



Preparation and Structure of Nickel Complex Ni(dppe)Cl₂

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 Ni(dppe)Cl₂ (dppe = Ph₂PCH₂CH₂PPh₂) was prepared by reaction of NiCl₂·6H₂O and dppe in CH₂Cl₂/methanol solution and its structure was determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group P2₁/c with a = 12.228(3), b = 15.235(4), c = 15.294(4) Å, α = 90.00, β = 105.933(4), γ = 90.00°, V = 2739.7(13) Å³, Z = 4, F₍₀₀₀₎ = 1256, D_c = 1.486 g/cm³, μ = 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_{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, Ni(dppe)Cl₂ 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 Ni(dppe)Cl₂.

EXPERIMENTAL

Crystal structure determination: The crystal of Ni(dppe)Cl₂ 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 (λ = 0.71073 Å) by using a phi and scan modes at 113(2) K in the range of 1.73° ≤ θ ≤ 27.87°. The crystal belongs to Monoclinic system with space group P2₁/c and crystal parameters of a = 12.228(3) Å, b = 15.235(4) Å, c = 15.294(4) Å, α = 90°, β = 105.933(4)°, γ = 90°, V = 2739.7(13) Å³, D_c = 1.486 g/cm³. The absorption coefficient μ = 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 F² 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 Uiso(H) = 1.2 Ueq(N). Other H atoms were positioned geometrically and refined using a riding model, with d(C--H) = 0.93-0.97 Å and Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(Cmethyl). The final full-matrix least squares refinement gave R = 0.0543 and wR = 0.1297.

Synthesis: To a methanolic solution of NiCl₂·6H₂O (1 mmol) was added a solution of dppe (1 mmol) in CH₂Cl₂. The mixture was stirred at room temperature for 1 h and then the solvent was reduced *in vacuo*. The residue was crystallized in CH₂Cl₂/hexane at room temperature and the red crystals were obtained after several days.

RESULTS AND DISCUSSION

Treatment of methanolic solution of NiCl₂·6H₂O with a solution of dppe in CH₂Cl₂ afforded the Ni(dppe)Cl₂ complex. Slow evaporation of the this complex in CH₂Cl₂/hexane gave red crystals.

Structure of the Ni(dppe)Cl₂: 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 F². 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 Ni(dppe)Cl₂ crystallizes in the monoclinic space group P2₁/c. The unit cell contains one molecule

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT OF Ni(dppe)Cl₂

Items	Values
Empirical formula	C ₂₇ H ₂₆ Cl ₄ 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	P2 ₁ /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 _(int) = 0.0620]
Final R indices [I > 2σ(I)]	R ₁ = 0.0543, wR ₂ = 0.1297

TABLE-2
SELECTED BOND LENGTHS [Å] OF Ni(dppe)Cl₂

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 Ni(dppe)Cl₂

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 Ni(dppe)Cl₂

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 Ni(dppe)Cl₂ and one molecule of CH₂Cl₂. 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

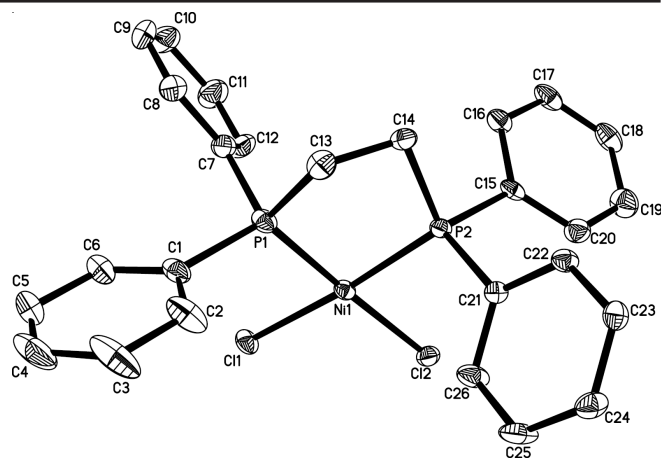


Fig. 1. Molecular structure of Ni(dppe)Cl₂

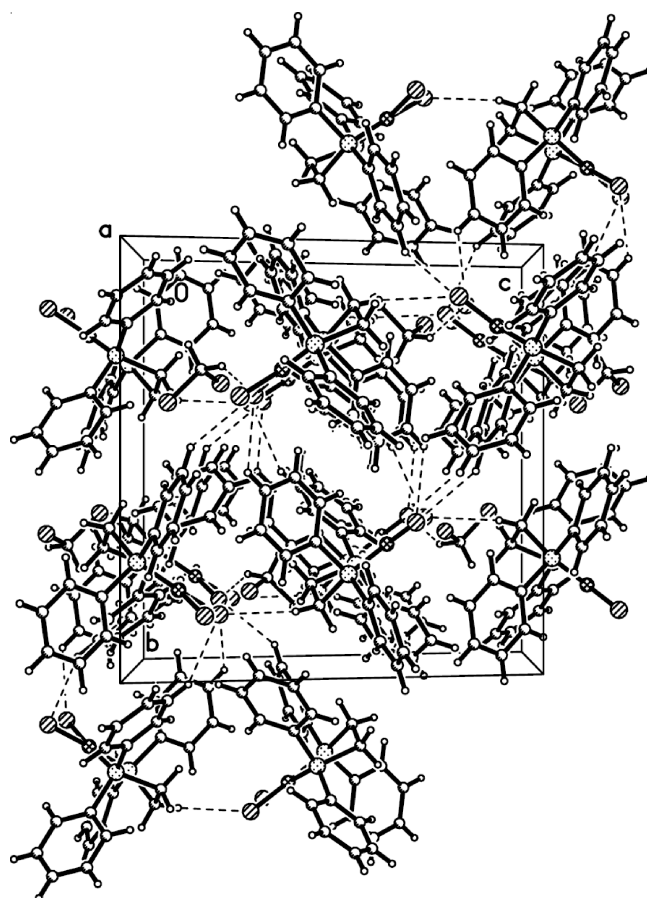


Fig. 2. Two-dimensional network of hydrogen bonds (dashed lines)

complex⁵. The P1-Ni1-P2 bond angle [87.46(4)°] are shorter than the corresponding angle in the crystal structure of Ni(dppe)Cl₂ [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).