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A novel fluorescence redox switch based on the formal Ni^{II}/Ni^{I} couple †

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The nickel(II) complex of the naphthalene-containing macrocyclic ligand **4** has been synthesized by a template reaction and structurally characterized. $[Ni(\mathbf{4})]^{2+}$, which in solution displays an emission spectrum typical of naphthalene derivatives, undergoes a reversible one-electron reduction process at a moderately negative potential value to give a formal nickel(I) species. The reduction process induces a distinct decrease of the emission intensity, but fluorescence is recovered after reoxidation to the original nickel(II) species. Thus, fluorescence can be switched OFF and ON through the redox reaction involving the formal Ni^{II}/Ni^{I} couple, which can be carried out both chemically (in MeCN : water) and electrochemically (in MeCN).

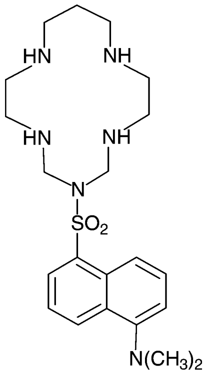
1 Introduction

The field of molecular switches has attracted great interest in the last few years because of their relevance in the development of molecular electronics and photonics.[1] Several examples of the latter are based on supramolecular devices whose optical properties (*i.e.* photochromism, luminescence, optical nonlinearity) can be switched (or modulated) by external stimuli such as chemical,[2] electrochemical,[3] and light inputs.[4] Nowadays, particular interest is devoted to molecular switches whose emission properties are influenced by redox potential, as they could find application, in conjunction with imaging techniques, in biology and biochemistry: fluorescent potentiometric probes based essentially on organic molecules have been proposed to map electric potential along neurons,[5] to detect synaptic activity[6] and, in general, to perform membrane potential measurements in organelles (*e.g.* mitochondria) and cells.[7]

A multicomponent supramolecular approach allows the design of fluorescence redox switches by assembling a redox active subunit (the control unit), which can exist in two different oxidation states of comparable stability (*i.e.* a *bistable* system), and a luminescent fragment (the active unit) whose emission depends on the oxidation state of the control unit.[8]

According to this approach, the organic redox couple quinone/hydroquinone has been used as the control unit in a luminescence molecular switch containing either a $[Ru(bipy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ group as the active unit,[9,10] while a few examples of inorganic redox couples involved in fluorescence switching processes have been also reported. The Cu^{II}/Cu^{I} couple inside a sulfur-containing macrocyclic ligand represents an efficient control unit to tune the emission of aromatic fluorophores, *e.g.* naphthalene and anthracene.[8,11]

Recently, the complexes of Ni^{II} with ligands **1** and **2** have been described as fluorescence switches based on the Ni^{III}/Ni^{II} couple. In particular the emission of $[Ni(\mathbf{1})]^{2+}$ and $[Ni(\mathbf{2})]^{2+}$ is distinctly quenched by performing the oxidation (both chemically and electrochemically) to the corresponding Ni^{III} complexes. The original emission spectra are restored upon reduction to the Ni^{II} species.[12]



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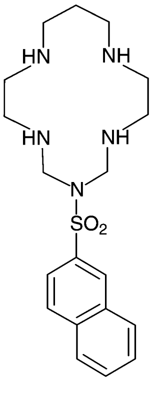

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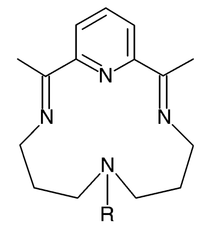

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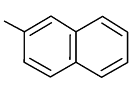
R =  : **4**

In this paper we report the synthesis and investigation of the switching behaviour of the novel two-component systems $[Ni(\mathbf{4})]^{2+}$ and $[Cu(\mathbf{4})]^{2+}$ containing a naphthalene moiety as the active unit and a metal–tetraazamacrocycle as the redox-active fragment. Electrochemical and spectrofluorimetric studies show that the nickel-containing two-component system $[Ni(\mathbf{4})]^{2+}$ behaves as a molecular device whose emission can be controlled (switched on and off) by variations of the redox potential.

