



Preparation and Structure of Nickel Complex $\text{Ni}(\text{dppe})\text{Cl}_2$

WEI GAO*, KAI LI and XIN-LING WANG

School of Pharmacy, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, P.R. China

*Corresponding author: E-mail: gaowei222@yahoo.cn; weigao415@yahoo.cn

(Received: 11 October 2012;

Accepted: 22 July 2013)

AJC-13831

Mononuclear nickel complex $\text{Ni}(\text{dppe})\text{Cl}_2$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) was prepared by reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and dppe in CH_2Cl_2 /methanol solution and its structure was determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group $\text{P2}_1/\text{c}$ with $a = 12.228(3)$, $b = 15.235(4)$, $c = 15.294(4)$ Å, $\alpha = 90.00^\circ$, $\beta = 105.933(4)^\circ$, $\gamma = 90.00^\circ$, $V = 2739.7(13)$ Å³, $Z = 4$, $F_{(000)} = 1256$, $D_c = 1.486$ g/cm³, $\mu = 1.231$ cm⁻¹, the final $R = 0.0543$ and $wR = 0.1297$. A total of 28157 reflections were collected, of which 6516 were independent ($R_{\text{int}} = 0.0620$).

Key Words: Synthesis, Crystal Structure, Nickel complex, Diphosphine.

INTRODUCTION

In past decades, nickel complexes with diphosphine ligands have been received considerable attention due to their potential application in catalytic reactions¹. Among these numerous nickel complexes with diphosphine ligands, $\text{Ni}(\text{dppe})\text{Cl}_2$ have been used in the carbon dioxide reaction². As we know, dppe is a common diphosphine ligand and easy to obtain. In order to develop the coordination chemistry of nickel complexes and novel structures, we carried out study on nickel complex with a bidentate ligand dppe . In this paper, we report the preparation and crystal structure of complex $\text{Ni}(\text{dppe})\text{Cl}_2$.

EXPERIMENTAL

Crystal structure determination: The crystal of $\text{Ni}(\text{dppe})\text{Cl}_2$ with dimensions of 0.20 mm × 0.16 mm × 0.12 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a ϕ and scan modes at 113(2) K in the range of $1.73^\circ \leq \theta \leq 27.87^\circ$. The crystal belongs to Monoclinic system with space group $\text{P2}_1/\text{c}$ and crystal parameters of $a = 12.228(3)$ Å, $b = 15.235(4)$ Å, $c = 15.294(4)$ Å, $\alpha = 90^\circ$, $\beta = 105.933(4)^\circ$, $\gamma = 90^\circ$, $V = 2739.7(13)$ Å³, $D_c = 1.486$ g/cm³. The absorption coefficient $\mu = 1.231$ mm⁻¹ and $Z = 4$. The structure was solved by direct methods with SHELXS-97³ and refined by the full-matrix least squares method on F^2 data using SHELXL-97⁴. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the

restraint $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{N})$. Other H atoms were positioned geometrically and refined using a riding model, with $d(\text{C}---\text{H}) = 0.93\text{--}0.97$ Å and $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$ or $1.5 \text{ Ueq}(\text{C}_{\text{methyl}})$. The final full-matrix least squares refinement gave $R = 0.0543$ and $wR = 0.1297$.

Synthesis: To a methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was added a solution of dppe (1 mmol) in CH_2Cl_2 . The mixture was stirred at room temperature for 1 h and then the solvent was reduced *in vacuo*. The residue was crystallized in CH_2Cl_2 /hexane at room temperature and the red crystals were obtained after several days.

RESULTS AND DISCUSSION

Treatment of methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with a solution of dppe in CH_2Cl_2 afforded the $\text{Ni}(\text{dppe})\text{Cl}_2$ complex. Slow evaporation of the this complex in CH_2Cl_2 /hexane gave red crystals.

Structure of the $\text{Ni}(\text{dppe})\text{Cl}_2$: The complex was confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles listed in Tables 2-4, respectively. 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 and the packing view of the title complex are shown in Figs. 1 and 2, respectively.

The complex $\text{Ni}(\text{dppe})\text{Cl}_2$ crystallizes in the monoclinic space group $\text{P2}_1/\text{c}$. The unit cell contains one molecule

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT OF $\text{Ni}(\text{dppe})\text{Cl}_2$

Items	Values
Empirical formula	$\text{C}_{27}\text{H}_{26}\text{Cl}_4\text{NiP}_2$
Formula weight	612.93
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	12.228(3)
b (Å)	15.235(4)
c (Å)	15.294(4)
Unit cell angles (°)	
α	90
β	105.933(4)
γ	90
Volume (Å ³)	2739.7(13)
Z	4
Temperature (K)	113(2)
Space group	$\text{P2}_1/\text{c}$
Wavelength (Å)	0.71073
Calculated density (g/cm ³)	1.486
Absorption coefficient (mm ⁻¹)	1.231
$F_{(000)}$	1256
Crystal size (mm)	0.20 × 0.16 × 0.12
Theta range for data collection (°)	1.73 – 27.87
Reflections collected	28157
Independent reflections	6516 [$R_{\text{int}} = 0.0620$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0543$, $wR_2 = 0.1297$

