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A Zig-Zag [Mn^{II}_4] Cluster from a Novel Bis(β-diketonate) Ligand

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A new ligand, H_5L3, has been synthesized featuring seven linearly arranged oxygen donors in form of two 1,3-diketone and three phenol groups. The X-ray structure of H_5L3 unveils a rare case where one of the diketones is in the enolic form and the other one in the bis(carbonyl) form. This structure is shown by ^1H NMR to persist in solution. Reaction of H_5L3 with $Mn(AcO)_2$ in pyridine leads to the novel tetranuclear cluster $[Mn_4(H_2L3)_2(OAc)_2(py)_5]$ (**1**), which displays an unusual core in form of a zig-zag chain. Bulk magnetic measurements revealed the existence of weak antiferromagnetic coupling within the molecule. Numerical fits to a model described by the Hamiltonian $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_2S_3)$ yield coupling constants of $J_1 = -2.23\ \text{cm}^{-1}$, $J_2 = -0.85\ \text{cm}^{-1}$ and $g = 2.08$.

The preparation of molecular cluster complexes of interacting transition-metal ions is useful to areas as important and diverse as molecular magnetism,[1,2] homogeneous catalysis[3] or bioinorganic chemistry.[4,5] A very successful approach for accessing such species has been the assembly of metal ions by means of small bridging ligands, such as carboxylates, where growth into infinite arrays is often prevented by additional terminal ligands.[6,7] Such a method has been sometimes termed “serendipitous approach” since it does not allow prediction of the structure of the final species.[8] An alternative strategy has been the design and preparation of complicated multidentate ligands favoring the assembly of metal ions into aggregates with topologies that may be anticipated from the structure of these ligands. This second course of action has led to the production of a large amount of polynuclear edifices displaying sophisticated shapes and architectures, such as helicates,[9] grids,[10] cylinders,[11] catenates,[12] and many more. Of these molecular species, only a minority have the metal ions disposed in close proximity so as to show cooperative effects resulting from strong magnetic-exchange interactions[13] or metal–metal bonding.[14] We have been interested in preparing new ligands incorporating various β-diketone units and other donor groups in a linear fashion (H_3L1 and H_4L2 in Scheme 1),[15,16] aimed at forming molecular strings of metal ions in close proximity. Maximum occupancy of their coordination pockets would result in tetranuclear clusters in form of [M_4] chains[17] for H_3L1 and aligned $[M_2]_2$ dimers of dimers for H_4L2. Reactions of the latter with $M(OAc)_2$ salts have resulted invariably in the formation of complexes of the type $[M_2(H_2L2)_2(S)_n]$ (n = 2 or 4; S = solvent; M = Mn, Ni, Co, Cu).[16] Similar dinuclear compounds have been obtained with H_3L1.[18] However, in the absence of a coordinating solvent, molecules exhibiting higher occupancy, $[Co_3(HL1)_3]$ and $[Mn_3(HL1)_3]$, were characterized, which represented a new asymmetric topology within the context of coordination helicates.[19] Inspired by these early results, we have now designed and synthesized a new ligand displaying as many as six adjacent coordination pockets (H_5L3, Scheme 1). Reaction of H_5L3 with Mn^{II} produces a very rare magnetically exchanged tetranuclear complex featuring an $[Mn_4O_6]$ core in form of a zig-zag chain.

The new ligand H_5L3 {2-hydroxy-1,3-bis[3-(2-hydroxyphenyl)-3-oxopropionyl]benzene} was prepared from the methoxide derivative H_4L4 (Scheme 1).[20] The latter is also a new molecule not described in the literature and constitutes a bis(β-diketone) with potentially interesting coordination chemistry. The NMR spectra (^1H and ^{13}C) of H_5L3 (Figure 1) do not reflect the symmetry presumed for this molecule in Scheme 1. The crystal structure of the compound (Figure 1),[21] obtained following its recrystallization from MeOH, threw light into the solution structure responsible of its ^1H NMR pattern, allowing its assignment, with help of a COSY spectrum (see Supporting Information). In fact, the molecule of H_5L3 crystallizes with one of its 1,3-diketone groups in its enolic form and the other one in the bis(carbonyl) form, constituting a very rare example where

