第 24卷第 1期 四川理工学院学报 (自然科学版) Vol.24 No.1
2011年 2月 Journal of Sichuan University of Science & Engineering (Natural Science Edition) Feb. 2011
文章编号: 1673-1549(2011)01-0086-08

Synthesis and Crystal Structure of 1, 10-Phenanthroline Bis (O, O'-di(2-phenylethyl) dithiophosphato) Nickel(II)

XIE Bin[1,2], ZOU Li-ke[1,2], LAI Chuan[3], HUANG Chun[3], WANG Jun[1,2], XIANG Yang-guang[3]

(1. Institute of Functional Materials, Sichuan University of Science & Engineering, Zigong 643000, China;
2. Key Laboratory of Green Chemistry of Sichuan Provincial University, Zigong 643000, China;
3. School of Material and Chemical Engineering, Sichuan University of Science & Engineering, Zigong 643000, China)

Abstract: Reaction of complex $Ni[S_2P(OCH_2CH_2PH)_2]_2$ with nitrogen base donor 1, 10-phenanthroline (phen) was carried out in petroleum ether and acetone solution to give green nitrogen base adduct 1, 10-phenanthroline bis (O, O'-di(2-phenylethyl) dithiophosphato) nickel(II), $Ni[S_2P(OCH_2CH_2Ph)_2]_2 \cdot phen$. The adduct was characterized by elemental analysis, UV-visible and IR spectra, thermal analysis and single-crystal X-ray diffraction. The crystal belongs to the monoclinic system, space group $P2_1/c$ with $a = 1.0987(9)$ nm, $b = 2.1432(9)$ nm, $c = 1.9025(5)$ nm, $\beta = 98.68(1)°$, $V = 4.429(4)$ nm^3, $Z = 4$, $Dc = 1.370$ Mg/m^3, $F(000) = 1904$, $\mu = 0.743$ mm^{-1}, the final $R = 0.057$ and $wR = 0.1492$ for 3498 observed reflections $(I > 2\sigma(I))$. The Ni(II) atom adopts a distorted octahedral geometry with four sulfur atoms from two O, O'-di(2-phenylethyl) dithiophosphate ligands and two nitrogen atoms from a phen ligand. The Ni-S distances rang from 0.2474(2) to 0.2505(17) nm, and the Ni-N distances are 0.2081(4) and 0.2090(5) nm. The overall structure of adduct consists of 1D chain-pair and 1D double-stranded helical chain, which formed from intermolecular π-π stacking, C-H…O and C-H…S hydrogen-bonding interactions. They are further extended to 3D supramolecular network via C-H…O hydrogen-bonding interactions.

Key words: O, O'-dialkyldithiophosphate; nickel(II) adduct; synthesis; characterization; crystal structure

CLC number: O614.12 **Document code**: A

Interest in the chemistry of metal complexes of O, O'-dialkyldithiophosphates continues to grow due to extensively employed as antioxidant and antiwear additives in rubber and lubricating oils[1-2]. The complexes exhibit remarkable variety in their coordination geometries, mono-, bi-, tetra-, or polynuclear, and the O, O'-dialkyldithiophosphate ligands act as monodentating, chelating, or bridging ligands in these complexes[3-8]. Furthermore, the structures of the O, O'-dialkyldithiophosphates and the categories of the metal can be modulated in an easily controlled manner to facilitate the individual application. The coordination system of nickel (II) is strongly dominated by mononuclearity with O, O'-dialkyldithiophosphates ligands, witch is much different from that of the readily-cluster-forming metals, cooper(I), zinc (II) and silver(I)[6-8]. And these square planar four-coordinate nickel(II) complexes can be stabilized by the formation of five-and six-coordinate adducts with neutral donor ligands, especially nitrogen bases, e.g. ethylenediamine (en), pyridine (py), quinoline, 2, 2'-bipyridine (bipy) and 1, 10-phenanthroline (phen). These nitrogen bases are usually added to lubricating oils when the metal complexes of O, O'-dialkyldithiophosphates serve as antioxidant additives of lubricating oils[9-10], thus many metal adducts of O, O'-dialkyldithiophosphates and nitrogen bases have been synthesized during the last two decade, but the alkyl groups of O, O'-dialkyldithiophosphates in these ad-

收稿日期: 2010-12-15
基金项目: 四川省科技厅科技支撑计划项目 (2010GZ0130); 四川省教育厅重点项目 (09ZA057); 材料腐蚀与防护四川省高校重点实验室重点项目 (2008CL03); 四川理工学院研究生创新基金项目 (y2009023)
作者简介: 谢斌 (1965-), 男, 四川荣县人, 教授, 主要从事功能有机材料方面的研究。

ducts are very simple, such as Me, Et, n-Pr, i-Pr, n-Bu and cyclohexthyl ect [9-16]. However, only several molecular and crystal structures of nitrogen bases adducts of nickel(II) complexes with aryl dithiophosphates have been reported, where aryls are $PhCH_2CH_2-$ [17-18] and p-MeC_6H_4- [19-20], so further studies on the influences of aromatic moiety to the coordinate behavior of nickel(II) are still necessary. Here we report the synthesis, characterization and crystal structure of 1, 10-phenanthroline adduct of bis(O, O'-di(2-phenylethyl) dithiophosphato) nickel (II), $Ni[S_2P(OCH_2CH_2Ph)_2]_2 \cdot$ phen.

1 Experimental

1.1 Reagents and Physical Measurements

Melting point was determined on a WC-1 melting point apparatus without correction. Elemental analyses for carbon, hydrogen, nitrogen and sulfur were carried out on a Carlo-Erba 1106 elemental analyzer. The infrared spectrum was taken on a Nicolet MX-1 spectrometer by using KBr pellets. The Ultraviolet-visible spectroscopy in $CHCl_3$ solution was obtained with a Jasco V-570 spectrophotometer. The thermal analysis was carried out with a Netzsch STA 409PC/PG in dry atmosphere at a heating rate of 10℃·min^{-1} from 35℃ to 700℃. Single crystal X-ray diffraction analysis was carried out on an Enraf-Nonius CAD4 X-ray diffractometer.

