Control of the Microarchitecture of a Double Helix − Electrochemical Synthesis and Characterisation of a Novel Dinickel(II) Helicate with Different Groove Sizes

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Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

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Self-assembly of nickel ions and the N_4 Schiff base **H_2PTs** [**H_2PTs**: *N,N′*-bis(2-tosylaminobenzylidene)-1,3-diaminopropane] in an electrochemical cell leads to the novel neutral double-stranded dinuclear helicate $[NiPTs]_2\cdot CH_3CN$ (**1**). Complex **1** was fully characterised by elemental analysis, IR and EPR spectroscopy, FAB mass spectrometry, and magnetic measurements. The single X-ray crystal structure of **1** shows that both ligands are asymmetrically positioned around the Ni–Ni axis, leading to a double-helical complex that presents a major and a minor groove.

Introduction

Helicate architectures have received a great deal of attention in recent years mainly due to DNA showing double-helical arrays.[1−8] However, the similarities between the structure of nucleic acids and that of synthetic metallo-helicates are very limited, principally because in most helicates the metal binding units are usually positioned symmetrically and on opposite sides of the helix, leading to two equivalent grooves. Hence, an important challenge of supramolecular chemistry is to design ligand strands that can associate on one side of the helical axis. This should lead to the isolation of asymmetrical helicates, which could be models of DNA structure.

Furthermore, it is highly desirable that these ligands are inexpensive, readily prepared, and easily modified donors, in order to enable wider access to this field. Schiff bases seem to be suitable ligands for this proposal.

By merging these two assumptions, one should try to find direct ways of preparing helical asymmetrical compounds with different groove sizes. However, very little work involving this concept has been published. In 1984 Van Koten et al.[9] described a binuclear $[Ag_2(N_4)_2]^{2+}$ dication with helical structure, where the N_4 donors are not symmetry re lated. More recently, Fabrizzi et al.[10] prepared a bis-iminoquinoline Cu^I helical cation with a certain degree of asymmetry, due to the reciprocal positioning of the ligand strands. It was not until 1999, however, that Hannon et al.[11] emphasised the significance of such asymmetry, and reported a Schiff base silver(I) double helical complex containing a major and a minor groove.

Our studies of the first-row transition metal complexes with imine-based ligands lead us to isolate mono-, di-, or trinuclear helical species.[12−15] As a continuation of this research, and considering that π-stacking interactions between benzylidene groups may provide a suitable tool for controlling the spatial orientation of ligand strands in a double-helical structure,[11] we have designed a new symmetric N_4 Schiff base ligand (see Scheme 1). This ligand contains four acyclic N donor atoms, an acyclic flexible spacer, and terminal bulky groups that should prevent the formation of undesired mononuclear species.[16−18] Furthermore, the Schiff base presents two benzylidene rings fused to the acyclic nitrogen atoms that could give rise to π-stacking interactions, as we have previously observed.[19] This could dictate a non-equivalent wrapping of the ligands around the M···M axis. The reaction of this potential bis-bidentate and dianionic ligand with nickel under electrochemical conditions was studied, and the results achieved are reported herein.

Results and Discussion

Design and Synthesis of the Ligand

The Schiff base **H_2PTs** [IUPAC name: *N,N′*-bis(2-tosylaminobenzylidene)-1,3-diaminopropane] has been prepared following a three-step procedure (Scheme 1) with a overall yield of 60%. The first step involves the oxidation of the

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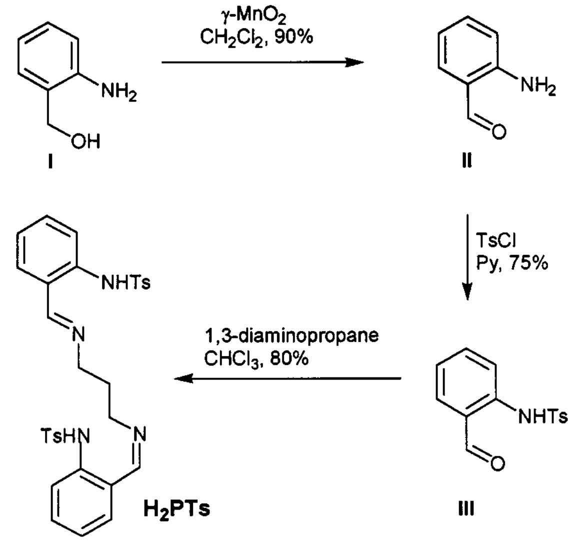

