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Dithiophosphonic acids and nickel(II) complexes

SOLVENT-FREE MECHANOCHEMICAL SYNTHESIS OF DITHIOPHOSPHONIC ACIDS AND CORRESPONDING NICKEL(II) COMPLEXES

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Abstract

We report a green chemistry route for dithiophosphonic acids of the type [HS₂P(OR)(4-MeOC₆H₄)] [R = H, (1); Me (2); Et (3); ^{*i*}Pr (4)]. The different dithiophosphonic acids formed through the stoichiometric addition of water or alcohols to Lawesson's Reagent (molar ratio 2:1), followed by an intimate grinding of the mixture (mechanochemistry). The products formed without the use of solvent or external heat in less than 5 minutes. The acids are formed with 100% atom economy, and because they form in essentially quantitative yield, are also formed with > 98% atom efficiency and an E-factor = 0, because no waste is produced. Of importance is that this methodology is different from conventional methods in forming dithiophosphonic acids where the use of organic solvents, added heat, long reaction times and lower yields are commonplace. We further demonstrate that nickel(II) complexes can form directly from the *insitu* generated acids. Thus, the reaction between **1-4** and NiCl₂ · 6 H₂O (molar ratio 2:1) lead to complexes of the type [Ni{S₂P(OR)(4-MeOC₆H₄)}₂] [R = H, (**5**); Me (**6**); Et (**7**); ⁱPr (**8**)] with no use of organic solvent. All compounds were characterized or verified by a combination of ¹H, ³¹P NMR, elemental analysis (solids), and FT-IR.

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Keywords

Green chemistry; dithiophosphonic acid; solvent-free; nickel(II) complexes; atom economy; hydrated

INTRODUCTION

Dithio-organophosphorus compounds are used in diverse and important areas of the chemical and allied industries. Applications range from anti-oxidant additives in the oil- and petroleum industry¹ to green lubricants², agricultural pesticide derivatives³ and metal ore extraction reagents in the mining industry⁴. While there is an initiative to become more aware of solvents from nature⁵, conventional synthetic methods still greatly rely on inherently wasteful organic solvents, which are toxic to the environment. Solvent-free methods are therefore considered more beneficial.⁶

The phosphorus-1,1-dithiolate class of compounds is multifaceted and includes, amongst others, the dithiophosphates **A**, dithiophosphinates **B**, and dithiophosphonates **C**, shown in Figure 1. The dithiophosphonato ligand, **C**, which is the focus of the present study, may be described as a hybrid of **A** and **B**.⁷ The literature reveals that $[HS_2PR(OR')]$ type acids are less common as compared to the better established $[HS_2PR_2]$ and especially $[HS_2P(OR)_2]$ counterparts.⁸ A reason for this may be the unavailability of key starting materials, but this problem was overcome with the development of dimers of the type $[RP(\mu-S)S]_2$ (R = aryl). Such dimers have traditionally been used by organic chemists to convert ketones into thiones.⁹

The preparation and characterization of the phenyl substituted dimer $[PhP(\mu-S)S]_2$ was first described in 1962 but the procedure is not in line with green chemistry procedures and requires the use of wasteful excess and toxic H₂S gas introduced sub-surface at elevated temperature (> 210°C) with the release of copious amounts of corrosive HCl as by-product.^{10,11} A significant improvement came in 1978 when Lawesson and co-workers reported¹² the reaction between the electron-rich aromatic anisole and P₄S₁₀ which leads directly to the formation of the dimer 2,4-bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide, [(4-MeOC₆H₄)P(μ -S)S]₂, Scheme 1. Anisole serves as both the solvent and reactant and this dimer has become known as Lawesson's Reagent (**LR**); it is commercially available and its general chemistry has been comprehensively reviewed.¹³

Although the conversion of ketones into thiones still occupy the largest part of **LR**'s utility, alcoholysis of dithiadiphosphetane dimers, including **LR**, yields the corresponding dithiophosphonic acid.¹⁴ A wide variety of alcohols are now known to be utilized in this manner,

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including unsaturated (allyl), sterically demanding (adamantyl), and quasi-strained (cyclopentyl) alcohol, as well as silanols and trialkyl silanols.¹⁵

As part of our ongoing studies on phosphorus-1,1-dichalcogenates of the late-transition metals (Groups 10-12),¹⁶ we report *i*) an entirely green and solvent-free synthesis of dithiophosphonic acids with 100% atom economy and *ii*) the direct formation of the corresponding nickel(II) complexes using the unmodified acid ligands.