All the chemicals were of analytical reagent grade and used directly without further purification. The compound $(PhCH_2CH_2O)_2PS_2NH_2Et_2$ [21] and the complex $Ni[S_2P(OCH_2CH_2PH)_2]_2$ [22] was prepared according to the literature methods.

1.2 Synthesis

A solution of 0.198 g (1 mmol) 1, 10-phenanthroline (phen) in 10 mL petroleum ether (90– 120℃) was added dropwise to a hot solution of $Ni[S_2P(OCH_2CH_2Ph)_2]_2$ (0.356 g, 0.5 mmol) in 25 mL petroleum ether (90 – 120℃) and 25 mL acetone under stirring. The solution was stirred at 40℃ for 30 min, the green gelatinous precipitate was filtrated out and purified by column chromatography on silica gel G (V(acetone) : V(petroleum ether) = 2∶1). The bright green solution was left to stand at room temperature, after two weeks pale green prismatic crystals $Ni[S_2P(OCH_2CH_2Ph)_2]_2 \cdot$ phen (**1**) suitable for X-ray analysis were obtained. Yield 45%, m. p. 150 – 152℃. Anal. calcd. for $C_{44}H_{44}N_2O_4P_2S_4Ni$: C 57.85, H 4.85, N 3.07, S 14.04; Found (%): C 57.95, H 5.02, N 3.13, S 14.35. UV-vis($CHCl_3$) λ_{max}: 382, 414, 661, 1122 nm; IR: ν_{max} /cm^{-1} (KBr): 3027 w, 2953 w, 2885 w, 1626 m, 1604 m, 1496 s, 1453 m, 1422 s, 1378 m, 1341 w, 1086 m, 1057 s, 1028 s, 996 vs, 870 s, 850 s, 795 s, 727 s, 701 s, 670 s, 656 s, 601 s, 495 s.

1.3 Crystallographic Measurements and Structure Determination

A pale green prismatic crystal of adduct **1** with dimensions of 0.35 mm × 0.20 mm × 0.15 mm was mounted on Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromaticed Mo Kα radiation (λ = 0.071073 nm) using the ω/2θ scan mode at 290(2) K. A total of 8025 reflections were measured in the range of 1.44 < θ < 25.01°, of which 7178 were independent with R_{int} = 0.0021 and 3498 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods using program SHELXS-97 [22] and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms on F^2 using program SHELXL-97 [23], spherical absorption correction was carried out by program WINGX (Version 1.70.01) [24]. All hydrogen atoms were placed in the geometrically idealized positions with C-H = 0.093 nm (aromatic), 0.099 nm (methylene) and refined as riding with U_{iso}(H) = 0.00110 nm^2 (aryl H) and 0.00129 nm^2 (methylene H).

Table 1 Crystal data and structure refinement of adduct 1

Empirical formula	$C_{44}H_{44}N_2NiO_4P_2S_4$
Formula weight	913.70
Temperature /K	290(2)
Volume/nm^3	4.429(4)
Crystal system	Monoclinic
Space group	$P2_1/c$
a /nm	1.0987(9)
b /nm	2.1432(9)
c /nm	1.9025(5)
β /(°)	98.68(4)
Z	4
ρ_{calcd} /(g·cm^{-3})	1.370
μ /mm^{-1}	0.743
F(000)	1 904
Crystal size	0.35 mm × 0.20 mm × 0.15 mm
h_{min}/h_{max}	–13/12
k_{min}/k_{max}	0/25
l_{min}/l_{max}	0/22
Reflections collected	8025
Independent refletions	7178(R_{int} = 0.0021)
Data/restraints/parameters	7178/2/516
Goodness-of-fit on F^2	1.067
Max and min transmission	0.8968, 0.7811
Refinement method	Full-matrix least-squares on F^2
R_1, wR_2 [$I > 2\sigma(I)$]	0.0577, 0.1282
R_1, wR_2 (all data)	0.01492, 0.1581
Largest diff peak and hole/e nm^{-3}	859/–478
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	a = 0.0619, b = 0.0000 $P = (F_o^2 + 2F_c^2)/3$

Table 2 Selected bond lengths (nm) and bond angles (°) of adduct 1

Ni(1)-N(1)	0.2090(5)	S(2)-P(1)	0.1972(3)
Ni(1)-N(2)	0.2081(4)	S(3)-P(2)	0.1975(2)
Ni(1)-S(1)	0.2474(2)	S(4)-P(2)	0.1978(2)
Ni(1)-S(2)	0.24839(18)	N(1)-C(1)	0.1337(7)
Ni(1)-S(3)	0.25065(17)	N(1)-C(12)	0.1351(7)
Ni(1)-S(4)	0.24970(18)	N(2)-C(10)	0.1332(6)
S(1)-P(1)	0.1974(2)	N(2)-C(11)	0.1365(6)
N(1)-Ni(1)-N(2)	79.69(16)	S(1)-Ni(1)-S(4)	90.95(5)
N(1)-Ni(1)-S(1)	170.23(12)	P(2)-S(3)-Ni(1)	82.52(7)
N(2)-Ni(1)-S(2)	95.09(11)	P(2)-S(4)-Ni(1)	82.70(7)
N(2)-Ni(1)-S(3)	167.39(12)	N(2)-Ni(1)-S(4)	97.30(12)
N(2)-Ni(1)-S(4)	90.19(11)	N(2)-Ni(1)-S(1)	95.12(12)
P(1)-S(1)-Ni(1)	84.49(7)	S(2)-Ni(1)-S(3)	94.54(6)
P(1)-S(2)-Ni(1)	84.27(8)	S(2)-Ni(1)-S(4)	170.94(5)
N(1)-Ni(1)-S(2)	90.89(12)	S(3)-Ni(1)-S(4)	81.36(5)
N(1)-Ni(1)-S(3)	92.06(12)	S(2)-P(1)-S(1)	109.81(10)
S(1)-Ni(1)-S(2)	81.27(5)	S(3)-P(2)-S(4)	111.21(10)
S(1)-Ni(1)-S(3)	94.36(6)		