Scheme 1. Synthesis of the ligand **H_2PTs**

OH group of **I** to give aldehyde **II**. Subsequently, *N*-tosylation of 2-aminobenzaldehyde **II** with tosyl chloride afforded aldehyde **III**.[20] Finally, treatment of **III** with 1,3-diaminopropane in chloroform under reflux conditions gave the N_4 Schiff base ligand **H_2PTs**.

The yellow powdery solid formed was satisfactorily characterised by elemental analysis, IR, ^1H NMR spectroscopy, and FAB mass spectrometry. Besides, the structure of the ligand was known by X-ray diffraction studies.[21] This structure shows that the bulky terminal tosyl groups are *trans* to each other, in order to minimise the steric hindrance. Thus, it seems that the ligand should preferably act as bis-bidentate, spanning two metal centres, and preventing the formation of mononuclear species, in order to avoid the tosyl groups getting closer. In addition, the benzylidene moieties, fused to the N-atoms of different ligands, give rise to π-stacking interactions when the ligand is free. These interactions could be also present in the corresponding complexes, as has been previously observed for similar systems,[19] and could predispose the ligands to associate asymmetrically around the helical axis, leading to helicates with different groove sizes.

Electrochemical Synthesis of the Nickel Complex

Complex **1** was obtained by electrochemical oxidation of a nickel anode in an acetonitrile solution of the ligand **H_2PTs**, in the presence of a small quantity of tetraethylammonium perchlorate as supporting electrolyte. The cell can be summarised as Pt(−)|H_2PTs + MeCN|Ni(+). This synthetic procedure yields the neutral $[NiPTs]_2$ complex with high purity and in high yield.[12−15,22]

The electrochemical efficiency of the cell E_f was close to 0.5 mol·F^{-1}, which is compatible with the reactions shown in Scheme 2.

$$\text{Cathode:}\quad 2H_2PTs + 4e^- \longrightarrow 2H_2(g) + 2PTs^{2-}$$

$$\text{Anode:}\quad 2PTs^{2-} + 2Ni \longrightarrow [NiPTs]_2 + 4e^-$$

Scheme 2

The green powder nickel complex formed by this synthetic route is insoluble in water and apolar organic solvents, and soluble in common polar organic solvents. It appears to be stable both in the solid state and in solution.

Crystal Structure

Green plate single crystals of $[NiPTs]_2.CH_3CN$ (**1**), suitable for X-ray diffraction studies, were grown by vapour diffusion of diethyl ether into an acetonitrile solution of the powder $[NiPTs]_2$. An Ortep view of the structure is shown in Figure 1. Experimental details are presented in Table 3

