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Volume 40 | Number 1 | January 2016 | Pages 1–846

NJC
New Journal of Chemistry
www.rsc.org/njc
A journal for new directions in chemistry

ISSN 1144-0546

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/x0xx00000x

1,2-bis(diphenylphosphino)ethane nickel(II) O,O′-dialkyldithiophosphates as Potential Precursors for Nickel Sulfides

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

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In this work, three heteroleptic Ni(II)dppe dithiophosphate complexes $[Ni\{S_2P(OC_2H_5)_2\}(dppe)]B(C_6H_5)_4$ (**1**), $[Ni\{S_2P(OCH(CH_3)_2)_2\}(dppe)]PF_6$ (**2**) and $[Ni\{S_2P(OCH(CH_3)_2)_2\}(dppe)]B(C_6H_5)_4$ (**3**) (dppe = 1,2-bis(diphenylphosphino)ethane) have been synthesized and characterized by analytical and spectroscopic techniques (microanalysis, IR, UV-Vis., ^1H, ^{13}C and ^{31}P NMR spectroscopy) as well as single crystal X-ray crystallography. The crystal structures of all complexes displayed a distorted square planar geometry around the Ni(II) center bonded through two sulfur atoms of the dithiophosphate ligand and two phosphorus atoms of the dppe. TGA results indicated that all three compounds display loss of solvents at the outset and decompose to Ni-S phase systems, hence, may act as potential precursor for nickel sulfides. Investigations indicated that the bulkiness of counter anions as well as alkyl fragment of the dithiophosphate ligands does not have any effect on the morphologies of as-synthesized nickel sulfide.

1. Introduction

Nickel sulfide is known to have various stoichiometries *viz.* Ni_3S_2, $Ni_{3+x}S_2$, Ni_4S_{3+x}, Ni_6S_5, Ni_7S_6, Ni_9S_8, Ni_3S_4, NiS_2 and NiS.[1] The existence of different stoichiometries make nickel sulfide an attractive and potentially important material in a diverse number of technical applications such as electrodes, battery materials, hydrogenation catalysts, and transformation tougheners for complex ceramics[2] and also a potential competitor for silicon in thin film solar cells.[3]

Various methods have been used to synthesize nickel sulfide nanostructures which utilizes solvothermal method[4] to synthesize urchin-like NiS and also uses γ-irradiation to produce NiS hollow nanospheres.[5] Alternatively, sonochemical method[6] and a microemulsion system[7] also produced NiS nanoparticles.

Additionally, a variety of single source molecular precursors have been utilized for the synthesis of nickel sulfides for example solventless thermolysis of a nickel alkylthiolate molecular precursor which produces nanorods and triangular nanoprisms of NiS.[8] Also, thermal decomposition of single-source precursors such as O-alkyl xanthates[9] and their pyridine adducts,[10] mercaptobenzothiazole,[11] $(tetramethylethylenediamine)Ni(SCOC_6H_5)$,[12] 1,1,5,5-tetra-iso-propyl-2-thiobiuret and dithiobiuret[13] produced nickel sulfide with varying morphologies and phases. Also, polysulfide $[Ni(N\text{-}methylimidazole)_6]S_8$ in a hot coordinating solvent formed a mixture of rods and spheres of NiS, ellipsoidal NiS nanoparticles, alpha or beta NiS nanocrystals, and NiS_2 or $Ni_{1-x}S$ nanocrystals.[14] Nickel(II) complexes with thio- and alkylthio-urea,[15] N-(dialkylcabrothioyl)-nitrosubstituted benzamide[16], dithioacetylacetonato[17] have also been deployed as a single source precursors for nickel sulfides. Nickel(II) dithiocarabamates have also been utilized as a single source precursors for nickel sulfides.[18,19] We had also reported the synthesis of nickel sulfide using heteroleptic Ni(II)dithiocarabamato(dppe) complex and monitored the influence of counter-anion on phase and morphology of as-synthesized material.[20]

Metal dialkyldithiophosphate,[21,22] dialkyldithiophosphinato[23] complexes and their selenium analogues[24] can also be the potentially ideal candidate as single-source precursors because of their accessible variety and stability.[25] The use of single-source precursors for the preparation of two different materials have been demonstrated earlier by O'Brien *et al.*[26] Just by changing the decomposition temperature, they have successfully prepared nickel selenide as well as nickel phosphide thin films using imido-bis-

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(diisopropylthioselenophosphinate) nickel(II), Ni[^{i}Pr$_2$P(S)NP(Se)^{i}Pr$_2$]$_2$ as single source precursor.