TABLE-2
SELECTED BOND LENGTHS [Å] OF $\text{Ni}(\text{dppe})\text{Cl}_2$

Bond lengths	X-Ray crystal	Bond lengths	X-Ray crystal
Ni(1)-P(1)	2.1306(11)	P(1)-C(1)	1.826(4)
Ni(1)-P(2)	2.1551(10)	P(1)-C(13)	1.867(4)
Ni(1)-Cl(2)	2.2021(10)	P(2)-C(15)	1.816(3)
Ni(1)-Cl(1)	2.2100(9)	P(2)-C(21)	1.818(3)
P(1)-C(7)	1.804(4)	P(2)-C(14)	1.829(3)

TABLE-3
SELECTED BOND ANGLES [°] OF $\text{Ni}(\text{dppe})\text{Cl}_2$

Bond angles	X-Ray crystal	Bond angles	X-Ray crystal
P(1)-Ni(1)-P(2)	87.46(4)	P(2)-Ni(1)-Cl(1)	175.56(4)
P(1)-Ni(1)-Cl(2)	175.21(4)	Cl(2)-Ni(1)-Cl(1)	95.50(4)
P(2)-Ni(1)-Cl(2)	88.59(4)	C(1)-P(1)-Ni(1)	119.38(12)
P(1)-Ni(1)-Cl(1)	88.54(4)	C(15)-P(2)-Ni(1)	118.01(11)

TABLE-4
SELECTED BOND ANGLES [°] TORSIONAL
ANGLES (°) OF $\text{Ni}(\text{dppe})\text{Cl}_2$

Bond angles	X-Ray crystal
P(2)-Ni(1)-P(1)-C(7)	103.37(13)
Cl(2)-Ni(1)-P(1)-C(7)	137.7(4)
Cl(1)-Ni(1)-P(1)-C(7)	-74.71(13)
P(2)-Ni(1)-P(1)-C(1)	-132.52(16)
Cl(2)-Ni(1)-P(1)-C(1)	-98.2(5)
Cl(1)-Ni(1)-P(1)-C(1)	49.40(16)
P(2)-Ni(1)-P(1)-C(13)	-12.78(13)
Cl(2)-Ni(1)-P(1)-C(13)	21.6(5)

of $\text{Ni}(\text{dppe})\text{Cl}_2$ and one molecule of CH_2Cl_2 . As can be seen in Fig. 1, the molecular structure of the title complex consists of a nickel atom coordinated by a dppe ligand and two chloride anions. The Ni-Cl bond lengths [2.2021(10) and 2.2100(9) Å] are close to the values found in the related nickel diphosphine