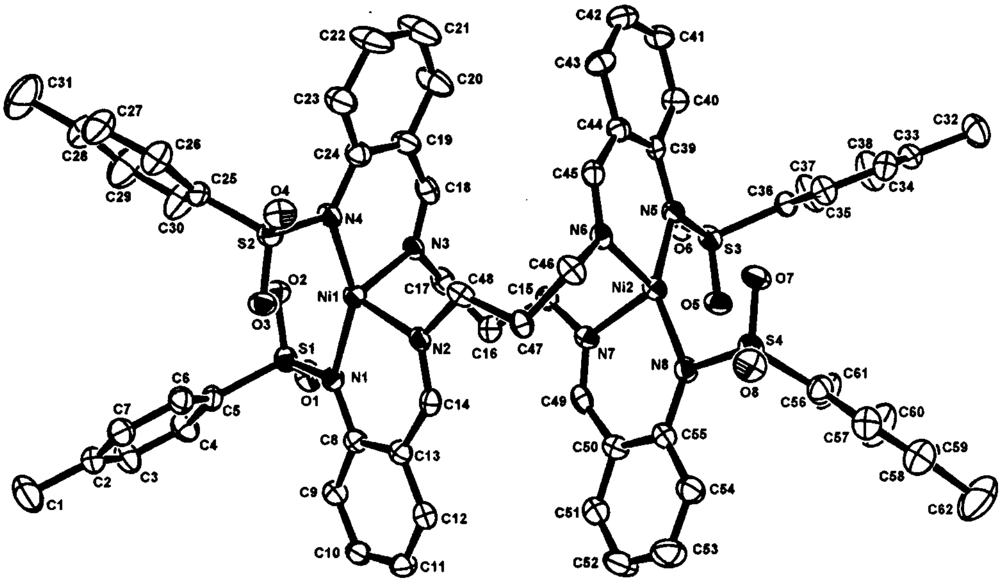

Figure 1. ORTEP view of complex **1** (thermal ellipsoids are drawn at 30% of probability level and hydrogen atoms and solvent molecules have been omitted for clarity)

Table 1. Main bond lengths [Å] for **1**

Ni(1)−N(1)	1.991(5)
Ni(1)−N(2)	1.999(6)
Ni(1)−N(3)	2.017(5)
Ni(1)−N(4)	1.985(5)
Ni(2)−N(5)	1.977(5)
Ni(2)−N(6)	2.016(6)
Ni(2)−N(7)	2.018(6)
Ni(2)−N(8)	1.971(6)

Table 2. Main bond angles [°] for **1**

N(1)−Ni(1)−N(2)	91.7(2)
N(4)−Ni(1)−N(1)	151.7(2)
N(4)−Ni(1)−N(2)	103.9(2)
N(4)−Ni(1)−N(3)	91.5(2)
N(2)−Ni(1)−N(3)	101.0(2)
N(1)−Ni(1)−N(3)	108.8(2)
N(8)−Ni(2)−N(5)	149.8(2)
N(8)−Ni(2)−N(6)	107.6(2)
N(5)−Ni(2)−N(6)	91.9(2)
N(8)−Ni(2)−N(7)	91.7(2)
N(5)−Ni(2)−N(7)	106.2(2)
N(6)−Ni(2)−N(7)	103.5(2)

and selected bond lengths and angles in Table 1 and Table 2.

The asymmetric unit contains a $[NiPTs]_2$ molecule with two acetonitrile solvates at 0.5 occupancy. The compound is a binuclear nickel complex, with the ligands spanning both metal centres, and intertwined to give a double helix. Both enantiomers (left- and right-handed) are observed in the unit cell.

Each ligand uses both nitrogen atoms of one binding moiety [N(1), N(2); N(3), N(4)] to coordinate one metal centre [Ni(1)]. The remaining imine nitrogen [N(6), N(7)] and amide nitrogen [N(5), N(8)] atoms of the second binding units of both $[PTs]^{2-}$ coordinate the second nickel atom [Ni(2)]. Thus, the environment of the metal centres can be described as distorted tetrahedral, with both ligands acting as bisbidentate N_4 donors. This distortion is shown by the angles between nitrogen and nickel atoms, which range from 91.7(2)° to 151.7(2)° for Ni(1) and from 149.8(2) to 91.7(2) for Ni(2). The longer angles [151.7(2)° and 149.8(2)°] are those between nickel and the amide nitrogen atoms, and this seems to be the result of the attempt to minimise the steric hindrance between the tosyl groups.

