Designed Assembly of Low-dimensional Molecular Units: Novel Neutral Coordination Polymers Based on (Phosphonodithioato)Ni^{II} Complexes

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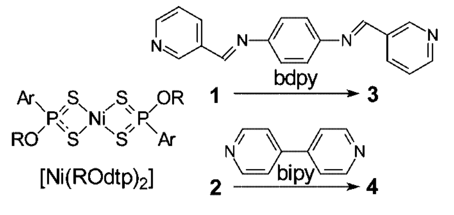
The reactions of phosphonodithioato complexes [Ni(ROdtp)$_2$] [where ROdtp = (4-MeOPh)(RO)PS$_2$; R = Et, Me] with 4,4′-bipy and *N*,*N*′-bis-(3-pyridinylmethylene)benzene-1,4-diamine (bdpy), respectively, yield the 1:1 coordination polymers [Ni(EtOdtp)$_2$(bipy)]$_8$ and [Ni(MeOdtp)$_2$(bdpy)]$_\infty$, whose syntheses and single-crystal X-ray diffraction analyses are reported.

Introduction

Crystal engineering is an important form of supramolecular synthesis, which utilises the understanding of intermolecular interactions in the design of new solids with desired physical and chemical properties.[1] In this view, the involvement of transition metals in crystal engineering can introduce specific physical properties,[2] such as optical properties,[3] electrical conductivity and magnetism,[4] and allows us to exploit a well-established know-how, based on the principles of coordination chemistry.[5] The most employed approach to coordination polymers with predetermined molecular architecture is the rational self-assembly of cleverly selected, multifunctional ligands and metal ions.[6] However, the nature of the counterion, the choice of the solvent, and various phenomena, such as supramolecular isomerism and interpenetration, introduce some uncertainty into the outcome of a particular experiment.[7] In this regard, by reducing the degrees of freedom of the system, for instance by using *cis*-protected metal blocks in place of the "naked" metal ions,[8] or by using a neutral, coordinatively unsaturated metal complex, less uncertainty can be expected. Moreover, the use of neutral synthons leads to self-reliant supramolecular assemblies, which do not require the presence of a counterion. Therefore, the use of suitable coordination compounds as molecular building blocks[9] is a logical extension of the self-assembly approach and is becoming an important synthetic strategy, as attested by the extensive work done on the use of di- and tricarboxylic acids to link adjacent equatorial sites in dimetal units and, more recently, on the use of axial linking to connect simple oligomers to form one- and two-dimensional polymers.[10] However, apart from the massive work on metal carboxylates,[10] this strategy remains largely untapped. Our aim in this study is to exploit this building strategy by using neutral coordinatively unsaturated (phosphonodithioato)Ni^{II} complexes, [Ni(ROdtp)$_2$], [where ROdtp = (4-MeOPh)(RO)PS$_2$; R = Me (**1**), Et (**2**)] and bipyridyl-type ligands as neutral building blocks.[11]

Results and Discussion

Recently, following the one-step reaction between alcohols and diorgano-dithiadiphosphetane disulfides (ArPS$_2$)$_2$ (where Ar = 4-MeOPh, Ph), in the presence of nickel chloride, square planar phosphonodithioato complexes have been synthesised.[12]



