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The first iron(III)–nickel(II) heterodinuclear complex containing both terminal and bridged phosphato ligands relevant to structural core models for dimetalloenzymes

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A novel iron(III)–nickel(II) heterodinuclear complex containing bidentate bridging and terminal monodentate coordinated diphenylphosphate ligands has been synthesized, and its structure and properties have been clarified.

The study of heterodimetallic complexes is interesting in regard to their potential in modeling the structures and reactivities of metalloenzymes containing two distinct metal ions in their active sites. The protein crystal structure of [NiFe] hydrogenase isolated from the bacterium *Desulfovibrio gigas* has disclosed a unique Ni–Fe heterometallic site.[1] The active site of red kidney bean purple acid phosphatase (RKBPAP) contains a Zn^{2+} and an Fe^{3+} ion, while those of the mammalian purple acid phosphatases isolated from beef spleen (BSPAP) and porcine uterine fluids (uteroferrin, Uf) contain an Fe^{3+} and an Fe^{2+} ion in their functional forms. A single oxygen atom from the carboxylate group of Asp-164 was found to be the endogenous bridging atom between the Fe^{III} and the Zn^{II} atoms in the recently reported crystal structure of RKBPAP.[2] Beef spleen purple acid phosphatases and Uf probably have related structures. However, the preparation of mixed-metal complexes is often a considerable challenge. Very few examples of heterodinuclear complexes relevant to dimetalloenzymes, such as phenolato bridged Fe^{III}–M^{II} (M = Zn, Cu, Ni, Co or Mn) heterodimetallic complexes as models for purple acid phosphatase (PAP),[3–5] have been reported so far.

For the purple acid phosphatase, the coordination mode of the phosphate group has been controversial while the coordinated phosphates have been detected in the oxidized form, PAP_o. Early investigations based on spectroscopic, magnetic, XANES and EXAFS studies have suggested that phosphate is bound in a terminal monodentate mode in $BSPAP_o{\cdot}PO_4$.[6] New EXAFS studies of uteroferrin and its anionic complexes favor the bidentate *O,O′*-bridging mode of phosphate.[7] Diiron-(II,III) and -(III,III) model compounds containing a bridging phosphate and phosphate ester have been synthesized and characterized in some cases.[8–11] The diiron complexes with terminally coordinated phosphate ligands, however, are poorly understood.[12,13] Very recently we reported a rare diiron complex $[Fe_2(HPTB)\{\mu\text{-}O_2P(OPh)_2\}\{O_2P(OPh)_2\}_2](ClO_4)_2$ (**1**), where HPTB is the anion of *N,N,N′,N′*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane (Fig. 1).[14] The crystal structure determined one diphenylphosphate in a bridging mode and two diphenylphosphates in terminal coordination modes. We report herein the synthesis and crystal structure determination of the iron(III)–nickel(II) heterodinuclear complex $[FeNi(HPTB)\{\mu\text{-}O_2P(OPh)_2\}\{O_2P(OPh)_2\}(CH_3OH)](ClO_4)_2{\cdot}2H_2O$ (**2**) with a bridging diphenylphosphate and a terminal diphenylphosphate.

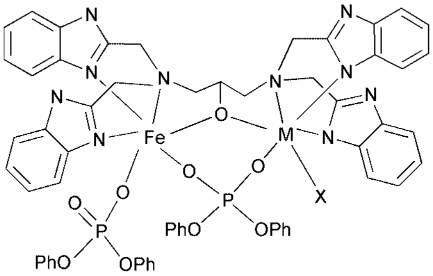

Fig. 1 Schematic structures of **1** and **2**.

The heterodinuclear complex **2** was synthesized in a U-tube with a glass frit by the diffusion method. H[HPTB], $Fe(ClO_4)_3{\cdot}9H_2O$ and $Ni(ClO_4)_2{\cdot}6H_2O$ were mixed at a 1 : 1 : 1 molar ratio (each of 0.1 mmol) in 5 ml CH_3OH to give a brown solution which was added to one side of the U-tube. A methanolic solution (5 ml) of $O_2P(OPh)_2$ (0.2 mmol) was placed in the other side. Brown crystals suitable for X-ray diffraction analysis were obtained in one month. The yield is about 10%. Metal ion analysis indicated iron and nickel ions to be present in a 1 : 1 ratio.† FAB MS measurement (VG ZAB-HS) was obtained and the fragment peak was observed at *m/z* 971, which corresponds to the bridged heterodinuclear core of $[FeNi(HPTB)\{\mu\text{-}O_2P(OPh)_2\}]$. All attempts to produce the heterodinuclear compound on a large scale by using the direct method which has already been used to synthesize the heterodinuclear Fe^{III}-Mn^{II},[3a] $Fe^{III}Ni^{II}$[3b] and $Fe^{III}Zn^{II}$[3c] complexes has so far been unsuccessful.