RESULTS AND DISCUSSION

Preparation of dithiophosphonic acids

The *conventional synthetic methodology* used to form dithiophosphonic acids, $HS_2PR(OR^2)$, typically starts with the anisyl substituted Lawesson's Reagent (**LR**), although the phenetyl¹⁷ and even ferrocenyl¹⁸ versions of the dimer have also been successfully utilized. **LR** is placed in a Schlenk tube and heated to ~80°C using an oil bath followed by the slow addition of the appropriate alcohol. A small amount of inert solvent such as toluene is added to give the magnetic stirrer bar mobility. The addition of solvent immediately leads to a dilution effect, which in turn results in more time needed for the reaction to proceed to completion. Afterward, the acid needs to be separated from the solvent, which requires further heating for distillation, and loss of yield is inevitable. The acid is generally very viscous and difficult to manipulate but can be precipitated as an ammonium salt by bubbling ammonia through the solution in an ice bath at 0°C which turns it into a free-flowing powder upon drying.

By contrast, the *green synthetic methodology* described in the present study circumvents many of these drawbacks. **LR** is placed in a Schlenk tube and is covered under a blanket of nitrogen to avoid hydrolysis, *vide infra*. At room temperature, 2 molar equivalents of mono-hydroxy alcohols (i.e. simple alcohols such as MeOH, EtOH, etc.) are dripped directly onto **LR**; higher alcohols such as diols (ethylene glycol), pentaerythritol, etc. would require different molar ratios. Mechanochemical synthesis in general terms refers to reactions induced by the input of mechanical energy, usually grinding.¹⁹⁻²⁰ Once the alcohol is added, the mixture is gently grinded, Scheme 2. This process appears very discouraging at first because it seems that no reaction is taking place. For this reason previous attempts of a mechanochemical synthesis for this system have been prematurely abandoned. But the reaction dynamics changes quite

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dramatically in less than 5 minutes when the mixture turns viscous, which was subsequently identified to be generated by the acid product. This highlights another advantage of the green method, namely the reaction both starts and finishes at room temperature, giving no opportunity for any alcohol to evaporate through extensive heating during the reaction. By contrast, conventional methods require much longer (> 30 min.) reaction times.

Theories to comprehensively explain the reaction taking place at the solid-liquid interface during solvent-free mechanochemical processes are lacking. Following from work by Paul and Curtin,²¹ Bala and Coville reviewed different scenarios for reactions in the melt²² (a sub-class of solvent-free reactions) most commonly observed for solid-solid and solid-gas reactions, which can be described as binary systems with a minimum eutectic temperature. In this study, the focus is on a solid-liquid interface system which appears to be a rare example for a reaction, for which both start and finish are at room temperature. We focused on alcohols in liquid form as reagents, which turned out to be very efficient for this particular transformation; we also attempted materials with alcohol functionalities in the solid state, such as cholesterol etc., but they were less efficient and require further optimization.

Preparation of nickel(II) dithiophosphonate complexes

Once we were able to routinely form dithiophosphonic acids **1-4**, we investigated their use as ligands to form metal complexes. Here the goal was not to produce new metal complexes through conventional solvent-based methods, but instead to show a new green chemistry and sustainable synthetic methodology. We started from the hexahydrate NiCl₂ · 6 H₂O (distinct green colour) and obtained the corresponding Ni(II) dithiophosphonates, which have a distinctly purple colour, allowing to detect product formation by simple colorimetric methods. The metal most frequently reported to form complexes with the dithiophosphonato ligand⁷, is Ni(II); yet to date these complexes were all formed by traditional methods. Our methodology differs from the conventional methods in a number of ways: *i*) we found no need to first convert the ligands to their respective ammonium or sodium salts, but used the ligands in the acid form directly; *ii*) this had the advantage that no filtration step (to remove NH₄Cl and/or NaCl) was later needed; *iii*) the reaction proceeded without solvent and at room temperature, and *iv*) there was no need to first isolate the ligand before using it for complex formation, since the ligand formed in > 98%

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yield in the first step, without unwanted side-products, and complex formation was immediate by adding the Ni(II) precursor. The yields for the acids were all exceptionally high, which we attribute to *i*) the 100% concentration of the reactants in intimate contact with each other (no solvents, no dilution effects) and *ii*) the oxophilic nature of the P atom which would always prefer P-O bonding to P-S bonding, the former providing a continuous driving force for the reaction to reach completion. The yields for the nickel(II) complexes were slightly lower but still much higher than could be achieved by synthesis through conventional methodology, which we ascribe to the absence of salt formation as a byproduct, which makes extraction and filtration steps unnecessary. The reaction is shown in Scheme 3.