Although homoleptic Ni(II) dialkyldithiophosphate complexes have been utilized as a single source precursors (*vide supra*). However, to the best of our knowledge and findings, nickel dithiophosphate complexes $[Ni(S_2P)(OR)_2(dppe)]^+X^-$ have been synthesized before with different counter anions by Zdeněk Trávníček *et al.*[27] but never be explored as possible single-source precursor for nickel sulfides. With these viewpoints and in the quest for new precursors for nickel sulfides in different morphologies, we wish to report the synthesis, characterization and thermal decomposition products of the heteroleptic complex cation $[Ni\{S_2P(OR)_2\}(dppe)]^+$ with different counter anions viz. PF_6^-, BPh_4^-.

2. Experimental

2.1 Materials and Physical Measurements

All synthetic manipulations were performed under ambient atmosphere. Solvents were dried and distilled before use by following standard procedures. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance III HD FTNMR spectrophotometers. Chemical shifts were reported in parts per million (ppm) using TMS as internal standard for ^{1}H and ^{13}C NMR and phosphoric acid for ^{31}P NMR. Elemental analysis was performed on an Exeter analytical Inc. "Model CE-440 CHN analyser". UV-Vis spectra, in dichloromethane solution, were recorded on a SPECORD 210 PLUS BU spectrophotometer. Structural characterization of the nickel sulfides was done using powder X-ray diffraction (PXRD) measurements using a Bruker AXS D8 Discover X-ray diffractometer, with Ni-filtered Cu Kα_1 radiation (λ = 1.5405 Å). Small quantities of the decomposed products were dispersed in ethanol by sonicating for about 3 min. 5 ml of the suspension was placed on copper grids using a microliter pipette for SEM measurements which were carried out using a Hitachi S-4800 scanning electron microscope.

2.2 General Syntheses

2.2.1 Synthesis of bis (O,O'-dialkyldithiophosphate)nickel(II)

Phosphorus pentasulfide (2.220 g, 5 mmol) was placed in a three necked round bottom flask equipped with N_2 inlet, chemical inlet and a condenser. Ethanol (5mL)/2-propanol (7.5 mL) was poured into the flask through the chemical inlet. The mixture was heated until the solution became clear yellow. Nickel chloride hexahydrate (3.00 g, 12.7 mol) was then added. The resulting purple precipitate was stirred for 10 minutes. Then the mixture was allowed to stand for 30 minutes at room temperature and after that the precipitate was filtered and washed with water 6-7 time.

2.2.2 *Synthesis of $[Ni\{S_2P(OC_2H_5)_2\}(dppe)](BPh_4)$* ***(1)***

$Ni(S_2P(OC_2H_5)_2)_2$ (0.429 g, 1 mmol) and $NaBPh_4$ (0.784 g, 2 mmol) were dissolved in methanol (10 mL) under vigorous stirring. To the resulting mixture 1,2-bis(diphenylphosphinoethane) (0.396 g, 1 mmol) dissolved in dichloromethane (10 mL) was added dropwise and the solution stirred for another 180 min. Then the solvent was removed and the dry residual was dissolved in dichloromethane (5 mL) and filtered through celite. The filtrate was concentrated and precipitated with petroleum ether to yield an orange solid.

Characterization data **1**: Yield (0.908 g, 94.38%); m.p. 145 ˚C; IR (KBr) ν_{max}: 3044 cm^{-1} (C_6H_5), 2978 (CH_3), 1008 [(P)OC], 740 (PO_2), 706 (P=S); ^{1}H NMR ($CDCl_3$, δ): 7.61-7.39 (m, 20 H, C_6H_5), 7.32 (s, 8H, C_6H_5), 6.86 (t, J = 7.2 Hz, 8H, C_6H_5), 6.77 (t, J = 6.9 Hz, 4H, C_6H_5), 4.06 (m, 4H, -OCH_2), 1.89 (d, J = 19.5 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 136.4, 133.1, 129.8, 126.9, 121.9 (C_6H_5), 65.3 (-OCH_2), 29.8 (CH_3), 25.7 (CH_2). ^{31}P NMR ($CDCl_3$, δ): 89.1 (PS_2), 65.8 (dppe).