R = Me (**1**), Et (**2**); Ar = 4-MeOPh

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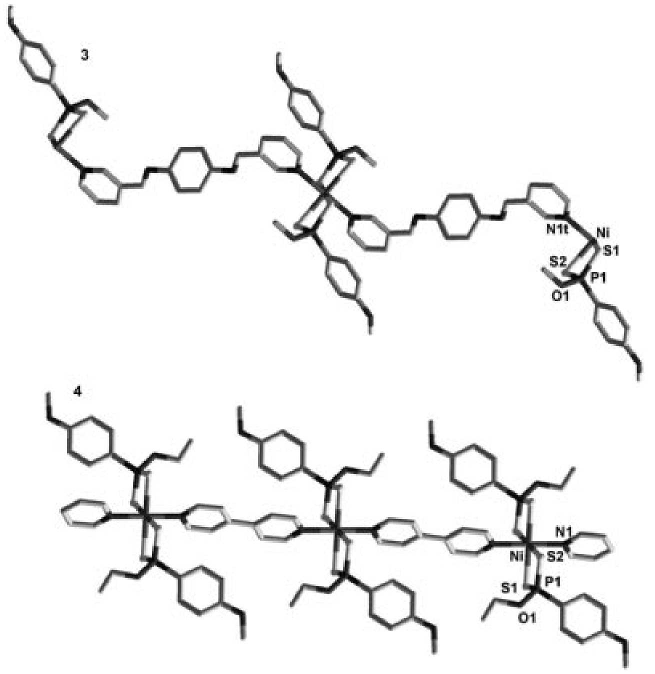

Figure 1. Linear and zigzag polymeric chains of compounds **3** and **4**; hydrogen atoms have been omitted for clarity

The reactivity of these complexes towards pyridine ligands to form octahedral adducts has been studied both in solution and in the solid state,[13] and given the high values of the formation constants of the corresponding adducts,[14] we decided to exploit the tendency of these square-planar (dtp)Ni complexes to be axially coordinated by N−R−N multidentate ligands, such as bidentate bipyridyl-based spacers, to form $[Ni(ROdtp)_2]-(N-R-N)-[Ni(ROdtp)_2]-(N-R-N)-$ neutral polymers. We report here the synthesis and the structural characterisation of the 1:1 coordination polymers $[Ni(MeOdtp)_2(bdpy)]_\infty$ (**3**) and $[Ni\text{-}(EtOdtp)_2(bipy)]_\infty$ (**4**), obtained by treating $[Ni(MeOdtp)_2]$ (**1**) with *N*,*N*′-bis-(3-pyridinylmethylene)-benzene-1,4-diamine (bdpy), and $[Ni(EtOdtp)_2]$ (**2**) with 4,4′-bipyridine (bipy), respectively. The bipy and bdpy spacers differ not only in the directionality of the two nitrogen donor atoms, but also in the distance between the N donor atoms, which is of about 7.2 and 14.1 Å for bipy and bdpy, respectively. In both **3** and **4** the nickel ion displays a distorted octahedral environment and the two bidentate phosphonodithioato units occupy the equatorial positions. Each pyridine unit of both bipy and bdpy is axially coordinated to the Ni^{II} ion of two $[Ni(ROdtp)_2]$ units [Ni−N, **3**: 2.129(3) Å; **4**: 2.136(2)], thus forming polymeric structures.