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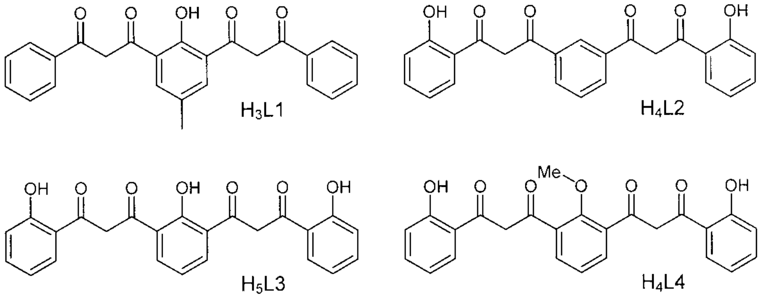


Scheme 1.

both forms are present simultaneously in one molecule. The only such previous example featured by the Cambridge data base is a cyclic polyketide lactone where the strain of the macrocycle is forcing the formation of the mixed tautomer.[22] In H_5L3, the simultaneous occurrence of both forms may be favored by the formation of five intramolecular [O–H···O] hydrogen bonds, which are all part of π-delocalized systems. The structural parameters within these delocalized systems follow indeed the criteria of resonance-assisted hydrogen bonding (RAHB).[23] According to this theory, intramolecular hydrogen bonds within β-diketone enols are reinforced by the existence of π-delocalization within the heterodienic O=C–C–C=O–H chain, translating into abnormally short O···O distances. The same phenomenon occurs, although less pronounced, within 2-hydroxybenzoketones, such as these present in H_5L3, and this trend is clearly observed on the crystal structure of the molecule. RAHB predicts a good correlation between *d*(O···O) and the ^1H NMR chemical shift of the proton concerned by the H-bond, and this criterion was used to assign this class of protons in H_5L3 (Figure 1).

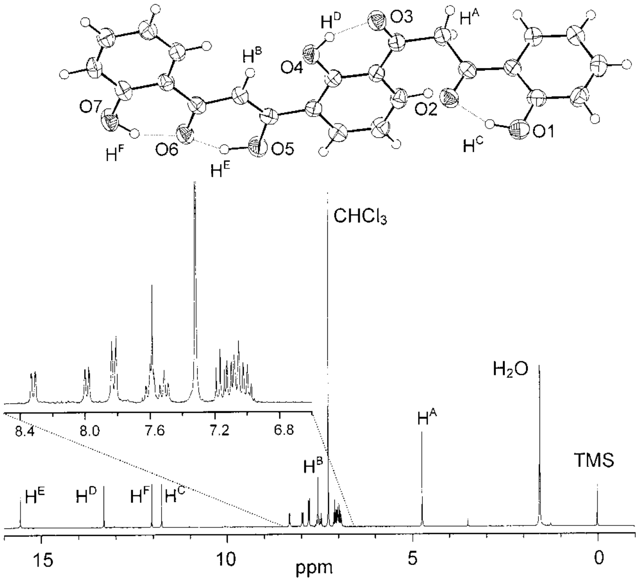


Figure 1. Top: ORTEP representation at the 50% probability level of the ligand H_5L3. Only the oxygen atoms are labeled. Intramolecular hydrogen bonds are shown as dashed lines. H-bond [O–H···O] distances [Å]: 2.578(2) (O1,O2), 2.533(2) (O3,O4), 2.488(2) (O5,O6), 2.536(2) (O6,O7). Bottom: 300 MHz ^1H NMR spectrum of H_5L3 in $CDCl_3$ reflecting the symmetry of the solid state. The assignment of the non-aromatic protons is shown (see text for details). Full assignments are given in the Supporting Information.