Again, as is the case for the acids, we propose a mechanochemical synthesis for this system, which had been overlooked due to the preconceived notion that the reaction always requires a solvent. For example in 1997, Verani and coworkers reported²³ a number of $[Ni{S_2P(OR)(4-MeOC_6H_4)}_2]$ (R = Me, Et, ⁱPr) complexes similar to those in the present study. A typical synthesis started in a favorable green chemistry manner by adding equivalent amounts of nickel(II) chloride and **LR**, but then turned to a conventional route by suspending the solids in a huge excess (100 mL) of the appropriate alcohol, ROH. The stirred reaction mixture was refluxed for 1--3 h, then filtered and the solvent was removed under vacuum. In the present study, we hope to demonstrate, that the excess alcohol is not required, thus making unnecessary additional reflux, filtration, and solvent and waste removal steps.

In another study, that used a large excess of alcohol, Ni(II) complexes similar to **6** and **7** were formed by mixing and refluxing two ROH solutions, namely **LR** and ROH (R = Me or Et, 0.02 M) and NiCl₂ and ROH (0.02 M) in a closed vial and single crystals were grown from the solution. These complexes were analysed solely by X-ray and IR studies, and it is thus not clear whether they formed from acids or by another mechanism, and whether the bulk material formed is the same as the single crystals.²⁴

We are aware of only two examples where Ni(II) had previously been used in a solvent-free system for any ligand, the one was obtained by mechanochemical and the other by thermochemical means. The use of dimethylglyoxime (H₂dmg) as a chelating agent for the gravimetric analysis of Ni(II) was discovered by Tschugaeff in 1905.²⁵ Yet the

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mechanochemical preparation of $[Ni(Hdmg)_2]$ and $[Ni(H_2dmg)_2]^{2+}$ from nickel halides and H₂dmg was only reported a century later.²⁶ Thermochemical work by Fabrizzi and coworkers focused²⁷ on a Ni(II) bis(diamine) complex having a pink-red nitro isomer and a blue coloured nitrito isomer. The facile reversible thermally induced nitro / nitrito interconversion for the design of thermochromic devices was studied.

Characterisation

We report the first series of characterized dithiophosphonic acids formed by green chemistry methods. Due to the viscous nature of the acids, we did not attempt to measure the boiling points. The melting points for the Ni(II) complexes were determined and the melting points of complexes 7 and 8 corresponded within 1°C to those from identical complexes previously reported through more cumbersome means.²³ Together with satisfactory elemental analysis (see Table 1) we were satisfied with the bulk purity. The determined melting point of complex 6differed substantially from the literature value,²³ but we did establish bulk purity based on elemental analysis and NMR results and concluded that after work-up the bulk powder contained no solvated molecules in the structure. We prepared and characterized complex 5, and came to the same conclusion. However, when 5 was formed in situ and dissolved in water for about 1 week (no further work-up), we discovered through X-ray analysis that it formed the hydrated ammonium salt of the Ni(II) complex, namely $(NH_4)_2[Ni\{S_2P(O)(4-C_6H_4-OMe)\}_2]$, 9. There are related neutral complexes reported²⁸ but with THF solvates, and not with H₂O, and with much higher melting points. In the ¹H NMR spectra the S-H signals for the acids 1-4 are the only peculiarity to point out. There are other reports where the S-H proton for acids of the related dithiophosphates are not observed or recorded.²⁹ We observed the NMR signal of the S-H proton for 1 at $\delta = 1.76$ and for 2 at $\delta = 3.41$ whilst no S-H signal was observed for 3 and 4. Note the distinct upfield shift for 1 compared to 2; a similar effect was observed for the corresponding complexes 5 and 6 in the 31 P NMR spectra, see below. We nevertheless substituted H₂O for D₂O (1) and MeOH for CD_3OD (2) and noted, that the previously observed S-H protons have now both disappeared. The ³¹P NMR spectra of all the acids show singlet peaks in the range 74 to 89 ppm, but this requires a cautionary note. Initially, we made no attempt to keep the reaction in an inert environment because we reasoned the product forms rapidly and there is not sufficient time