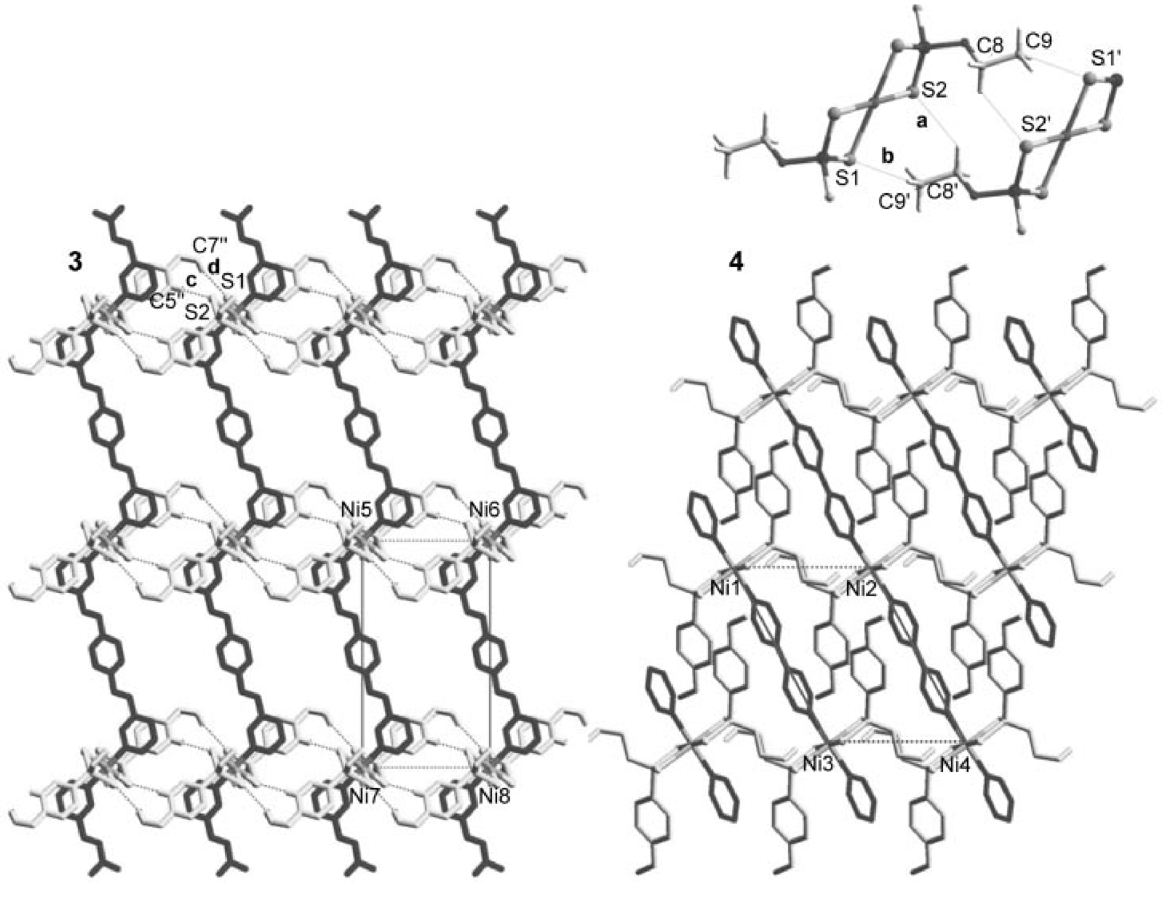

Figure 2. 2D grids viewed down the crystallographic axes *c* and *b* for **3** and **4**, respectively; bipy and bdpy are shaded to evidence the coordination polymers; interactions **a**···**b** (enlarged at the top for clarity reasons) and **c**···**d** connect adjacent chains: **a** S2···C8′ 3.76, H···S 2.96 Å; **b** S1···C9′ 3.90, H···S 3.01 Å; **c** S2···C5′′ 3.74, H···S 2.80 Å; **d** S1···C7′′ 4.00, H···S 3.05 Å; Ni1···Ni2 8.12; Ni1···Ni3 11.38; Ni5···Ni6 10.02, Ni5···Ni7 16.72 Å. Ni2−Ni1−Ni3 60°; Ni5−Ni6−Ni7 90°; ′: 1 + x, *y*, *z*; ′′: −x, −*y*, −*z*; hydrogen atoms except those involved in the described interactions have been omitted for clarity

The coordination of the pyridyl bases causes an increase in the Ni−S bond lengths [**1**: 2.2330(6), 2.2340(6); **2**: 2.2197(8), 2.2225(8); **3**: 2.4729(9), 2.4997(9); **4**: 2.4646(10), 2.4763(8) Å] and variations in the bond angles in the PS_2Ni metallacycle [S1−Ni−S2, **1**: 88.24(2), **2**: 88.14(3), **3**: 82.19(3), **4**: 82.54(2)°; S1−P−S2, **1**: 102.15(3), **2**: 101.57(4), **3**: 110.16(5), **4**: 109.43(4)°]. These variations closely resemble those found in analogous molecular adducts between phosphonodithioato complexes and pyridine derivatives.[13]

