

An unprecedented example of a *cis*-phosphonodithioato nickel(II) complex built by an extensive hydrogen bonding supramolecular network

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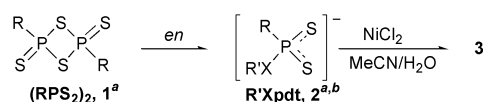
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The P–N bond hydrolysis of the 4-methoxyphenyl-ammonium ethylamido-phosphonodithioato ligand during its complexation to Ni^{II} leads to the first example of phosphonodithioato nickel(II) complex having a *cis* configuration; this complex is stabilised in the solid state by an extensive and intricate network of hydrogen bondings involving the released ethylenediamine and a water molecule.

Existing design strategies for the synthesis of extended inorganic networks follow two principal methods based on the different nature of the interactions responsible for networking. In one approach, which is the more frequently used, coordinative covalent bonds engaged between transition-metal ions and various organic 'linkers', such as 4,4'-bipyridine, propagate the coordination geometry into infinite architectures of various dimensionality and topology.¹ The other method, still far less common, exploits weaker intermolecular forces (particularly π – π interactions, hydrogen bonding, and halogen bonding) as a guide to the assembly of molecular coordination complexes into extended networks.²

We present here a very novel case of a 'one-pot' self-assembly of a 3D extended network by a combination of coordinative and hydrogen bonds.

The reaction between alcohols^{3,4} and amines³ R'XH (X = NH, O; R' = alkyl) and diorgano-dithiadiphosphetane disulfides (RPS₂)₂ (R = 4-MeOPh, Ph) to give the corresponding phosphonodithioato anions R(R'X)PS₂[–] (R'Xpdt), through a P₂S₂ ring opening, has recently been described. The subsequent reaction with Group 10 metal ions gives square-planar phosphonodithioato complexes [M(R'Xpdt)₂] (M = Ni, Pd, Pt) that are always crystallised as *trans*-isomers. This is a very simple way to prepare the phosphonodithioato and amido-phosphonodithioato complexes, whose chemistry had been scarcely explored because of synthesis difficulties.³ In an attempt [Scheme 1] to test the reactivity of (RPS₂)₂ towards bidentate nucleophilic reagents HXR'XH, we have performed the reaction of Lawesson's reagent [R = 4-MeOPh, **1**] with ethylenediamine (en). As expected, the 4-methoxyphenyl-ammoniumethylamido-phosphonodithioato inner salt [(4-MeOPh)-(+NH₃CH₂CH₂NH)PS₂[–], **2**] was obtained,[†] and structurally characterised.[‡] Instead of yielding the corresponding *trans*-amidophosphonodithioato complex, the reaction of **2** with NiCl₂[†] results in purple crystals whose X-ray structure corresponds to the formulation [(HOpdt)₂Ni-en-H₂O]_∞ (**3**).[‡]



^aR = 4-MeOPh; ^bR'X = ⁺H₃N(CH₂)₂HN

Scheme 1

(HOpdt)₂Ni being the very novel complex *cis*-bis[(4-methoxyphenyl) *O*-hydrogenphosphonodithioato]nickel(II). In *cis*-(HOpdt)₂Ni (Fig. 1) the nickel ion is coordinated to two HOpdt anions through the sulfur atoms in a square planar arrangement. The NiS₄ core is strictly planar (deviations from the average plane 0.04 Å) and the Ni–S distances [average value 2.222(6) Å] are coincident with those of analogous phosphonodithioato and amidophosphonodithioato nickel(II) complexes.³ The distinctive feature of this complex is the *cis* arrangement of the 4-MeOPh appendages with respect to the coordination plane. To the best of our knowledge, this is the first case of a phosphonodithioato complex isolated in the solid state only in a

