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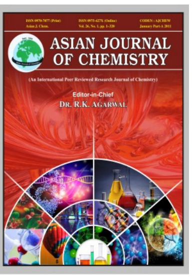

Synthesis, Characterization and Crystal Structure of Nickel Complex (dppv)Ni($C_7H_4NS_2$)$_2$

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Reaction of 2-mercaptobenzothiazole with (dppv)NiCl$_2$ (dppv: Ph$_2$PCH=CHPPh$_2$) in the presence of Et$_3$N affords the title complex (dppv)Ni($C_7H_4NS_2$)$_2$ in 92 % yield. The new complex was fully characterized by elemental analysis, TGA, IR and ^{1}H (^{13}C, ^{31}P) NMR spectroscopies. In addition, the molecular structure of the title complex was established by X-ray crystallography. The crystal of (dppv)Ni($C_7H_4NS_2$)$_2$·CH$_2$Cl$_2$ crystallizes in monoclinic, space group P2/n with a = 15.927(9), b = 8.3553(5), c = 16.3728(8) Å, α = 90.00, β = 112.417(4), γ = 90.00°, V = 2014.22(19) Å^3, Z = 2, $C_{40}H_{30}N_2NiP_2S_4$·CH$_2$Cl$_2$, M$_r$ = 872.48, D$_c$ = 1.439 g/cm^3, F(000) = 896 and μ(MoK$_\alpha$) = 0.934 mm^{-1}. The final R = 0.0920 and wR = 0.2220 for 2572 observed reflections with I > 2σ(I) and R = 0.1171 and wR = 0.2434 for all data. The geometry at the Ni centre in the title complex is square-planar with the NiP$_2$S$_2$ chromophore.

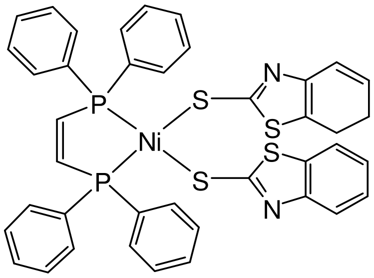
Keywords: dppv, 2-Mercaptobenzothiazole, Synthesis, X-ray crystallography.

INTRODUCTION

Since the discovery of nickel could be used in place of palladium in Suzuki-type coupling of boronic acids and the active site of [NiFe] hydrogenases consists of a [NiFe$_2$S] cluster core, (diphosphine)NiCl$_2$ (diphosphine = dppe, dppv, dppf) have been received special attention[1-6]. A series of [NiFe] hydrogenases models (dppe)Ni(μ-S)$_2$Fe$_2$(CO)$_6$ and (dppf)Ni(μ-S)$_2$Fe$_2$(CO)$_6$ have been synthesized by treatment of (μ-SLi)$_2$Fe$_2$(CO)$_6$ with (dppe)NiCl$_2$ and (dppf)NiCl$_2$, respectively[7-11]. Especially, Schmidt prepared an important complex (dppe)Ni(pdt) by reaction of (dppe)NiCl$_2$ with HSCH$_2$CH$_2$CH$_2$SH[12, 13], which has been used to synthesized [NiFe] hydrogenases model complex (dppe)Ni(μ-pdt)Fe(CO)$_3$[14], that attracted our interest. Here we reported the synthesis, characterization and crystal structure of (dppv)Ni($C_7H_4NS_2$)$_2$(I) (**Scheme-1**), we expect it can be used to synthesize the [NiFe] hydrogenases models.

EXPERIMENTAL

All reactions were carried out in a N$_2$ atmosphere using standard Schlenk techniques. All solvents were dried using standard procedures and distilled under N$_2$. Ni(dppv)Cl$_2$[15] was prepared according to literature procedures. 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. ^{1}H (^{13}C, ^{31}P) 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.



(I)

Scheme-I: Structure of Ni(II) complex (**I**)

Synthetic procedure: A solution of Ni(dppv)Cl$_2$ (0.263 g, 0.5 mmol) in THF (15 mL) was treated with 2-mercaptobenzothiazole (0.167 g, 1 mmol) in the presence of Et$_3$N (0.140 mL, 1 mmol). The mixture was stirred at room temperature for 1 h, volatiles were removed under vacuum and the residue was subjected to TLC using CH$_2$Cl$_2$/*n*-hexane (v/v = 5:1) as eluent. From the main red band, the title complex (**I**) (0.360 g, 92 %) was obtained as a red solid. m.p.: 214-216 °C . Anal.

calcd. (%) for $C_{40}H_{30}N_2NiP_2S_4$: C, 61.00, H, 3.84, N: 3.56; Found : C, 61.27, H, 3.92, N, 3.48. IR (KBr, ν_{max}, cm^{-1}): 3052, 1642, 1485, 1433, 1102, 1076, 1034, 995, 751, 724, 691. ^1H NMR (400 MHz, DMSO, TMS) δ ppm: 7.08-7.85 (m, 30H, $4C_6H_5$, $2C_6H_4$, CH=CH) ppm. ^{13}C NMR (100.6 MHz, DMSO, TMS) δ ppm: 113.11, 122.11, 124.49, 127.48, 128.97, 131.95, 133.94, 133.97, 142.40 (C_6H_5, C_6H_4, CH=CH), 190.09 (C=N). ^{31}P NMR (162 MHz, DMSO, 85 % H_3PO_4) δ ppm: 64.73 (s).