The main, common, structural feature of **3** and **4** is the presence of $[Ni(ROdtp)_2]$−N−R−N−$[Ni(ROdtp)_2]$−N−R−N− neutral parallel chains running in linear and zigzag lines with an Ni−Ni distance, through coordinate bonds, of 16.72 and 11.38 Å for **3** and **4**, respectively (see Figure 1). It is interesting to note that in **3** and **4** the 4-MeOPh rings bound to the phosphorus atom show different torsion angles with respect to the P−S bonds [**3**: S2−P−C1−C2 164.4(3)°; **4**: S1−P−C1−C2 99.1(2)°]. Moreover, the orientations of the 4-MeOPh groups with respect to the pyridyl rings in **3** and **4** are different: the mean planes of the two types of rings form an angle of 19.7° in the case of **3**, and 72.5° in the case of **4** (Figure 1). Weak hydrogen bonds, especially of the C−H···S type,[15] between the phosphonodithioato units connect the linear polymers in 2D rectangular and rhombic grids in the case of **3** and **4**, respectively, due to the different geometries of the spacers (see Figure 2). In the case of **3**, the grids feature openings of about 10 × 17 Å; however, in the crystal lattice two sets of symmetry-equivalent parallel and specular grids, shifted by *a*/2, *b*/2, *c*/2, pack in such a way that the bulky nodes of one net are complementary to the spaces within the other net (see Figure 3). Moreover, the sheets interact through weak hydrogen bonds between the bdpy and ROdtp units generating a three-dimensional network. In contrast, in the case of **4**, due to the short length of the bipy rods, the rhombic grids, arising from hydrogen bonding of the chains, do not have enough room to host anything else but the 4-MeOPh rings of two different ligand units (Figure 2).

In conclusion, the use of neutral (phosphonodithioato)Ni^{II} complexes, with predefined coordination sites, as molecular building blocks and suitable bipyridyl-based spacers allows us to assemble one-dimensional coordination polymers. The architecture of the polymers strongly depends on the geometrical features of the spacers and on the weak hydrogen bonds involving the substituents at the

