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SHORT COMMUNICATION

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Synthesis and Spectroscopic Characterisation of a Heterodinuclear Iron(III)-Copper(II) Complex Based on an Asymmetric Dinucleating Ligand System

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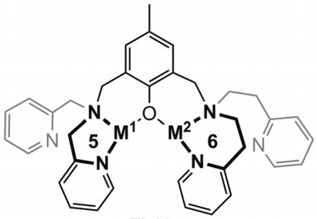
The site-directed generation of a heterodinuclear $Fe^{III}Cu^{II}$ complex by using a new asymmetric dinucleating ligand FloH is reported. The iron(III) ion is introduced first on the preferential metal-binding site of the ligand that leads to the formation of the thermodynamically favored five-membered chelate rings upon metal-binding. Copper(II) is introduced in the next step. The stepwise metalation strategy reported here may be extended to the preparation of other heterometallic complexes with the view of avoiding a statistical distribution. Such complexes can offer novel spectroscopic properties, electronic structures, and reactivities in comparison to their homometallic analogues.

Introduction

The study of heterodimetallic complexes is interesting in regard to their potential in modelling the structures and reactivities of metalloenzymes containing two different metal ions at their active sites.[1–4] Moreover, this may lead to the possible discovery of novel species exhibiting alternative reactivity patterns relative to their symmetric counterparts.[5] The synthesis of heterodinuclear complexes, however, presents a special challenge because of the possibility of disproportionation and selectivity problems resulting in the formation of mixtures of homo- and heterodinuclear complexes, as well as metal-site isomers. This is, in part, due to the symmetrical nature of most of the dinucleating ligands in which the two coordination sites are equivalent. These difficulties can be overcome by designing asymmetric ligands that bind metals selectively in one pocket or strongly enough to prevent disproportionation and metal mixing. A limited number[6–8] of synthetic asymmetric dinucleating ligands are reported to form heterodimetallic $Fe^{III}M^{II}$ (M = Fe, Cu, Co, Cd, and Zn) complexes in good yields by utilizing hard and anionic oxygen donors on one side to selectively bind the Fe^{III} ion, and soft and neutral nitrogen donors on the other side to preferentially bind the divalent metal ions. A few symmetric ligands[9–11] have also been successfully utilized in the synthesis of heterodinuclear complexes by treating the ligands with equimolar amounts of two different metal salts; the factors that contribute to the sole formation of the heterodinuclear complexes without the contamination of the homodinuclear units are, however, not clear in these cases.

In our efforts to achieve systematic generation of heterometallic complexes in high yield and purity, we present here the synthesis of a new phenolate-based dinucleating ligand system, FloH. This ligand possesses two distinct metal-binding sites: a preferential metal-binding site provided by the bis(2-pyridylmethyl)amino moiety and a second binding site involving the bis(2-pyridylethyl)amino group. The thermodynamic driving force for preferential binding to the bis(2-pyridylmethyl)amino site arises because of its ability to form more favored five-membered chelate rings,[12] as opposed to the six-membered chelate rings arising from binding to the bis(2-pyridylethyl)amino moiety. The unsymmetrical nature of FloH allows the site-directed generation of a heteronuclear $Fe^{III}Cu^{II}$ complex in high yield. A detailed structural and spectroscopic characterization of the Fe^{III}-Cu^{II} complex is reported.