This tetrahedral geometry is quite unusual for dinickel helical complexes, where the nickel atom is usually six-coordinated.[13−14,23−25] Thus, in nickel complexes with imine-based ligands of the hydrazone type, composed by two bidentate arms and a spacer with a donor atom, two different possibilities of reaching the coordination number 6 have been described.[13−14,23] The most general one is the linking of two bidentate arms and two central donor atoms, which act as bridges, to the same metal atom.[13−14,23] When this type of complex is recrystallised in a donor solvent, the central bridges break and the donor atoms of the spacers are now linked to only one metal centre, acting as terminal donors. This would lead to a coordination number of six for one metal atom and to a coordination number of four for the other one. The two free coordination positions of the second nickel atom are now filled by donor solvent molecules, giving rise to a [6 + 4 + (2)] helix.[13−14]

However, when the ligand does not contain a donor atom in the spacer group, the octahedral environment with bisbidentate Schiff bases is normally achieved by simultaneous coordination of three strands to two metal centres. Thus, the most common nickel helical complexes with Schiff bases described in literature are the dinuclear triple helical ones.[24−25] In this case study, two factors can prevent the coordination of a third $[H_2PTS]$ ligand or solvent molecules in order to achieve a coordination number six: 1) the steric hindrance of the bulky tosyl groups; 2) the closeness of some of the tosyl oxygen atoms to Ni(1) [O(2) and O(3)] and Ni(2) [O(5) and O(7)]. These distances of ca. 2.5 Å seem to indicate that one oxygen atom of each tosyl group is weakly interacting with one metal atom. Thus, the aforementioned distances could be taken as secondary intramolecular bonds, since they are too long to be considered true coordinated bonds. This fact could have a profound influence on the adopted tetrahedral geometry, as maybe these oxygen atoms are too close to the nickel centres to allow any other ligand to complete their environment requirements.

Each ligand forms two six-membered chelate rings, one around each metal atom, which are nearly planar, with angles between the chelate rings of 85.75° and 80.18° around Ni(1) and Ni(2), respectively. The Ni−N(imine) bond lengths [Ni(1)−N(2) = 1.999(6) Å, Ni(1)−N(3) = 2.017(5) Å, Ni(2)−N(6) = 2.018(6) Å, and Ni(2)−N(7) = 2.018(6) Å] are shorter than those found for octahedral triple dinickel helicates with Schiff bases.[25] This could be a reflection of the lower coordination number in the latter complexes. The same occurs with the Ni−N(amide) bonds [Ni(1)−N(1) = 1.991(5) Å, Ni(1)−N(4) = 1.985(5) Å, Ni(2)−N(5) = 1.977(6) Å, and Ni(2)−N(8) = 1.971(6) Å], which are shorter than the Ni−Ni(amide) distances found for hexa-coordinated nickel Schiff base complexes containing the NTos radical.[26] The Ni(1)···N(2) distance of 6.207 Å is shorter than the ones reported for nickel triple helical complexes[24−25] (about 11 Å), but longer than the ones for double helical nickel complexes with hydrazone ligands,[13−14,23] as was expected.

All these distances and angles also show the non-equivalence of the environment of the nickel atoms and of both Schiff bases, giving rise to a certain degree of asymmetry. This asymmetry leads to the formation of two grooves of different size. The two distinct grooves (major and minor) seem to be exacerbated by aromatic π-stacking interactions between the benzylidene rings of the binding moieties. Two interactions of different strength can be observed between aromatic rings of different ligand strands, as is shown in Figure 2. From now we will call A and B the two benzylidene rings of the dark strand, and C and D those of the light strand. Interaction between A and D (Figure 2, left) gives

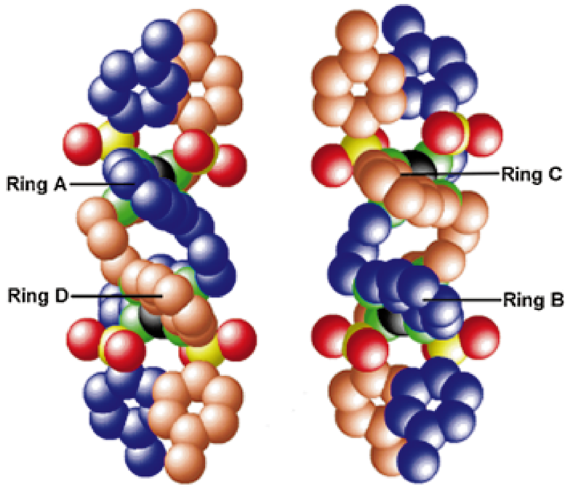

Figure 2. Space-filling representation of complex **1**, showing the minor (left) and major (right) grooves. Both representations correspond to the same enantiomer, turned 180°

