

含双二苯基膦乙烷镍配合物的合成与性质

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在氯仿中通过取代反应制备了含双二苯基膦乙烷(dppe)的镍配合物 $[\text{Ni}(\text{dppe})\text{Cl}_2]$, 并通过元素分析、热分析、红外光谱、核磁、电导测定、光电子能谱及X-射线单晶分析表征了配合物的结构和性质, 晶体属于单斜晶系, 空间群为 $P2_1/c$ 。晶胞参数如下: $a = 11.429(2)$, $b = 13.346(2)$, $c = 15.953(7)$ Å; $\beta = 99.13(3)^\circ$, $V = 2402.5 \text{ Å}^3$, $Z = 4$, $F(000) = 1088$, $D_{\text{calc.}} = 1.460 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 11.782 \text{ cm}^{-1}$, $R = 0.04470$, $R_w = 0.05352$ 。分析结果表明, 配合物中双二苯基膦乙烷属双齿配体, 氯离子是单齿配体。

关键词: 镍 晶体结构 配合物
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Synthesis and Properties of Nickel (II) Complex Containing Bis(Diphenylphosphino) Ethane

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Mononuclear nickel (II) complex $[\text{Ni}(\text{dppe})\text{Cl}_2]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) has been synthesized by replacement reaction in CHCl_3 and characterized by specific elemental analyses, molecular weight determination, IR spectra, XPS, conductivity and X-ray single crystal analysis. The crystal is monoclinic, space group $P2_1/c$, $a = 11.429(2)$, $b = 13.346(2)$, $c = 15.953(7)$ Å; $\beta = 99.13(3)^\circ$, $V = 2402.5 \text{ Å}^3$, $Z = 4$, $F(000) = 1088$, $D_{\text{calc.}} = 1.460 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 11.782 \text{ cm}^{-1}$, $R = 0.04470$, $R_w = 0.05352$. The results show that dppe coordinates as bidentate ligand to the Ni (II) atoms, and Cl anion behaves as a monodentate ligand in the prepared complex.

Keywords: nickel crystal structure complex

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0 Introduction

Nickel (II) displays wide diversity in its structural chemistry, the nickel coordination number ranging from two to six. Procedures to synthesize nickel (II) complexes itself are of great interest because of the diversity of products resulting from almost the same methodology. The compound Ni(dppe)₂ is a catalyst of carbon dioxide catalytic reaction. In order to imitate the structure and functions of the active center of the relative catalyst, artificial systems should be developed^[1]. Coordination compounds with latent biological significance or with novel structures should be prepared. Many examples of metal complexes containing dppe are known with a variety of metals, oxidation and stereochemistries^[2]. Dppe belongs to efficient four-electron-donor bidentate ligand. This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of dppe compounds. Dppe and related phenylsubstituted diphosphines exhibit antitumor activity in several murine tumor models^[3]. In the present work, we reported the preparation and crystal structure of the complex [Ni(dppe)Cl₂].

1 Experimental

Commercially available purest samples of various chemicals were used for the preparation of the complex. Solvents were dried and distilled prior to use. Elemental analyses were performed on an Carlo-Erba 1106 instrument(Italy). Ni and P content were determined using a JA96 970 spectrometer. Molecular weight determinations were made on CHCl₃ solutions at 25° using CORONA-117 analyser(American instrument). I. r. spectra were recorded on a Nicolet 170SX IR spectrophotometer. Conductivity measurements were carried out in MeOH solutions thermostatted at 25° using a Shanghai DDS-11A conductometer and DJS-1 type platinum black electrode. Melting points were determined on an electrothermal apparatus and are uncorrected. ³¹P-NMR spectra were taken on a DPX-400 NMR spectrometer. ³¹P-NMR spectra were measured in CDCl₃ with 85% H₃PO₄ as external reference. XPS spectra were recorded on VG ESCALAB MK II instrument with AlK α radiation. High voltage, electric current and vacuum were set at 12.5 kV, 20 mA and 6 $\times$ 10⁻⁸ mbar, respectively.

1.1 Synthesis of the complex

1.1.1 [Cu(dppe)₂](NO₃)₂

Dppe(1.536 g, 4 mmol) and solid Cu(NO₃)₂ · 3H₂O(0.482 g, 2mmol) were added to hot ethanol(60 mL) to form a colorless solution. The resulting solution was subsequently allowed to evaporate slowly at room temperature to a final volume of 20 ~ 25 mL. Polyhedral, colorless crystals of [Cu(dppe)₂](NO₃)₂ were obtained, which were separated by filtration, washed with ethanol, and dried in air. Yield: 69%. M. p.: 189-191°C dec.. Anal. Found: C, 63.08; H, 4.68; P, 12.1; Cu, 6.12; N, 2.68%. Calc. for C₃₂H₄₈P₄CuN₂O₆: C, 63.45; H, 4.88; P, 12.6; Cu, 6.46; N, 2.85%. ¹H NMR(ppm): δ 6.9-7.3(40H, C₆H₅), 3.2-3.3(8H, CH₂). IR data(cm⁻¹): 1482m, 1436s, 1405m, 1381s, 1041s, 828m.

