



Synthesis and Crystal Structure of O-Methyldithiophosphato Nickel Complex [Ni(S₂P(O)OCH₃)(dppe)]

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O-Methyldithiophosphato nickel complex [Ni(S₂P(O)OCH₃)(dppe)] (**I**) (dppe = Ph₂PCH₂CH₂PPh₂) has been synthesized by treatment of (dppe)NiCl₂ with (CH₃O)₂P(S)SH·Et₂NH in THF solution. The new complex (**I**) was fully characterized by elemental analysis, TGA, IR, ¹H, ¹³C, ³¹P NMR spectroscopies. In addition the molecular structure of the complex was established by X-ray crystallography. The crystal of [Ni(S₂P(O)OCH₃)(dppe)] crystallizes in monoclinic, spacegroup P21/n with a = 9.2762(3), b = 17.1214(5), c = 18.8627(6) Å, α = 90.00, β = 96.813(3), γ = 90.00°, V = 2974.66(15) Å³, Z = 4, C₂₇H₂₇O₂P₃S₂Ni, Mr = 599.23, D_c = 1.338 g/cm³, F(000) = 1240 and μ(MoKα) = 0.976 mm⁻¹. The final R = 0.0521 and wR = 0.1303 for 6073 observed reflections [I > 2σ(I)].

Key Words: Ph₂PCH₂CH₂PPh₂, Dithiophosphate, Synthesis, X-ray crystallography.

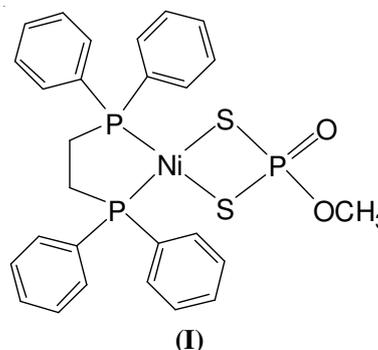
INTRODUCTION

The nickel complexes (diphosphine)NiCl₂ (diphosphine = dppe, dppv, dppf) have been received special attention, largely because of their unique structure and their use in Suzuki-type coupling of boronic acids¹⁻⁵. The main advantage of nickel in this application is that it reacts more readily with aryl chlorides and methane sulfonates than does the Pd system. In recent years, the nickel complexes (diphosphine)NiCl₂ have also been used to synthesize [NiFe] hydrogenases models. A series of [NiFe] hydrogenases models (dppe)Ni(μ-S)₂Fe₂(CO)₆ and (dppf)Ni(μ-S)₂Fe₂(CO)₆ have been synthesized by treatment of (μ-SLi)₂Fe₂(CO)₆ with (dppe)NiCl₂ and (dppf)NiCl₂, respectively⁶⁻¹⁰. Especially, Schmidt prepared an important complex (dppe)Ni(pdt) by reaction of (dppe)NiCl₂ with HSCH₂CH₂CH₂SH^{11,12}, which has been used to synthesized [NiFe] hydrogenases model complex (dppe)Ni(μ-pdt)Fe(CO)₃¹³, that attracted our interest.

In view of the above information and as a continuation of our studies on such complexes, we herein report the synthesis and crystal structure of O-methyldithiophosphato nickel complex [Ni(S₂P(O)OCH₃)(dppe)] (**I**), we expect it can be used to synthesis the [NiFe] hydrogenases models.

EXPERIMENTAL

All solvents were dried using standard procedures and distilled under N₂. Ni(dppe)Cl₂ was prepared according to



Structure of the title complex (**I**)

literature procedures¹⁴. Some other materials were available commercially. Melting points were determined on a SGW X-4 microscopic melting point apparatus and were uncorrected. Elemental analyses for carbon, hydrogen were performed on a Perkin-Elmer 240C analyzer. IR spectra were recorded at room temperature on a Bruker Vector 22 infrared spectrophotometer. ¹H, ¹³C, ³¹P NMR spectra were obtained on a Varian Mercury Plus 400 NMR spectrometer. TGA measurement was carried out on a NETZSCH STA 409 PC/PG instrument.