Crystal structure determination: Single crystal of the present nickel complex (**I**) suitable for X-ray diffraction analysis was grown by slow evaporation of the CH_2Cl_2/hexane solution at -10 °C. The crystal of (**I**) with dimensions of 0.28 mm × 0.24 mm × 0.21 mm was mounted on a CCD area detector equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using by using an ω scan mode at 296(2) K in the range of 1.52º ≤ θ ≤ 25.01°. The crystal belongs to monoclinic system with space group P2/n and crystal parameters of a = 15.927(9) Å, b = 8.3553(5) Å, c = 16.3728(8) Å, α = 90.00°, β = 112.417(4)°, γ = 90.00°, V = 2014.22(19) $Å^3$, D_c = 1.439 g/cm^3. The absorption coefficient μ = 0.934 mm^{-1} and Z = 2. Absorption correction was performed by the CRYSTALCLEAR program[16]. The structure was solved by direct methods using the SHELXS-97 program[17] and refined by full-matrix least-squares techniques on F^2 data using SHELXL-97[18]. The empirical absorption corrections were applied to all intensity data. All the Hydrogen atoms were located by using the geometric method, with d(C-H) = 0.95-0.98 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C_{methyl})$. The final full-matrix least squares refinement gave R = 0.0920, wR = 0.2220 ($w = 1/[\sigma^2(F_o)^2 + (0.1021P)^2 + 10.4125P]$, where $P = (F_o^2 + 2F_c^2)/3$), S = 1.089, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta\rho)_{max}$ = 1.380 and $(\Delta\rho)_{min}$ = -1.120 e/$Å^3$.

RESULTS AND DISCUSSION

The single crystal of the present 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 title complex (I): Crystallographic and refinement parameters are listed in Table-1. The selected bond lengths and angles are given in Tables 2 and 3. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all non-hydrogen 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 present nickel complex (**I**) was determined by X-ray diffraction ORTEP and crystal packing diagram of the title complex (I) are shown in Figs. 1 and 2, respectively.

As can be seen in Fig. 1, the crystal of the complex (**I**) contain a dichloromethane molecule, the geometry at the Ni centre in the title complex (**I**) is square -planar with the NiP_2S_2 chromophore. The Ni atom is coordinated by two sulfur atoms from 2-mercaptobenzothiazole and two phosphorus atoms from dppv ligand. The crystallographic study of the title complex (**I**) revealed that the Ni(1)-P(1) bond length (2.1437(19) Å) is shorter than the corresponding bond of complex (dppe)Ni(pdt) (Ni(1)-P(1) = 2.1637(7) Å; Ni(1)-P(2) = 2.1554(7) Å), while the Ni(1)-S(1) bond length (2.267(2) Å) is slightly longer than the corresponding bond of complex (dppe)Ni(pdt)(Ni(1)-S(1) = 2.1966(7) Å; Ni(1)-S(2) = 2.2077(7) Å)[14]. The selected bond angels P(1)-Ni(1)-P(1A) 87.92(10)°, P(1)-Ni(1)-S(1A) 88.41(7)°, S(1)-Ni(1)-S(1A) 95.28(11)°, P(1A)-Ni(1)-S(1) 88.41(7)° for the title complex (**I**) indicated that the coordination geometry around nickel is distorted from an ideal arrangement (sum of the angles is

TABLE-1

Items	Values
Empirical formula	$C_{41}H_{32}Cl_2N_2NiP_2S_4$
Formula weight	872.48
Crystal system	Monoclinic
Unit cell dimensions	
a (Å, °)	15.9275(9)
b (Å, °)	8.3553(5)
c (Å, °)	16.3728(8)
Unit cell angles (°)	
α	90.00
β	112.417(4)
γ	90.00
Volume ($Å^3$)	2014.22(19)
Z	2
Temperature (K)	296(2)
Space group	P 2/n
Wavelength (Å)	0.71073
Calculated density (g cm^{-3})	1.439
Absorption coefficient μ (mm^{-1})	0.934
F(000)	896
Crystal size (mm^3)	0.28 x 0.24 x 0.21
θ range for data collection (°)	1.52 – 25.01
Limiting indices	-18 < = h < = 18, -9 < = k< = 9, -19 < = l < = 18
Reflection collected	9234
Independent reflection	3452 (R_{int} = 0.0545)
Completeness to θ_{max} (%)	97.0
Data/restraints/parameters	3452/348/236
Goodness-of-fit on F^2	1.102
Final R indices [I > 2σ(I)]	R_1 = 0.0920, wR_2 = 0.2220
R indices (all data)	R_1 = 0.1171, wR_2 = 0.2434
Largest diff.e peak and hole (e A^{-3})	1.120 and -1.380