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for side-products to form. But the ³¹P NMR spectrum for each acid we obtained, under those circumstances, showed two singlets ca > 10 ppm apart, with the upfield signal of lower intensity but with growing intensity over time, and with further signals also appearing upfield over time. What we observed with regards to by-product formation was akin to a reported series of elegant hydrolysis studies performed by Burn et al.³⁰⁻³² more than 2 decades ago. They followed mechanisticaly and kinetically by ³¹P NMR the hydrolysis of zinc(II) dithiophosphate $[Zn{S_2P(OEt)_2}]$ in 10-fold water excess at 85°C and could observe the replacement of S atoms by O atoms, as well as C-O bond cleavage, giving rise to further signals at higher field, right to the final hydrolysis product, H_3PO_4 , at 0 ppm. It is clear from those studies that the ultimate fate of possibly all phosphorus-1,1-dithiolate acids, salts, and complexes, in the presence of moisture (hydrolysis) and oxygen (oxidation), is phosphoric acid, but this can be well avoided by excluding both H₂O and O₂ from the system. The ³¹P NMR spectrum of the Ni(II) complexes showed singlets for both $[Ni{S_2P(OH)(4-MeOC_6H_4)}_2]$ 5 at 58.1 ppm and for $[Ni{S_2P(OCH_3)(4-MeOC_6H_4)}_2]$ $MeOC_6H_4$]₂] 6 at 104.4 ppm; a remarkable difference of 46 ppm between seemingly closely related complexes. The chemical shift observed for 5 is similar to that reported for the complex $[Ni{S_2P(OH)(4-MeOC_6H_4)}_2(THF)_2]$ by Rothenberger and coworkers, but in their case they found two resonance peaks at 42.3 and 56.9 ppm, which they assign to partial decomposition.²⁸ We found only one peak, however. It should also be pointed out that the heavily solvated tetranuclear Ni(II) complex [Ni₂{AnP(O)S₂}₂(THF)₂(H₂O)₂]₂ displays a ³¹P NMR resonance at 56.1 ppm.³³

Complex **5** was obtained in high yield and displayed a singlet ³¹P NMR peak closely related to similar compounds. The starting complex NiCl₂ \cdot 6 H₂O (0.50 g) leads to the release of 12.62 mmol of water (*ca*. 0.23 mL) upon reaction with the acid ligand. This is a sufficient volume to already wet all generated powder of the product and only requires a few additional drops of water to partly solubilise the complex. Amongst all Ni(II) complexes **5-8** formed, complex **5** was by far the most soluble in water. As a result, we attempted to grow crystals of **5** from a water solution. X-ray quality single crystals indeed formed from the aqueous solution by slow evaporation of the solvent, but instead of **5**, X-ray diffraction revealed the isolated crystals to be complex **9**. At first glance it appears as though the ligand had undergone a reduction in going

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from a negative to double negative charge, as shown in Figure 2A. But closer inspection revealed that a double deprotonation occurred, followed by the coordination of the ligand resulting in the best binding mode to the Ni(II) center (i.e. $NiS_4 vs. NiO_2S_2$), shown in Figure 2B, while the proposed formation of complex **9** is shown in Scheme 4.

This is the first example of a decidedly 'green structure' for any Ni(II) dithiophosphonate complex and contains only water in the crystal, all other reported solvated structures contain organic molecules, especially THF. The structure is shown in Figure 3. The molecular structure is unsurprising, showing a 4-coordinate, slightly distorted square-planar geometry around the Ni(II) center. The bond lengths and angles are comparable with related structures⁷ and the P = O groups are in a *trans* orientation with respect to each other, generated by the Ni atom that acts as a crystallographic inversion center. Details of the X-ray data are shown in Table 2.

Although this paper describes solvent-free methods to form acids and corresponding complexes, knowledge about the solubility of compounds is often useful. To this end, a series of qualitative solubility tests were performed on all the compounds, **1-8**. A variety of solvents were tested over a wide range of dielectric constants, including protic/aprotic and polar/non-polar solvents. Noteworthy is for example how the acids are soluble in protic solvents such as water and ethanol, but the corresponding complexes are insoluble in those solvents. Results are shown in Table 3.