1.1.2 [Ni(dppe)Cl₂](1)

NiCl₂ · 2H₂O(0.331 g, 2 mmol) was added with stirring to a solution of [Cu(dppe)₂](NO₃)₂

(0.984 g, 1 mmol) in 30 mL of CHCl_3 . The addition of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ caused the colorless solution immediately turn to orange yellow. The mixture was stirred at room temperature for 50 min. Orange cubic crystals were obtained from the filtration. Yield: 86%. M.P. = 236-238°C. Ni, 9.51 (9.78); P, 9.11 (9.54); C, 66.1 (66.5); H, 4.35 (4.62)%. ^1H NMR(ppm): 3.3 (4 H, b, CH_2); 6.9-7.3 (20 H, m, ph).

1.2 X-ray data collection, structure determination and refinement

A single crystal of dimensions (0.1 × 0.1 × 0.15 mm) of the title complex was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator and $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Unit-cell dimensions and intensity data were measured at room temperature. Final unit cell dimensions, calculated from a leastsquares treatment of the accurately centred reflections are given. Reflections were collected using $\omega/2\theta$ scans (scan width $1.00 + 0.35 \tan \theta$), 4658 of which were considered unique and 2519 observed [$I \geq 3\sigma(I)$]. No significant change was detected in the intensity of the three standard reflections. Lorentz, polarization and absorption corrections were applied to the intensity data (empirical method, ψ -scan). The structure was solved by direct methods and Fourier syntheses. The structure was refined by full-matrix least-squares method. Computations were performed using the SDP program on a PDP11/44 computer. Atomic coordinates and thermal parameters are given in Table 1. Selected bond lengths and angles are given in Table 2. Crystal data: $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{P}_2\text{Ni}$, $M = 528.05$, Space group $P2_1/c$, monoclinic, $a = 11.429(2)$; $b = 13.346(2)$; $c = 15.953(7)$; $\beta = 99.13(3)^\circ$, $V = 2402.5 \text{ \AA}^3$, $Z = 4$, $F(000) = 1088$, $D_{\text{calc.}} = 1.460 \text{ g} \cdot \text{cm}^{-3}$, $\mu_{\text{calc.}} = 11.782 \text{ cm}^{-1}$, $2^\circ \leq 2\theta \leq 50^\circ$, $S = 2.450$, $\Delta/\sigma = 0.036$, $\Delta\rho_{\text{max}} = 0.937 \text{ e} \cdot \text{\AA}^{-3}$, $R = 0.04470$, $R_w = 0.05352$.

Table 1 Atomic Coordinates and Thermal Parameters

atom	x	y	z	B/ $\text{\AA}^2$	atom	x	y	z	B/ $\text{\AA}^2$
Ni	0.12630(8)	0.21966(6)	0.70628(5)	2.61(2)	Cl(1)	0.2852(2)	0.2030(2)	0.8030(1)	4.28(4)
Cl(2)	0.0110(2)	0.2660(2)	0.7972(1)	4.30(4)	P(1)	-0.0266(2)	0.2112(1)	0.6095(1)	2.48(3)
P(2)	0.2307(2)	0.1820(1)	0.6098(1)	2.61(3)	C(1)	0.0163(6)	0.1408(5)	0.5204(4)	3.0(1)
C(2)	0.1354(7)	0.1807(5)	0.5070(4)	3.2(1)	C(11)	-0.0839(6)	0.3296(5)	0.5652(4)	3.0(1)
C(12)	-0.1384(8)	0.3367(6)	0.4824(5)	4.7(2)	C(13)	-0.185(1)	0.4270(7)	0.4495(6)	6.1(2)
C(14)	-0.1767(8)	0.5099(6)	0.5007(6)	5.3(2)	C(15)	-0.1219(9)	0.5049(6)	0.5821(6)	5.7(2)
C(16)	-0.0737(9)	0.4154(6)	0.6160(5)	4.5(2)	C(21)	-0.1510(6)	0.1428(5)	0.6394(4)	2.8(1)
C(22)	-0.2584(7)	0.1873(6)	0.6427(5)	3.9(2)	C(23)	-0.3502(8)	0.1332(7)	0.6674(6)	5.4(2)
C(24)	-0.3339(8)	0.0335(7)	0.6881(6)	5.3(2)	C(25)	-0.2272(8)	-0.0113(6)	0.6852(5)	4.8(2)
C(26)	-0.1356(7)	0.0422(6)	0.6624(5)	4.0(2)	C(31)	0.3527(6)	0.2644(5)	0.5944(4)	2.9(1)
C(32)	0.4051(7)	0.3285(6)	0.6570(5)	3.9(2)	C(33)	0.4934(8)	0.3929(6)	0.6422(5)	4.7(2)
C(34)	0.5308(7)	0.3944(6)	0.5649(5)	4.7(2)	C(35)	0.4793(7)	0.3324(6)	0.5019(5)	4.4(2)
C(36)	0.3905(7)	0.2679(6)	0.5150(4)	3.7(2)	C(41)	0.2834(6)	0.0535(5)	0.6198(4)	3.0(1)
C(42)	0.2379(7)	-0.0105(6)	0.6768(4)	4.0(2)	C(43)	0.2682(9)	-0.1107(6)	0.6799(5)	5.0(2)
C(44)	0.3445(8)	-0.1482(6)	0.6301(6)	5.0(2)	C(45)	0.3870(9)	-0.0860(6)	0.5739(6)	6.2(2)
C(46)	0.3565(8)	0.0136(6)	0.5691(5)	5.2(2)					