FloH

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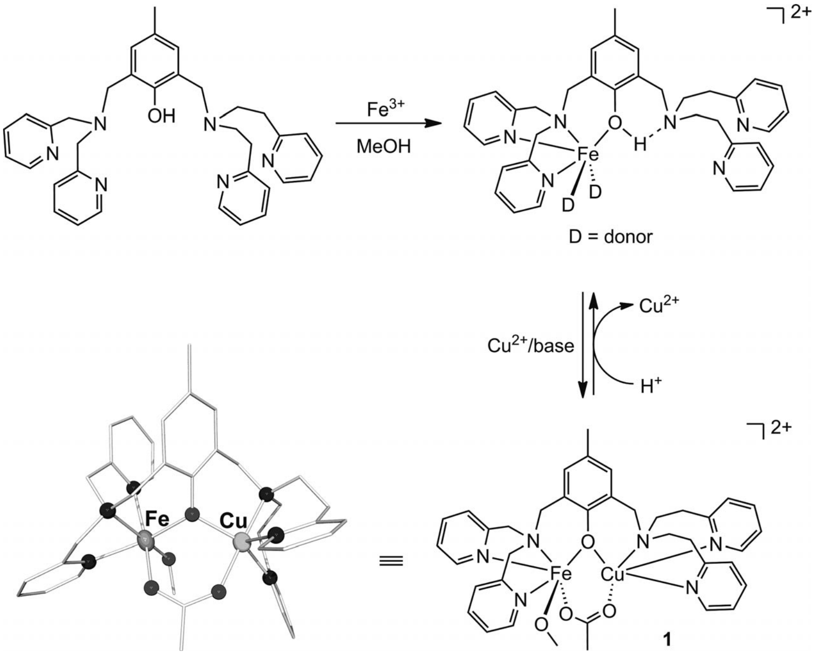
Results and Discussion

The six-step synthesis of the ligand FloH utilizing a precedented,[13] relatively general synthetic pathway is shown in Scheme S1. The introduction of asymmetry, the key step in the synthesis, is realized in the first step through oxidation of a single hydroxymethyl group by manganese dioxide. Subsequent chlorination and alkylation of bis(2-picolyl)amine generates the first metal-binding site involving the bis(2-pyridylmethyl)amino moiety. Borohydride reduction of the carbonyl regenerates the hydroxymethyl group, which is similarly chlorinated for introduction of the bis(2-pyridylethyl)amino moiety. By using this procedure, FloH can be obtained in gram quantities with an overall yield of 21%.

The synthesis of the heterodinuclear $Fe^{III}Cu^{II}$ complex **1** is achieved by the stepwise metalation of FloH, as shown in Scheme 1. Reaction with $Fe(NO_3)_3$ leads to the initial binding of the Fe^{III} ion into the bis(2-pyridylmethyl)amino site leading to the formation of a deep-blue solution containing the monoiron complex (λ_{max} = 583 nm, ε = 970 $L\,mol^{-1}\,cm^{-1}$) (Figure S1). The X-band EPR spectrum of the resultant solution shows a signal at g_{iso} = 4.2, typical for asymmetric high-spin complexes of iron(III) (Figure S2). Addition of $Cu(OAc)_2$ to the resultant blue solution leads to the formation of a new species with a band at λ_{max} = 453 nm (ε = 1333 $L\,mol^{-1}\,cm^{-1}$; shoulder). Subsequent anion metathesis with sodium tetraphenylborate results in the precipitation of **1** as the tetraphenylborate salt (96% yield, based on the Fe^{III} salt), for which the ratio of Cu/Fe is determined to be 1.007 by inductively coupled plasma optical emission spectroscopy (ICP-OES). X-ray diffraction studies on crystals obtained from dichloromethane/methanol reveal a dinuclear complex with the iron and the copper atoms bridged by the phenolate oxygen atom of FloH and one carboxylato ligand (Scheme 1). The Cu^{II} site is found to be intermediate between trigonal-bipyramidal and square-pyramidal (τ = 0.52). The Fe^{III} site has an octahedral coordination environment involving the phenolate oxygen atom, three nitrogen atoms of the bis(2-pyridylmethyl)amino moiety, the bridging acetate group and an additional methanol ligand presumably derived from the recrystallization solvent.[14] Fe–O bond lengths vary in the range of 1.834(4)–2.004(4) Å, whereas Fe–N bonds are generally longer [2.133(4)–2.249(5) Å]. For the Cu–O and Cu–N bonds similar trends are found [1.965(4)–1.976(4) Å for Cu–O and 2.014(5)–2.183(4) Å for Cu–N]. Energy-dispersive X-ray spectroscopy (EDX) measurement on a single crystal of **1** is also performed so as to confirm the presence of both iron and copper in **1** (Figure S3). The IR spectrum of **1** shows two intense signals for the symmetric and antisymmetric carboxylate stretching frequency of the bridging acetate at 1559 cm^{-1} and 1428 cm^{-1}, respectively (Figure S4).