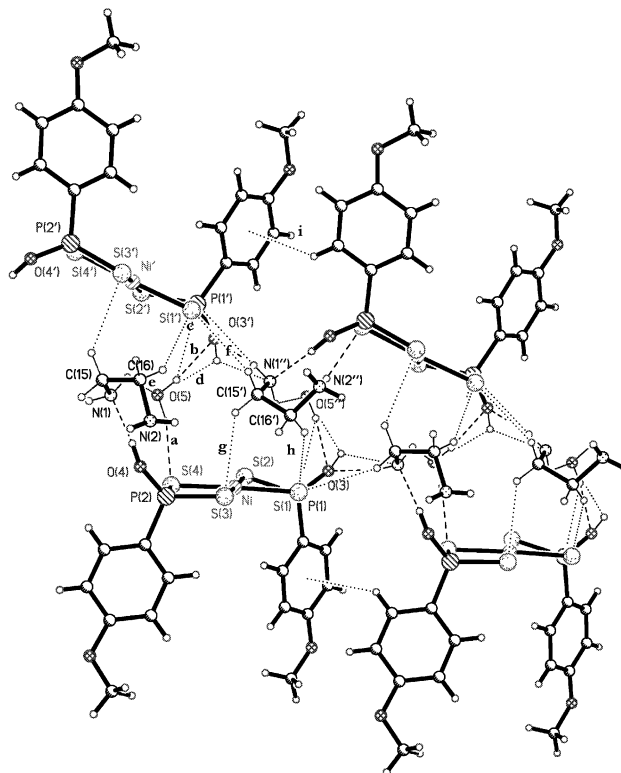


Fig. 1 Herringbone-like ribbons formed by coupled chains built by propagating **3** along the *c* direction. Besides the hydrogen bonds described in the text, a secondary weak hydrogen bond between H(O(3)) and N(1'') [H...N 2.40 Å], as well as a P(1)···H(N(1'')) contact (2.93 Å) contribute to bind the units into chains. Interactions **a–h** couple the chains into ribbons: **a**: O(5)···S(4) 3.21, H···S 2.28 Å; **b**: O(5)···O(3') 2.81, H(O(5))···O(3') 1.97 Å; **c**: P(1')···O(5) 3.49, P(1')···H(O(5)) 2.80 Å; **d**: H(O(3'))···O(5) 2.39 Å; **e**: O(5)···N(1) 2.94; O(5)···H(N(1)) 2.47 Å; **f**: C(15')···S(1) 3.62, H(C(15'))···S(1) 2.90 Å; **g**: C(15')···S(3) 3.62, H(C(15'))···S(3) 2.87 Å; **h**: C(16')···S(1) 3.63, H(C(16'))···S(1) 2.79 Å.

cis configuration. Even though the existence of *cis*-phosphonodithioato complexes was demonstrated by Fackler and Thompson,⁵ who explored the *cis*–*trans* isomerisation of the Ni^{II}, Pd^{II} and Pt^{II} complexes of *O*-ethylphenylphosphonodithioato [EtO(Ph)PS₂][–] anion in several organic solvents by ¹H NMR spectroscopy, until now these complexes have been known to crystallise only in a *trans* configuration. The only other example of a phosphonodithioato complex in a *cis* arrangement is [Au(S₂P(OH)Ph)₂]Cl, which anyway co-crystallised as a mixture of the *cis* and *trans* isomers in a 1:2 ratio.⁶

It is interesting to note that compound **2** by itself is stable in the CH₃CN–H₂O mixture,[†] and undergoes the hydrolysis of the P–N bond when reacted with NiCl₂, yielding the *cis*-(HOpdt)₂Ni complex, where a hydroxo group is bonded to the phosphorus atom instead of the ethylenediamine molecule. Consequently, the reaction of NiCl₂ with **2** completely differs from those of all other R(R'X)PS₂[–] ligands (X = O, NH; R' = alkyl), which always give the *trans*-Ni^{II}-complexes in the same experimental conditions, with the chemical environment of the phosphorus atom unchanged.³

A further aspect of the chemistry of these complexes is noteworthy: the *trans*-[Ni(R'Xpdt)₂] complexes readily add nitrogen bases, including ethylenediamine,⁷ to form green paramagnetic octahedral adducts.⁸ In the present case, since the formation of the *cis*-(HOpdt)₂Ni complex is accompanied by the release in solution of two ethylenediamine molecules, the formation of an octahedral nickel(II) complex by addition of en would be expected. However, not only does en not interact with the metal centre, but even the addition of an excess of en to the solution of **3**, does not result in any octahedral adduct formation. In contrast, the mutual recognition between en and the *cis*-(HOpdt)₂Ni complex occurring at the second coordination sphere level, leads to the supramolecular assembly [(HOpdt)₂Ni-en-H₂O]_∞, promoted by the numerous hydrogen bonding interactions.

The supramolecular structure [(HOpdt)₂Ni-en-H₂O]_∞ is made up of discrete molecules of *cis*-(HOpdt)₂Ni, en, and water, held together by an extended network of hydrogen bonds. Units of *cis*-(HOpdt)₂Ni are bridged head-to-tail by ethylenediamine molecules to give infinite 1-D chains running along the *c* direction (Fig. 1). The H-bonds between the P–OH moieties and the N(1)H₂ amino groups hold together the infinite chains [O(3)⋯N(1) 2.87, O(4)⋯N(1) 2.67; (N(1))H⋯O(3) 2.03, (O(4))H⋯N(1) 1.81 Å]. Also the aromatic substituents at the phosphorus atoms, which are disposed on either side of the chains, bridge adjacent molecules of *cis*-(HOpdt)₂Ni through CH⋯π contacts (2.97 Å, 135°, **i** in Fig. 1).