The reaction of H_5L3 with 2 equiv. of $Mn(OAc)_2{\cdot}H_2O$ in pyridine affords a dark orange solution that produces orange crystals upon layering with Et_2O. This product was identified by single-crystal X-ray diffraction to be $[Mn_4(H_2L3)_2(OAc)_2(py)_5]$ (**1**).[24] The structure of **1** (Figures 2 and 3)[21] reveals a linear tetranuclear array of Mn^{II}, assembled by the action of two triply deprotonated μ_4-$(H_2L3)^{3-}$ ligands located face-to-face, through four adjacent chelating units per side constituted by the five central oxygen donors of each ligand. All chelating units form six-membered rings. The peripheral ones, formed by the 1,3-diketonate units, deviate significantly from planarity [Cremer and Pople puckering amplitude in the range 0.0756(13)–0.2321(15) Å],[25] although not as much as the central ones, involving the phenoxide moiety [puckering amplitudes in the range 0.3804(15)–0.8351(16) Å]. The latter can be described as in a distorted boat, twist-boat or screw-boat conformation. The ionizable protons remaining on each $(H_2L3)^{3-}$ moiety are those of the peripheral neutral phenol groups and are involved in internal hydrogen bonds, as seen with the free ligand. Interestingly, each chelating pocket binds a metal ion disposed in *cis* configuration with respect to its counterpart from the other ligand. This is presumably because the ionic radius of Mn^{II} is too large to accommodate the four metal ions in a linear array with the chelating units disposed equatorially (i.e. *trans*). The result is an $[Mn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2Mn]$ chain with a very unusual "zig-zag" shape. In complex **1**, each peripheral pair of metal ions is further bridged by one μ-OAc^- ligand, while pyridine ligands complete the six- (Mn1, Mn2 and Mn4) or seven-donor (Mn3) coordination spheres present in this system. Thus, the external Mn_2 pairs are bridged by one *syn,syn*-OAc and two alkoxide-type μ-O donors, while the central Mn_2 is linked by just two phenoxide-type bridges. The bond lengths around the metal ions range from 2.066(1) to 2.488(2) Å, within the limits expected for Mn^{II} ions (ranges for each type of bond are listed in the caption of Figure 2). The average nearest and second-nearest neighbor Mn···Mn separations are 3.378 and 5.826 Å, respectively.

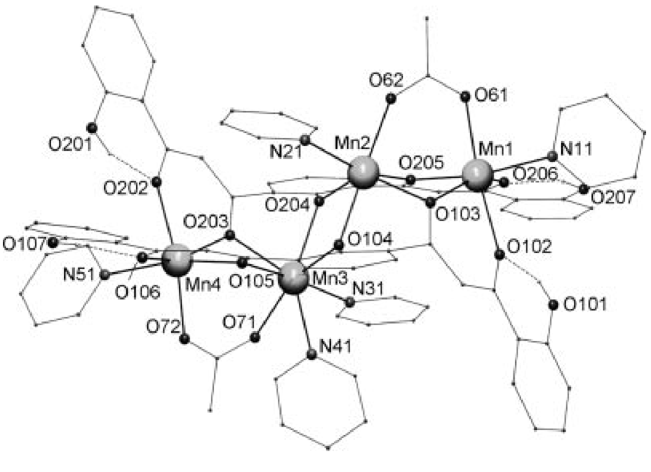


Figure 2. Labeled Pov-ray representation of $[Mn_4(H_2L3)_2(AcO)_2(py)_5]$ (**1**). Only hydroxy H-atoms are shown. Intramolecular hydrogen bonds are shown as dashed lines. Ranges of selected interatomic distances [Å] and angles [°]: Mn–O 2.0661(14) to 2.4031(14), Mn–N 2.2660(18) to 2.488(2), Mn1···Mn2 3.2876(6), Mn2···Mn3 3.4950(7), Mn3···Mn4 3.3502(6), Mn2···Mn4 5.7526(9), Mn3···Mn1 5.8984(9), Mn1···Mn4 8.8046, Mn1–Mn2–Mn3 120.80(2), Mn2–Mn3–Mn4 114.35(2), O107–H···O106 2.513(2), O207–H···O206 2.500(2), O101–H···O102 2.501(2), O201–H···O202 2.495(2).