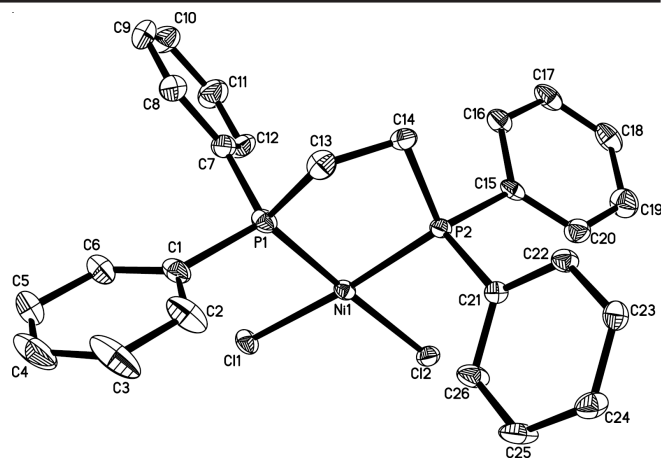


Fig. 1. Molecular structure of $\text{Ni}(\text{dppe})\text{Cl}_2$

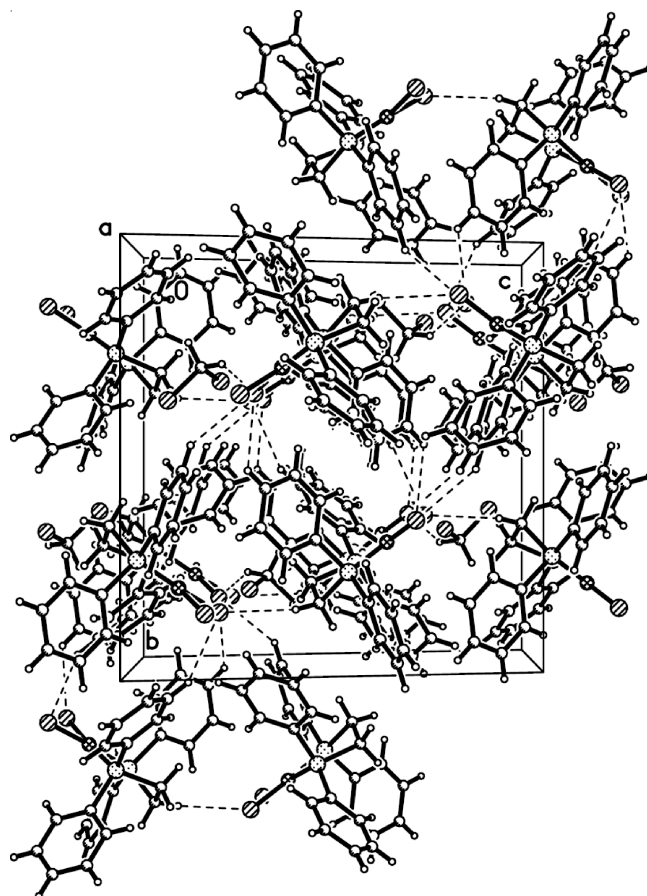


Fig. 2. Two-dimensional network of hydrogen bonds (dashed lines)

complex⁵. The P1-Ni1-P2 bond angle [87.46(4)°] are shorter than the corresponding angle in the crystal structure of $\text{Ni}(\text{dppe})\text{Cl}_2$ [131.0(4)°]. The phenyl rings (C1, C2, C3, C4, C5, C6), (C7, C8, C9, C10, C11, C12), (C15, C16, C17, C18, C19, C20) and (C21, C22, C23, C24, C25, C26) are fairly planar with plane equation $4.902x + 11.020y + 7.477z = 11.2291$, $-8.274x + 9.506y + 8.589z = 2.3887$, $-3.285x + 5.131y + 14.400z = 1.3027$ and $9.755x + 0.860y + 5.480z = 9.1137$, respectively. The largest deviation from the least squares plane is 0.0103 Å⁶.

As shown in Fig. 2, there are intermolecular C-H...Cl hydrogen bonds in the crystal packing. These interactions can help to stabilize the crystal structure.

Supplementary material

CCDC 901592 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support from the Doctoral Research Fund of Henan University of Traditional Chinese Medicine.

REFERENCES

1. J.A. Rahn, A. Delian and J.H. Nelson, *Inorg. Chem.*, **28**, 215 (1989).
2. R.N. Yang, L.F. Zhang, Y.M. Hou, X.-Y. Hu, D.M. Jin and B.S. Luo, *Chin. J. Inorg. Chem.*, **16**, 445 (2000).
3. G.M. Sheldrick, SHELXS97, A Program for Crystal Structure Solution; University of Göttingen: Germany (1997).
4. G.M. Sheldrick, SHELXL97, A Program for Crystal Structure Refinement; University of Göttingen: Germany (1997).
5. (a) J.A.S. Bonofim, F.P. deSouza, C.A.L. Filguerras, A.G. de Souza and M.T.P. Gambardella, *Polyhedron*, **22**, 1567 (2003); (b) J.C. Davison, M.R. Foreman, R.A. Howie, M.J. Plater and J.M.S. Stakle, *Acta Crystallogr.*, **C57**, 690 (2001).
6. (a) X.H. Liu, C.X. Tan and J.Q. Weng, *Phosphorus Sulfur Silicon Rel. Elem.*, **186**, 552 (2011); (b) X.H. Liu, C.X. Tan and J.Q. Weng, *Phosphorus Sulfur Silicon Rel. Elem.*, **186**, 558 (2011); (c) P.Q. Chen, C.X. Tan, J.Q. Weng and X.H. Liu, *Asian J. Chem.*, **24**, 2808 (2012); (d) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 3016 (2012); (e) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 1571 (2012); (f) X.F. Liu and X.H. Liu, *Acta Cryst.*, **E67**, o202 (2011); (g) X.H. Liu, L. Pan, C.X. Tan, J.Q. Weng, B.L. Wang and Z.M. Li, *Pestic. Biochem. Physiol.*, **101**, 143 (2011); (h) X.H. Liu, J.Q. Weng, C.X. Tan and H.J. Liu, *Acta Cryst.*, **E67**, o1940 (2011); (i) X.H. Liu, J.Q. Weng, C.X. Tan, L. Pan, B.L. Wang and Z.M. Li, *Asian J. Chem.*, **23**, 4031 (2011); (j) H.J. Liu, J.Q. Weng, C.X. Tan and X.H. Liu, *Acta Cryst.*, **E67**, o1940 (2011).