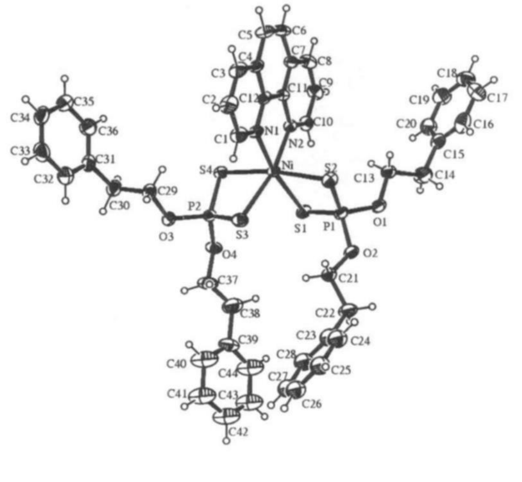

Figure 1 Perspective view of adduct 1 showing 30% probability thermal ellipsoids

2 Results and Discussion

2.1 Crystal Structure

Single-crystal X-ray diffraction analysis reveals that the nitrogen base adduct **1** crystallizes in the monoclinic, space group $P2_1/c$. The ORTEP view of **1** drawn at 30% probability displacement ellipsoids and the packing diagram in a unit are shown in Fig. 1, Fig. 2, Fig. 3, and Fig. 4 respectively. The crystal data and structure refinement for adduct **1** are given in Table 1. The selected bond lengths and angles of adduct **1** are given in Table 2. The hydrogen bond lengths and angles of adduct **1** are given in Table 3.

The space group $P2_1/c$ allows the two expected optical isomers to be present in the crystal lattice. Ni(II) ion adopts a distorted octahedral geometry with four sulfur atoms from two *O*, *O'*-di(2-phenylethyl) dithiophosphate ligands and two nitrogen atoms of phen ligand. In adduct 1, the square planar structure of Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$[22] has readily accommodated the bidentate phen ligand, with two nitrogen atoms occupying *cis*-positions, while maintaining the integrity of the two bidentate *O*, *O'*-di(2-phenylethyl) dithiophosphate ligands. Similar coordination geometry is seen in some six-coordinate analogues complex or adduct, Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$ · bipy[17], Ni[$S_2P(OC_6H_4$-Me-*p*)]$_2$ · bipy[19], and Ni[$S_2P(OC_6H_4$Me-*p*)]$_2$ · phen[20].

In adduct **1**, the Ni–S distances range from 0.2474(2) to 0.25065(17) nm, which are in the range of other six-coordinate analogues, Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$ · bipy[17] (0.2488(5) to 0.2513(5) nm), Ni[$S_2P(OC_6H_4$Me-*p*)]$_2$ · bipy[19] (0.24757(7) to 0.25096(6) nm), Ni[$S_2P(OC_6H_4$Me-*p*)]$_2$ · phen[20] (0.2486(1) to 0.2532(1) nm) and Ni[$S_2P(OMe)_2$] · phen[14] (0.247(1) to 0.252(1) nm). And the Ni-S distances in adduct **1** are much longer than those in the square planar four-coordinate Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$ (0.22202(11) and 0.22228(13) nm)[22], resulting from the change of coordination-geometry and the increase in steric hindrance. The Ni-N distances are fairly similar in adduct **1** (0.2081(3) and 0.2090(5) nm) which is also in good agreement with the bond lengths found in these six-coordinate, Ni[$S_2P(OMe)_2$] · phen[14] (0.208(1) to 0.209(1) nm), Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$ · bipy[17] (0.2072(13) to 0.2086(13) nm), Ni[$S_2P(OC_6H_4$Me-*o*)]$_2$ · bipy[19] (0.2060(1) to 0.2079(1) nm), Ni[$S_2P(OC_6H_4$Me-*p*)]$_2$ · phen[20] (0.2082(3) to 0.2086(3) nm). The average distances of the four P – S bonds (0.1975(2) nm) in adduct **1** is shorter than that in Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$[22] (0.19889(15) nm), which shows that the increase in steric hindrance has no significant influence on the partial double bond character of these P – S bonds. All other bond distances are normal.

The N1-Ni-N2, S1-Ni-S2 and S3-Ni-S4 bite angles in adduct 1 are similar to the values found previously in the six-coordinate adducts Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$ · bipy[17], *Ni[$S_2P(OC_6H_4$-Me-o)]$_2$ · bipy*[19], *Ni[$S_2P(OC_6H_4$Me-p)]$_2$ · phen*[20], and *Ni[$S_2P(OMe)_2$] · phen*[14], which are 79.69(16), 81.27(5) and 81.36(5)°, respectively. The small bite angles of the phen and *O*, *O'*-di(2-phenylethyl) dithiophosphate ligands result in very acute bond angles for an octahedral geometry. This distortion is also reflected in the bond angles between the *trans* ligands. The S2-Ni-S4 bond angle is 170.94(5)° compared to 170.23(12) and 167.39(12)° for the N1-Ni-S1 and N2-Ni-S3 bond angles. The deviated of these angles from idealized octahedral geometry is also duo to the fact that two four-member chelating rings occur for the chelating *O, O'*-di(2-phenylethyl) dithiophosphates while phen forms five-member chelating ring. Therefore, small bite angles for phen and *O, O'*-di(2-phenylethyl) dithiophosphate ligands as well as four-and five-member chelating rings lead to a very distorted octahedron for adduct **1**.