2.2.3 Synthesis of $[Ni\{S_2P(OCH(CH_3)_2)_2\}(dppe)]X$ (X^- = PF_6^- ***(2)****, BPh_4^-* ***(3)****)*

A similar procedure was applied to $Ni\{S_2P(OCH(CH_3)_2)_2\}$ (0.485 g, 1 mmol) and KPF_6 (**2**) (0.368 g, 2 mmol)/$NaBPh_4$ (**3**) (0.784g, 2 mmol) to yield an orange solid.

Characterization data **2**: Yield (0.575 g, 67.56%); m.p.180 ˚C; IR (KBr), ν_{max}: 2978 (CH_3), 974 [(P)OC], 784 (PO_2), 684 (P=S); ^{1}H NMR ($CDCl_3$, δ): 7.77-7.44 (m, 40 H, C_6H_5), 4.72 (m, 2H, CH), 2.87 (s, 4H, -CH_2), 1.78 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$, δ): 133.1, 129.8, 126.6 (C_6H_5), 74.1 (CH), 27.4 (CH_2), 24.0 (CH_3). ^{31}P NMR ($CDCl_3$, δ):88.9 (PS_2), 65.9 (dppe), -142.8 (J = 176.0 Hz, PF_6^-).

Characterization data **3**: Yield (0.909 g, 91.91%); m.p.160 ˚C; IR (KBr), ν_{max}: 3056 (C_6H_5), 2978 (CH_3), 996 [(P)OC], 740 (PO_2), 706 (P=S); ^{1}H NMR ($CDCl_3$, δ): 7.59-7.45 (m, 20 H, C_6H_5), 7.32 (s, 8H, C_6H_5), 6.87 (t, J = 7.2 Hz, 8H, C_6H_5), 6.77 (t, J = 6.9 Hz, 4H, C_6H_5), 4.62 (m, 2H, CH), 2.80 (s, 4H, CH_2), 1.90 (d, J = 19.4 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$, δ): 136.4, 133.1, 129.8, 126.9, 121.9 (C_6H_5), 75.5 (CH), 26.2 (CH_2), 23.8 (CH_3); ^{31}P NMR ($CDCl_3$, δ): 84.7 (PS_2), 65.8 (dppe).

2.2.4 Preparation of nickel sulfides

Decomposition of the precursor complex salts **1**, **2** and **3** was performed at 500 °C for 5 h in an argon gas atmosphere in a tubular furnace (heating rate 10 °C min^{-1}). The obtained nickel sulfides were washed thrice with de-ionised water (15 mL) and air-dried.

2.3 X-ray crystallography

Intensity data for **1-3** were collected at 150(2) K on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation λ = 0.71073 Å. Unit cell determination, data scaling, and corrections for Lorentz and polarization effects were performed with Denzo-SMN.[28] The structures were solved by direct methods (SIR97) [29] and refined by a full-matrix least-squares procedure based on F^2(SHELXL-2014).[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed onto calculated positions and refined using a riding model. Molecular structures were constructed using ShelXle.[31]

Crystal Data **1**: $C_{54}H_{54}BNiO_2P_3S_2$, M = 961.52, Monoclinic, P2_1/c, a = 14.2516(2) Å, b = 18.8126(2) Å, c = 18.1568(3) Å, β = 100.6942(6)°, V = 4783.46(12) Å^3, Z = 4, D_c = 1.335 mg m^{-3}, F(000) = 2016, crystal size 0.30 × 0.15 × 0.10 mm, reflections collected 93811, independent reflections 10966 [R_{int} = 0.1032], Final indices [$I > 2\sigma(I)$] R_1 = 0.0454, wR_2 = 0.0849,