Zero-field Mössbauer spectra of a powdered sample of **1** have been recorded at 50 K and 3 K (Figure 1). Both spectra show composite quadrupole-split doublets appearing as two asymmetric absorptions with isomer shift (δ) and quadrupole splitting (ΔE_Q) values typical of a high-spin $S = 5/2$ iron(III) ion (δ = 0.46 mm/s and ΔE_Q = 1.12 mm/s at 50 K; δ = 0.48 mm/s and ΔE_Q = 1.16 mm/s at 3 K).[15] The δ value slightly decreases with increasing temperature because of the second-order Doppler effect.[16] Similarly, the quadrupole splitting values show little dependence upon the temperature between 50 and 3 K, as expected for high-spin Fe^{III}



Scheme 1. Sequential metalation reaction of the asymmetric dinucleating ligand FloH with $Fe(NO_3)_3$ and $Cu(OAc)_2$. Metathesis with $NaBPh_4$ leads to the precipitation of **1** as the tetraphenylborate salt. Addition of H^+ [triflic acid, or $HClO_4$ (70%)] results in the decoordination of the Cu^{II} ion in **1** leading to the formation of the monoiron species (Figures S5 and S8).

ions.[17] Complex **1** is also found to be EPR-silent (Figure S5) in normal X-band measurements, which is consistent with the high-spin (S = 5/2) Fe^{III} ion undergoing antiferromagnetic or ferromagnetic interaction with the S = 1/2 Cu^{II} center to result in an integer-spin S = 2 or S = 3 ground state, respectively. DFT calculations were performed on **1**, with the aim to compute the energy difference between the optimized structures of **1** in the S = 2 (Figure S6, Table S1) and S = 3 (Table S2) states. As described in the methods section, the broken-symmetry[18] approach was applied to represent the antiferromagnetic coupling between the Fe and Cu centers. It turned out that the high-spin state arising from the ferromagnetic coupling is 1.8 kJ/mol less stable than the antiferromagnetically coupled state. The calculated magnetic exchange coupling is $-58.6\ cm^{-1}$, in reasonable agreement with that previously reported for related systems.[8a,11] Analysis[19] of the Mössbauer spectrum of **1** in an applied field of 4 T at 3 K (Figure S7) also predicts an S = 2 ground state, consistent with the results of the DFT calculations. The effective magnetic moment (μ_{eff}) of **1** at room temperature (298 K) is determined to be 5.24 μ_B by Evan's method.[20] This value is close to that previously reported for a related system at 298 K.[8a]

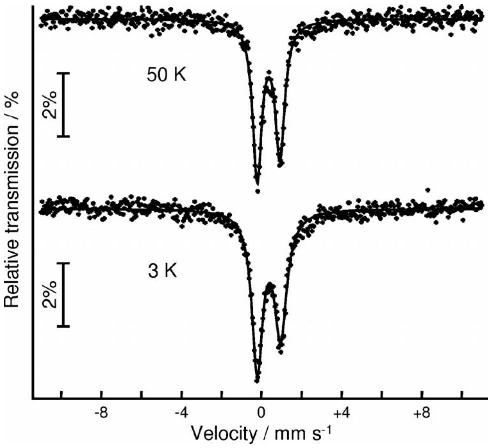


Figure 1. ^{57}Fe Mössbauer spectra of **1** obtained at 50 and 3 K.

The preferential binding ability of the bis(2-pyridylmethyl)amino unit over the bis(2-pyridylethyl)amino moiety in the ligand FloH, therefore enables us to synthesize the heterodinuclear $Fe^{III}Cu^{II}$ complex in high yield and purity without contamination from the corresponding homodinuclear species. The stronger chelation of the bis(2-pyridylmethyl)amino unit is also revealed in the decay of **1** in the presence of acid; treatment of **1** with triflic acid results in the demetalation of the bis(2-pyridylethyl)amino moiety to generate the monoiron complex. The formation of the monoiron complex is confirmed on the basis of the appearance of the UV/Vis band at λ_{max} = 583 nm (Figure S8) and the S = 5/2 high-spin Fe^{III} signal (together with S = 1/2 Cu^{II} signal) in the EPR (Figure S5). This process is found to be reversible, and **1** can be regenerated by adding sodium methoxide. We also performed geometry optimizations of **1** after the protonation of the phenolate oxygen atom; such optimizations allowed us to show that protonation favors the breaking of the Cu–O bond, a result that nicely fits the experimental observation. Thus, the deprotonation of the phenol oxygen atom is necessary for the second metalation step. In the protonated form of FloH, the phenol hydrogen atom, as proposed earlier for a related ligand system,[8a] may form hydrogen bonds with the amine nitrogen atom of the bis(2-pyridylethyl)amino group, thereby inhibiting any metal coordination in that site (Scheme 1).