The phen ligand and the nickel atom of adduct 1 lie approximately in one plane. Atom C2 shows a maximum deviation of 0.0075 nm from the least-squares chelating plane. The atom P1 has a maximum deviation of 0.0013 nm from the least-squares chelating plane defined by atoms Ni, S1, P1, and S2. The largest deviation from the least-squares chelating plane of Ni, S3, P2, and S4 is 0.0128 nm for P2, much larger than that of P1 (0.00013 nm).

Interestingly, weak π-π stacking and hydrogen bond interactions are found in the crystal structure. There exist weak intermolecular C3-H…S1[i] hydrogen-bonding interactions [symmetry code (i): -1+*x*, *y*, *z*] between molecules having the same configuration, with distance of 0.3761(7) nm, which is shorter than that in complex $[Mn(NCS)_2(Eim)_4]$ (0.3856nm, where Eim is 1-ethylimdazole)[25]. The C3-H…S1[i] hydrogen-bonding interactions link the molecules into a 1D chain along the *a*-axis, as showed in Fig. 2. And inter-chain face-to-face π-π stacking interactions occur between aromatic rings of phen ligands in the adjacent 1D chains, C4~C7/C11~C12 and $C4^{ii}$ ~ $C7^{ii}$ / $C11^{ii}$ ~ $C12^{ii}$ [symmetry code (ii) 1*x*, *y*, *z*], with dihedral angles of 0.00° and inter-planar distance of 0.3604(2) nm, centroid-to-centroid distance of 0.3652(4) nm, and slippage distance of 0.0594(3) nm. The inter-planar distance is shorter than that in complex $Cu(phth)_2(H_2O)$[26] (0.3647nm) and $[Co(p\text{-}ClC_6H_4CO_2)_2(phen)(H_2O)_2]$[27] (0.3684nm), meanwhile, the centroid separation is shorter than that of $[Zn(H_2O)_6](HL)$[28] (0.3672 nm, H_2L is 1-(4-hydroxylphenyl)-5-thioacetatetetrazol). Thus a 1D chain-pair structure unit along the *a*-axis is assembled through the inter-chain π-π stacking interactions and weak inter-chain C9-H…O4[iii] hydrogen-bonding interactions [symmetry code (iii): 2-*x*, -*y*, -*z*, with distance of 0.3415(7) nm] (Fig. 2). An interesting feature of the 1D chain-pair resides in that all molecules constructing a 1D chain have the same configuration and molecules in the adjacent different 1D chain have the apposite configuration.

Table 3 Hydrogen bonds length (nm) and bonds angle (°) for adduct 1

D-H…A	d(D-H) /nm	d(H…A) /nm	d(D…A) /nm	∠(DHA) /(°)
C3-H…S1 i	0.093	0.2868	0.3761(7)	162.74(3)
C9-H…O4 iii	0.093	0.2481	0.3415(7)	177.56(2)
C34-H…S2 iv	0.093	0.2958	0.3476(6)	143.47(3)
C30-H30A…O2 v	0.097	0.2593	0.3469(8)	152.23(6)

* Symmetry transformations used to generate the equivalent atoms: i -1+*x*, *y*, *z*; iii 2-*x*, -*y*, -*z*; iv 4 1-*x*, -1/2+*y*, 1/2-*z*; v: 2-*x*, -1/2+*y*, 1/2-*z*

The most striking structural feature of adduct **1** is that it forms 1D helical chain structure through potentially weak intermolecular C34-H…S2[iv] hydrogen-bonding interactions [symmetry code (iv): 1-*x*, -1/2+*y*, 1/2-*z*, with distance of 0.3476(6) nm] (Fig. 3(A))[29-31]. Obviously, the hydrogen bonds undoubtedly steer the rotation direction of the helix. The adduct **1** is uniformly spaced column along the *b*-axis. The nearest Ni…Ni distance within the columns is 2.1432nm, and the repeating period in the helical chain is identical with the former. In addition, unlike the most double-helical complexes[32-37], the adjacent helical chains in adduct **1**, one exhibiting left-handedness and the other right-handedness, are not entangled together but hydrogen bonding which are alternatively offered by two helical chains to generate a 1D double-stranded helical chain, as showed in Fig. 3 (A). To illustrate this clearly, the left-and right-handed helical chains are represented respectively in Fig. 3(B), 3(C). Because left-handed and right-handed helical chains coexist in the crystal structure, the whole crystal is mesomeric and does not exhibit chirality[38].

Furthermore, the another inter-chain C30-H30A…O2[v] hydrogen-bonding interactions [symmetry code (v): 2-*x*, -1/2+*y*, 1/2-*z*, with distance of 0.3469(8) nm] link the 1D chain-pair and the double-stranded helical chain into a 3D supramolecular network.