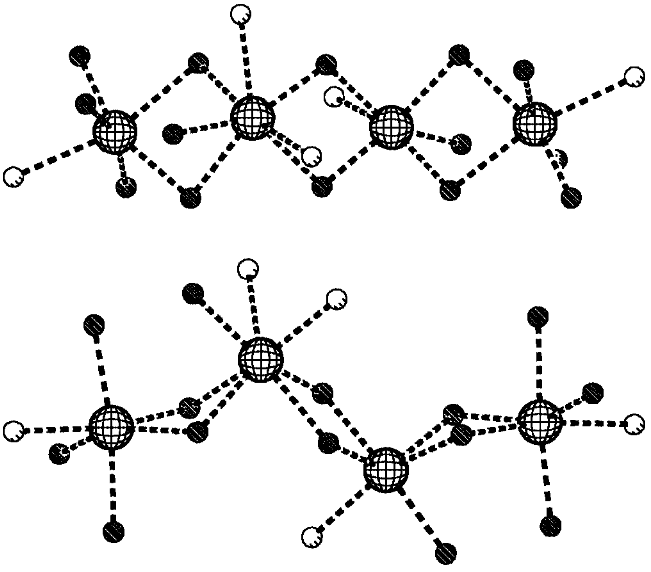
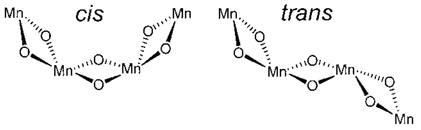


Figure 3. Platon representation of the core of $[Mn_4(H_2L3)_2(AcO)_2(py)_5]$ (**1**) emphasizing two different views. Code for atoms: large, Mn; small hatched, O; shaded, N.

Tetranuclear manganese clusters are interesting from the magnetic point of view,[26] or as synthetic models of the dioxygen-evolving complex of photosystem II.[27] Of the dozens of examples existing in the literature only three types consist of linear arrays of fused $[Mn_2(\mu\text{-}O)_2]$ moieties as in **1**; the $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ cation,[28,29] the $[Mn_2^{III}Mn_2^{II}(Me\text{-}hmp)_6Cl_4]$ cluster [Me-hmpH = 2-(hydroxymethyl)-6-methylpyridine],[30] and the cations $[Mn_4^{II}L_6]^{2+}$ [HL = a (2-hydroxyphenyl)bipyridine or -phenanthroline ligand].[31,32] All of these display a *cis* conformation with respect to the central $[Mn_2O_2]$ unit (Scheme 2), while complex **1** is the first example of the *trans* form as forced presumably by the structure of the $(H_2L3)^{3-}$ ligand.



Scheme 2.

The magnetic exchange within complex **1** was examined by means of variable-temperature (2–300 K) bulk-magnetization measurements under a constant magnetic field of 0.3 T. The results are given in Figure 4 in form of a $\chi_M T$ vs. T plot. The product $\chi_M T$ at 300 K is 18.43 $cm^3 \cdot K \cdot mol^{-1}$ (quite near to the value of 17.5 $cm^3 \cdot K \cdot mol^{-1}$ for four independent high-spin Mn^{II} centers with $g = 2$), and it decreases slowly and then more rapidly near 70 K to reach a value of 1.22 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. This indicates the presence of dominant antiferromagnetic interactions within the cluster. A fit of the experimental data was obtained through a matrix diagonalization procedure using the program CLUMAG,[33] by considering the Heisenberg spin Hamiltonian $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_2S_3)$, where S_i is the spin angular momentum operator of Mn_i ($S_i = 5/2$) and the interaction between the metal ions of both external Mn_2 pairs was assumed to be equal (see inset in Figure 4). Good fits were obtained for two sets of solutions. One was reached for values $J_1 = -1.37\ cm^{-1}$, $J_2 = +0.77\ cm^{-1}$ and $g = 2.06$, which leads to a total spin ground state of $S_T = 0$. Since $J_1 > J_2$, a very similar behavior is expected if J_2 were instead negative but with comparable absolute value. This turns out to be the case if the fit is performed by restricting both coupling constants to be antiferromagnetic, yielding the parameters $J_1 = -2.23\ cm^{-1}$, $J_2 = -0.85\ cm^{-1}$ and $g = 2.08$. The latter fit is preferred since it yields a smaller error factor R ($R = \Sigma[\chi_M T_{exp} - \chi_M T_{calc}]^2/\Sigma[\chi_M T_{exp}]^2$) than the first fit ($R = 7.73 \cdot 10^{-5}$ vs. $1.62 \cdot 10^{-4}$). The value of g is similar in both cases; however, it must be taken with caution, since this parameter is the most affected by errors in the molecular weight used for treatment of the magnetic data. The bridging arrangement found within the Mn_{1-2} and Mn_{3-4} pairs (see above) is very uncommon for Mn^{II} ions; however, the few reports showing preliminary magnetic studies on systems containing this moiety suggest weak antiferromagnetic coupling as found in **1**.[34,35] The central $[Mn_2O_2]$ unit on the other hand, is bridged by two phenoxide-type ligands. Such a type of link between divalent Mn centers has been reported to lead to both, ferro-[31,36–39] and antiferromagnetic interactions.[40–43] The actual magnetic behaviour depends strongly on the efficiency of the overlap between $d_{x^2-y^2}$ orbitals of the metal ions through the phenoxide O-donors, which is considered the main pathway to antiferromagnetism. In **1**, the latter is expected to be much reduced, given the weakening of antiferromagnetic pathways that might be caused by the severe distortion in the coordination geometry shown by the metal ions. The coupling appears thus antiferromagnetic and very weak in any case, as for all previous analogous cases.