2 Results and discussion

Nickel (II) chloride reacted with $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ to form an orange yellow nickel (II) complex $[\text{Ni}(\text{dppe})\text{Cl}_2]$. But nickel (II) chloride reacted with dppe giving the product $[\text{Ni}(\text{dppe})_2]\text{Cl}_2$. The

molecular weight determination result (Found: 526, calcd.: 528) strongly suggests that the complex (1) containing dppe, is mononuclear. Nickel (II) complex with dppe and monodentate coordinated Cl^- can be obtained with high yields. The elemental analysis of the complex agreed well with its formulation. Conductance data (methanol solution: $8 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) show that the title complex is nonelectrolyte^[4], confirming its mononuclear nature and the coordination character of dppe. The product is an air-stable, orange yellow crystalline material, soluble in polar solvents such as MeOH, acetonitrile, dimethylformamide, and dimethylsulfoxide. It is, however, insoluble in water. The complex has limited solubility in toluene, ether, hexane and tetrahydrofuran.

Table 2 Selected Bond Lengths(Å) and Bond Angles(°) for Complex (1)

Ni(1)-Cl(1)	2.200(2)	Ni(1)-Cl(2)	2.198(2)	Ni(1)-P(1)	2.143(2)
Ni(1)-P(2)	2.151(2)	P(1)-C(1)	1.836(7)	P(1)-C(11)	1.811(7)
P(1)-C(21)	1.815(7)	P(2)-C(2)	1.820(6)	P(2)-C(31)	1.822(7)
P(2)-C(41)	1.817(7)	C(1)-C(2)	1.508(11)	C(11)-C(12)	1.371(10)
Cl(1)-Ni(1)-Cl(2)	94.61(8)	Cl(1)-Ni(1)-P(1)	171.07(9)	Cl(1)-Ni(1)-P(2)	89.31(8)
Cl(2)-Ni(1)-P(1)	89.10(7)	Cl(2)-Ni(1)-P(2)	175.36(8)	P(1)-Ni(1)-P(2)	87.37(7)
Ni(1)-P(1)-C(1)	107.3(2)	Ni(1)-P(1)-C(11)	116.0(2)	Ni(1)-P(1)-C(21)	114.9(2)
C(1)-P(1)-C(11)	105.6(3)	C(1)-P(1)-C(21)	105.3(3)	C(11)-P(1)-C(21)	107.0(3)
Ni(1)-P(2)-C(2)	109.1(3)	Ni(1)-P(2)-C(31)	118.6(2)	Ni(1)-P(2)-C(41)	111.8(2)
C(2)-P(2)-C(31)	104.2(3)	C(2)-P(2)-C(41)	102.3(3)	C(31)-P(2)-C(41)	109.4(3)
P(1)-C(1)-C(2)	106.7(4)	P(1)-C(1)-H(1)	110.9(6)		

2.1 IR and ^{31}P NMR

The i. r. spectra(in CsI) of complex (1) exhibit the expected bands due to the dppe ligand: 1485s, 1186w, 1098m, 783m, 740s, 718m, and 690s cm^{-1} ^[5]. The P-Ph absorption at about 1090 cm^{-1} ^[5], shows an increase in frequency and intensity, which is characteristic of P-metal coordination. In the 1500 ~ 700 cm^{-1} range, the characteristic absorption bands of nitrate anion of $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ disappear in the title compounds, exhibiting nitrate has been substituted.