2 Results and discussion

In our search for new metal-containing control units to be used in redox fluorescence switches, we considered nickel(II) and copper(II) complexes of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, known as CR[13] and of its *N*-methyl derivative, **3**, which are characterized by a reversible monoelectronic reduction process at moderately negative potentials[14–16] and can behave as *bistable* systems.

The complexes $[Cu(\mathbf{4})]^{2+}$ and $[Ni(\mathbf{4})]^{2+}$ were prepared by a template reaction involving 2,6-diacetylpyridine, copper or nickel chloride and the appropriate naphthalene-functionalized triamine fragment as depicted in Scheme 1.

The complexes $[Cu(\mathbf{4})]^{2+}$ and $[Ni(\mathbf{4})]^{2+}$ were isolated as perchlorate or hexafluorophosphate salts; crystals suitable for X-ray structural investigations were obtained by slow diffusion of diethyl ether into acetonitrile solutions of the complexes.

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† Dedicated to Professor Dr. Ernst-G. Jäger, on the occasion of his 65th birthday

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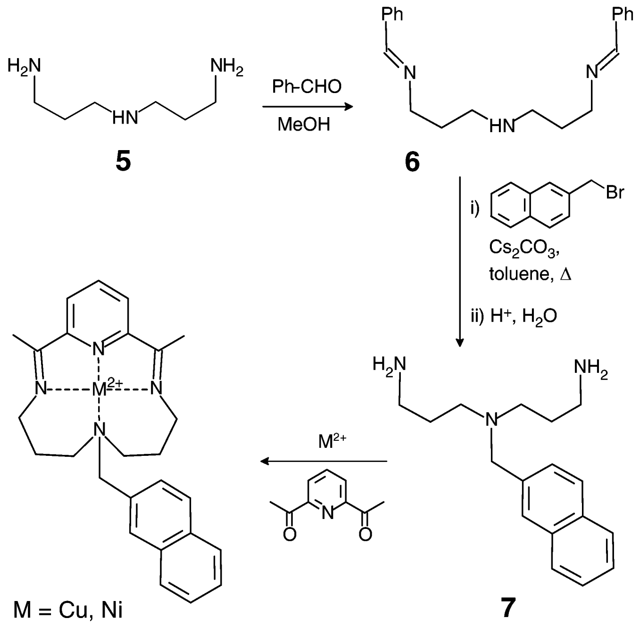


Scheme 1

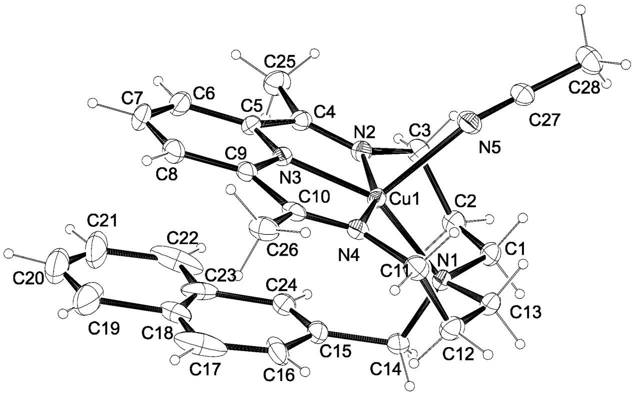


Fig. 1 Crystal structure of [Cu(**4**)(CH$_3$CN)](ClO$_4$)$_2$ (counter ions have been omitted for clarity).