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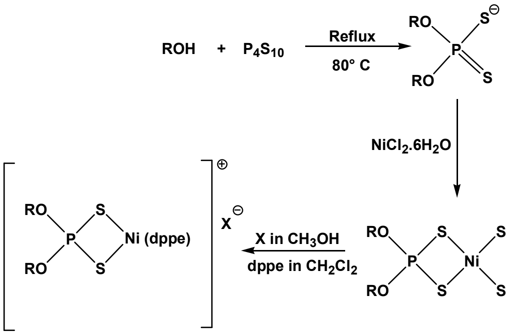
R indices (all data) R_1 = 0.0823, wR_2 = 0.0965, gof 1.035, Largest difference peak and hole 0.319 and -0.311 e Å^{-3}. **CCDC No.: 1508397**

Crystal Data **2**: $C_{32}H_{38}F_6NiO_2P_4S_2$, *M* = 815.33, Monoclinic, P2$_1$/c, *a* = 9.51170(10) Å, *b* = 17.2102(2) Å, *c* = 22.5279(3) Å, β = 100.9207(7)°, *V* = 3620.99(7) Å^3, *Z* = 4, D_c = 1.496 mg m^{-3}, *F*(000) = 1680, crystal size 0.50 × 0.50 × 0.25 mm, reflections collected 48394, independent reflections 8135 [R_{int} = 0.0759], Final indices [$I > 2\sigma(I)$] R_1 = 0.0593, wR_2 = 0.1291, *R* indices (all data) R_1 = 0.0802, wR_2 = 0.1370, gof 1.115, Largest difference peak and hole 0.860 and -0.637 e Å^{-3}. **CCDC No.: 1508396**

Crystal Data **3**: $C_{112.50}H_{117}B_2ClNi_2O_4P_6S_4$, *M* = 2021.60, Triclinic, P-1, *a* = 11.9740(2) Å, *b* = 14.1021(2) Å, *c* = 17.2015(4) Å, α = 102.5046(7)°, β = 101.1188(7)°, γ = 106.1991(7)°, *V* = 2621.90(8) Å^3, *Z* = 1, D_c = 1.280 mg m^{-3}, *F*(000) = 1061, crystal size 0.50 × 0.40 × 0.30 mm, reflections collected 53581, independent reflections 11899 [R_{int} = 0.0581], Final indices [$I > 2\sigma(I)$] R_1 = 0.0452, wR_2 = 0.0963, *R* indices (all data) R_1 = 0.0660, wR_2 = 0.1034, gof 1.112, Largest difference peak and hole 0.359 and -0.391 e Å^{-3}. **CCDC No.: 1508395**



R = C_2H_5; X = $B(C_6H_5)_4^-$ (1)

R = $CH(CH_3)_2$; X = PF_6^- (2)

R = $CH(CH_3)_2$; X = $B(C_6H_5)_4^-$ (3)

Scheme 1 Synthetic routes for the preparation of the complexes.

3. Result and Discussion

3.1 Synthesis and Spectroscopy

All three compounds *viz.* [Ni{$S_2P(OC_2H_5)_2$}(dppe)]$B(C_6H_5)_4$ (**1**), [Ni{$S_2P(OCH(CH_3)_2)_2$}(dppe)]PF_6 (**2**) and [Ni{$S_2P(OCH(CH_3)_2)_2$}(dppe)]$B(C_6H_5)_4$ (**3**) were obtained by addition of stoichiometric amounts of dppe and the counter anions PF_6^- and BPh_4^- in a methanol-dichloromethane mixture (Scheme 1). They were air-stable and soluble in halogenated solvents but insoluble in petroleum ether. Crystals of **1-3** suitable for X- ray analysis were obtained by slow evaporation of the dichloromethane-methanol mixture. The observed Λ_M is lying in the range of Λ_M 110-115 cm^2 S mol^{-1} in 10^{-3} M dichloromethane solution and shows their 1:1 electrolytic behavior.[32]

The purity and composition of the complexes were checked by ^{1}H NMR spectroscopy that integrated well to the corresponding aliphatic and aromatic fragments of the ligands and the counter anions. The ^{13}C NMR signals also corresponds to the corresponding carbon atoms in the molecules. A signal at ~δ 66 ppm in the {^{1}H}^{31}P NMR spectra indicates that both phosphorus donors of the dppe ligands are magnetically equivalent and signals lying in the range of 84.7-89.1 are indicative of the PS_2 function in the dithiophosphate ligand. Additionally, in the case of **2**, the septet centered at δ -142.8 with ^{1}J(PF) 708.7 Hz corresponds to the phosphorus centre of the PF_6^-. In the IR spectra two medium to strong bands obtained at 1108-1008 and 996-974 cm^{-1} are assigned to ν [(P)–O–C] and [ν P–O–(C)].[33, 34] In the case of **2,** a strong peak at 829 cm^{-1} can be assigned to $\nu_{(P-F)}$.