Synthetic procedure: (CH₃O)₂P(S)SH·Et₂NH (0.227 g, 1.0 mmol), Ni(dppe)Cl₂ (0.264 g, 0.5 mmol) and THF (15 mL) are added to a 3-neck round bottomed flask. The mixture was stirred at room temperature for 1 h. Then volatiles were

removed under vacuum and the residue was subjected to TLC using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ($v/v = 5:1$) as eluent. From the main red band, the title complex (**I**) (0.255 g, 85 %) was obtained as an orange solid. m.p. 200–202 °C. Anal. calcd. (%) for $\text{C}_{27}\text{H}_{27}\text{NiO}_3\text{P}_3\text{S}_2$: C, 54.12, H, 4.54; Found (%): C, 54.01, H, 4.83. IR (KBr, ν_{max} , cm^{-1}): 3052, 2986, 1607, 1503, 1435, 1203, 1161, 1100, 998, 889, 691, 557. ^1H NMR (400 MHz, DMSO, TMS) δ/ppm : 2.51–2.65 (m, 4H, $\text{PCH}_2\text{CH}_2\text{P}$), 3.52 (s, 3H, CH_3), 7.54–7.80 (m, 20H, $4\text{C}_6\text{H}_5$). ^{13}C NMR (100.6 MHz, DMSO): 26.72 ($\text{PCH}_2\text{CH}_2\text{P}$), 53.48 (OCH_3), 115.50, 127.57, 129.55, 130.16, 132.20, 133.00, 133.39 (C_6H_5) ppm. ^{31}P NMR (162 MHz, DMSO, 85 % H_3PO_4) δ/ppm : 56.86 (q), 63.73 (s) ppm.

Crystal structure determination: Single crystal of the title complex (**I**) suitable for X-ray diffraction analysis was grown by slow evaporation of the $\text{CH}_2\text{Cl}_2/\text{hexane}$ solution at -5 °C. The crystal of (**I**) with dimensions of 0.40 mm \times 0.36 mm \times 0.24 mm was mounted on a Rigaku RAXIS-RAPID diffractometer equipped with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using an ω scan mode at 143(10) K in the range of $3.25^\circ \leq \theta \leq 26.37^\circ$. The crystal belongs to monoclinic system with space group P21/n and crystal parameters of $a = 9.2762(3)$ Å, $b = 17.1214(5)$ Å, $c = 18.8627(6)$ Å, $\alpha = 90.00^\circ$, $\beta = 96.813(3)^\circ$, $\gamma = 90.00^\circ$, $V = 2974.66(15)$ Å³, $D_c = 1.338$ g/cm³. The absorption coefficient $\mu = 0.976$ mm⁻¹ and $Z = 4$. Absorption correction was performed by the CRYSTALCLEAR program¹⁵. The structure was solved by direct methods using the SHELXS-97 program¹⁶ and refined by full-matrix least-squares techniques on F^2 data using SHELXL-97¹⁷. The empirical absorption corrections were applied to all intensity data. All the Hydrogen atoms were located by using the geometric method, with $d(\text{C-H}) = 0.95$ – 0.98 Å and $U_{\text{iso}(\text{H})} = 1.2 U_{\text{eq}(\text{C})}$ or $1.5 U_{\text{eq}(\text{C-methyl})}$. The final full-matrix least squares refinement gave $R = 0.0521$, $wR = 0.1303$ ($w = 1/[\sigma^2(\text{F}_o)^2 + (0.0633\text{P})^2 + 2.5119\text{P}]$, where $\text{P} = (\text{F}_o^2 + 2\text{F}_c^2)/3$), $S = 1.086$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.883$ and $(\Delta\rho)_{\text{min}} = -0.534$ e/Å³.

RESULTS AND DISCUSSION

The single crystal of the title complex (**I**) was obtained by slow diffusion of *n*-hexane to the dichloromethane solution of the complex, which was crystallized as air-stable red crystals. The elemental analyses, IR and NMR spectra are in good agreement with the formulae proposed by the X-ray crystallography.

Structure of the Ni(II) complex (I): Crystallographic and refinement parameters are listed in Table-1. The selected bond lengths and angles are given in Tables 2-3. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2 . The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure of the title complex (**I**) is shown in Fig. 1. The crystal packing diagram of the title complex (**I**) is shown in Fig. 2.