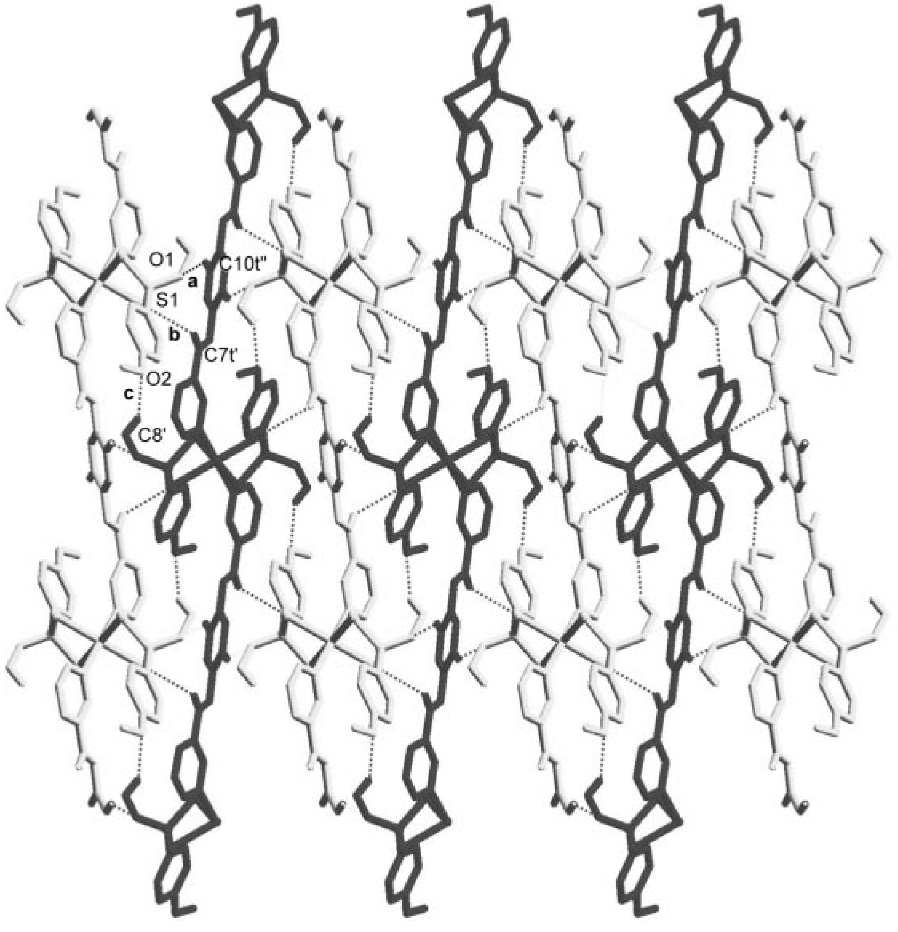

Figure 3. 2D view (*bc* plane) of **3** showing the complementary arrangement of the two sets of grids (dark and light) formed by H bonding of the chains. Hydrogen interactions: **a** O1···C10t'' 3.42, H···O 2.61 Å; **b** S1···C7t' 3.80, H···S 2.99 Å; **c** O2···C8' 3.17, H···O 2.35 Å; ': −x − 1/2, y − 1/2, −z − 1/2; '': x + 1/2, −y + 3/2, z + 1/2; hydrogen atoms except those involved in the described interactions have been omitted for clarity.

phosphorus atoms, which play an important role in the packing of the molecules. Further systematic work is now in progress in our laboratories with the aim of studying the effects of the structural features of building blocks on the resulting supramolecular structures.

Experimental Section

Materials and Methods: Solvents and reagents were Aldrich products and used as purchased. The degree of purity of each compound was checked by CHNS and TLC analyses. Elemental analyses were performed with an EA1108 CHNS-O Fisons instrument. Infrared spectra were recorded on a Bruker IFS55 spectrometer at room temperature using a flow of dried air. Far-IR (500−50 cm^{-1}) spectra (resolution 2 cm^{-1}) were recorded as polythene pellets with a Mylar beam splitter and polythene windows. Middle-IR spectra (resolution 2 cm^{-1}) were recorded as KBr pellets, with a KBr beam splitter and KBr windows. FT-Raman spectra were recorded on the solid sample, dispersed in a KBr matrix (resolution of 2 cm^{-1}) on a Bruker RFS100 FT-Raman spectrometer, fitted with an In-Ga-As detector (room temperature) operating with a Nd-YAG laser (excitation wavelength 1064 nm) with an 180° scattering geometry, at an excitation power of 350 mW.

Syntheses: *N*,*N′*-Bis-(3-pyridinylmethylene)benzene-1,4-diamine (bdpy) was synthesised by an adaptation of literature procedures.[16] Compounds **1** and **2** were prepared as previously reported.[12]

$[Ni(MeOdtp)_2(bdpy)]_\infty$ (3): **1** (26.4 mg, 0.05 mmol) and bdpy (14.6 mg, 0.05 mmol) were reacted at 100 °C in a high-pressure Aldrich tube in 40 mL of a $MeOH/CHCl_3$ (1:1 v/v) mixture. After the reagents had completely dissolved, the reaction mixture was slowly cooled to room temperature. **3** (20.6 mg, 0.025 mmol, 50 % yield) was obtained as bright green crystals; m.p. 190 °C (decomp.). $C_{34}H_{34}N_4O_4P_2S_4Ni$ (811.55): calcd. C 50.3, H 4.2, N 6.9, S 15.8; found C 50.3, H 4.2, N 7.0, S 15.6. FT-IR: 1700 w, 1653 mw, 1625 ms, 1593 vs, 1541 mw, 1498 s, 1456 ms, 1365 mw, 1319 mw, 1305 m, 1295 ms, 1255 vs, 1182 s, 1112 vs, 1006 vs, 893 ms, 835 s, 800 s, 777 vs, 694 s, 659 vs, 645 s, 623 s, 546 vs, 525 m, 438 m, 418 mw, 383 m, 353 w, 326 w, 302 w, 280 mw, 267 w, 247 w, 227 mw, 203 w, 172 mw, 151 m, 140 mw, 121 mw, 101 m, 91 w cm^{-1}. FT-Raman (solid state, relative intensities in parentheses related to the highest peak taken equal to 10.0): 3054 (0.4), 1630 (2.6), 1582 (10.0), 1429 (0.6), 1320 (0.2), 1193 (2.1), 1157 (3.4), 1111 (0.7), 1034 (1.0), 984 (0.5), 892 (0.2), 824 (0.2), 664 (0.2), 545 (0.9), 399 (0.3), 265 (0.7), 136 (2.1), 89 (2.8) cm^{-1}.