EXPERIMENTAL

General

Mechanochemical grinding was carried out in a standard Schlenk tube (~2 cm diameter) using a ball head glass rod under a blanket of nitrogen. Lawesson's reagent was either purchased from Aldrich or prepared according to literature procedures.¹⁵ All other reagents were purchased from Aldrich and used as received. ¹H and ³¹P NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer. Proton NMR chemical shifts (δ_{H}) are given in ppm and referenced internally to the residual proton impurity in the deuterated solvent. ³¹P NMR chemical shifts are reported relative to an 85% H₃PO₄ in D₂O as external standard. All NMR measurements were performed at 298 K. The yields were determined by performing the reaction in a dry pre-weighed Schlenk

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tube, weighing the sample after drying. Infrared spectra were recorded in the range 4000--380 cm^{-1} with a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

Synthesis

Hydroxy-4-methoxyphenyldithiophosphonic acid (1)

Lawesson's Reagent (1.00 g, 2.48 mmol) was placed in a clean and dry Schlenk tube, and distilled water (0.10 mL, 4.90 mmol) was added. The reactants were ground together for 15 min. This derivative took the longest to complete the reaction compared to alcohols, that took < 5 min. A viscous liquid formed. (1.06 g, 98.6%). ³¹P NMR (CDCl₃): δ = 74.1, ¹H NMR (CDCl₃): δ = 1.76 (s, 1H, SH), 3.71 (s, 3H, ArOMe), 6.83 (dd, ⁴*J*_{PH} = 2.6 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *m*-ArH), 7.51 (s, 1H, OH), 7.78 (dd, ³*J*_{PH} = 13.8 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *o*-ArH). Selected FT-IR (4000-350 cm⁻¹): 2945 (m), 2305 (b), 1595 (s), 1501 (s), 1256 (s), 1120 (s), 1023(s), 892(b), 803 (w), 612 (w), 526 (m).

(Methoxy)-4-methoxyphenyldithiophosphonic acid (2)

To Lawesson's Reagent (1.00 g, 2.48 mmol) in a clean and dried Schlenk tube, methanol (0.2 mL, 4.9 mmol) was added. The reactants were ground together for about 2 min. A viscous liquid resulted. (1.14 g, 98.5%). ³¹P NMR (CDCl₃): $\delta = 89.5$. ¹H NMR (CDCl₃): $\delta = 3.41$ (s, 1H, SH), 3.81 (d, ²*J*_{HH} = 8.7 Hz, 3H, CH₃), 3.85 (s, 3H, ArOMe), 6.92 (dd, ⁴*J*_{PH} = 3.5 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *m*-ArH), 7.88 (dd, ³*J*_{PH} = 14.4 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *o*-ArH). Selected FT-IR (4000-350 cm⁻¹): 2941 (m), 2433 (b), 1593 (s), 1498 (s), 1256 (s), 1114 (s), 827 (w), 679 (s), 530 (m).

(Ethoxy)-4-methoxyphenyldithiophosphonic acid (3)

To Lawesson's Reagent (1.00 g, 2.48 mmol) in a clean and dried Schlenk tube, ethanol (0.30 mL, 4.90 mmol) was added. The reactants were ground together for 3 min until a viscous liquid formed. (1.21 g, 98.9%). ³¹P NMR (CDCl₃): $\delta = 86.4$. ¹H NMR (CDCl₃): $\delta = 1.36$ (t, ³*J*_{HH} = 7.1 Hz, 3H, CH₃), 3.78 (s, 3H, ArOMe), 4.25 (m, ³*J*_{HH} = 7.2 Hz, 2H, CH₂), 6.92 (dd, ⁴*J*_{PH} = 3.3 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *m*-ArH), 7.88 (dd, ³*J*_{PH} = 14. 7 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *o*-ArH). Selected FT-IR (4000-350 cm⁻¹): 2941 (m), 2433 (b), 1593 (s), 1498 (s), 1256 (s), 1114 (s), 827 (w), 679 (s), 530 (m).

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Bis (Isopropoxy)-4-methoxyphenyldithiophosphonic acid (4)

To Lawesson's reagent (1.00 g, 2.48 mmol) in a clean and dried Schlenk tube, isopropanol (0.4 mL, 4.9 mmol) was added. The reactants were ground together for 3 min until viscous liquid formed. (1.27 g, 98.7%). ³¹P NMR (CDCl₃): $\delta = 84.3$. ¹H NMR (CDCl₃): $\delta = 1.40$ (d, ³*J*_{HH} = 6.0 Hz, 6H, CH₃), 3.82 (s, 3H, ArOMe), 5.08 (sept, ³*J*_{HH} = 6.4 Hz, 1H, CH), 6.95 (d, ³*J*_{HH} = 9.0 Hz, 2H, *m*-ArH), 7.90 (dd, ³*J*_{PH} = 14.6 Hz, ³*J*_{HH} = 9.0 Hz, 2H, *o*-ArH,). Selected FT-IR (4000--350 cm⁻¹): 2977 (m), 2434 (b), 1595 (s), 1499 (s), 1255 (s), 1111 (s), 961 (m), 828 (m), 617 (s), 530 (m).