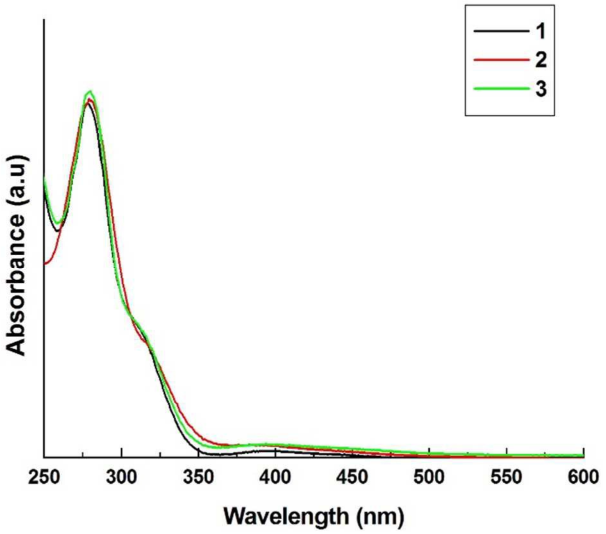


Fig. 1 Electronic absorption spectra of the complexes in 10^{-5} M dichloromethane solution.

Electronic adsorption spectra of the three compounds in dichloromethane, exhibited (Fig. 1) bands in the range 230-400 nm due to the ligand centered π→π* and intraligand charge transfer transition.[35, 36] The very weak broad absorptions ~400 nm is assignable to L→M, ligand-to-metal charge transfer (LMCT) transitions consistent with square planar geometry about the metal center.[37]

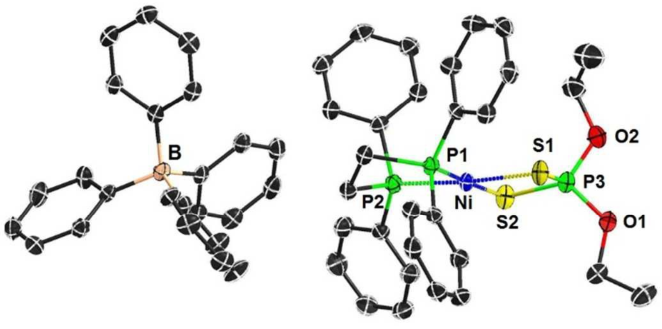


Fig. 2 View of the asymmetric unit of **1** with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

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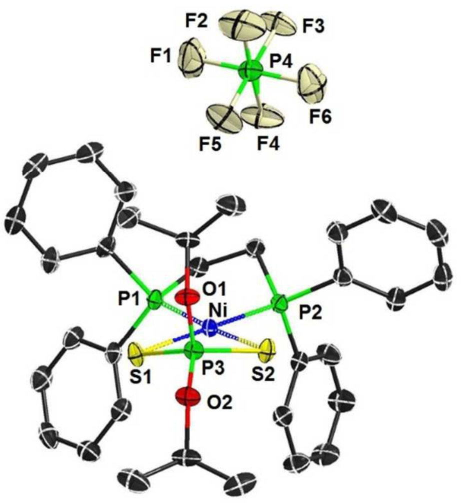

Fig. 3 View of the asymmetric unit of **2** with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

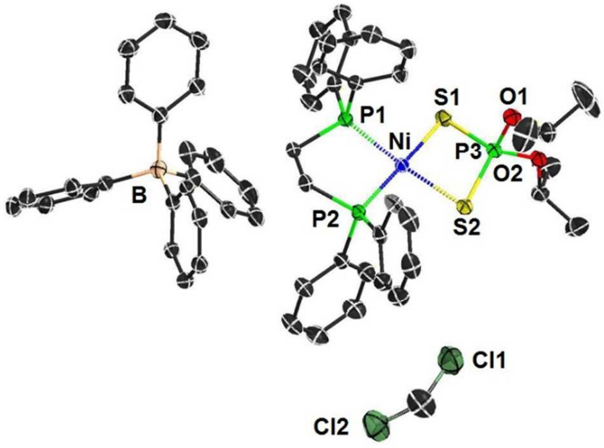

Fig. 4 View of the asymmetric unit of **3** with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.'

