional theoretical (DFT) study[19] at the B3LYP/TZDP level provided strong evidence that the ground state of unsubstituted porphycene corresponds to the *trans* tautomer. At this level of theory the optimized N–H and NH$\cdots$N distances for the *trans* tautomer are 1.041 and 1.703 Å, which corresponds to a geometrical asymmetry of 0.662 Å for the N-H$\cdots$N unit. The *trans* →*cis* activation barrier, corrected for zero-point energy effects, was predicted to be only 2.1 kcal mol^{-1}, which is consistent with the lack of change in the NMR spectra down to 165 K. In contrast, the N$\cdots$H distances involving each hydrogen-bonded proton in the optimized geometry of dibenzoporphycene[20] are nearly identical, namely, 1.23 and 1.26 Å, which corresponds to a geometrical asymmetry of 0.03 Å. This minute geometrical asymmetry is at, or beyond, the limit of what can be reliably predicted with DFT, which raises the intriguing prospect that the dibenzoporphycenes may provide a rare, if not unique, example of a symmetrical N$\cdots$H$\cdots$N hydrogen bond. XPS provides a convenient means for examining this issue and here we report an XPS[21] study of 2,3,6,7,12,13,16,17-octaethylporphycene (OEPnH$_2$),[22] 2,7,12,17-tetra-*n*-propylporphycene



Scheme 1. Free-base porphycenes studied in this work.

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($TPrPnH_2$),[23] and 2,7,12,17-tetra-(*tert*-butyl)-3,6-13,16-dibenzo[cde;mno]porphycene (T*t*BuDBPnH_2: Scheme 1).[24]

Table 1 lists the N 1s and C 1s peak maxima obtained by XPS and Figure 1 shows the N 1s XPS spectra. The energy splitting between the different ionization potentials of the nitrogen core ($\Delta I_{\text{N-1s}}$) decreases along the series $TPPH_2$ (2.1 eV), $OEPnH_2$ (1.75 eV), $TPrPnH_2$ (1.4 eV), and T*t*BuDBPnH_2 (0.95 eV). The two types of nitrogen atoms appear as well-resolved peaks in all cases except for T*t*BuDBPnH_2 where the splitting of 0.95 eV approaches the limit of the instrument resolution. The results afford a number of interesting conclusions as well as provoke some significant unanswered questions, as discussed below.

Table 1. XPS peak maxima [eV] of different compounds studied.

Compound	N 1s	$\Delta I_{\text{N-1s}}$	C 1s
$TPPH_2$	397.4, 399.5	2.1	284.6
$OEPnH_2$	397.9, 399.65	1.75	285.0
$TPrPnH_2$	397.8, 399.2	1.4	284.9
T*t*BuDBPnH_2	397.95, 398.9	0.95	284.6