rise to distances of 2.455−3.179 Å between the atoms of A and mean plane of D, with an angle between their least-square planes of 16.0°. Similarly, C overlaps with B (Figure 2, right) leading to a longer distance (2.682−3.755 Å) and to a bigger acute angle (25.2°). Thus, to the best of our knowledge, this is the first example where π-stacking interactions between aromatic rings of the binding moieties (not of the spacer group) control the micro-architecture of the helix, and lead to an asymmetrical double-stranded helicate with a major and a minor groove.

However, no specific π-stacking interactions (face-face or face-edge π-π) are identifiable between the terminal tosyl aromatic rings, which probably appear separated to minimize the steric repulsion.

Finally, the helical turn, defined as the angle subtended by the centroids of the inner benzylidene rings of the ligand along the Ni−Ni axis (helical axis), are 174.8° and 179.6° for each strand.

IR Spectroscopy and FAB Mass Spectrometry

The IR spectra of **1** shows a strong band at ca. 1625 cm^{-1} due to the imine ν(C=N) mode, which exhibit a shift of 10 cm^{-1} to lower energy from the free ligand value, indicative of coordination of the ligand to nickel. In addition, the band due to ν(C−N) mode undergoes a negative shift (1303 vs. 1340 cm^{-1} in the free ligand). This behaviour is compatible with the participation of both imine an amide nitrogen atoms in the coordination to nickel centres.[27−28]

The FAB mass spectrum of **1** presents a peak at *m*/*z* = 646 due to the fragment $[NiPTs]^+$, that confirms the coordination of the ligand to the metal centre. Besides a prominent peak at *m*/*z* = 1292 is assigned to the fragment $[NiPTs]_2{}^+$, which seems to indicate a dinuclear nature of complex **1**, as the X-ray structure shows.

Magnetic and EPR Characterisation

Nickel(II) tetrahedral complexes usually exhibit a large magnetic moment, due to the largely unquenched orbital momentum; this is usually observed together with a large dependence of the magnetic moment on temperature. However, distortion from ideal tetrahedral symmetry may remove the orbital degeneration of the ground state, thus reducing both the temperature dependence and the absolute value of the magnetic moment.[29−31]

The high temperature value of the magnetic moment of **1** (1.36 emu K per mol of Ni^{2+}at 280 K) is quite low for a tetrahedral nickel(II), thus indicating that, as expected from the structural data, large distortions from tetrahedral symmetry are active in reducing the orbital contribution to the magnetic moment. The temperature dependence of the product (shown in Figure 3) is quite small. In agreement with this interpretation, on lowering the temperature, χT slowly decreases to 1.20 emu K per mol of Ni^{2+} centre at 22 K. Only below this temperature does it drop until it reaches 0.32 emu K mol^{-1} at 2 K. As the two tetrahedral units of Ni^{2+} are quite far from each other (6.207 Å), and there are no bridging ligands capable of transmitting the exchange coupling interaction between them, it seems reasonable to attribute this behaviour to a large Zero Field Splitting of the $S = 1$ ground state, which is a well-known characteristic of nickel(II) complexes.