Pairs of infinite symmetry-related chains arranged on parallel planes shifted by *c*/2, are coupled together into infinite herringbone-like ribbons. The water molecules play the main role in forming these ribbons by H-bonding the S(4) atom of one chain [O(5)⋯S(4) 3.21, H⋯S 2.28 Å, **a**] with the opposite O(3') atom [O(3)⋯O(5) 2.81, (O(5))H⋯O(3') 1.97 Å, **b**]. Other secondary bonds and contacts are described in Fig. 1.

The ribbons are interpenetrated by interacting through H⋯ring centroid type C–H⋯π contacts (3.08 Å, 151°),⁹ forming 2-D sheets (*bc* planes) as shown in Fig. 2. These sheets pack on top of each other along the axis *a* by interacting through hydrogen bonds involving the N(2)H₂ amino group and the O(3) and O(5) atoms of neighbouring sheets [N(2)⋯O(3) 2.73; N(2)⋯O(5) 2.80; (N(2))H⋯O(3)/(5) 1.92/1.96 Å].

We believe this to represent the first example of a one-pot self assembly of a transition metal complex-organo network, where both building blocks [en and *cis*-(HOpdt)₂Ni] are formed *in situ* from a single starting material (**2**). Actually, the supramolecular crystallisation process seems to be, in our opinion, the driving force for the unusual hydrolytic P–N bond cleavage, the subsequent releasing of en, and the generation of *cis*-(HOpdt)₂Ni.

The possibility of incorporating metal ions into extended hydrogen-bonded arrays using a single starting material could represent a brand new one-pot synthetic route to the crystal

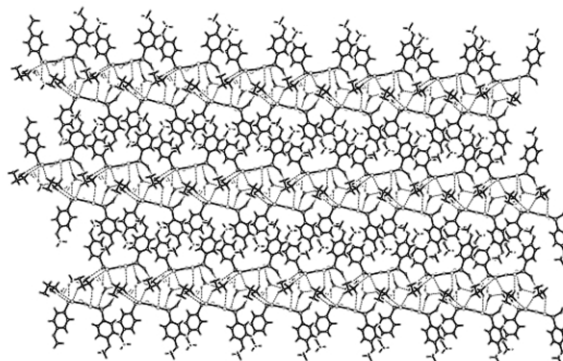


Fig. 2 2-D view (*bc* plane) of [(HOpdt)₂Ni-en-H₂O]_∞ showing alternate inorganic/organic interacting layers through H⋯ring centroid type C–H⋯π contacts (3.08 Å, 151°).

engineering of innovative materials based on hydrogen-bonded networks between co-crystallised transition metal complexes and organic molecules.

A deeper insight into the reactivity of the new ligand **2** and its derivatives is currently in progress at our laboratories.

Notes and references

[†] *Syntheses*: [(4-MeOPh)(⁺NH₃CH₂CH₂NH)PS₂[–], **2**]; **1** and en were reacted in CHCl₃ at reflux for 10–15 min in different molar ratios (1:2, 1:4, and a large excess of en); compound **2** was always obtained as the only product as a white solid, and was recrystallised from a CH₃CN–H₂O mixture; found (calc. for C₉H₁₅N₂OPS₂): C, 41.6 (41.2); H, 5.8 (5.8); N, 10.8 (10.7); S, 24.4 (24.4)%. [(HOpdt)₂Ni-en-H₂O]_∞: **2** (0.45 g, 1.7 mmol) was reacted with NiCl₂·6H₂O (0.23 g, 1.0 mmol) in 40 mL of a CH₃CN–H₂O (1:1 v/v) mixture. After refluxing for 10 min the reaction mixture was allowed to cool at room temperature. The product was quantitatively obtained as purple crystalline flakes; found (calc. for C₁₆H₂₆N₂NiO₅P₂S₄): C, 33.3 (33.4); H, 4.3 (4.5); N, 4.8 (4.9); S, 22.5 (22.3)%.
[‡] CCDC reference numbers 178335 and 178336 for **2** and **3**, respectively. See <http://www.rsc.org/suppdata/cc/b2/b200414c/>

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