Schematic structures of **1** and **2** are shown in Fig. 1. The crystal structure of **2**‡ (Fig. 2) reveals that the iron(III) and nickel(II) ions in the binuclear complex are coordinated by the heptadentate ligand HPTB; each metal atom is bound to two benzimidazole moieties and one tertiary nitrogen atom as well as to the bridging endogenous alkoxo oxygen atom and exogenous bidentate *O,O′*-diphenylphosphate ligand. The distorted octahedral environments of the iron(III) and nickel(II) ions are completed by one terminal monodentate coordinated diphenylphosphate ligand and one methanol molecule, respectively. The structural parameters found in **2** are similar to those in the dinuclear iron(III) model complexes **1** and $[Fe_2Cl_2(HPTB)\{O_2P(OPh)_2\}(CH_3OH)](ClO_4)_2{\cdot}3CH_3OH$ (**3**) which includes two terminally coordinated diphenylphosphate ligand.[12] A comparison of structural parameters of **1**, **2**, and **3** is shown in Table 1.

The magnetic susceptibility in the range of 4.2 to 300 K (Fig. 3) has been measured by using a SQUID magnetometer. The observed magnetic moment decreases with temperature suggesting operation of intramolecular antiferromagnetic interaction between the iron(III) and nickel(II) centres. The magnetic data could be fitted on the basis of an isotropic Heisenberg model $\boldsymbol{H} = -2J\boldsymbol{S}_1\boldsymbol{S}_2$ ($\boldsymbol{S}_1 = 5/2$ and $\boldsymbol{S}_2 = 1$) and the

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Table 1 Selected structural parameters of the model complexes with an HPTB ligand

Complex	Fe···M/Å	Fe–O_{HPTB}–M/°	Fe–O^a/Å	Fe–O^b/Å M–O^b/Å	M–O_{HOCH_3}/Å	Ref.
1	3.712	131.82	1.971 1.956	1.944 1.950		14
2	3.684	131.7	2.014	1.945 2.038	2.075	This work
3	3.700	130.9	1.996		2.053	12

[a] Bond distance between iron and the terminally coordinated oxygen atom of $O_2P(OPh)_2$. [b] Bond distance between metal and the bridging oxygen atom of $O_2P(OPh)_2$.