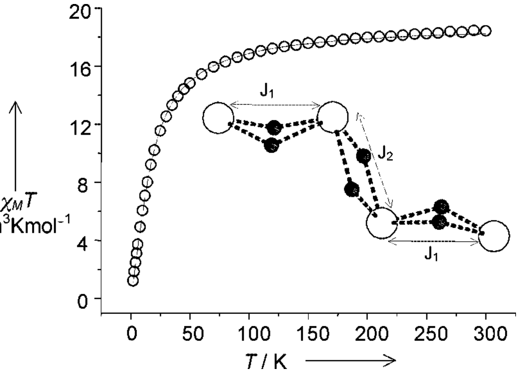


Figure 4. Plot of $\chi_M T$ vs. T per mol of $[Mn_4(H_2L3)_2(AcO)_2(py)_5]$ (**1**). The solid line is a fit to the experimental data (see text for details). The inset shows the model and spin coupling scheme used for the fitting procedure.

The preparation of H_5L3 and its association with Mn^{II} ions have demonstrated that rigid ligands with linearly disposed O-donors do provide access to metallic coordination chains with interesting magnetic properties, difficult to obtain otherwise. The preparation of **1** offers a very promising prospect in this direction. We are currently exploring the coordination chemistry of this new ligand with other metals and in the presence of other small co-ligands.

Supporting Information (see footnote on the first page of this article): This material includes the description of the preparation of ligands H_5L3 and H_4L4, full ^1H NMR characterization of the ligands and the COSY diagram of H_5L3.

