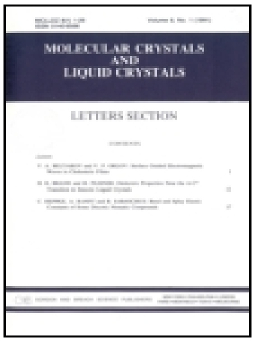

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Synthesis and Crystal Structure of Mononuclear Nickel Ethanedithiolate Complex with 1,2-bis(diphenylphosphino)ethane

WEI GAO*

School of Pharmacy, Henan University of Traditional Chinese Medicine,
Zhengzhou, People's Republic of China

The title complex (dppe)Ni(edt) [dppe = 1,2-bis(diphenylphosphino)ethane, edt = ethanedithiolate] was prepared by treatment of (dppe)NiCl$_2$ with HSCH$_2$CH$_2$SH in the presence of Et$_3$N in CH$_2$Cl$_2$ at room temperature and structurally characterized by ^{1}H NMR, ^{31}P{^{1}H} NMR, ^{13}C{^{1}H} NMR and ESI-MS spectroscopy. In addition, the molecular structure was determined by single crystal X-ray diffraction analysis. The title complex consists of a distorted square planar NiP$_2$S$_2$ core coordinated by dppe and edt. The van der Waals' interactions stabilize the solid state in the crystal packing.

Keywords crystal structure; dppe; nickel complex; Synthesis

Introduction

Over past decades, the mononuclear nickel complexes have received special attention due to their potential application in olefin polymerization and copolymerization [1–5]. The diphosphine ligands such as dppm [bis(diphenylphosphino)methane], dppe, dppp [1,3-bis(diphenylphosphino)propane], or diphosphinoamine have been widely used in transition metal chemistry [6–8]. The mononuclear nickel ethanedithiolate complex (dppe)Ni(edt) was previously reported by Roundhill [9] and its structure was only characterized by ^{1}H NMR spectroscopy. Recently, the mononuclear nickel complexes with diphosphine ligands and dithiolphosphato [10] or 2-thioxo-1,3-dithiol-4,5-dithiolate dianion [11] were synthesized and structurally characterized by spectroscopy and X-ray analysis. On the basis of our previously work on nickel complex [12], we carried out a study on the mononuclear nickel complex and successfully prepared the title complex in good yield and its molecular structure was confirmed by X-ray crystallography. In this paper, we report the synthesis and X-ray crystal structure of mononuclear nickel dithiolate complex (dppe)Ni(edt).

Experimental

Synthesis of the Title Complex

To a solution of (dppe)NiCl$_2$ [13] (0.528 g, 1.0 mmol) and HSCH$_2$CH$_2$SH (0.084 mL, 1.0 mmol) in CH$_2$Cl$_2$ (30 mL) was added Et$_3$N (0.28 mL, 2.0 mmol) and the new mixture

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*Address correspondence to Wei Gao, School of Pharmacy, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, People's Republic of China. E-mail: weigao415@aliyun.com

Table 1. Crystal data and structure refinements details

Empirical formula	$C_{28}H_{28}NiP_2S_2$
Formula weight	549.27
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2$ (1)
a (Å)	9.4653 (19)
b (Å)	15.802 (3)
c (Å)	9.7233 (19)
α (°)	90
β (°)	115.29 (3)
γ (°)	90
V (Å^3)	1314.9 (5)
Z	2
D_{calc} (g$^{\text{å}}$cm^{-3})	1.387
μ (mm^{-1})	1.033
F(000)	572
Crystal size (mm^3)	0.20 × 0.18 × 0.12
$\theta_{\min}$, $\theta_{\max}$ (°)	2.32, 29.12
Reflections collected/unique	14016/6029
R_{int}	0.0329
hkl range	$-12 \le h \le 12$
	$-19 \le k \le 21$
	$-13 \le l \le 12$
Completeness to $\theta_{\max}$ (%)	97.7
Data/restraints/parameters	6029/31/298
Goodness of fit on F^2	0.993
R_1/wR_2 $(I>2\sigma(I))$	0.0430/0.1073
R_1/wR_2 (all data)	0.0617/0.1177
Largest diff peak and hole/e Å^{-3}	0.918/−0.515

was stirred for 1 h at room temperature. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2 as eluent. From the main red band afforded 0.416 g (76%) of the title complex as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.81–7.77 (m, 8H, *o*-PPh*H*), 7.50–7.43 (m, 12H, *m*-Ph*H* and *p*-Ph*H*), 2.78 (s, 4H, 2SCH_2), 2.24 (d, $J = 4.4$ Hz, 4H, 2PCH_2) ppm. ^{31}P{^{1}H} NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 58.08 (s) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 133.41 (t, $J_{\text{P-C}} = 5.1$ Hz, *m*-Ph*C*), 131.02 (s, *p*-Ph*C*), 130.16 (dd, $J_{\text{P-C}} = 23.7$, 21.8 Hz, *i*-Ph*C*), 128.72 (t, $J_{\text{P-C}} = 5.2$ Hz, *o*-Ph*C*), 40.72 (t, $J_{\text{P-C}} = 8.0$ Hz, S*C*H_2), 26.98 (t, $J_{\text{P-C}} = 22.9$ Hz, P*C*H_2) ppm. ESI-MS: *m/z* 549.051503 [M^++H] (calcd. 549.053944).