3.2 Molecular Structure Description

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. The $[\mathrm{Ni}\{S_2P(OC_2H_5)_2\}(\mathrm{dppe})]^+$ core is cationic and a $B(C_6H_5)_4^-$ anion is also present in the system for neutrality (Fig. 2). The immediate distorted square planar geometry around the Ni(II) center is defined by two sulfur atoms S(1), S(2) of the dithiophosphate ligand and P(1) and P(2) of the dppe. The Ni–S and Ni–P bond distances lie in the range of 2.2304(7)-2.2414(7) Å and 2.1598(7)-2.1614(7) Å, respectively, which indicates almost symmetrical bidentate behavior of both dithiophosphate and dppe ligands.[27] The S(1)–Ni–S(2) bite angle of 88.72(3)° in the four membered chelate ring shows very small distortion from the square planar geometry.[27] The bite angle P(1)–Ni–P(2) for the five membered ring is 87.12(3)° and offers significantly lower distortion for the square planar geometry[27] because of the relatively greater flexibility. The dihedral angle between the planes formed by the four- and five-membered chelate ring is 4.75°.

Like **1**, complex **2** crystallizes in the monoclinic space group P2$_1$/c. The $[\mathrm{Ni}\{S_2P(OCH(CH_3)_2)_2\}(\mathrm{dppe})]^+$ core is cationic and a PF_6^- anion is also present in the system for neutrality (Fig. 3). The immediate distorted square planar geometry around the Ni(II) center is defined by two sulfur atoms S(1), S(2) of the dithiophosphate ligand and P(1) and P(2) of the dppe. The Ni–S and Ni–P bond distances lie in the range of 2.2308(11)- 2.2350(11) and 2.1529(11)- 2.1584(11) Å, respectively which indicates almost symmetrical bidentate behavior of both dithiophosphate and dppe ligands.[27] The S(1)–Ni–S(2) bite angle of 89.09(4)° in the four membered chelate ring shows very small distortion from the square planar geometry. [27] The bite angle P(1)–Ni–P(2) for five membered ring is 87.12(4)° and offers significantly lower distortion for the square planar geometry.[27] The dihedral angle between the planes formed by the four- and five-membered chelate ring is 20.41°. Complex **3** crystallizes in triclinic space group P-1. The $[\mathrm{Ni}\{S_2P(OCH(CH_3)_2)_2\}(\mathrm{dppe})]^+$ core is cationic and a $B(C_6H_5)_4^-$ anion is also present in the system for neutrality. Additionally, a partially occupied (25%) dichloromethane solvent molecule co-crystallizes per asymmetric unit (Fig. 4). The immediate distorted square planar geometry around the Ni(II) center is defined by two sulfur atoms S(1), S(2) of the dithiophosphate ligand and P(1) and P(2) of the dppe. The Ni–S and Ni–P bond distances lie in the range of 2.2380(7)-2.2449(6) and 2.1550(7)-2.1650(7) Å, respectively which indicates almost symmetrical bidentate behavior of both dithiophosphate and dppe ligands. [27] The S(1)–Ni–S(2) bite angle of 89.08(2)° in the four membered chelate ring shows very small distortion from the square planar geometry. The bite angle P(1)–Ni–P(2) for the five membered ring is 86.59(3)° and offers significantly lower distortion for the square planar geometry. The dihedral angle between the planes formed by the four- and five-membered chelate ring is 14.47°. The geometrical parameters for all the three complexes are in agreement with the previously reported $[\mathrm{Ni(dtp)(dppe)}]^+$ complex cations.[27]

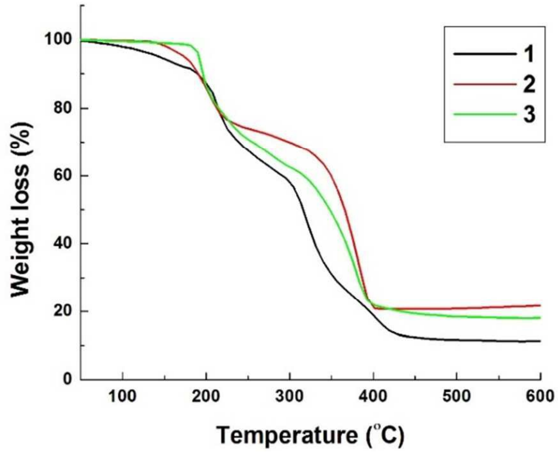

Fig. 5 TGA curves for the complexes **1**-**3**.