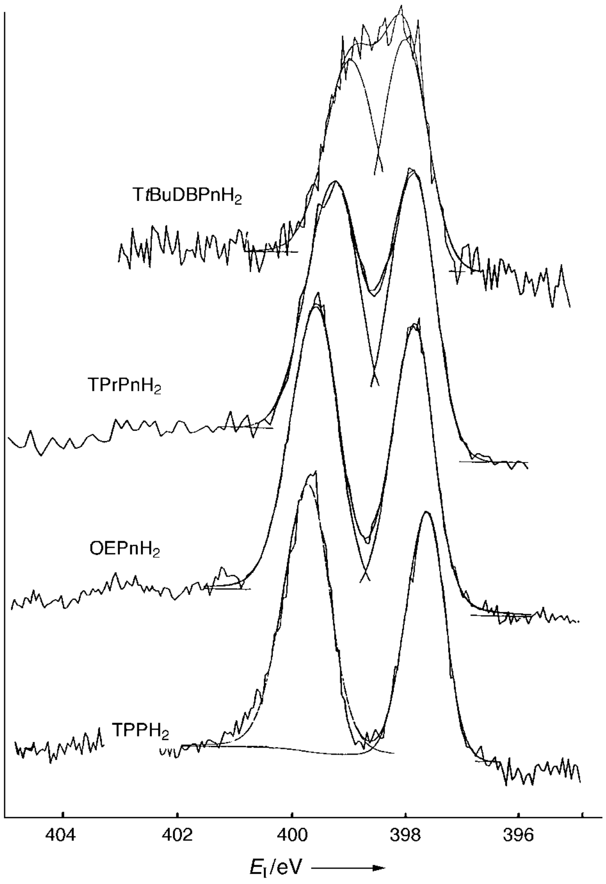

Figure 1. Nitrogen 1s maxima of the various compounds studied by XPS. The *x* axis gives IPs or binding energies in eV. The spectral intensities along the *y* axis are in arbitrary units. The lower signal-to-noise ratio in the case of the spectrum of T*t*BuDBPnH_2 is a consequence of the extra high instrument resolution used relative to the other samples.

All the compounds studied have localized, albeit rapidly tautomerizing, central protons. The assignment of the spectra are straightforward, based on previous XPS studies[11] as well as ab initio Hartree–Fock[11] and DFT equivalent-core[25] calculations: for each molecule, the higher IP of the nitrogen core corresponds to the protonated nitrogen atoms.[11c]

The core IPs of the "unprotonated" nitrogen atoms increases along the series of compounds $TPPH_2$, $OEPnH_2$, $TPrPnH_2$, and T*t*BuDBPnH_2, while the core IPs of the "protonated" nitrogen atoms decreases.[26] However, although the difference in the electronic character between the protonated and unprotonated nitrogen atoms narrows across this series of compounds, the two types of nitrogen atoms do not quite equalize. Remarkably, even for T*t*BuDBPnH_2, whose hydrogen bonds are almost perfectly symmetrical in a geometrical sense,[20] a significant charge asymmetry persists across the $N\cdots H\cdots N$ units.

The decrease in the $\Delta I_{\text{N-1s}}$ value, or the increase in the hydrogen-bond strength, along the series $TPPH_2$, $OEPnH_2$, $TPrPnH_2$, and T*t*BuDBPnH_2, correlates with a decrease in the $N\cdots N$ separations in the $N\cdots H\cdots N$ hydrogen-bonded units in these compounds, with the $N\cdots N$ distances being 2.93,[27] 2.79–2.80,[22] 2.61–2.62,[23] and 2.51 Å,[24c] respectively, for the four compounds (Figure 2). This correlation also explains a somewhat puzzling aspect of the data shown in Table 1: the $\Delta I_{\text{N-1s}}$ value of $TPrPnH_2$ (1.4 eV) is significantly smaller than that of $OEPnH_2$ (1.75 eV). On the basis of the foregoing argument it appears that this anomaly results from differences in the skeletal geometry between the two compounds. Indeed, there appears to be a monotonic relationship between the $\Delta I_{\text{N-1s}}$ values and the $N\cdots N$ separations that also extends to other tetrapyrroles, such as different porphyrin and corrole isomers.[9, 28] We shall report XPS results, along with DFT equivalent-core simulations, on these substances in a forthcoming paper.[29]

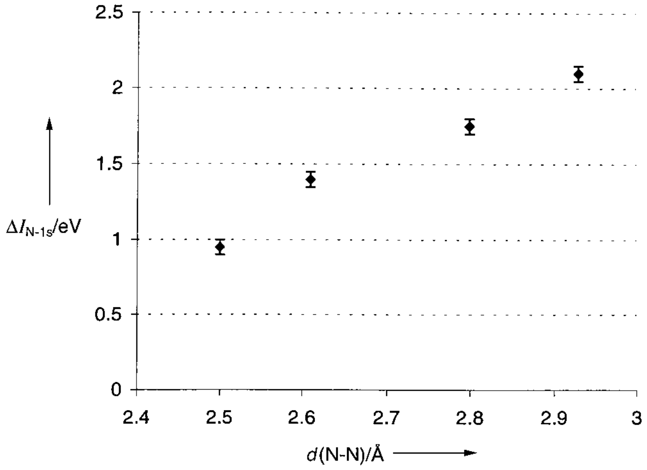

Figure 2. Variation of the $\Delta I_{\text{N-1s}}$ [eV] values with $N\cdots N$ separation [d(N–N), Å]. From left to right: the data points are for T*t*BuDBPnH_2, $TPrPnH_2$, $OEPnH_2$, and $TPPH_2$.