2.2 IR and UV-vis Spectra Studies

The IR spectrum of the nitrogen base adduct **1** shows two strong intensity bands present at 1057 and 996 cm^{-1} are assigned to ν[(P)-O-C)] stretching vibrations, while a strong band at 868 cm^{-1} is assigned to ν[P-O-(C)] stretching vibration. Two strong bands due to PS_2 asymmetric and symmetric stretching vibrations in the adduct are observed at 670 and 601 cm^{-1}, respectively[17, 19]. The weak band at 3027 cm^{-1} may be

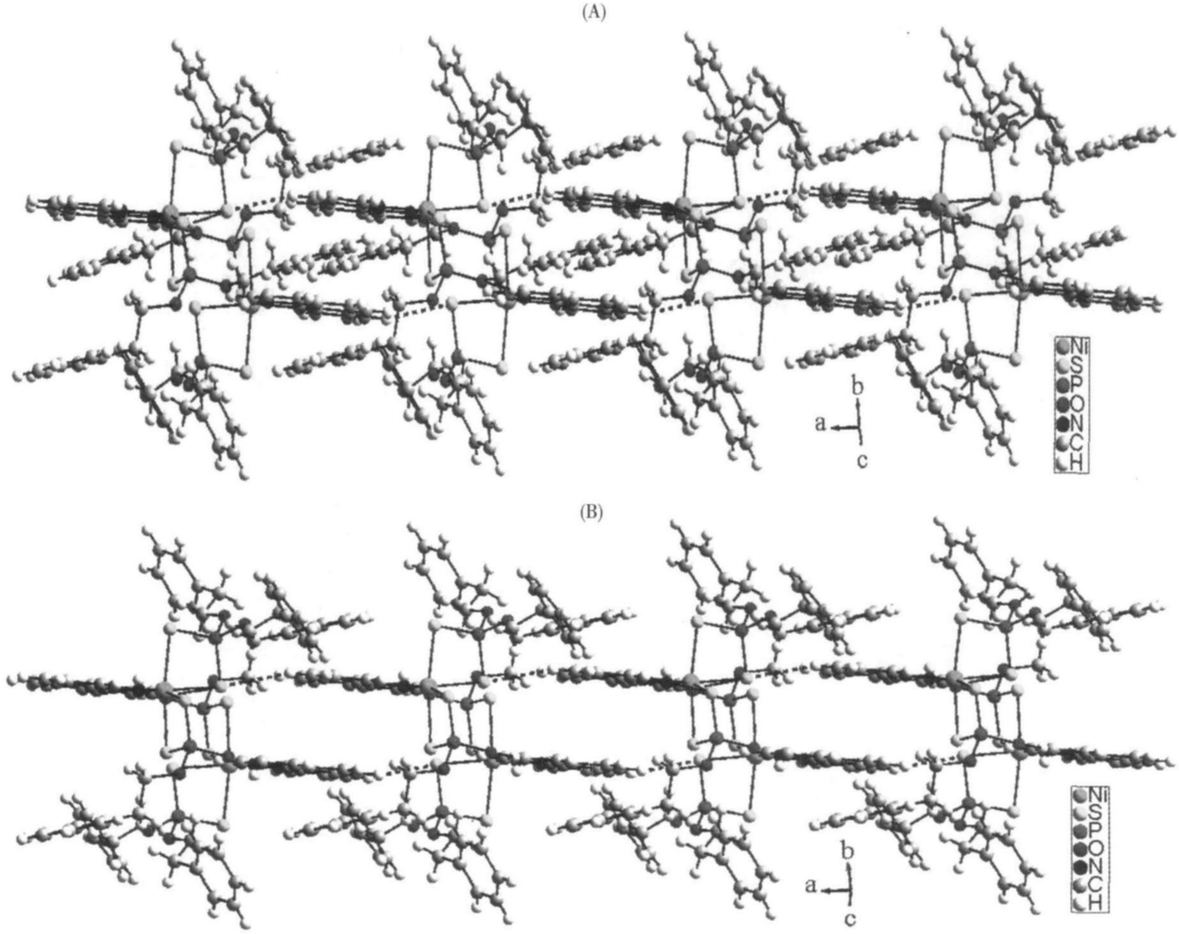

Figure 2 1D chain-pair structure consist from π-π stacking, C3-H…S1[i] interactions, and C9-H…O4[iii] interactions (A), dotted line indicating the hydrogen bonds (B) with party of phenylethyl groups omitted for clear

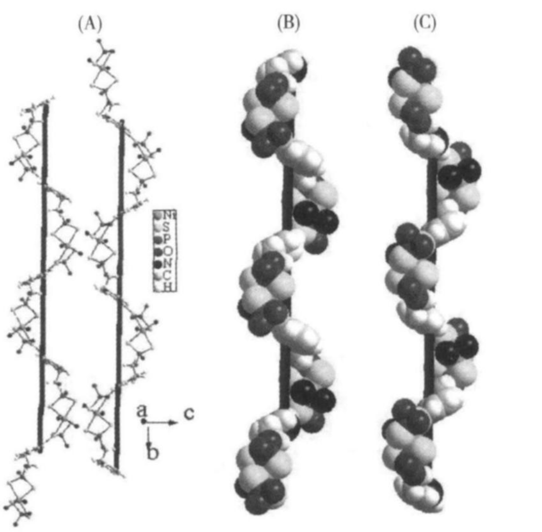

Figure 3 (A) 1D double-stranded helical chain formed by C34-H…S2[iv] hydrogen-bonding interactions, (B) left-handed, and (C) right-handed (phen ligands and party of phenylethyl groups omitted for clarity)

assigned to the unsaturated C-H bond stretching vibrations of the phenyl group and 1, 10-phenanthroline ligand. The bands at 1604, 1494, 1453 and 1422 cm^{-1} may be attributed to the skeleton vibrations of the phenyl group and 1, 10-phenanthroline ligand, but the bond at 1626 cm^{-1} duo to ν(C=N) stretching vibration of phen ligand[15].