The molecular structure of the copper(II) complex is shown in Fig. 1. Copper(II) is five-coordinate, bonding to the four nitrogen atoms from the macrocycle and one from an acetonitrile molecule. The Cu–N distances reflect the different hybridization states of the nitrogen atoms [Cu–N(py) 1.911(4) Å; Cu–N(imine) 1.990(5) and 1.995(4) Å; Cu–N(amine) 2.017(4) Å]. The overall geometry at the metal centre can be described as a distorted square pyramid with the acetonitrile molecule at the apex [Cu–N(acetonitrile) 2.256(5) Å]. The Cu atom lies 0.286(1) Å out of the N$_4$ mean plane. Both saturated six-membered rings are in a chair conformation [apex–apex distances: Cu1–C2 3.276(7) Å; Cu1–C12 3.276(7) Å; Cu1 and C2 are displaced with respect to the N1–C1–N2–C3 mean plane by 0.689(1) Å and −0.648(7) Å, respectively; Cu1 and C12 are displaced with respect to the N1–C13–N4–C11 mean plane by −0.688(1) Å and 0.673(7) Å, respectively] while the molecular moiety containing the pyridine ring and the two imino groups is planar. The mean deviation from the best plane calculated using 15 atoms is 0.065 Å, while the largest deviation is 0.142(8) Å for C7. As expected, the naphthalene is also essentially planar; the mean deviation from the least-squares plane calculated using all ten carbon atoms is 0.027 Å, while the largest deviation is 0.057(15) Å. The ligand is bent so that the naphthalene is hanging over the pyridine ring: the planes containing the two aromatic systems are almost parallel forming an angle of 4.60° and the distance between them ranges from 3.123 to 3.589 Å. The almost perfect superposition of the two aromatic moieties results also from the torsion angle Cu1–N1–C14–C15 which is 1.6°. All these considerations may suggest an intramolecular π–π interaction.

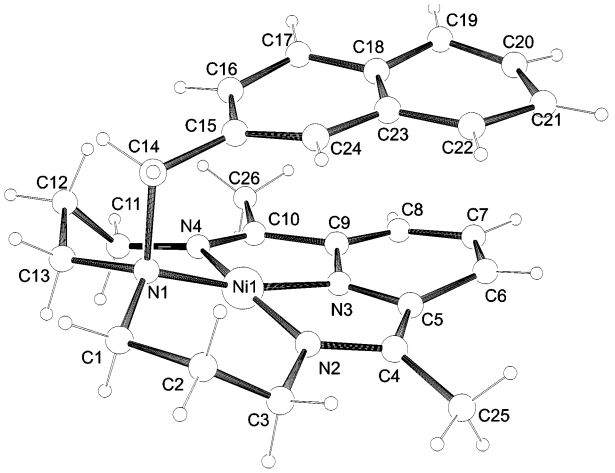


Fig. 2 Crystal structure of [Ni(**4**)](PF$_6$)$_2$ (counter ions have been omitted for clarity).

The nickel(II) complex (Fig. 2) closely resembles the copper(II) complex described above. Unfortunately, in this case the low quality of the crystallographic data (see Experimental section) does not allow an accurate analysis of the structural model. At any rate, as in the [Cu(**4**)]$^{2+}$ complex, the ligand is bent and the naphthalene is hanging over the pyridine ring. The distances between the pyridine and the naphthalene planes range from 3.075 to 3.566 Å. Nickel(II) is four-coordinated in an almost square planar geometry [Ni1 is 0.089(2) Å out of the N$_4$ mean plane].

The folded arrangement with a pendant naphthalene subunit over the macrocyclic cavity, although unusual, has been recently observed in another naphthalene-containing tetraazamacrocyclic Ni^{II} complex.[2g]

Electrochemical investigations (cyclic voltammetry, CV and differential pulse voltammetry, DPV) showed that [Cu(**4**)]$^{2+}$ undergoes a quasi-reversible reduction process in acetonitrile solution at a potential value of −0.986 V *vs.* Fc$^+$/Fc (−0.561 V *vs.* SCE) which can be ascribed to the Cu^{II}/Cu^{I} couple. Previous studies performed on the reference systems [Cu^{II}(**3**)]$^{2+}$ and [Cu^{II}(CR)]$^{2+}$ gave potential values of −0.398 and −0.492 V *vs.* SCE respectively.