Can we understand or rationalize these large charge asymmetries, as measured by $\Delta I_{\text{N-1s}}$, across exceedingly low-barrier hydrogen bonds in terms of a simple physical picture? Simple electrostatics provides part of the answer. Consider a proton P placed in a vacuum approximately halfway between two points A and B so that the distances $P \cdots A$ and $P \cdots B$ are 1.23 and 1.26 Å, respectively (these being the NH distances in an optimized structure of dibenzoporphycene as mentioned above). A simple calculation shows that the geometrical asymmetry of 0.03 Å with respect to the proton results in a fairly significant difference in the electrostatic potential (about 0.3 V) between points A and B. For $P \cdots A = 1.21$ Å and $P \cdots B = 1.27$ Å, the difference in the electrostatic potential between points A and B is about 0.6 V. These simple-minded "proton-in-vacuum" calculations help somewhat in demystifying how geometrical asymmetries of less than 0.1 Å may engender electrostatic potential differences of several tenths of an eV (as measured by $\Delta I_{\text{N-1s}}$ in this study) across the termini of a low-barrier hydrogen bond. Clearly, obtaining a proper understanding the charge distribution of LBHBs involves much more than these crude considerations and we hope to present a theoretical analysis of the experimental results reported here in the not too distant future.

A brief comment may be in order on the question of whether perfectly symmetrical hydrogen bonds (that is, with single-well potential energy minima) exist. The bifluoride ion HF_2^- is believed to provide the prototypical example of such bonding. Another well-studied example of an LBHB system with at least near-perfect geometrical asymmetry is provided by the $[(CO)_5Cr\text{-}CN \cdots H \cdots NC\text{-}Cr(CO)_5]^-$ ion.[30] However, in light of the present results, these as well as other LBHB systems are well worth reexamining by XPS.

Finally, how might the present results relate to current research on the role of LBHBs in enzyme catalysis? How similar are the LBHBs in porphycenes and those found in biological systems? Although these questions remain unanswered at this point, we felt obliged to articulate them here because, eventually, the large and diverse body of results on LBHBs, including the present findings, must come together in a coherent picture.

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[1] W. W. Cleland, P. A. Frey, J. A. Gerlt, *J. Biol. Chem.* **1998**, *273*, 25529.

[2] a) B. Schwartz, D. G. Drueckhammer, *J. Am. Chem. Soc.* **1996**, *118*, 9826; b) Y. Kato, L. M. Toledo, J. Rebek, Jr., *J. Am. Chem. Soc.* **1996**, *118*, 8575; c) C. J. Smallwood, M. A. McAllister, *J. Am. Chem. Soc.* **1997**, *119*, 11277.

[3] B. Schiøtt, B. B. Iversen, G. K. H. Madsen, F. K. Larsen, T. C. Bruice, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 12799; b) B. Schiøtt, B. B. Iversen, G. K. H. Madsen, T. C. Bruice, *J. Am. Chem. Soc.* **1998**, *120*, 12117.

[4] a) G. A. Gerlt, P. G. Gassman, *J. Am. Chem. Soc.* **1993**, *115*, 11552; b) G. A. Gerlt, P. G. Gassman, *Biochemistry* **1993**, *32*, 11943.

[5] W. W. Cleland, M. M. Kreevoy, *Science* **1994**, *264*, 1887.

[6] P. A. Frey, S. A. Whitt, J. B. Tobin, *Science* **1994**, *264*, 1927.

[7] A. Warshel, A. Papazyan, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 13665.