The UV-vis spectrum of the adduct **1** in $CHCl_3$ is shown in Fig. 4. The adduct shows an absorption bond at 268 nm that can be attributed to ligand absorption band and /or ligand-to-metal charge transfer band (LMCT). As expected for high-spin octahedral Ni(II) complex, spin allowed d-d bands are observed at 661 and 1122 nm that are assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}$(F) and $^3A_{2g} \rightarrow {}^3T_{2g}$(F) transition, respectively. A weak band at 900 nm is duo to the spin-forbidden $^3A_{2g} \rightarrow {}^3E_{1g}$ transition. The bands at 382 and 414 nm are attributed to the third d-d ($^3A_{2g} \rightarrow {}^3T_{1g}$(P)) for d^8 octahedral Ni(II) complex[19, 39]

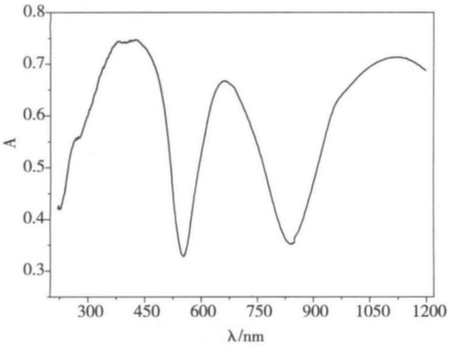

Figure 4 Ultraviolet-visible spectroscopy of adduct 1

2.3 Thermal Analysis

Fig 5 indicates the TG-DSC curves at atmosphere from 35℃ to 700℃. The adduct **1** has a sharp endothermic peak and has no weight loss at 152.3℃, which is attributed to heat-absorbing of adduct **1** melting. The adduct **1** begin to loss at 179.0–279.0℃ corresponding to two 2-phenylethyloxyl groups (anal 25.46%, calc 26.52%), which is assigned to the second weak broad endothermic peak at 206.7℃. Then the weight loss of 18.22% for the adduct **1** at 297.0–422.0℃ corresponding to **1**, 10-phenanthroline ligand (calc 17.09%), which is assigned to the first exotherm ic peak at 379.4℃ and the third endothermic peak at 387.9℃. And last, the continuous weight loss for adduct 1 is observed above 422.0℃ corresponding to removing the residual organic ligands continuously and there isn't thermo-effect any more at DSC curve.

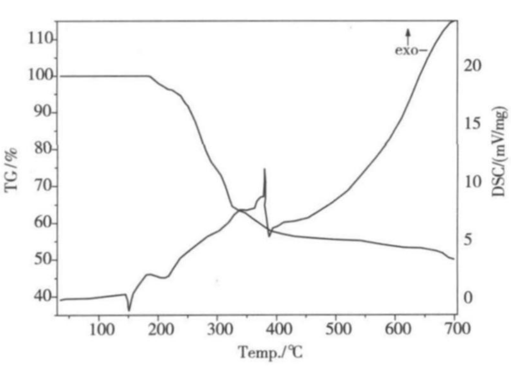

Figure 5 TG-DSC curves of adduct 1

3 Conclusions

A nitrogen base adduct 1, 10-phenanthroline bis *(O, O'*-di(2-phenylethyl) dithiophosphato) nickel(II), $Ni[S_2P(OCH_2CH_2Ph)_2]_2 \cdot phen$ (Ⅰ) has been synthesized. X-ray crystallography shows that adduct **1** consist of 1D chain-pair and 1D double-stranded helical chain, which formed from π-π stacking of phen ligands and hydrogen-bonding interactions of C-H…S and C-H…O. they are further extended to 3D supramolecular network by C-H…S hydrogen-bonding interactions.

Note:

Crystallographic data excluding structure factors for the structural analysis has been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. 774426 for adduct **1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/deposit.html (or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, by Fax 0044-1223-336-033 or E-mail deposit@ccdc.cam.ac.uk).

References:

[1] Masuko M, Sato H, Suzuki A, et al. Prevention of oxidative degradation of ZnDTP by microcapsulation and verification of its antiwear performance[J]. Tribology International, 2008, 41(11): 1097-1102

[2] Hu J Q, Wei X Y, Dai G L, et al. Tribological behaviors and mechanism of sulfur and phosphorus-free organic molybdate ester with zinc dialkyldithiophosphate[J]. Tribology International, 2008, 41(6): 549-555.

[3] Larsson A C, Ivanov A V, Antzutkin O N, et al. Complexation of lead(II) with O, O'-dialkyldithiophosphate ligands ^{31}P and ^{13}C CP/MAS NMR and single-crystal X-ray diffraction studies[J]. Inorg Chim. Acta, 2004, 357: 2510-2518

[4] Ivanov M A, Antzutkin O N, Sharutin V V, et al. Preparation and structural organization of heteroleptic tetraphenylantimony (V) complexes comprising unidentately and bidentately coordinated O, O'-dialkyldithiophosphate groups. Multinuclear(^{31}C, ^{31}P) CP/MAS NMR and single-crystal X-ray diffraction studies [J]. Inorg Chim. Acta, 2007, 360: 2897-2904.

[5] Maheshwari S, Drake J E, Kori K M, et al. Synthesis and spectroscopic characterization of tris(O, O'-ditolyldithio-phosphato) arsenic/antimony/bismuth(III) compounds. Crystal structures of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3] \cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ [J]. Polyhedron, 2009, 28(4): 689-694.

[6] Liu C W, Irwin M D, Mohamed A A, et al. Cluster self-assembly of centered cubes of copper(I) with dialky-ligands. X-ray structures of $[Cu_8(DDP)_6(\mu_8\text{-}X)]PF_6$ ($DDP = S_2P(O^iPr)_2$; X = Cl or Br) and their relationship to oxide and sulfide centered zinc (II) dialkyldithiophosphates, $[Zn_4(DDP)_6(\mu_4\text{-}S\ or\ O)]$[J]. Inorg. Chim. Acta, 2004, 357: 3950-3956

[7] Menzer S, Phillips J R, Slawin A M Z, et al. Structural characterization of basic zinc O, O'-dialkyldithiophos-phosphate and two iso-

meric examples of zinc mono-thiophosphates[J]. J Chem. Soc, Dalton Trans, 2000(19): 3269-3273.