$[Ni(EtOdtp)_2(bipy)]_\infty$ (4): **2** (10.2 mg, 0.018 mmol) and bipy (4.8 mg, 0.03 mmol) were reacted at 100 °C in a high-pressure Aldrich tube in 35 mL of an $EtOH/CHCl_3$ (1:1 v/v) mixture. After the reagents had completely dissolved, the reaction mixture was slowly cooled to room temperature. The product was obtained quantitatively as tiny yellow-green needles. M.p.: 230 °C (decomp.). $C_{28}H_{32}N_2O_4P_2S_4Ni$ (709.45): calcd. C 47.4, H 4.5, N 3.9, S 18.1; found C 47.4, H 4.2, N 4.0, S 17.4. FT-IR : 1598 vs, 1568 m, 1531 mw, 1500 s, 1484 m, 1455 m, 1440 m, 1403 ms, 1389 mw, 1297 s, 1259 vs, 1216 m, 1178 ms, 1114 vs, 1064 m, 1029 vs, 949 vs, 830 m, 810 ms, 784 s, 728 mw, 660 ms, 646 s, 628 ms, 545 s, 521 mw, 500 w, 475 w, 438 m, 383 m, 353 w, 326 w, 302 w, 279 mw, 254 w, 247 w, 227 mw, 203 w, 176 w, 151 m, 140 mw, 121 mw, 101 m, 91 w cm^{-1}. FT-Raman (solid state, relative intensities in parentheses related to the highest peak taken equal to 10.0): 3066 (1.2), 3045 (1.5), 2941 (1.6), 2924 (1.6), 1604 (8.7), 1284 (10.0), 1113 (5.7), 1062 (3.1), 1018 (8.1), 659 (1.7), 633 (1.1), 545 (5.8), 379 (0.9), 359 (1.5), 101 (9.3), 68 (6.7) cm^{-1}.

X-ray Crystal Structure Determination: Data collection for **3** was performed on a Bruker SMART APEX CCD area detector diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), equipped with an Oxford Cryosystems open-flow cryostat.[17] Data collection for **4** was performed on a Siemens SMART CCD diffractometer with a monochromated synchrotron radiation (λ = 0.68710 Å, ω rotation with narrow frames) using a silicon 111 monochromator, at 120(2) K. SADABS corrections were applied for **3**, while no absorption corrections were applied for **4**. The structures were solved by direct methods using SHELXS-97[18] and all non-hydrogen atoms were located using subsequent difference Fourier methods.[19] Hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, except for the methyl groups for **4**, which were located by difference Fourier methods and treated as rigid rotors. All crystal structure diagrams were prepared using the OLEX program.[20]

Compound 3: $C_{34}H_{34}N_4NiO_4P_2S_4$, monoclinic, space group $P2_1/n$, a = 10.016(2) Å, b = 16.724(3) Å, c = 11.412(2) Å, β = 103.902(4)°, V = 1855.6(11) Å^3, Z = 2, $D_{calcd.}$ = 1.452 Mg/m^3. R = 0.0465, wR = 0.0908 for 2670 observed independent data.

Compound 4: $C_{28}H_{32}N_2NiO_4P_2S_4$, triclinic, space group $P\bar{1}$, a = 8.13(3) Å, b = 9.910(3) Å, c = 10.126(3) Å, α = 89.479(7), β = 76.330(5), γ = 77.675(6)°, V = 773.0(4) Å^3, Z = 1, $D_{calcd.}$ = 1.524 Mg/m^3. R = 0.0397, wR = 0.0884 for 2981 observed independent data.

CCDC-227421 for **3** and CCDC-227422 for **4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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