Conclusions

We have reported the synthesis of a new asymmetric dinucleating ligand FloH that has been designed with two sets of metal-ion binding groups suited to selective complexation. The regiocontrolled synthesis of the mononuclear iron(III) and the heterodinuclear $Fe^{III}Cu^{II}$ (**1**) complexes of FloH have been demonstrated. The strategy reported in this paper may be extended to the preparation of other heterometallic complexes with the view of avoiding a statistical distribution. Such complexes can offer novel spectroscopic properties, electronic structures, and reactivities in comparison to their homometallic analogues.

Experimental Section

General: All reagents were purchased from Sigma Aldrich, ABCR, Acros and TCI Europe and used as received, unless otherwise mentioned. UV/Vis studies were performed by using an HP8453A diode array spectrometer equipped with a cryostat from Unisoku Scientific Instruments (Osaka, Japan). Electrospray ionization mass spectrometry experiments were carried out with a Finnigan LTQ fourier transform ion cyclotron resonance mass spectrometer (Therma Electron Co. Bremen). EPR spectra were recorded with the X-band spectrometer ERS 300 (ZWG/Magnettech Berlin/Adlershof, Germany) equipped with a fused quartz Dewar for measurements at liquid-nitrogen temperature. The g factors were calculated with respect to a Cr^{3+}/MgO reference (g = 1.9796). IR measurments were performed with an FTIR-8400S infrared spectrometer (Shimadzu). The EDX spectrum was measured with a Quantax system (Röntec) in ultra-high vacuum (UHV; $<10^{-7}$ mbar) with an energy-dispersive Si-Li detector attached to a scanning electron microscope JSM 6060 (Joel). ICP analyses were obtained with a VISTA-MPX CCD Simultaneous ICP-OES spectrometer (Varian); the solution was prepared by extraction of **1** by heating a suspension of about 8 mg of the complex, 2.5 mL of concd. HNO_3 and 0.5 mL of H_2O_2 (30%) in a microwave oven (MLS easywave) at 200 °C for 45 min, followed by dilution with deionized water. The Mössbauer spectra were acquired by using a conventional spectrometer in the constant-acceleration mode equipped with a ^{57}Co source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to α-Fe at room temperature. The sample was inserted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat, which has a split-pair superconducting magnet system with the field of the sample oriented perpendicular to the γ-ray direction, while the sample temperature can be varied between 3.0 and 300 K. 3 K temperature could be achieved by pumping the sample space. Fits of the Mössbauer spectra were obtained with the NORMOS program.[21] ^1H NMR spectra were measured with a Bruker DPX-300 (300 MHz) NMR spectrometer. The spin state of **1** was determined by using the modified ^{1}H NMR method of Evans[20] at room temperature. For the measurements a sealed capillary tube containing 40 µL of the blank CD_2Cl_2 solvent [with 1.0% tetramethylsilane (TMS)] was inserted into a normal NMR tube containing **1** (600 µL, 9.8×10^{-3} M) dissolved in CD_2Cl_2 (with 0.5% TMS). All geometry optimizations were carried out by using the density functional theory at the B3LYP/TZVP level[22] with the TURBOMOLE suite.[23] The broken-symmetry (BS) approach[18] was applied to model antiferromagnetic coupling of metal spins. Prediction of magnetic exchange coupling constants has been performed as described previously.[24]