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3.3 Decomposition Study

Thermal decomposition of the three complexes **1-3** was performed under argon atmosphere with a heating rate of 10 °C min^{-1} and shows a two-step decomposition (Fig. 5). First, weight loss for **1-2** occurs at around 100 °C but for **3** at around 200 °C and the second major weight loss for the three complexes takes place above 300 °C. The residual percentages for **1-3** from the TGA plots were found to be 12.28%, 20.80% and 18.38%, respectively. The calculated residual mass for the formation of the NiS_2 at the end of decomposition in complex **1** was 12.78% which is very close to the observed value of 12.28%. For **2** the calculated mass of NiS and NiS_2 is 11.12% and 15.04%, respectively. Out of these two calculated values, NiS_2 is much closer to the observed value. Also for **3**, the calculated mass of NiS and NiS_2 is around 9.61% and 12.31% respectively in which NiS_2 is very close to the observed values. In all the three cases the calculated values are lower than the observed value. The probable reason may be the presence of an amorphous impurity as well as the formation of an impurity phase as suggested by X-ray diffraction studies (*vide infra*).

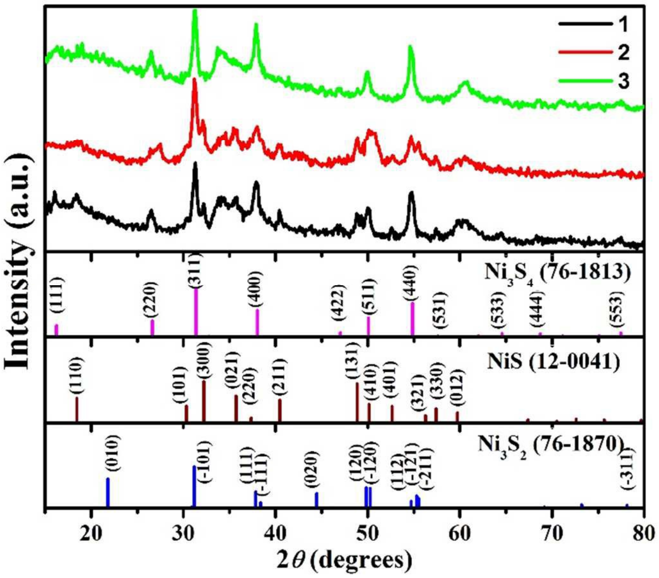

Fig. 6 Powder X-ray diffractograms of the nickel sulfides obtained from the decomposition of the precursors at 500 °C for 6 h.

3.4 PXRD and SEM

The XRD pattern of the decomposition products of **1-3,** at 500 °C under inert atmosphere, are showing mixed pattern (Fig. 6) comprising of mainly Ni_3S_4 cubic polydymite phase (JCPDS No. 76-1813, space group: Fd-3m (227), $a = b = c = 9.457$ Å; $\alpha = \beta = \gamma = 90°$) alongwith NiS rhombohedral Millerite phase (JCPDS No. 12-0041, space group: R3m (160), $a = b = 9.6200$ Å; $c = 3.1490$ Å and $\alpha = \beta = 90°$ $\gamma = 120°$).[38] In addition, traces of Ni_3S_2 rhombohedral Heazlewoodite phase (JCPDS No. 76-1870, space group: R32 (155), $a = b = c =$ 4.0730 Å and $\alpha = \beta = \gamma = 89.42°$) is also present.[38] Differences in TGA and XRD results is possibly arising because of the formation of amorphous impurities along with other impurity phases formed during the decomposition of precursors **1-3**. However, from scanning electron microscopic studies, it is observed that decomposition products of **1** and **2** have a similar flower like morphology while the decomposition product of **3** has aggregated nanoparticle.[18a] It is interesting that precursors of **1** and **2** have similar morphologies although they have different counter anions *viz.* BPh_4^- and PF_6^-, respectively. They also differ in alkyl groups *viz.* ethyl (**1**) and isopropyl (**2**) groups on dithiophosphate ligands. These results indicates that neither the counter anions nor the ligands have any effect on the morphology. It is the stability of the compounds which decided the respective morphologies of as-synthesized nickel sulfide.