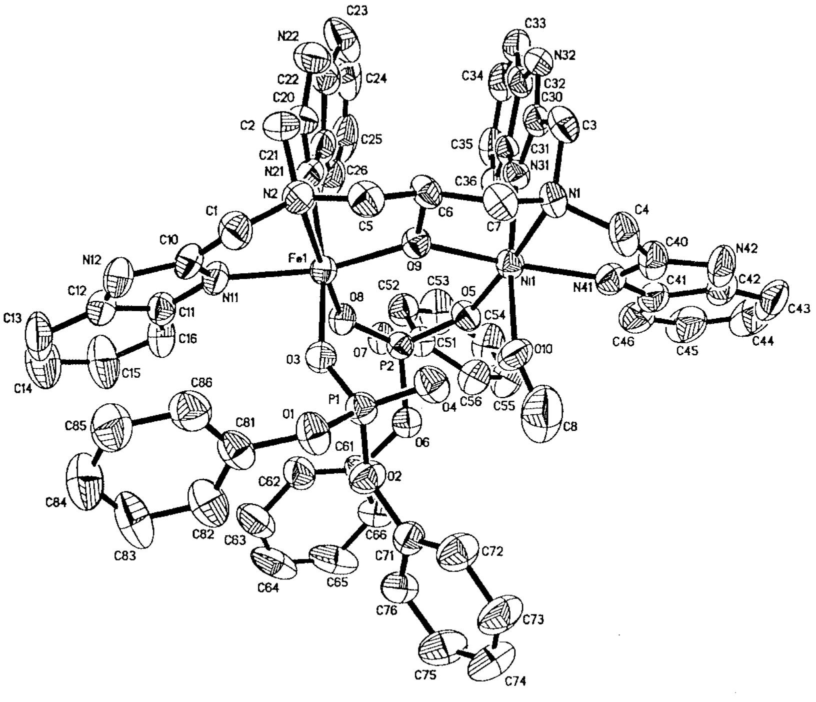

Fig. 2 Structure of the cation $[FeNi(HPTB)\{\mu\text{-}O_2P(OPh)_2\}\{O_2P(OPh)_2\}(CH_3OH)]^{2+}$ in **2**. Selected bond lengths (Å) and angles (°): Fe···Ni 3.684(2), Fe(1)–O(9) 1.936(4), Fe(1)–O(8) 1.945(4), Fe(1)–O(3) 2.014(4), Fe(1)–N(11) 2.100(5), Fe(1)–N(21) 2.120(6), Fe(1)–N(2) 2.270(5), Ni(1)–O(9) 2.101(4), Ni(1)–O(5) 2.038(4), Ni(1)–O(10) 2.075(5), Ni(1)–N(1) 2.165(5), Ni(1)–N(31) 2.024(5), Ni(1)–N(41) 2.051(6); Fe(1)–O(9)–Ni(1) 131.7(2), Fe(1)–O(8)–P(2) 136.8(3), Fe(1)–O(3)–P(1) 146.9(3), N(11)–Fe(1)–O(9) 155.8(2), Ni(1)–O(5)–P(2) 134.6(3), Ni(1)–O(10)–C(8) 122.5(7), O(9)–Ni(1)–N(41) 159.2(2), O(8)–P(2)–O(5) 118.0(3).

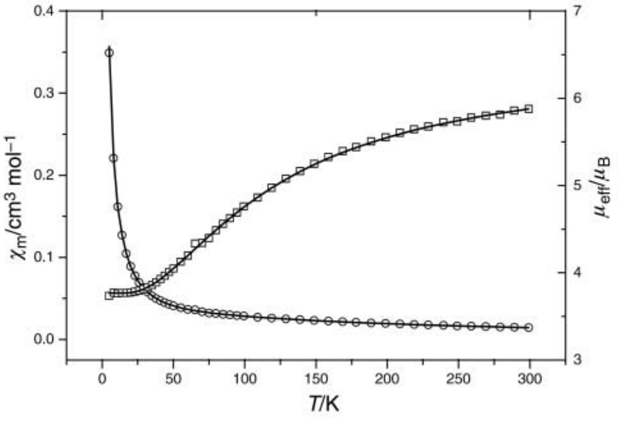

Fig. 3 The experimental data and fitted curves of magnetic susceptibilities (○) and magnetic moments (□) *versus* temperature for **2**.

parameters found were $J = -18.1$ cm^{-1}, $g_{Ni} = 2.07$ and $g_{Fe} = 1.98$. The zero-field splitting parameters are not considered in the fitting procedure because they are important only at very low temperatures (below 10 K). This value is in agreement with that previously observed in an Fe^{III}–Ni^{II} system.[3b] Compared with the Fe^{III}–Fe^{III} analogue **1** ($J = -10.0$ cm^{-1}), the exchange interaction between Fe^{III} and Ni^{II} ions in **2** is stronger.

In summary, the H[HPTB] ligand has proven to be suitable for the synthesis of homobinuclear complexes, such as model complexes of urease,[15] PAP,[12,14,16] hemocyanin,[17] and manganese pseudocatalase,[18] *etc.* For the first time, a heterobinuclear complex has been isolated. The structure of this dimetallic complex including both terminal and bridging diphenylphosphate helps us gain an insight into the dimetallic coordination core of the enzymes. Further investigations in this area are currently underway.

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Notes and references

† C, H, N and metal content analyses were performed on a Perkin-Elmer Model 240 Elemental Analyser and WYX-904 Atomic Absorption Spectrophotometer, respectively. Anal. calcd. for $C_{60}H_{61}Cl_2FeN_{10}NiO_{20}P_2$: C, 48.34; H, 4.10; N, 9.40; Fe, 3.76; Ni, 3.96. Found: C, 48.39; H, 3.95; N, 8.97; Fe, 3.00; Ni, 3.75%.

‡ Crystal data for **2**: $C_{60}H_{61}Cl_2FeN_{10}NiO_{20}P_2$: $M_r = 1489.59$, monoclinic, $P2_1/c$, $a = 17.3028(15)$ Å, $b = 20.5989(19)$ Å, $c = 20.1296(19)$ Å, $\beta = 111.796(2)°$, $V = 6661.7(11)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_c = 1.485$ Mg mm^{-3}, μ(Mo-Kα) = 0.711 mm^{-1}. 11663 Unique reflections ($R_{int} = 0.0971$) of which 5111 with $I \geq 2\sigma(I)$ were measured ($1.27 = \theta = 25.03°$) on a Siemens SMART/CCD area detector. The structure was solved by direct methods, and refined by least-squares treatment on F^2 using the SHELXS-97 and the SHELXL-97 programs,[19] $R1 = 0.0767$ and

$wR2 = 0.1725$ with GOF = 0.970. CCDC reference number 158045. See http://www.rsc.org/suppdata/dt/b1/b100498k/ for crystallographic data in CIF or other electronic format.

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