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[1] J. S. Miller, M. Drillon, in: *Magnetism: Molecules to Materials V* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2005**.
[2] G. Aromí, E. K. Brechin, *Struct. Bonding*, DOI: 10.1007/430_022.
[3] R. D. Adams, F. A. Cotton, in *Catalysis by Di- and Polynuclear Metal Cluster Complexes* (Eds.: R. D. Adams, F. A. Cotton), Wiley-VCH, New York, **1999**.
[4] H. A. O. Hill, P. J. Sadler, A. J. Thompson, in *Metal Sites in Proteins and Models* (Eds.: H. A. O. Hill, P. J. Sadler, A. J. Thompson), Springer, Berlin, **1999**, vol. 1–3.
[5] P. V. Rao, R. H. Holm, *Chem. Rev.* **2004**, *104*, 527.
[6] R. E. P. Winpenny, *Adv. Inorg. Chem.* **2001**, *52*, 1.
[7] G. Aromí, S. M. J. Aubin, M. A. Bolcar, G. Christou, H. J. Eppley, K. Folting, D. N. Hendrickson, J. C. Huffman, R. C. Squire, H. L. Tsai, S. Wang, M. W. Wemple, *Polyhedron* **1998**, *17*, 3005.
[8] R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* **2002**, 1.
[9] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005.
[10] G. S. Hanan, D. Volkmer, J. M. Lehn, *Can. J. Chem. – Rev. Can. Chim.* **2004**, *82*, 1428.
[11] D. W. Johnson, J. D. Xu, R. W. Saalfrank, K. N. Raymond, *Angew. Chem. Int. Ed.* **1999**, *38*, 2882.
[12] D. J. Cardenas, J. P. Collin, P. Gavina, J. P. Sauvage, A. De Cian, J. Fischer, N. Armaroli, L. Flamigni, V. Vicinelli, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 5481.
[13] L. Thompson, *Can. J. Chem. – Rev. Can. Chim.* **2005**, *83*, 77.
[14] Y. H. Chen, C. C. Lee, C. C. Wang, G. H. Lee, S. Y. Lai, F. Y. Li, C. Y. Mou, S. M. Peng, *Chem. Commun.* **1999**, 1667.
[15] G. Aromí, P. Gamez, P. C. Berzal, W. L. Driessen, J. Reedijk, *Synth. Commun.* **2003**, *33*, 11.
[16] G. Aromí, C. Boldron, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, H. Stoeckli-Evans, J. Ribas, J. Reedijk, *Dalton Trans.* **2004**, 3586.
[17] G. Aromí, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, S. Teat, E. MacLean, H. Stoeckli-Evans, J. Reedijk, *Chem. Eur. J.* **2004**, *10*, 6476.
[18] G. Aromí, P. Gamez, O. Roubeau, P. Carrero-Berzal, H. Kooijman, A. L. Spek, W. L. Driessen, J. Reedijk, *Eur. J. Inorg. Chem.* **2002**, 1046.
[19] G. Aromí, P. C. Berzal, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, W. L. Driessen, J. Reedijk, *Angew. Chem. Int. Ed.* **2001**, *40*, 3444.
[20] See Supporting Information for experimental details on organic synthesis and characterization of H_5L3 and H_4L4.
[21] Crystals of H_5L3 and **1** were measured with a Nonius KappaCCD diffractometer on a rotating anode (θ_{max} = 25.3°, T = 150 K, Mo-K_α radiation, λ = 0.71073 Å, no absorption correction). The structures were solved with direct methods and refined on F^2 (SHELXL-97). Pertinent data for H_5L3: $C_{24}H_{18}O_7$, yellow block-shaped crystal ($0.10\times0.25\times0.35$ mm), orthorhombic, space group *Pbcn* (no. 60) with a = 13.9229(15), b = 8.5263(12), c = 32.190(5) Å, V = 3821.3(9) Å^3, Z = 8, 18194 reflections measured, 3410 independent, R_{int} = 0.1106, R_σ = 0.0664. The structure was solved with SHELXS-86. All hydrogen atoms could be located on a difference Fourier map and their coordinates were refined. Refinement of 334 parameters converged at a final wR_2 value of 0.1254, R_1 = 0.0468 [for 2302 reflections with $I > 2\sigma(I)$], S = 1.044, $-0.22 < \Delta\rho < 0.20$ e·Å^{-3}. Pertinent data for **1**: $C_{77}H_{61}Mn_4N_5O_{18}$+solvent (vide infra), pale orange blockshaped crystal ($0.05\times0.18\times0.35$ mm), triclinic, space group $P\bar{1}$ (no. 2) with a = 10.8441(10), b = 18.591(2), c = 20.904(3) Å, α = 85.172(15), β = 77.893(15), γ = 87.872(15)°, V = 4105.1(9) Å^3, Z = 2, 83947 reflections measured, 14832 independent, R_{int} = 0.0443, R_σ = 0.0330. The structure was solved with SHELXL-97. Electron density in a cavity with a volume of 896 Å^3, filled with a disordered mixture of Et_2O and pyridine, was taken into account in the refinement with PLATON/SQUEEZE. A total number of 321 electrons per unit cell were found. Where relevant, data cited above are given without disordered solvent contribution. The coordinated pyridine molecule containing N11 is disordered and is described with a two-site disorder model. The hydroxy hydrogen atoms could be located on a difference Fourier map and their coordinates were refined. All other hydrogen atoms were included with calculated positions and riding on their carrier atoms. Refinement of 967 parameters converged at a final wR_2 value of 0.1203, R_1 = 0.0407 [for 11825 reflections with $I > 2\sigma(I)$], S = 1.074, $-0.44 < \Delta\rho < 0.59$ e·Å^{-3}. CCDC-293439 and -293440 contain 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] K. Tatsuta, M. Chino, N. Kojima, S. Shinojima, M. Nakata, M. Morooka, S. Ohba, *Tetrahedron Lett.* **1993**, *34*, 4957.
[23] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *J. Chem. Soc., Perkin Trans. 2* **1997**, 945.
[24] Elemental analysis reveals partial substitution of pyridine by water upon exposure to air. Calcd. (found) for **1** (– 1.5py + $1\cdot5H_2O$): C 56.69 (56.86), H 3.87 (3.68), N 3.33 (3.09).
[25] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354.
[26] H. Andres, R. Basler, H. U. Güdel, G. Aromí, G. Christou, H. Buttner, B. Ruffle, *J. Am. Chem. Soc.* **2000**, *122*, 12469.