[8] Matsumoto K, Tanaka R, Shimomura R, et al. Synthesis and X-ray structures of octanuclear silver(I) cluster [Ag_8(μ_6-S){$S_2P(OC_2H_5)_2$}$_6$] and its copper(I) analogue [Cu_8(μ_8-S){$S_2P(OC_2H_5)_2$}$_6$][J]. Inorg Chim. Acta, 2000, 304: 293-296.

[9] Drew M G B, Hasan M, Hobson R J, et al. Reaction of [Zn{$S_2P(OPr^i)_2$}$_2$]$_2$·$H_2NCH_2CH_2NH_2$ and [Zn{$S_2P(OPr^i)_2$}$_2$]·NC_5H_5[J]. J Chem. Soc, Dalton Trans, 1986(6): 1161-1166.

[10] Harrison P G, Begley M J, Kabhai T, et al. Zinc(II) bis-(O,O'-dialkyldithiophosphates): complexation behavior with pyridine and other multidentate nitrogen donor molecules. The crystal and molecular structures of the 1:1 complexes of bis(O,O'-di-isopropyldithiophosphato) zinc(II) with pyridine, 2,2'-bipyridine, and 2,2':6',2''-terpyridine and of (1,11-diamino-3,6,9-triazaundecane) zinc(II) bis(O,O'-diethyl dithiophosphate)[J]. J Chem. Soc, Dalton Trans, 1986(5): 929-938.

[11] Harrison P G, Begley M J, Kabhai T, et al. Complexes of lend(II) bis(O,O'-dialkyldithiophosphates) with nitrogen donor ligands. The crystal structures of Pb[$S_2P(OEt)_2$]·en (en=ethylenediamine) Pb[$S_2P(OEt)_2$]$_2$·bipy (bipy=2,2'-bipyridine) and {Pb[$S_2P(OEt)_2$]$_2$}$_2$]·en[J]. J Chem. Soc, Dalton Trans, 1989(12): 2443-2448.

[12] Drew M G B, Forsyth G A, Hasan M, et al. Reactions of copper(II) with [$S_2P(OR)_2$](R=Et or Pr^i) and single-crystal X-ray studies of Cu[$S_2P(OEt)_2$]·bipy and Cu[$S_2P(OEt)_2$]·2PPh_3[J]. J Chem. Soc, Dalton Trans, 1987(5): 1027-1033.

[13] Li Z H, Li J R, Du S W. Construction of three novel luminescent polymers containing {$CuS_2P(OR)_2$} (R=Me, Et) building blocks linked by 4,4'-bipyridine ligands[J]. J Mol Struct, 2006, 783(6): 116-121.

[14] Shetty P S, Fernando Q. Structures of five- and six-coordinated mixed-ligand chelates of nickel(II) containing sulfur and nitrogen donor atoms[J]. J Am. Chem. Soc, 1970, 92(13): 964-3969.

[15] 刘世雄,林墀昌,徐正,等.双-(O,O'-二正 基二硫代磷酸酯)合镍-二吡啶加合物的晶体结构和分子结构[J].有机化学,1987,7(5): 369-373.

[16] 游效曾,徐正,徐昕,等.双-(O,O'-二环己基二硫代磷酸酯)合镍(II)与苄胺的加合常数及加合物 Ni[$(C_6H_{11}O)_2PS_2$]$_2$·$2NH_2CH_2C_6H_5$的晶体结构[J].化学通报,1991,36(17): 1308-1311.

[17] 谢斌,程煜,邹立科,等.三元配合物 Ni[$S_2P(OCH_2CH_2Ph)_2$]$_2$·bipy的合成与晶体结构[J].化学通报,2009,72(1): 70-74.

[18] Zou L K, Xie B, Zhao B, et al. Bis[O,O'-bis(2-phenylethyl) dithiophosphato]dipyridinenickel(II)[J]. Acta Cryst, 2006, 62: 2830-2830.

[19] Bingham A L, Drake J E, Hursthouse M B, et al. Synthesis, characterization and spectral studies of nitrogen base adducts of bis(O,O'-ditolyldithiophosphato) nickel(II). Crystal structures of Ni[$S_2P(OC_6H_4Me$-p$)_2$]$_2$·$C_{10}H_8N_2$ and Ni[$S_2P(OC_6H_4Me$-o$)_2$]$_2$·$_{14}H_{12}N_2$·$_6H_6$[J]. Polyhedron, 2007, 26(12): 2672-2678.

[20] Hao Q, Fun H K, Chantrapromma S, et al. Bis(O,O'-di-p-tolyldithiophosphato-S,S')(1,10-phenanthroline-N,N')nickel(II)[J]. Acta Cryst, 2001, 57: 717.

[21] 谢斌,李可彬,邹立科,等.含四氮杂大环的双(O,O'-二(2-苯乙基)二硫代磷酸根)合镍(II)或铜(II)配合物的合成和晶体结构[J].结构化学,2004(23): 324-331.

[22] Zou L K, Xie B, Xie J Q, et al. Kinetic study of the hydrolysis of a carboxylic acid ester promoted by the complex bis(O,O'-di(2-phenylethyl) dithiophosphato) nickel II)[J]. Transition Met Chem., 2009, 4(4): 395-401.

[23] Sheldrick G M. SHELXTL, Structure determination software program. Version 5.10, Bruker analytical X-ray systems[M]. Inc Madison, WI, 1997.

[24] Frarrugia L J. WinGX suite for small-molecule single-crystal crystallography[J]. J Appl Cryst, 1999, 32: 837.

[25] 刘法谦,李荣勋,李少香.四(1乙基咪唑)二异硫氰酸锰的晶体结构和热性能[J].无机化学学报,2008,24(1): 141.