[8] a) A. Warshel, A. Papazyan, P. A. Kollman, *Science* **1995**, *269*, 102; b) W. W. Cleland, M. M. Kreevoy, *Science* **1995**, *269*, 104; c) P. A. Frey, *Science* **1995**, *269*, 104.

[9] a) E. Vogel, *J. Heterocycl. Chem.* **1996**, *33*, 1461; b) for another account of the same area, see J. L. Sessler, S. J. Weghorn, *Expanded, Contracted, and Isomeric Porphyrins*, Elsevier, Amsterdam, **1997**.

[10] a) A. Ghosh in *The Porphyrin Handbook*, *Vol. 7* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, Chap. 47, p. 1; b) A. Ghosh, *Acc. Chem. Res.* **1998**, *31*, 189.

[11] a) A. Ghosh, J. Fitzgerald, P. G. Gassman, J. Almlöf, *Inorg. Chem.* **1994**, *33*, 6057; b) A. Ghosh, *J. Org. Chem.* **1993**, *58*, 6932; c) P. G. Gassman, A. Ghosh, J. Almlöf, *J. Am. Chem. Soc.* **1992**, *114*, 9990.

[12] For other applications of XPS to the study of hydrogen bonds, see for example: a) E. Hasselbach, A. Henriksson, F. Jachimowicz, J. Wirz, *Helv. Chim. Acta* **1972**, *55*, 1757; b) K. Wozniak, H. Y. He, J. Klinowski, T. L. Barr, P. Milart, *J. Phys. Chem.* **1996**, *100*, 11420.

[13] a) T. Butenhoff, C. B. Moore, *J. Am. Chem. Soc.* **1988**, *110*, 8336; b) Z. Smedarchina, M. Z. Zgierski, W. Siebrand, P. M. Kozlowski, *J. Chem. Phys.* **1998**, *109*, 1014; c) for a review of NH tautomerism in porphyrins, see D. K. Maity, T. N. Truong, *J. Porphyrins Phthalocyanines*, in press.

[14] a) C. B. Storm, Y. Teklu, *J. Am. Chem. Soc.* **1972**, *94*, 1745. For more detailed analyses of NH tautomerism in porphyrins, including isotope labeling, see b) M. Schlabach, H.-H. Limbach, E. Bunnenberg, A. Y. L. Shu, B.-R. Tolf, C. Djerassi, *J. Am. Chem. Soc.* **1993**, *115*, 4554; c) C. J. Medforth in *The Porphyrin Handbook*, *Vol. 5* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, Chap. 35, p. 1.

[15] Among the free-base derivatives of tetrapyrrolic porphyrin isomers with N_4 cores, porphycene is as stable as, or slightly more stable than, porphyrin. This reflects the presence of short, strong hydrogen bonds in free-base porphycenes: Y.-D. Wu, K. W. K. Chan, C.-P. Yip, E. Vogel, D. A. Plattner, K. N. Houk, *J. Org. Chem.* **1997**, *62*, 9240. However, among metallotetrapyrroles, metalloporphyrins are thermodynamically more stable than their isomers, including the metalloporphycenes: A. Ghosh, T. Vangberg, *Inorg. Chem.* **1998**, *37*, 6276.

[16] E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausmann, M. Kisters, M. Aukauloo, P. Richard, R. Guilard, *Angew. Chem.* **1993**, *105*, 1670; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1600.

[17] E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, O. Ermer, *Angew. Chem.* **1987**, *99*, 909; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 928.

[18] For a ^{15}N NMR study of proton transfer in polycrystalline porphycene, see U. Langer, C. Hoelger, B. Wehrle, L. Latanowicz, E. Vogel, H.-H. Limbach, *J. Phys. Org. Chem.* **2000**, *13*, 23.

[19] P. M. Kozlowski, M. Z. Zgierski, J. Baker, *J. Chem. Phys.* **1998**, *109*, 5905.

[20] Y.-D. Wu, K. W. K. Chan, *THEOCHEM* **1997**, *398*, 325.