[Cu^{II}(**4**)]$^{2+}$ displays a very weak emission ($\Phi < 0.001$) both in acetonitrile and in 4 : 1 acetonitrile : water 10^{-5} M solutions. Copper(II), as already observed in similar systems, can induce a fluorescence quenching of the adjacent naphthalene subunit through either an electron tranfer (eT) or an energy transfer (ET) mechanism.[17] The chemical reduction performed by adding SO$_3^{2-}$ or ascorbate to a solution of [Cu^{II}(**4**)]$^{2+}$ 10^{-5} M in 4 : 1 acetonitrile : water did not induce any appreciable variation of the fluorescence intensity (I_F). Similar results were obtained when 2,5-di-*tert*-butylhydroquinone was added as a reductant to acetonitrile solutions of the copper(II) complex. The [Cu^{I}(**4**)]$^+$ species, which is reasonably stable on the electrochemical experimental time scale, may decompose in the cuvette before the emission spectrum is registered. Any attempt to shorten the spectral acquisition time after the reduction was unsuccessful. In conclusion, the [Cu^{II}(**4**)]$^{2+}$ complex does not display any interesting switching behaviour since it maintains its emission OFF in both of its states.

On the other hand, [Ni^{II}(**4**)]$^{2+}$ in acetonitrile solution displays the typical fluorescence spectrum of naphthalene derivatives with a maximum I_F at 335 nm ($\lambda_{exc} = 290$ nm) and is distinctly more emissive ($\Phi = 0.013$) than its copper(II) analogue. Although nickel(II) has been described as a quencher of vicinal fluorophores *via* eT and ET mechanisms,[17] it seems to be less efficient than copper(II) in the fluorescence quenching processes, as confirmed by other examples of nickel(II) tetraazamacrocycle–fluorophore conjugates whose residual emission was strong enough to make them suitable for fluorescence switching applications.[2g,12]

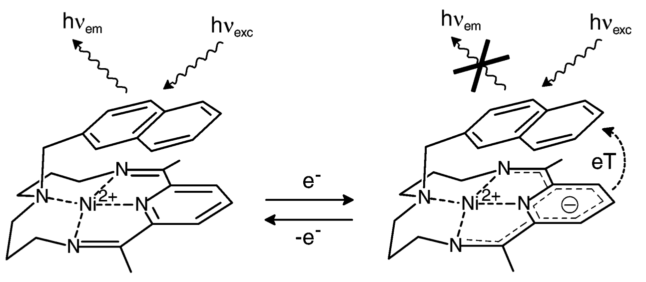
Electrochemical investigations performed on acetonitrile solutions of $[Ni^{II}(\mathbf{4})]^{2+}$ showed that it behaves as expected for a $[Ni^{II}(CR)]^{2+}$ derivative. CV and DPV profiles are consistent, with a one-electron reversible process at -0.953 V and a non-reversible one at -1.645 V *vs.* Fc^+/Fc in the cathodic region. Moreover, a quasi-reversible oxidation wave at 1.148 V *vs.* Fc^+/Fc was observed. The anodic process can be reasonably assigned to the Ni^{III}/Ni^{II} couple,[14] while the two reduction processes can be assigned on the basis of the results obtained in investigations previously performed on $[Ni^{II}(\mathbf{3})]^{2+}$ and $[Ni^{II}(CR)]^{2+}$. In particular, it is generally observed that the first reduction process of these systems involves mainly the unsaturated conjugated ligand, thus giving rise to a Ni^{II}–radical anion ligand complex, $[Ni^{II}(L^{\bullet -})]^{+}$, while the second reduction is a genuine metal ion one.[14,15]