TABLE-2

Bond lengths	X-ray crystal
Ni(1)-P(1)	2.1437(19)
Ni(1)-S(1)	2.267(2)
N(1)-C(14)	1.291(10)
P(1)-C(2)	1.815(8)
P(1)-C(1)	1.820(7)
P(1)-C(8)	1.807(7)
S(1)-C(14)	1.714(8)
S(2)-C(14)	1.762(8)

TABLE-3

Bond angles	X-ray crystal
P(1)-Ni(1)-P(1A)	87.92(10)
P(1)-Ni(1)-S(1)	176.19(8)
P(1)-Ni(1)-S(1A)	88.41(7)
S(1)-Ni(1)-S(1A)	95.28(11)
C(14)-S(1)-Ni(1)	91.8(3)
C(15)-S(2)-C(14)	88.8(5)
C(14)-N(1)-C(16)	112.2(8)
C(1)-P(1)-Ni(1)	109.0(2)

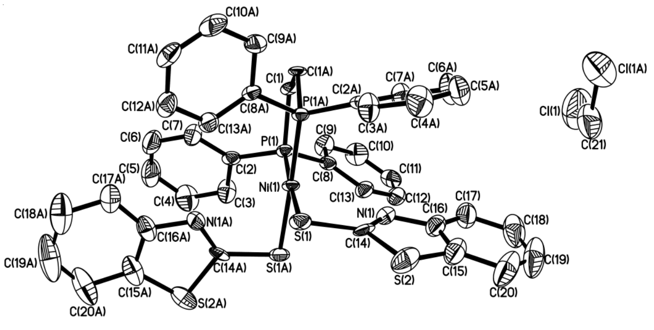


Fig. 1. Molecular structure of (**I**) with 30 % probability thermal ellipsoids

360.02°). The bond angels C(14)-S(1)-Ni(1) and C(14A)-S(1A)-Ni(1) are both 91.8(3)°, the bond angel P(1)-Ni(1)-S(1) is 176.19(8)°. In addition, as shown in Fig. 2, a lD linear chain is formed *via* S···H intramolecular interactions. The distances of S1B and H1, S1AA and H1A are both 2.919 Å.

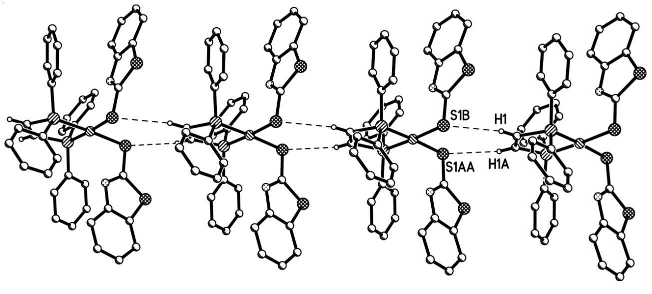


Fig. 2. Crystal packing diagram of (**I**)

TGA analysis: 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 1000 °C, shown in Fig. 3. The TGA curve indicates that the weight loss below 240 °C is 20.22 %, which is attributed to 2-mercaptobenzothiazole molecule (Cacld. 21.1 %). With the temperature increasing to 400 °C, the ligand dppv and 2-mercaptobenzothiazole are completely decomposed.

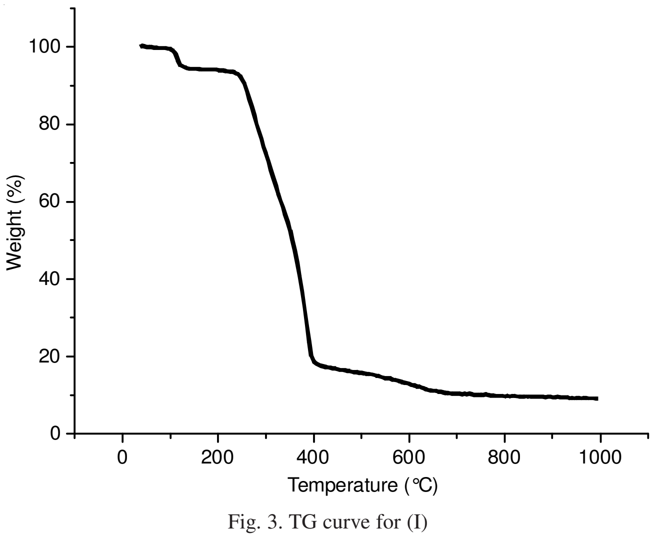


Fig. 3. TG curve for (I)

Conclusion

In summary, the nickel complex (dppv)Ni($C_7H_4NS_2$)$_2$ (I) has been synthesized and structurally characterized by elemental analysis, TGA, IR and ^{1}H (^{13}C, ^{31}P) NMR spectra. Particularly, the molecular structure of the complex (**I**) was determined by single-crystal X-ray diffraction analysis.

Supplementary data

CCDC-914957 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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