$[Ni{S_2P(OH)(4-C_6H_4-OMe)}_2] (5)$

Non-green route: Ammonia gas was bubbled into compound **1** (1.00 g, 4.54 mmol) and NiCl₂ \cdot 6 H₂O (0.45 g, 1.92 mmol) was added and ground together for 5 min. The immediate formation of a purple complex resulted which was subsequently used for analysis and following work-up, gave the same result as that found for the 'green route'. Note: In the absence of further work-up, X-ray quality crystals of **9** were grown by slow evaporation of an aqueous solution. Because of the NH₄⁺ counterion, the same structure (**9**) can thus not be obtained by following the green route below.

Green route: Solid NiCl₂ · 6 H₂O (0.45 g, 1.92 mmol) was added to acid **1** (1.0 g, 4.54 mmol) and ground together for 5 min. The complex was dried under vacuum to give a purple solid (1.09 g, 96.3%). M.p.: 125°C. Anal. Calcd. for C₁₄H₁₆O₄P₂S₄Ni: C, 33.81; H, 3.24. Found: C, 32.91; H, 3.55%. ³¹P NMR (DMSO): $\delta = 58.1$. ¹H-NMR (DMSO): $\delta = 3.80$ (s, 3H, ArOMe), 6.95 (d, J = 8.0 Hz, 1H, *m*-ArH), 8.25 (d, J = 19.3 Hz, 1H, *o*-ArH). Selected FT-IR (4000--350 cm⁻¹): 3109 (m), 2559 (b), 1593 (s), 1499 (s), 1260 (s), 1113 (s), 1028 (s), 937 (s), 800 (w), 768 (s), 619 (s), 546 (s).

$[Ni{S_2P(OMe)(4-C_6H_4-OMe)}_2](6)$

A mixture of NiCl₂ · 6 H₂O (0.50 g, 2.13 mmol) and viscous acid **2** (1.00 g, 4.30 mmol) were ground together and an immediate purple complex resulted. The complex precipitated upon addition of water and was then filtered under vacuum to give a dry purple solid (1.08 g, 96.8%). Anal. Calcd. for C₁₆H₂₀O₄P₂S₄Ni: C, 36.59; H, 3.84. Found: C, 36.65; H, 3.77%. ³¹P NMR (CDCl₃): $\delta = 104.4$. ¹H NMR (CDCl₃): $\delta = 3.87$ (s, 3H, ArOMe), 3.99 (d, J = 14.8 Hz, 3H,

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CH₃), 7.00 (d, J = 5.9 Hz, 2H, *m*-ArH), 7.99 (d, J = 5.4 Hz, 2H, *o*-ArH). Selected FT-IR (4000-350 cm⁻¹): 2968 (m), 2292 (b), 1593 (s), 1501 (s), 1259 (s), 1116 (s), 962 (b), 827 (w), 616 (s), 549 (s).

$[Ni{S_2P(OEt)(4-C_6H_4-OMe)}_2](7)$

A mixture of NiCl₂ · 6 H₂O (0.48 g, 2.02 mmol) and viscous acid **3** (1.00 g, 4.00 mmol) was ground and an immediate purple complex resulted. Workup was performed as for **6** above. Dry purple solid (1.09 g, 97.8%). Anal. Calcd. for C₁₈H₂₄O₄P₂S₄Ni: C, 39.08; H, 4.37. Found: C, 39.12; H, 4.29%. ³¹P NMR (CDCl₃): $\delta = 101.9$. ¹H NMR (CDCl₃): $\delta = 1.35$ (t, J = 7.1 Hz, 3H, CH₃), 3.80 (s, 3H, ArOMe), 4.29 (d, J = 17.1 Hz, 2H, CH₂), 6.97 (d, J = 8.7 Hz, 2H, *m*-ArH), 7.91 (dd, J = 8.8 Hz, 14.6 Hz, 1H, *o*-ArH). Selected FT-IR (4000-350 cm⁻¹): 2971 (m), 2288 (b), 1593 (s), 1498 (s), 1257 (s), 1112 (s), 1020 (s), 800 (m), 616 (s), 551 (s).