[27] H. Chen, M.-N. Collomb, C. Duboc, G. Blondin, E. Rivière, J. W. Faller, R. H. Crabtree, G. W. Brudvig, *Inorg. Chem.* **2005**, *44*, 9567.
[28] B. C. Dave, R. S. Czernuszewicz, *New J. Chem.* **1994**, *18*, 149.
[29] C. Philouze, G. Blondin, J. J. Girerd, J. Guilhem, C. Pascard, D. Lexa, *J. Am. Chem. Soc.* **1994**, *116*, 8557.
[30] J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L. C. Brunel, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, *40*, 4604.
[31] J. C. Jeffery, P. Thornton, M. D. Ward, *Inorg. Chem.* **1994**, *33*, 3612.
[32] D. A. Bardwell, J. C. Jeffery, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1995**, 3071.
[33] D. Gatteschi, L. Pardi, *Gazz. Chim. Ital.* **1993**, *123*, 231.
[34] S. Brooker, V. McKee, T. Metcalfe, *Inorg. Chim. Acta* **1996**, *246*, 171.
[35] Z. J. Zhong, X. Z. You, *Polyhedron* **1994**, *13*, 2157.
[36] E. O. Gao, S. Q. Bai, Z. He, C. H. Yan, *Inorg. Chem.* **2005**, *44*, 2566.
[37] M. Mikuriya, K. Nakadera, T. Tokii, *Inorg. Chim. Acta* **1992**, *194*, 129.
[38] H. R. Chang, S. K. Larsen, P. D. W. Boyd, C. G. Pierpont, D. N. Hendrickson, *J. Am. Chem. Soc.* **1988**, *110*, 4565.
[39] D. Luneau, J. M. Savariault, P. Cassoux, J. P. Tuchagues, *J. Chem. Soc., Dalton Trans.* **1988**, 1225.
[40] I. A. Koval, M. Huisman, A. F. Stassen, P. Gamez, M. Lutz, A. L. Spek, D. Pursche, B. Krebs, J. Reedijk, *Inorg. Chim. Acta* **2004**, *357*, 294.
[41] C. Hureau, E. Anxolabehere-Mallart, M. Nierlich, F. Gonnet, E. Rivière, G. Blondin, *Eur. J. Inorg. Chem.* **2002**, 2710.
[42] M. Qian, S. H. Gou, S. Chantrapromma, S. S. S. Raj, H. K. Fun, Q. D. Zeng, Z. Yu, X. Z. You, *Inorg. Chim. Acta* **2000**, *305*, 83.
[43] T. C. Higgs, K. Spartalian, C. J. O'Connor, B. F. Matzanke, C. J. Carrano, *Inorg. Chem.* **1998**, *37*, 2263.

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