As shown in Fig. 1, the Ni(1) atom is coordinated by two phosphorus atoms (P(1), P(2)) from dppe and two sulfur atoms

TABLE-1
CRYSTAL DATA AND STRUCTURAL
REFINEMENT FOR COMPLEX I

Items	Values
Empirical formula	$\text{C}_{27}\text{H}_{27}\text{NiO}_3\text{P}_3\text{S}_2$
Formula weight	599.23
Crystal system	Monoclinic
Unit cell dimensions	
a (Å, °)	9.2762(3)
b (Å, °)	17.1214(5)
c (Å, °)	18.8627(6)
Unit cell angles (°)	
α	90.00
β	96.813(3)
γ	90.00
Volume (Å ³)	2974.66(15)
Z	4
Temperature (K)	143(10)
Space group	P 21/n
Wavelength (Å)	0.71073
Calculated density (g cm ⁻³)	1.338
Absorption coefficient μ (mm ⁻¹)	0.976
$F(000)$	1240
Crystal size (mm ³)	0.40 \times 0.36 \times 0.24
θ range for data collection (°)	3.25 – 26.37
Limiting indices	$-11 \leq h \leq 11$, $-21 \leq k \leq 18$, $-23 \leq l \leq 22$
Reflection collected	14774
Independent reflection	6073 ($R_{\text{int}} = 0.0282$)
Completeness to θ_{max} (%)	99.79
Data/restraints/parameters	6073/0/317
Goodness-of-fit on F^2	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1303$
R indices (all data)	$R_1 = 0.0713$, $wR_2 = 0.1425$
Largest diff.e peak and hole (e Å ⁻³)	0.883 and -0.534

TABLE-2
SELECTED BOND LENGTHS (Å) FOR COMPLEX I

Bond lengths	X-ray crystal
Ni(1)-S(1)	2.2192(10)
Ni(1)-S(2)	2.2147(11)
Ni(1)-P(1)	2.1500(10)
Ni(1)-P(2)	2.1756(10)
S(1)-P(3)	2.0265(16)
S(2)-P(3)	2.0283(15)
O(1)-P(3)	1.588(4)
O(2)-P(3)	1.474(3)

TABLE-3
SELECTED BOND ANGLES (°) FOR COMPLEX I

Bond angles	X-ray crystal
S(2)-Ni(1)-S(1)	88.35(4)
P(1)-Ni(1)-S(1)	88.14(4)
P(1)-Ni(1)-S(2)	176.47(4)
P(1)-Ni(1)-P(2)	88.18(4)
P(2)-Ni(1)-S(1)	173.98(4)
P(2)-Ni(1)-S(2)	95.35(4)
P(3)-S(1)-Ni(1)	85.87(5)
P(3)-S(2)-Ni(1)	85.95(5)
S(1)-P(3)-S(2)	99.28(6)
O(1)-P(3)-S(1)	109.42(14)

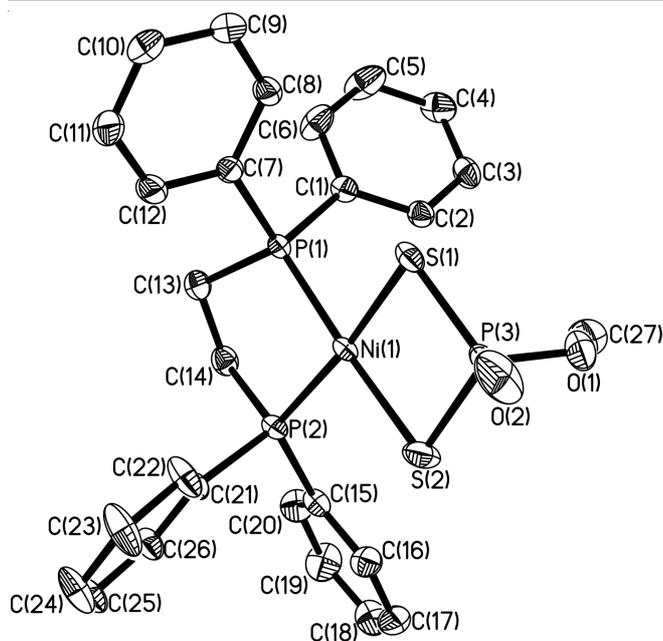


Fig. 1. Molecular structure of complex I with 30 % probability thermal ellipsoids