The fluorescence switching behaviour was tested by measuring the emission intensity of $[Ni^{II}(\mathbf{4})]^{2+}$ at 335 nm before and after a controlled potential electrolysis experiment, performed in acetonitrile with the platinum electrode potential set at -1.15 V *vs.* Fc^+/Fc. After the reduction cycle, the I_F value is distinctly lower ($\Phi < 0.001$) than that of the emission spectrum displayed by the initial $[Ni^{II}(\mathbf{4})]^{2+}$ solution ($\Phi = 0.013$). A subsequent controlled potential electrolysis experiment, carried out at -0.75 V *vs.* Fc^+/Fc, affords reoxidation of the reduced complex to the parent Ni^{II} species with an almost complete recovery of the pristine fluorescence ($\Phi = 0.011$). The incomplete restoring of I_F could be due to a partial decomposition occurring in the course of the reduction process.

The switching behaviour was also tested by performing chemical reduction and reoxidation of the complex. The addition of aqueous SO_3^{2-} to a $[Ni^{II}(\mathbf{4})]^{2+}$ solution 10^{-5} M in 4 : 1 MeCN : water makes the I_F measured at 335 nm ($\lambda_{exc} = 290$ nm) decrease by about 10 fold. The reoxidation performed by adding aqueous $S_2O_8^{2-}$ to the previously prepared reduced metal complex solution induces a fluorescence increase to the original I_F value. Thus, one can switch the fluorescence OFF and ON by alternatively adding a reducing or an oxidizing agent to the solution of $[Ni^{II}(\mathbf{4})]^{2+}$. Emission measurements performed in glassy ethanol at 77 K showed that in frozen solutions no I_F variations occurred upon reduction: this is the expected behaviour when an eT process is active. In contrast to an energy transfer process, the occurrence of a photoinduced electron transfer induces the formation of an ion-pair species which is stabilized by the reorientation of solvent dipoles. Such reorientation cannot take place in frozen media and the ion-pair experiences only a very small stabilization.[17,18] With the exception of a few examples of ultrafast eT processes,[19] the reviving of fluorescence in frozen solution can therefore be considered as evidence that an eT rather than an ET process is active.

These considerations enable us to assume that an eT process from the reduced complex subunit to the excited naphthalene is responsible for the fluorescence quenching in the $[Ni(\mathbf{4})]^{+}$ system. Such an event can be favoured by a folded arrangement in solution similar to the one observed in the solid state, which provides a spatial proximity between the two subunits involved in the eT process. The fluorescence redox switching behaviour is pictorially illustrated in Scheme 2.

The reversible electrochemical and photophysical nature of the molecular switch $[Ni^{II}(\mathbf{4})]^{2+}$, allows a redox titration experiment to be performed. An aliquot of a 4 : 1 MeCN : water solution was titrated with aqueous SO_3^{2-} and I_F was measured after each addition: the emission intensity decreased and reached a minimum value after the addition of one equivalent of reductant. No further decrease was observed upon addition of excess SO_3^{2-}. In a separate experiment, addition of aqueous $S_2O_8^{2-}$ to a second aliquot of the solution of the complex previously reduced by addition of one equivalent of SO_3^{2-} determined an increase of I_F which reached the original value after the addition of one equivalent of oxidant. Combination of the titration plots originates the apparently parabolic profile shown in Fig. 3.