^{31}P NMR spectra of the title complex at room temperature show a single resonance at $\delta = 8.6$ ppm, showing that all phosphorus atoms are chemically equivalent (free dppe: -12.6 ppm). The corresponding phosphorus resonance shifted to higher field, compared with that shown by the precursor complex $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ ($\delta = -7.8$ ppm).

2.2 XPS

The XPS spectra of the complex gives information concerning nickel-ligand binding. The binding energy of $\text{P}2p$ in the title complex is at 133.6 eV. The binding energy $\text{P}2p$ (133.6 eV) of dppe in the complex is larger than the relative value ($\text{P}2p$: 132.4 eV) of free dppe, compared with that shown by the precursor complex $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ ($\text{P}2p$: 133.5 eV). This can be attributed to electronic density reduction of P atom from dppe because of the formation of $\text{Ni} \leftarrow \text{P}$ bond in the complex.

2.3 Thermal analysis and UV-Vis

The results of the thermogravimetric analyses of the complex shown the thermal stability of dppe increases upon complexation (free dppe decomposition temperature: 420°C). The TG curve of the title complex corresponds to a pronounced weight loss of 72% and is due to the decomposition of the

ligand dppe(weight loss calcd. : 75%) giving NiCl_2 as the residue in the 200 ~ 489°C range.

The electronic spectra of the complex in methanol solution shows transitions near $\lambda_{\text{max}} = 208$ nm which can be assigned to the high-energy transitions from internal ligand $\pi-\pi^*$ orbital transition. The appearance of absorption at $\lambda_{\text{max}} = 265$ nm arises from metal-to-ligand charge-transfer (MLCT).

2.4 Crystal structure

The molecular structure of the complex (1) is depicted in Fig. 1. The solid-state consists of a neutral molecular unit with one nickel atom coordinated by one dppe ligand. In addition, each nickel atom is terminally bound by Cl^- anion in a monodentate fashion. The observed Ni-Cl distances [2.198(2) ~ 2.200(2) Å] and P(1)-Ni-P(2) angle [131.0(4)°] are comparable to the values found for the corresponding P(1)-Ni-P(2) angle found in the related mononuclear dppe complex^[6,7].

Thus, each nickel atom is four-coordinate, with phosphorus atoms from dppe ligand occupying two of the coordination sites and the Cl^- atom occupying the third and the fourth, resulting in a planar square coordination geometry. The sum of bond angles [$\angle \text{Cl}(1)-\text{Ni}(1)-\text{Cl}(2) = 94.61(8)^\circ$, $\angle \text{Cl}(1)-\text{Ni}(1)-\text{P}(2) = 89.31(8)^\circ$, $\angle \text{Cl}(2)-\text{Ni}(1)-\text{P}(1) = 89.10(7)^\circ$, $\angle \text{P}(1)-\text{Ni}(1)-\text{P}(2) = 87.37(7)^\circ$] is 360.39°.

In summary, the bis(diphenylphosphine)ethane complex $[\text{Ni}(\text{dppe})\text{Cl}_2]$ has been structurally characterized by single-crystal X-ray methods. The central nickel atom belongs to planar square coordination geometry.

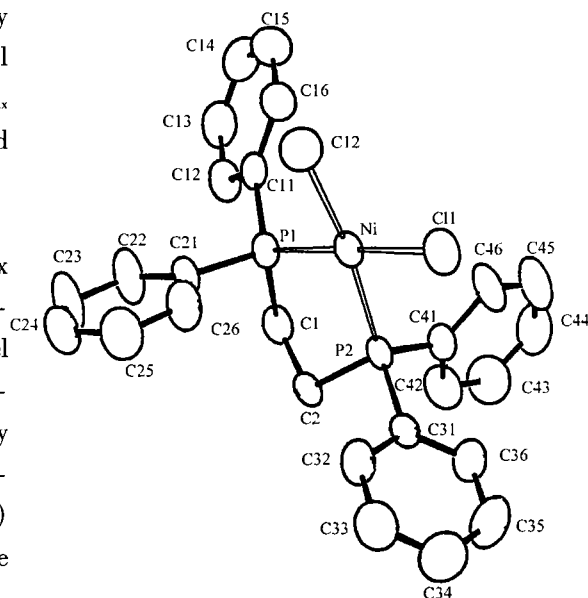


Fig. 1 Molecular structure of $[\text{Ni}(\text{dppe})\text{Cl}_2]$

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