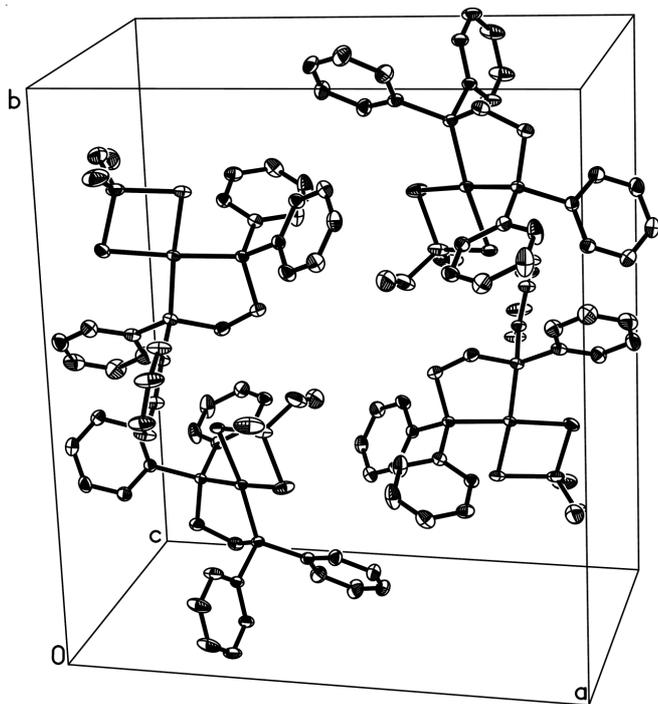


Fig. 2. Crystal packing diagram of complex I

(S(1), S(2)) from one O-methyldithiophosphato. The geometry at the Ni centre in the title complex (I) is square-planar with the NiP_2S_2 chromophore. The Ni(1)-P(1) bond length (2.1500(10) Å), Ni(1)-P(2) bond length (2.1756(10) Å), Ni(1)-S(1) bond length (2.2192(10) Å) and Ni(1)-S(2) bond length (2.2147(10) Å) are almost the same length as the corresponding bonds of the complex $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OCH}_2\text{CH}_3)(\text{dppe})]$ (Ni(1)-P(3) bond length (2.1414(6) Å), Ni(1)-P(2) bond length (2.1608(6) Å), Ni(1)-S(1) bond length (2.2224(6) Å), Ni(1)-S(2) bond length (2.2124(6) Å)¹⁸, which proves that phosphorus and sulfur atoms coordinate to nickel atom. The O(2)=P(3) double bond length (1.474(3) Å) is shorter than the O(1)-P(3)

single bond length (1.588(4) Å), which is consistent with the results of IR spectra. The sum of the selected bond angles P(2)-Ni(1)-P(1) (88.18(4)°), P(1)-Ni(1)-S(1) (88.14(4)°), S(1)-Ni(1)-S(2) (88.35(4)°) and P(2)-Ni(1)-S(2) (95.35(4)°) is 360.02°, which indicated that the coordination geometry around nickel is distorted from an ideal arrangement. In addition, as shown in Fig. 2, one cell contains four molecule structural units.

TGA analysis for the present Ni(II) complex (I): To reveal the thermal stabilities of the title complex, TGA measurement has been carried out on a NETZSCH STA 409 PC/PG instrument with a flow of dry air at a heating rate of 5 °C/min from room temperature to 800 °C, shown in Fig. 3. With the temperature increasing to 460 °C, the complex is completely decomposed.

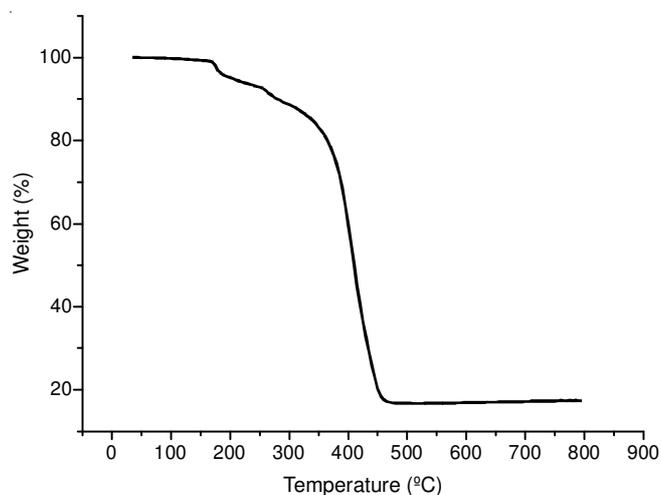


Fig. 3. TG curve for the title complex I

Conclusion

In summary, O-methyldithiophosphato nickel complex $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OCH}_3)(\text{dppe})]$ (I) has been synthesized and structurally characterized by elemental analysis, TGA, IR and ^1H , ^{13}C , ^{31}P NMR spectra. Particularly, the molecular structure of the complex (I) was determined by single-crystal X-ray diffraction analysis. Compared to the traditional way to synthesize the O-alkyldithiophosphato nickel complexes with diphosphine ligands¹⁸, our synthesis route is found to be simple and efficient.

Supplementary data

CCDC-920344 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or E-mail: deposit@ccdc.cam.ac.uk).

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