Scheme 2

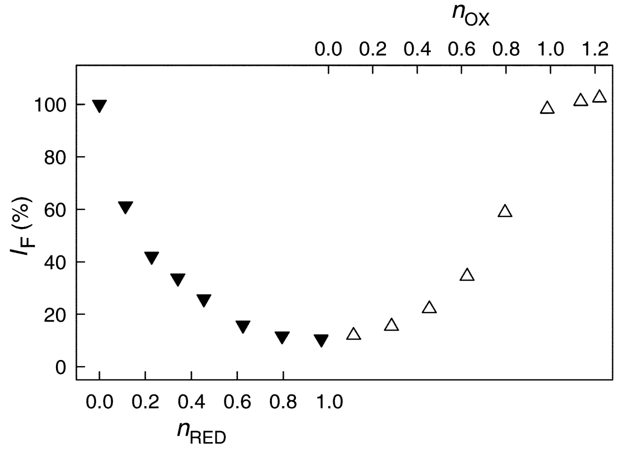


Fig. 3 Combination of the titration profiles of $[Ni^{II}(\mathbf{4})]^{2+}$with SO_3^{2-} (full triangles) and $S_2O_8^{2-}$ (open triangles) in 4 : 1 MeCN : water. n_{RED} = equiv. of added SO_3^{2-}; n_{OX} = equiv. of added $S_2O_8^{2-}$.

The shape observed in the combined plots, with a particular regard to the oxidation part, can be interpreted by taking into account the different kinetic behaviour of SO_3^{2-} and $S_2O_8^{2-}$. The former reacts quickly, giving a hyperbolic titration plot, while the latter reacts rather slowly and the titration plot has a distorted sigmoidal shape.

The redox switches reported in previous papers[8–12] can be classified as OFF/ON switches because the fluorescence is quenched (OFF) when the system is in the oxidized form, while it is restored (ON) in the reduced one. On the contrary, $[Ni^{II}(\mathbf{4})]^{2+}$ is the first example of a two-component system behaving as an ON/OFF switch, in which the oxidized form (Ni^{II}) is emissive and the reduced one (the $[Ni^{II}(L^{\bullet -})]^{+}$ complex) is not.

3 Experimental

General remarks

All chemicals were used as purchased without further purification.

UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Emission spectra were taken on a Perkin-Elmer LS-50B luminescence spectrometer (excitation wavelength 290 nm; maximum emission intensities at 335 nm). The relative quantum yields of fluorescence were obtained through the optically diluted method[20] using naphthalene ($\Phi = 0.21$ in EtOH) as reference.[21] Emission spectra at 77 K were measured in ethanol (10^{-5} M) using quartz sample tubes and the same luminescence spectrometer equipped with a Perkin-Elmer low temperature luminescence accessory. Mass spectra were obtained with a Finnigan TQS 700 mass spectrometer.

Table 1 Crystal and refinement data

	$[Cu(\mathbf{4})(CH_3CN)](ClO_4)_2$	$[Ni(\mathbf{4})](PF_6)_2$
Formula	$CuN_5H_{33}C_{28}Cl_2O_8$	$NiN_4H_{30}C_{26}P_2F_{12}$
Molecular weight	702.04	747.19
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a/Å	19.473(3)	6.922(5)
b/Å	7.613(2)	18.364(10)
c/Å	21.797(4)	11.729(10)
β/°	110.79(2)	101.91(6)
V/Å^3	3020.7(18)	1458.8(17)
Z	4	2
d_{calc}/g cm^{-3}	1.544	1.701
μ/mm^{-1}	0.958	0.878
θ Range/°	2–26	2–30
Tot. reflns measured	6072	6074
Unique reflections	5911 ($R_{int} = 0.0345$)	4374 ($R_{int} = 0.1620$)
Refined parameters	445	198
R_1	0.0624 (3654 reflns with $I > 2\sigma_I$)	0.1020 (915 reflns with $I > 2\sigma_I$)
R_{all}	0.1241	0.2292
wR_2	0.1880	0.3160

Redox potential values were determined by voltammetric techniques, on a Princeton Applied Research Model 273 potentiostat–galvanostat. Investigations in MeCN solutions, made 0.1 M in Bu_4NClO_4, were carried out in a conventional three-electrode cell using a platinum microsphere as a working electrode, and a silver wire as a pseudo-reference electrode which was calibrated *vs.* the Fc^+/Fc couple used as an internal standard.[22]

CAUTION: perchlorate salts of metal complexes are potentially explosive and should be handled with care. In particular, they should never be heated as solids.[23]

Syntheses

$[Ni(4)](ClO_4)_2$. *(i).* A solution of *N*-(3-aminopropyl)-1,3-propanediamine, **5** (4.2 ml, 0.03 mol) in MeOH (20 ml) was slowly added to a magnetically stirred solution of benzaldehyde (6 ml, 0.06 mol) in MeOH (20 ml). After stirring for one night at room temperature the solvent was distilled off and the resulting viscous liquid (the protected amine, **6**) used without further purification.