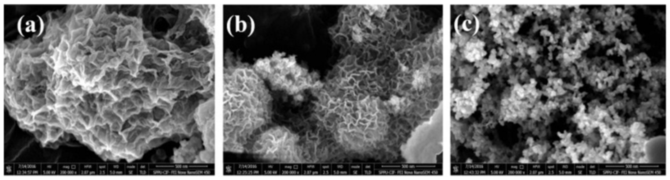

Fig. 7 SEM micrographs for the obtained nickel sulfides obtained from the precursors (a) **1**, (b) **2** and (c) **3**.

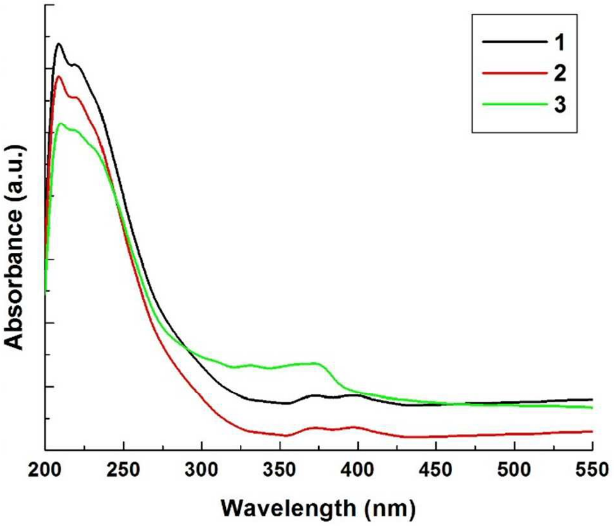

Fig. 8 Electronic absorption spectra of the nickel sulfides obtained by the decomposition of the precursors **1-3**

The UV-Vis spectra for the synthesized nickel sulfides dispersed in the distilled water through ultrasonication is presented in figure 8. The absorption band observed around 210 nm confirms the formation of nano-sized nickel sulfide particles, while their narrow particle size distribution and uniformity of particles is confirmed based on the narrow width of this absorption peak.[39] **1** and **2** shows two very weak absorption around 360 and 400 while **3** shows absorption at 330 and 375 nm. The phenomenon of blue shift in the absorption band of **1-3** in comparison to bulk nickel sulfide observed at 590 nm can be ascribed to decrease in particle size which in turn increases the band gap of the newly synthesized nickel sulfide nanoparticles.[40]

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DOI: 10.1039/C6NJ03186B

Conclusion

On the basis of present investigations it can be concluded that the synthesized 1,2-bis(diphenylphosphino)ethane O,O′-dialkyldithiophosphatenickel(II) complexes with different alkoxy substituents and counter-ions can be used as a single source precursor for the nickel sulphide. Also, it has been found that the bulkiness of counter anions as well as alkyl fragment of the dithiophosphate ligands does not have any effect on the morphologies of as-synthesized nickel sulfides. This observation is in contrast to our previous report with 1,2-bis(diphenylphosphino)ethane nickel(II) dithiocarbamates[20] where nature and bulkiness of the counter-anions affected the phase as well as the morphologies of as-synthesized nickel sulfides. These results indicates the application of 1,2-bis(diphenylphosphino)ethane nickel(II) dithiophosphates complexes as potential single source precursor for nickel sulphide which on decomposition yield nickel sulfide with same phase under ambient conditions.

Acknowledgements

AK is thankful to the Department of Science and Technology, New Delhi for financial support in the form of project (SB/FT/CS-018/2012).

Notes and references

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The crystallographic data in CIF format has been deposited with CCDC (CCDC deposition number is **1508395-1508397**. 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: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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DOI: 10.1039/C6NJ03186B

Three new 1,2-bis(diphenylphosphino)ethane nickel(II) dithiophosphates with different counter anions synthesized and decomposed to obtain the Ni-S systems having same phase independent of the nature of counter anion and alkyl fragment.