[21] X-ray photoelectron spectra were acquired at room temperature with a Physical Electronics 5800 spectrometer, equipped with a hemispherical analyzer, and 350 W of monochromatized $Al_{K\alpha}$ radiation. Sample preparation consisted of rubbing a tiny speck of the porphyrin or porphycene into a thin film on gold foil. The films, which appeared as a colored sheen on gold, were so thin that they showed no evidence of charging in the course of X-ray bombardment. Likewise, flooding the samples with low-energy electrons did not change the positions or shapes of the XPS peaks, again proving the absence of sample charging. The binding energies reported here (Table 1) are externally referenced to the Au $4f_{7/2}$ binding energy of the gold substrate at 84.0 eV and were reproducible to ±0.1 eV. The carbon 1s peak maxima given in Table 1 may be regarded as additional internal binding energy references. Alternatively, high-quality spectra, which allow accurate measurements of energy splittings between different peaks but leave the absolute binding energy scale somewhat less defined, could also be obtained with powder samples by using suitable charge-neutralization techniques. For any particular compound, energy differences between different binding energies (for example, between two N 1s peaks) were highly reproducible (to within ±0.05 eV) regardless of whether the sample was used as a thin film on gold or as a powder.

[22] E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausmann, M. Kisters, M. Aukauloo, P. Richard, R. Guilard, *Angew. Chem.* **1993**, *105*, 1670; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1600.

[23] E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, O. Ermer, *Angew. Chem.* **1987**, *99*, 909; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 928.

[24] a) E. Vogel, *Pure Appl. Chem.* **1993**, *65*, 143–152; b) U. Hübsch, PhD Thesis, University of Cologne, **1994**;. c) D. Donnerstag, PhD Thesis, University of Cologne, **1993**.

[25] A. Ghosh, *J. Phys. Chem. B* **1997**, *101*, 3290.

[26] The terms "protonated" and "unprotonated" are artificial in the context of LBHBs and are simply used for convenience.

[27] This value is taken from a DFT(VWN-PW91)/TZDP optimization: A. Ghosh, T. Vangberg, *Theor. Chem. Acc.* **1997**, *97*, 143.
[28] A. Ghosh, K. Jynge, *Chem. Eur. J.* **1997**, *3*, 823.
[29] A. Ghosh, T. Vangberg, M. Bröring, E. Vogel, unpublished results.
[30] H. Benedict, H.-H. Limbach, M. Wehlan, W.-P. Fehlhammer, N. S. Golubev, R. Janoschek, *J. Am. Chem. Soc.* **1998**, *120*, 2939.

Cyano-Bridged 4f–3d Coordination Polymers with a Unique Two-Dimensional Topological Architecture and Unusual Magnetic Behavior**

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Cyano-bridged dimetallic hybrid Prussian Blue one- to three-dimensional (1D–3D) coordination polymers based on $[M(CN)_6]^{3-}$ (M = Fe, Cr, Mn) have attracted great attention because of their rich and interesting structures and magnetic behavior.[1] These studies were mainly focused on transition metals. In principle, it would be possible to enhance the coercive field by the introduction of paramagnetic lanthanide ions because these possess rather large and anisotropic magnetic moments. However, the magnetism, rarely investigated, for known cyano-bridged lanthanide / transition metal complexes such as ion pairs, dinuclear, trinuclear, tetranuclear, and one-dimensional chains,[2], does not seem exciting, since the couplings between the lanthanide and transition metals are very weak, because of the effective shielding of the 4f electrons by the outer-shell electrons. However, the 3D polymer $[SmFe(CN)_6]\cdot 4H_2O$, with strong anisotropic coercive field, exhibits a long-range ferrimagnetic ordering below 3.5 K, and that $[TbCr(CN)_6]\cdot 4H_2O$ has the highest known Curie temperature ($T_C = 11.7$ K) for 4f–3d molecule-based magnets.[3] This implies that increasing the number of dimensions may enhance and improve bulk magnetic properties. Our strategy for the rational synthesis of a high-dimensional network is to use a suitable combination of cyanide groups and other bridging ligands. Here, 2,2′-bipyrimidine (bpym) was selected, in preference to 4,4′-bipyridine and pyrazine, because it is more capable of transmitting magnetic interactions[4] and its bis(chelating) coordination modes facilitate connection between lanthanide ions. Unexpectedly, two novel coordination polymers $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (M = Fe (**1**), Co (**2**)) were obtained, which have a unique 2D topological architecture, and exhibit unusual magnetic behavior.