(ii). 2-Bromomethylnaphthalene (2.82 g, 0.0128 mol) and **6** (3.92 g, 0.0128 mol) were dissolved in toluene (50 ml). Finely podwered Cs_2CO_3 (4.17 g, 0.0128 mol) was added and the resulting mixture heated at 100 °C in a nitrogen atmosphere under vigorous mechanical stirring for one night. After cooling, the inorganic salts were filtered off and the solvent removed at the rotary evaporator. The oily residue was dissolved in 1 M aqueous HCl and the solution stirred for 6 h. An extraction with Et_2O (3 × 30 ml) was performed to eliminate benzaldehyde, then the aqueous phase was made alkaline with NaOH and extracted with CH_2Cl_2 (3 × 30 ml). The organic phase was desiccated over Na_2SO_4 and the functionalized amine, **7**, was obtained as a yellow oil, after removing the solvent (2.468 g, 71%); δ_H (400 MHz; solvent $CDCl_3$; 25 °C) 1.3 (broad s, NH_2), 1.5–1.6 (m, 4H, CH_2–CH_2–NH_2), 2.55–2.7 (m, 8H, CH_2–NH_2 and CH_2N), 3.6 (s, 2H, benzylic), 7.25–7.4 (m, 3H, aromatic), 7.6–7.8 (m, 4H, aromatic).

(iii). 2,6-Diacetylpyridine (0.14 g, 0.85 mmol) and $NiCl_2\cdot 6H_2O$ (0.2 g, 0.85 mmol) were dissolved in MeOH (25 ml) and the solution heated to 40 °C. Compound **7** (0.235 g, 0.85 mmol) was added and the resulting mixture heated and stirred for 12 h. The reaction mixture was concentrated (to about 10 ml) and an aqueous saturated solution of $NaClO_4$ (7 M, 6 ml) was added, to give a brown precipitate of $[Ni(\mathbf{4})](ClO_4)_2$, which was recrystallized from water. (0.422 g, 74%). Found: C, 47.31; H, 4.74; N, 8.41. $C_{26}H_{30}Cl_2N_4NiO_8$ requires: C, 47.59; H, 4.61; N, 8.54%. MS (ESI) *m*/*z* (%): 555 (15) M − ClO_4, 455 (100) M − ClO_4 − $HClO_4$.

Table 2 Selected bond distances (Å) and angles (°)

$[Cu(\mathbf{4})(CH_3CN)](ClO_4)_2$

Cu1–N1	2.017(4)	Cu1–N4	1.990(5)
Cu1–N2	1.995(4)	Cu1–N5	2.256(5)
Cu1–N3	1.911(4)		
N1–Cu1–N2	99.1(2)	N2–Cu1–N4	159.6(2)
N1–Cu1–N3	151.8(2)	N2–Cu1–N5	93.1(2)
N1–Cu1–N4	99.3(2)	N3–Cu1–N4	79.5(2)
N1–Cu1–N5	94.9(2)	N3–Cu1–N5	113.4(2)
N2–Cu1–N3	80.0(2)	N4–Cu1–N5	94.2(2)

$[Ni(\mathbf{4})](PF_6)_2$

Ni1–N1	1.89(1)	Ni1–N3	1.81(1)
Ni1–N2	1.76(2)	Ni1–N4	1.98(2)
N1–Ni1–N2	97(1)	N2–Ni1–N3	80(1)
N1–Ni1–N3	166.2(5)	N2–Ni1–N4	162.1(6)
N1–Ni1–N4	99.2(9)	N3–Ni1–N4	85(1)

The corresponding hexafluorophosphate salt was simply obtained by adding excess NH_4PF_6 to a methanol solution of $[Ni(\mathbf{4})](ClO_4)_2$.The orange-yellow precipitate was filtered off, dissolved in acetonitrile and used to obtain single crystals by slow diffusion of diethyl ether.