X-ray Crystallography: The crystal-structure determination was performed at 100 K with a Stoe IPDS 2T diffractometer by using Mo-K_α radiation (λ = 0.71073 Å). The radiation source was a sealed X-ray tube with graphite monochromator. A multi-scan absorption correction was applied (μ = 0.510, $T_{\min}$ = 0.8493, $T_{\max}$ = 0.9766, R_{int} = 0.1060). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[25] All non-hydrogen atoms were refined anisotropically. H atoms were introduced in their idealized positions and refined as riding model. The suitability indexes are: R_1 = 0.0869, wR_2 = 0.2387. 48673 reflections were collected, 16166 unique, 9583 observed. **1** crystallizes in the space group $P\bar{1}$ [a = 12.3923(5), b = 14.9659(6), c = 22.1871(9) Å, α = 88.650(3), β = 77.729(3), γ = 76.482(3)°].

Synthesis of FloH [2-({Bis[2-(pyridin-2-yl)ethyl]amino}methyl)-6-{[bis(pyridin-2-ylmethyl)amino]methyl}-4-methylphenol]: To a solution of bis(pyridylethyl)amine (0.31 g, 1.36 mmol) and NEt_3 (1.52 mL, 10.88 mmol) in THF (15 mL) was added 2-{[bis(pyridin-2-ylmethyl)amino]methyl}-6-(chloromethyl)-4-methylphenol (0.50 g, 1.36 mmol)[13] in small portions. The reaction mixture was refluxed for 4 h and stirred at room temperature for 20 h followed by filtration of the reaction mixture and concentration of the filtrate under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed twice with a pH = 7.5 buffer containing NaOH and KH_2PO_4. The organic phase was dried with $MgSO_4$, and the solvents were evaporated to dryness under reduced pressure. Column chromatography on silica gel ($CHCl_3$/MeOH, 8:2) gave 0.51 g (0.90 mmol, 66%) of FloH as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) (Figure S9): δ = 10.38 (br. s, 1 H, OH), 8.49 (d, J = 4.8 Hz, 2 H, Py), 8.41 (d, J = 4.2 Hz, 2 H, Py), 7.57 (dt, J = 1.8, 7.6 Hz, 2 H, Py), 7.46 (dt, J = 1.9, 7.7 Hz, 2 H, Py), 7.09 (dt, J = 1.2, 4.9 Hz, 2 H, Py), 7.03 (dd, J = 1.0, 7.5 Hz, 2 H, Py), 7.03 (dt, J = 1.0, 7.5 Hz, 2 H, Py), 6.97 (d, J = 1.7 Hz, 1 H, 5′-phenol), 6.80 (s, 1 H, 3′-phenol), 3.82 (s, 4 H, CH_2), 3.66 (s, 2 H, $ArCH_2N$), 3.03 (m, 8 H, CH_2Py), 2.18 (s, 3 H, CH_3), 1.41 (s, 2 H, $ArCH_2N$) ppm. ESI-MS: m/z (%) = 559.292 (62) [$C_{35}H_{39}N_6O^+$] {calcd. 559.319}, 360.191 (100) [$C_{22}H_{24}N_4O^+$] {calcd. 360.195}, 332.161 (55) [$C_{21}H_{22}N_3O^+$] {calcd. 332.176}.