[26] 武文,谢吉民.之字链配合物 $Cu(phth)_2(H_2O)_2$ 的合成、表征及晶体结构[J].人工晶体学报,2008,37(5): 1172-1176.

[27] 金晶,刘佳操,赵力民,等.Co(II)配位超分子的水热合成、晶体结构及光物理性能[J].辽宁师范大学学报:自然科学版,2008,31(4): 478-481.

[28] 张曙光,冯云龙,温一航.H键连接的三维超分子化合物[$M(H_2O)_6$]$(HL)_2$的合成、表征与结构[H_2L=1-(4-羟基苯)-5-四氮唑乙酸,M=Mn^{II},Co^{II},Ni^{II},Zn^{II}][J].无机化学学报,2008,24(4): 581-585.

[29] Gluaker J P, Lewis M, Rossi M. Crystal structure analysis for chemists and biologists[M], New York: VCH Publishers Inc, 1994.

[30] Steiner T. C-H…O Hydrogen bonding in crystals[J]. Crystallogr Rev, 1996, 6(1): 1-51.

[31] Hunter R H, Haueisen R H, Irving A. The first water-dependent liquid clathrate: X-ray evidence in the solid for a C-H…π(heteroarene)…H-C interaction[J]. Angew. Chem., Int Ed Engl, 1994, 33(5): 566-568.

[32] Lu C Z, Wu C D, Lu S F, et al. A three-dimensional zeolite-like organic-inorganic hybrid material constructed from {$CuMo_2O_8N$}$_n$ double helical chains linked via [Cu(4,4'-bpy)]$_n$ fragments[J]. Chem. Commun, 2002(2): 152-153.

[33] Wang Y, Yu J H, Guo M, et al. [{$Zn_2(HPO_4)_4$}{$Co(dien)_2$}]H_3O: A zinc phosphate with multidirectional intersecting helical channels[J]. Angew. Chem., Int Ed Engl, 2003, 42(34): 4089-4092.

[34] Qin C, Wang X L, Li Y G, et al. Three-dimensional mesomeric networks assembled from helix-linked sheets: syntheses, structures, and magnetisms[J]. J Chem. Soc, Dalton Trans, 2005(15): 2609-2614.

[35] Wu Z, Chen Q, Xiong S, et al. Double-stranded helicates, triangles, and squares formed by the self-assembly of pyrrol-2-ylmethyle-

neamines and Zn[II] ions[J]. Angew. Chem. Int Ed, 2003, 42(28): 3271-3274

[36] Barboiu M, Vaughan G, Graff R, et al. Self assembly, structure, and dynamic interconversion of metallosupramolecular architectures generated by Pb(II) binding-induced unfolding of a helical ligand[J]. J Am. Chem. Soc, 2003, 125(34): 10257-10265

[37] Wang X L, Qin C, Wang E B. An unusual polyoxometalate-encapsulating 3D polyrotaxane framework formed by molecular squares threading on a twofold interpenetrated diamondoid skeleton[J]. Chem Commun., 2007, 41: 4245-4247.

[38] Wang X L, Qin C, Wang E B, et al. Syntheses, structures, and photoluminescence of a novel class of d[10] metal complexes constructed from pyridine-3, 4-dicarboxylic acid with different coordination architectures[J]. Inorg. Chem. 2004, 43(6): 1850-1856.

[39] Holz R C, Evdokimov E A, Gobena F T. Two-dimensional [1]H NMR studies on octahedral nickel (II) complexes[J]. Inorg Chem., 1996, 35(13): 3808-3814.

1, 10-林菲啰啉·双 (O, O'-二(2-苯乙基)二硫代磷酸)合镍(II)的合成与晶体结构

谢 斌[1,2], 邹立科[1,2], 赖 川[3], 黄 春[3], 王 军[1,2], 相阳光[3]

(1. 四川理工学院功能材料研究所, 四川 自贡 643000; 2. 绿色催化四川省高校重点实验室, 四川 自贡 643000; 3. 四川理工学院材料与化学工程学院, 四川 自贡 643000)

摘 要: 在石油醚和丙酮溶液中, 配合物 $Ni[S_2P(OCH_2CH_2PH)_2]_2$ 与 1, 10-邻菲啰啉(phen)反应得到了绿色的氮碱加合物 1, 10-林菲啰啉·双 (O, O'-(二 2-苯乙基)二硫代磷酸)合镍(II), 用元素分析、紫外-可见光谱、红外光谱、热分析和 X-射线单晶衍射进行了表征。加合物属单斜晶系, $P2_1/c$空间群。晶胞参数为 $a = 1.0987(9)$ nm, $b = 2.1432(9)$ nm, $c = 1.9025(5)$ nm, $\beta = 98.68(1)^\circ$, $V = 4.429(4)$ nm^3, $Z = 4$, $Dc = 1.370$ Mg/m^3, $F(000) = 1904$, $\mu = 0.743$ mm^{-1}, 可观测衍射点为 3498, $R = 0.057$, $wR = 0.1492$ $(I > 2\sigma(I))$。加合物为畸变八面体构型, 配位原子来自于两个O, O'-二(2-苯乙基)二硫代磷酸根的 4 个硫原子和配体 phen的 2 个氮原子。Ni-S键的键长在 0.2474(2)-0.2505(17) nm范围内, Ni-N键的键长分别为 0.2081(4) nm和 0.2090(5) nm。因分子间存在 π-π 堆积、C-H…O 和 C-H…S氢键作用, 加合物的晶体结构形成了一维链对和一维双链螺旋链。一维链对和一维双链螺旋链通过 C-H…O氢键作用进一步延展为三维结构。

关键词: O, O'-二烃基二硫代磷酸; 镍(II)加合物; 合成; 表征; 晶体结构