$[Ni{S_2P(OiPr)(4-C_6H_4-OMe)}_2](8)$

A mixture of NiCl₂ · 6 H₂O (0.45 g, 1.92 mmol) and viscous acid **4** (1.00 g, 3.8 mmol) were ground together and an immediate purple complex resulted. Workup was performed as for **6** above. Dry purple solid (1.07 g, 96.7%). Anal. Calcd. for C₂₀H₂₈O₄P₂S₄Ni: C, 41.32; H, 4.85. Found: C, 41.39; H, 4.82%. ³¹P NMR (CDCl₃): $\delta = 97.8$. ¹H NMR (CDCl₃): $\delta = 1.41$ (d, J = 6.2 Hz, 6H, (CH₃)₂), 3.81(s, 3H, ArOMe), 5.22 (d, J = 1.2 Hz, 1H, CH), 7.00 (d, J = 5.8 Hz, 2H, *m*-ArH), 8.01 (d, J = 5.2 Hz, 1H, *o*-ArH). Selected FT-IR (4000--350 cm⁻¹): 2967(m), 2274 (b), 1593 (s), 1501 (s), 1260 (s), 1116 (s), 1023(s), 959(m), 800 (w), 616 (s), 550 (m).

Crystallography

A crystal of complex **9**, $(NH_4)_2[Ni\{S_2P(O)(4-C_6H_4-OMe)\}_2]$, with approximate dimensions $0.106 \times 0.256 \times 0.432$ mm, was mounted on a glass fibre with epoxy resin. All intensity and geometric data were collected on a Bruker APEXII CCD diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). APEXII software was used for preliminary determination of the unit cell.³⁵ Determination of integrated intensities and unit cell refinement were performed using SAINT.³⁶ The SADABS program was used to apply an empirical absorption correction.³⁷ The integration of the data yielded a total of 21960 reflections

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to a maximum θ angle of 28.51° (0.74 Å resolution). XPREP determined the space group to be C 1 2/c 1, with Z = 4 for the formula unit, C₁₄H₁₄NiO₄P₂S₄ · 2 NH₄ · 2 H₂O.³⁸ The structure was solved with XS³⁹ and subsequent structure refinements were performed with XL.⁴⁰ A complete listing of crystallographic data and parameters are reported in Table 2.

CONCLUSIONS

The first mechanochemical synthesis procedure is described for the formation of dithiophosphonate acid derivatives by using green chemistry methods with 100% atom economy and essentially 100% atom efficiency. The procedure circumvented tedious consecutive steps such as heating, reflux, filtration and solvent removal. In a proof-of-concept experiment, the acids were then used *in situ* to form Ni(II) dithiophosphonate complexes in high yield. A comparative analysis of the solubilities for all the compounds were also performed. The present study focuses on common alcohols in the liquid phase under ambient conditions. We are in the process of investigating the more challenging mechanochemical reaction where precursor alcohols are in the solid phase.

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Entry	Yield	m.p.	³¹ P	Elem.	
	(%)	(°C)	NMR	anal.	
			(ppm)	(%)	
				Н	С
1 ^a	98	visc.	74.1	N/O	
		liquid			
2	98	visc.	89.5	N/O	
		liquid			
3	99	visc.	86.4	N/O	
		liquid	(102.9) ^h		
4	98	visc.	84.3 /	N/O	
		liquid	84.4 ^c		
5 ^b	96	125	58.1	3.55	32.91
		$(N/A)^d$	(56.1) ^e	(3.24)	(33.82)
6	96	160	104.4	3.77	36.65
		(184) ^f	(105.7) ^g	(3.84)	(36.59)
7	97	130	101.9	4.29	39.12
		(131) ^f	(102.2) ^g	(4.37)	(39.08)
8	97	167	97.8	4.82	41.39
		(168) ^f	(99.1) ^g	(4.85)	(41.32)

Table 1 Yield, melting points, ³¹P NMR and elemental analyses data for 1-8

N/O: not obtained. a: all four acids (1-4) are viscous colourless liquids; b: all four Ni(II) complexes (5-8) are purple solids; c: in d_6 -DMSO; d: N/A = not available; m.p. for related THF solvated [Ni{S₂P(OH)(4-MeOC₆H₄)}₂(THF)₂] and [Ni{S₂P(OH)(4-MeOC₆H₄)}₂(THF)₄] is 195 (dec.) and 250°C (dec.), respectively, ref. 28; e: [Ni₂{AnP(O)S₂}2(THF)₂(H₂O)₂]₂ δ = 56.1 ppm (An = anisyl), ref. 33; f: ref. 23; g: ref. 34; h: as ammonium salt, ref. 15.