Compounds **1** or **2** were obtained by the slow diffusion of $K_3[Fe(CN)_6]$ or $K_3[Co(CN)_6]$ and bpym with $Nd(NO_3)_3$ in a 1:1:1 molar ratio in aqueous solution (30 mL); X-ray diffraction analysis reveals that the compounds are isomorphous.[5] The structure of **1** (Figure 1) consists of a 2D net with alternating fused rows of rhombuslike $Fe_2Nd_2(CN)_4$ rings and six-sided $Fe_4Nd_4(CN)_8$ rings. Each Nd^{3+} ion is nine coordinate being bound by two N atoms from one chelating bpym molecule (the mean length of Nd–N = 2.7084 Å), four O atoms from water molecules (the mean length of Nd–O = 2.4706 Å) and three N atoms from three bridging CN^- groups (the mean length of Nd–N = 2.5825 Å), yielding a monocapped square anti-prism. The top and bottom planes are defined by O1, O2, N2, N10A and O3, O4, N1, N5, respectively, and N8 occupies the cap position. The bpym ligand coordinates to the Nd ions in a chelating fashion, and the remaining two N atoms form the hydrogen bonds with the coordinated water molecules of neighboring Nd^{3+} ion (not shown: O3···N3A 2.929 Å, O3–H5···N3A 155.80°; O2···N4A 2.850 Å, O2–H3···N4A 160.08°; symmetry: A: x, $y+1$, z). Although on chelation bpym and 2,2′-bipyridine (bipy) ligands have similar steric effects, they give different structures with $K_3[Fe(CN)_6]$ and $Nd(NO_3)_3$. For the latter, an ion pair compound $[FeNd_2(CN)_6(bipy)_4(H_2O)_8][Fe(CN)_6]\cdot 8H_2O$ is formed.[2f] The difference is tentatively attributed to the different affinity of both ligands.

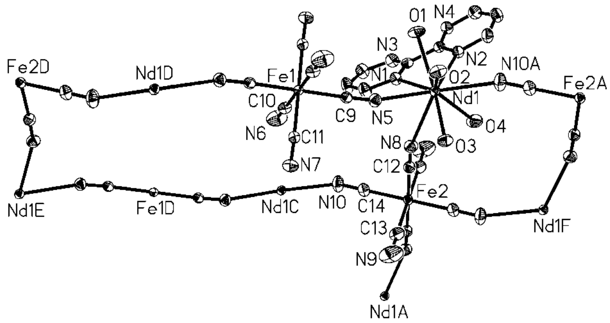

Figure 1. ORTEP plot of **1**. Selected bond lengths [Å]: Nd1-O1 2.423510), Nd1-O2 2.4524(11), Nd1-O3 2.4739(11), Nd1-N5 2.5105(10), Nd1-O4 2.5326(10), Nd1-N10A 2.5972(15), Nd1-N8 2.6399(13), Nd1-N1 2.6875(13), Nd1-N2 2.7293(10) (Symmetry codes: A: $x+1$, y, z).

In the structure of **1** there are two crystallographically unequal Fe atoms per asymmetric unit; they are located at inversion centers. The Fe2 center employs four CN^- groups in the same plane to connect the Nd^{3+} ions, giving rise to a double strand chain as found in $[\{Cu(dien)_2Cr(CN)_6\}_n][\{Cu(dien)(H_2O)Cr(CN)_6\}_n]\cdot 4nH_2O$ (dien = diethylenetri-

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