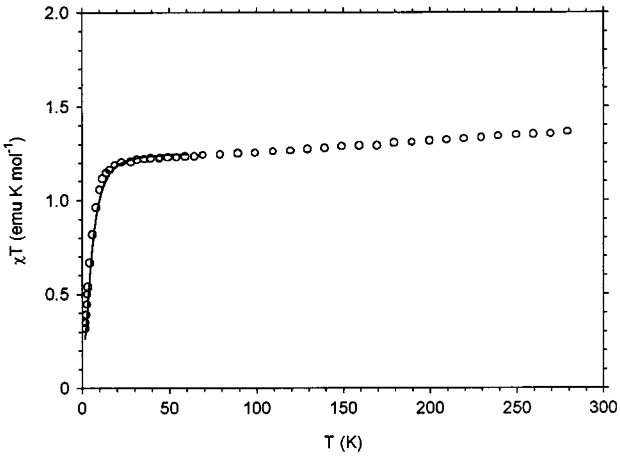

Figure 3. Plot of χ*T* versus *T* for **1**, in the range 2−280 K

This hypothesis was confirmed both by the absence of any X-Band EPR signal at 4.2 K, and by the behaviour of the *M* vs. *H* curve, measured at 3 K. As shown in Figure 4, the magnetisation is slowly increasing with the field and it

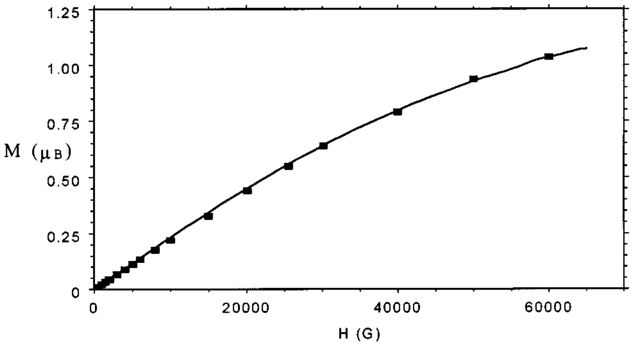

Figure 4. Magnetisation plot (*M*) versus *H* for **1**

is still far from saturation at 6.0 T (1.04 μ_B per Ni^{2+}). The magnetisation curve was fairly well reproduced (Figure 4, continuous line) assuming a D value of 13.0 ± 0.2 cm^{-1} and a g value of 2.20 ± 0.03, in agreement with what was expected for Ni^{2+}. Assuming the same parameters, we were then able to reproduce (Figure 3, continuous line) the low temperature part of the χT curve. The large D value may be due to the presence of low-lying excited states admixed through spin-orbit coupling. As far as the slight difference in the two tetrahedral units is concerned, it should be stressed that these parameters represent an average between the values of each single centre.

Conclusion

This work shows that careful selection and design of Schiff base ligands can yield helical nickel complexes. The presence of bulky terminal groups in the N_4 donor **H_2PTs** described herein constrains the ligand to act as binucleating. Besides, the presence of benzylidene moieties in the ligand strands seems to play a fundamental role in the asymmetrical structure of the helix. Thus, a neutral double-stranded dinickel helical complex, so scarce in literature, can be isolated by means of the electrochemical synthesis. In addition, internal π-stacking interactions between ligand binding domains control the micro-architecture of the double helix, leading to a helicate with different size grooves, reminiscent of DNA structure.

Variation of the length and rigidity of the spacer, as well as studies of further factors that can affect the spatial orientation of ligand strands in metallo-supramolecular compounds, are in progress in our laboratory.

Experimental Section

Elemental analysis was performed on a Carlo Erba EA 1108 analyser. − The NMR spectra were recorded on a Bruker WM-250 spectrometer using $CDCl_3$ as solvent. − Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range of 4000−600 cm^{-1}. − Mass spectrometry (FAB) was performed on a Micromass Autospec mass spectrometer, employing *m*-nitrobenzyl alcohol as a matrix. − The EPR spectrum of **1** was recorded using a Varian ESR9 spectrometer equipped with a ^{4}He continuous flow cryostat. − Magnetic measurements between 2 and 280 K were performed using a Cryogenics Squid magnetometer with field up to 6.5 T. The data were corrected for sample holder contribution and diamagnetism of the sample using Pascal constants.

Syntheses: All the starting materials were purchase from Aldrich and used without further purification. 2-tosylaminobenzaldehyde **III** was prepared according to a method previously reported in literature,[20] as shown in Scheme 1.