Synthesis of [(FloH)Fe$^{\text{III}}$Cu$^{\text{II}}$(OAc)(OMe)] (1): To a solution of FloH (0.20 g, 0.36 mmol) in MeOH (5 mL) was added $Fe(NO_3)_3 \cdot 9H_2O$ (0.12 g, 0.29 mmol) in MeOH (2 mL). The reaction mixture was stirred at room temperature for 18 h. After that time, $Cu(OAc)_2$ (0.06 g, 0.29 mmol) in MeOH (3 mL) was added, and the mixture was stirred again at room temperature for 10 h. $NaBPh_4$ (0.31 g, 0.90 mmol) in MeOH (5 mL) was then added, and a red precipitate was formed immediately. After stirring for 10 h, the precipitate was filtered, washed with a small amount of MeOH and dried in vacuo to obtain 0.39 g (0.28 mmol; 96% based on Fe) of a red solid. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a CH_2Cl_2/MeOH solution. $C_{86}H_{83}B_2CuFeN_6O_4$ (1405.63): calcd. C 73.48, H 5.95, N 5.98; found C 73.18, H 5.84, N 6.22. ESI-MS: m/z = 383.099 [$C_{38}H_{43}CuFeN_6O_4{}^{2+}$] {calcd. 383.099}, 376.091 [$C_{37}H_{41}CuFeN_6O_4{}^{2+}$] {calcd. 376.092} (from hydrolysis of the methoxide ligand). IR (KBr): $\tilde{\nu}$ = 3433 (br.), 3054 (m), 3034 (m), 2998 (m), 2983 (m), 2918 (w), 1607 (s), 1576 (m), 1559 (s), 1480 (s), 1443 (s), 1428 (s), 1307 (w), 1288 (w), 1265 (w), 1158 (w), 1098 (w), 1053 (w), 1026 (w), 733 (s), 704 (s), 611 (m) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Scheme of the ligand synthesis; UV/Vis, NMR, EPR, EDX, IR and DFT data.

Acknowledgments

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[14] Unexpectedly, neither the precipitant (dichloromethane) nor the solvent itself (methanol) filled the cavities of the crystal structure, although both are much smaller than the title compound and the tetraphenylborate counter anion. This led to large voids in the three-dimensional packing pattern and concomitantly to one totally disordered tetraphenylborate molecule. Fortunately, the dimetalated complex is only slightly affected by disorder so that the discrimination between Fe^{III} and Cu^{II} based on crystallographic criteria (thermal ellipsoids, suitability indexes) was still unambiguous. We cross-checked the refinement of the switched structure (Fe ↔ Cu) and found significant discrepancies in the suitability indexes, which strongly support our findings. For compound **1**, R_1 = 8.69 and wR_2 = 23.47; for the switched structure, R_1 = 9.63 and wR_2 = 29.68. Moreover, the Fe^{III} and Cu^{III} ADPs (thermal ellipsoids) are similar in size in the original structure as expected [U_{eq}(Fe) = 0.04445 Å^2, U_{eq}(Cu) = 0.04278 Å^2]. This is not the case for the switched structure [U_{eq}(Fe) = 0.03243 Å^2, U_{eq}(Cu) = 0.05802 Å^2].

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[19] The effective magnetic field at the Fe^{III} nucleus, H_{eff}, which is the sum of the applied (H_{appl}) and magnetic hyperfine (H_{hf}) fields, is determined to be 45 T on the basis of the simulation of the magnetic Mössbauer spectrum (Figure S7) at 4 T and 3 K. The hyperfine interaction for a 3d^5 electron configuration expected from the Fermi contribution is 55 T (or ca. 11 T per S = 1/2: N. N. Greenwood, T. C. Gibbs, *Mössbauer Spectroscopy*, Chapman and Hall Ltd., London, **1971**. If we extract H_{hf} from H_{eff}, then we obtain a value of 41 T, which is very close to the value expected for four S = 1/2 spins. Although this is not a common technique for calculating the spin state, nevertheless roughly we can say that the spin of this molecule is equal to 2, which fits very well with the data obtained from the DFT calculations.

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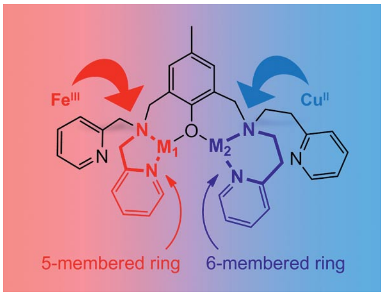
Heterodimetallic Complexes

The synthesis of a new asymmetric dinucleating ligand FloH, designed with two sets of metal ion binding groups suited to selective complexation, is reported. The site-directed generation of a heterodinuclear $Fe^{III}Cu^{II}$ complex is performed in high yield and purity by using FloH.



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Synthesis and Spectroscopic Characterisation of a Heterodinuclear Iron(III)-Copper(II) Complex Based on an Asymmetric Dinucleating Ligand System

Keywords: Bioinorganic chemistry / Unsymmetric ligands / Heterometallic complexes / Copper / Iron