$[Cu(4)](ClO_4)_2$. The copper(II) complex was prepared in 81% yield under the same experimental conditions from $CuCl_2\cdot 2H_2O$, 2,6-diacetylpyridine and **7**. Found: C, 46.18; H, 4.68; N, 8.34. $C_{26}H_{30}Cl_2CuN_4O_8\cdot H_2O$ requires: C, 45.99; H, 4.75; N, 8.25%. MS (ESI) *m*/*z* (%): 560 (55) M − ClO_4, 460 (100) M − ClO_4 − $HClO_4$.

X-Ray crystallography

Crystal data for complexes $[Cu(\mathbf{4})(CH_3CN)](ClO_4)_2$ and $[Ni(\mathbf{4})](PF_6)_2$ are reported in Table 1 while selected bond lengths and angles are reported in Table 2.

Unit cell parameters and intensity data were obtained on an Enraf-Nonius CAD-4 four-circle diffractometer at room temperature using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). Cell dimensions were determined by least-squares fitting of 25 centered reflections monitored in the range $7.35 < \theta < 12.11°$ for the Cu complex and $5.32 < \theta < 11.58°$ for the Ni complex. Calculations were performed with the WinGX-97 software.[24] Correction for Lp was applied. For both crystals, no suitable reflections for a ψ scan were found in the range $80 < \phi < 90°$ and the empirical absorption correction was not applied. Both structures were solved by SIR-92[25] and refined by full-matrix least-squares using SHELX.[26] Atomic scattering factors were taken from ref. 27. Diagrams of the molecular structure were produced by the ORTEP-3 program.[28]

For the $[Cu(\mathbf{4})(CH_3CN)](ClO_4)_2$ crystal all the non-hydrogen atoms were refined anisotropically while the hydrogen atoms were inserted in the calculated positions and not refined. Rotational disorder for one perchlorate group was detected and alternative positions for the oxygen atoms were refined with occupancy factors 0.60 and 0.40, respectively.

The poor quality of the $[Ni(\mathbf{4})](PF_6)_2$ crystal did not allow the achievement of a good resolution for the structural model. Only a few reflections were observed so that only Ni and P atoms could be refined anisotropically. All other non-H atoms were refined isotropically while the hydrogen atoms were inserted in the calculated positions and not refined. This crystal structure is almost centrosymmetric (91%)[29] and could be described in space group $P2_1/m$ rather than in the chiral space group $P2_1$. In the former case, the two alternative positions for the naphthalene system could not be refined even with the use of geometrical constraints. Structural refinement of 114 parameters in space group $P2_1/m$ would yield a final R_1 factor of ≈4% and chemically unacceptable bond distances and angles for the naphthalene rings ($R_1 = 10.2\%$ for 198 refined parameters in $P2_1$). The Flack parameter is very close to zero with a very low standard uncertainty [0.02(8)] indicating a clear absolute configuration and confirms the choice of the $P2_1$ space group. Nevertheless, this study is important since the molecular conformation of the Ni^{II} complex has been revealed and a comparison with the analogous Cu^{II} complex was therefore allowed. At any rate, the structural investigation must be considered as preliminary and it will be revised as soon as more suitable crystals become available.

CCDC reference numbers 162666 and 162667.

See http://www.rsc.org/suppdata/dt/b1/b101310f/ for crystallographic data in CIF or other electronic format.

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