***N,N′*-Bis(2-tosylaminobenzylidene)-1,3-diaminopropane (H_2PTs):** To a solution of 2-tosylaminobenzaldehyde **III** (5.0 g, 18.2 mmol) in chloroform (150 mL) 1,3-diaminopropane (0.8 mL, 9.1 mmol) was added and the mixture was heated under reflux. The volume of the solution was reduced over a 4 h period to ca. 50 mL, using a Dean−Stark trap, and was then allowed to cool. The resultant yellow solution was concentrated to ca. 10 mL. The solid, which precipitated, was collected by filtration, washed with diethyl ether (3 mL) and dried in vacuo. Yield 4.3 g (80%). m.p.: 145 °C. − $C_{31}H_{32}N_4O_4S_2$ (588.8): calcd. C 63.24, H 5.48, N 9.52, S 10.89; found C 63.0, H 5.3, N 9.4, S 10.5. FAB-MS: m/z = 589.2 [M^+]. − ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 13.0 (s, 2 H), 8.4 (s, 2 H), 7.7 (d, 4 H), 7.6 (d, 2 H), 7.2 (m, 6 H), 7.1 (d, 2 H), 7.0(dt, 2 H), 3.8 (t, 4 H), 2.3 (s, 6 H), 2.2 (q, 2 H). − IR (KBr, cm^{-1}): ν(C=N) 1635 s, ν(C−N) 1340 s, $\nu_{as}(SO_2)$ 1287 s, $\nu_s(SO_2)$ 1163 s.

$[NiPTs]_2$: A solution of H_2PTs (0.2 g, 0.3 mmol) in acetonitrile (80 mL), containing 10 mg of tetramethylammonium perchlorate as supporting electrolyte, was electrolysed for 3.6 h using a current of 5 mA and 7.2 V. Concentration of the resultant solution to a third of its initial volume yielded a green solid that was washed with diethyl ether and dried in vacuo. Yield: 0.2 g (86%). − $C_{62}H_{60}N_8Ni_2O_8S_4 \cdot CH_3CN$ (1333.9): calcd. C 57.7, H 4.7, N 9.5, S 9.6; found C 58.0, H 4.6, N 9.5, S 9.8. FAB-MS, m/z (%) = 646 (54, NiPTs), 1292 (42, Ni_2PTs_2). − IR (KBr, cm^{-1}): ν(C=N) 1625 s, ν(C−N) 1303 s, $\nu_{as}(SO_2)$ 1260 s, $\nu_s(SO_2)$ 1129 s.

Recrystallisation of the green powder in acetonitrile yields crystals of $[NiPTs]_2 \cdot CH_3CN$ **1** suitable for X-ray diffraction studies.

CAUTION: Perchlorate salts are potentially explosive and should therefore be handled with the appropriate care.

X-ray Crystallography: Crystals of **1** suitable for X-ray diffraction studies were grown as previously detailed. X-ray data were collected on a Siemens SMART CCD area-detector diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) operating at room temperature, using ω scans (Table 3). The structure was solved by direct methods[32] and refined by full-matrix least-squares on F^2. Absorption and incident beam corrections were applied (SADABS). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142926. Copies of the data can be obtained free of charge

Table 3. Crystal data and details of the structure determination of **1**

Empirical formula	$C_{64}H_{63}N_9Ni_2O_8S_4$
Molecular weight [g/mol]	1331.89
Crystal system	monoclinic
Space group	$P2(1)/c$
a [Å]	18.941(1)
b [Å]	24.802(1)
c [Å]	15.580(1)
β [°]	108.88°
V [A^3]	6970.2(2)
Z	4
$D_{calcd.}$ [Mg/m^3]	1.269
$F(000)$	2776
μ [mm^{-1}]	0.716
Crystal size [mm]	0.40 × 0.25 × 0.05
Crystal colour	green
Reflections collected/unique	24294/11983
Restraints	6
Parameters	811
Goodness-of-fit on F^2	1.006
Final $R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0692, 0.1391
Final $R1$, $wR2$ [all data]	0.1869, 0.1936

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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