Table 2. Crystal data and	i structure refinement of 9.	
Empirical formula	$C_{14}H_{14}NiO_4P_2S_4\cdot 2NH_4\cdot$	
	2H ₂ O	
Formula weight	567.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>C</i> 2/ <i>c</i> (no. 15)	
Unit cell dimensions	a = 23.7087(15) Å	$\Box \Box = 90^{\circ}.$
	b = 7.4340(4) Å	$\Box \Box = 105.507(4)^{\circ}.$
	c = 13.4003(7) Å	$\Box = 90^{\circ}.$
Volume	2275.8(2) Å ³	
Z	4	
Density (calculated)	1.6555 g/cm^3	
Absorption coefficient	1.394 mm ⁻¹	
F(000)	1176.00	
Crystal size	$0.559 \times 0.322 \times 0.106 \text{ mm}$	
Theta range for data	1.78 to 28.51°.	
collection		
Index ranges	$-31 \le h \le 31, -9 \le k \le 9, -17$	
	≤1≤17	
Reflections collected	21960	
Independent reflections	$2865 (R_{int} = 0.0290)$	
Completeness to theta =	99.34%	
28.5138°		
Absorption correction	Semi-empirical from	
	equivalents	
Max. and min.	0.866 and 0.509	
transmission		
Refinement method	Full-matrix least-squares on	
	F ²	
Data / restraints /	2865 / 0 / 147	
parameters		

Table 2. Crystal data and structure refinement of

Goodness-of-fit on F ²	1.0318	
Final R indices	R1 = 0.0473, wR2 = 0.1262	
[I>2sigma(I)]		
R indices (all data)	R1 = 0.0492, wR2 = 0.1282	
Largest diff. peak and	1.8737 and -0.5040 e · Å ⁻³	
hole		

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Entry	Acetone	CH ₃ CN	EtOH	Hexane	Ether	CH ₂ Cl ₂	Water	THF
1	Ι	S	VS	Ι	PS	PS	VS	S
2	Ι	S	VS	Ι	PS	PS	S	S
3	Ι	Ι	VS	Ι	PS	PS	VS	S
4	Ι	S	VS	Ι	PS	PS	S	S
5	PS	Ι	PS	Ι	PS	S	S	VS
6	PS	Ι	PS	Ι	PS	VS	Ι	VS
7	PS	Ι	PS	Ι	PS	VS	Ι	VS
8	PS	Ι	PS	Ι	PS	VS	Ι	VS

Table 3. Solubility data for compounds 1-8

Key to table: I = Insoluble (the material was quantitatively recovered after filtration); PS = PartlySoluble (10% of the material dissolved); S = Soluble (80% of the material dissolved); VS = Very Soluble (a clear solution emerged immediately). The solubility data is based on the following experimental criteria: 0.02 g of the compound was dissolved in 1.0 mL of the appropriate solvent and was hard shaken for 5-10 seconds at 23°C

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Figure 1 Different types of the most common phosphor-1,1,-dithiolates.

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Figure 2. Complex 9 formed through a double deprotonation of the ligand (A), followed by coordination resulting in the best binding mode (B).

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Figure 3. ORTEP representation of the molecular structure of Ni(II) complex **9**. Symmetry code for the symmetry generated atoms: -x, 2-y, -z. Selected bond lengths (Å) and angles (°): Ni-S(1) 2.214(1), Ni-S(2) 2.219(1), S(1)-P(1) 2.044(1), S(2)-P(1) 2.042(1), P(1)-O(1) 1.510(2), P(1)-C(1) 1.801(3), S(1)-Ni-S(2) 88.9(1), Ni-S(2)-P(1) 84.9(1), S(1)-P(1)-S(2) 98.9(1), S(1)-P(1)-O(1) 115.6(1), S(1)-P(1)-C(1) 107.6(1), A complete listing can be found in the Supplementary information.

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Scheme 1 Synthesis of the dimer $[PhP(\mu-S)S]_2$ (above) and of Lawesson's Reagent (LR) (below).

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Scheme 2 Comparison between the "traditional" and "green" method for the formation of dithiophosphonic acids. Note the differences in terms of solvent, temperature and time.

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Scheme 3 Synthesis of the Ni(II) complexes 5-8.

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Scheme 4. Proposed formation of complex 9 from aqueous solution.

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