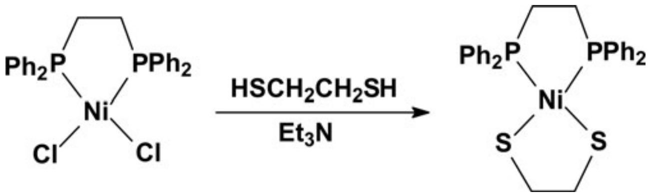
X-ray Structure Determination

Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/^{i}PrOH solutions at 4 °C. A single crystal was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 293(2) K by using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω-ϕ scanning mode. Data collection, reduction and absorption correction were performed by *CRYSTALCLEAR* program [14]. The structure was solved by direct methods using the SHELXS-97 program [15] and refined by full-matrix least-squares techniques SHELXL-97 [16] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

Results and Discussion

Synthesis and Characterization

Similar to Roundhill's procedure [9], treatment of (dppe)$NiCl_2$ with $HSCH_2CH_2SH$ in the presence of Et_3N in CH_2Cl_2 gave the title complex in 76% yield (Scheme 1).



Scheme 1. Preparation of the title complex.

The title complex was characterized by NMR and MS spectroscopy. The ^{1}H NMR spectra showed two multiplets at δ 7.79 and 7.50 ppm for phenyl protons, a singlet at δ 2.78 ppm for SCH_2 groups and a doublet at δ 2.24 ppm with a coupling constant $J_{\text{P-H}} =$ 4.4 Hz for PCH_2 groups (Fig. 1). The ^{13}C{^{1}H} NMR spectra displayed two triplets at δ 133.41 and 128.72 ppm, a singlet at δ 131.02 ppm and a doublet of doublets at δ 130.16 ppm for its phenyl carbons and two triplets at δ 40.72 and 26.98 ppm for SCH_2 and PCH_2 groups, respectively (Fig. 2).

X-ray Crystal Structure

The molecular structure of the title complex has been confirmed by single-crystal X-ray diffraction analysis. While the ORTEP and packing views are shown in Figs. 3 and 4, selected bond lengths and angles are presented in Table 2, respectively. The title complex crystallizes in monoclinic space group P2(1). As shown in Fig. 3, the molecular structure contains mononuclear nickel atom coordinated by two phosphorus atoms of dppe and two sulfur atoms of edt. The nickel atom is at the center of a distorted square planar NiP_2S_2 core. The NiP_2S_2 core is almost planar with the mean deviation formed by Ni1, P1, P2, S1, S2 of 0.1191 Å and the dihedral angle between the planes Ni1, P1, C15, C16, P2 and Ni1, S1, C1, C2, S2 is 1.8°. The Ni-S bond lengths [2.1722(14) and 2.1773(13) Å] and Ni-P bond lengths [2.1505(12) and 2.1619(14) Å] are comparable to those previously reported nickel dithiolate complexes with diphosphine ligands [17–19].

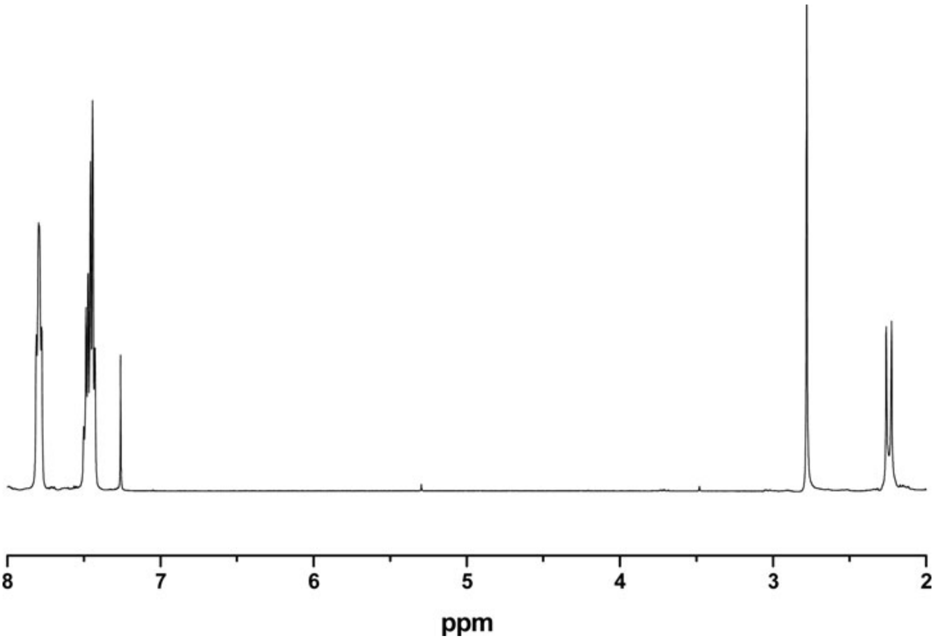


Figure 1. ^{1}H NMR spectra of the title complex.

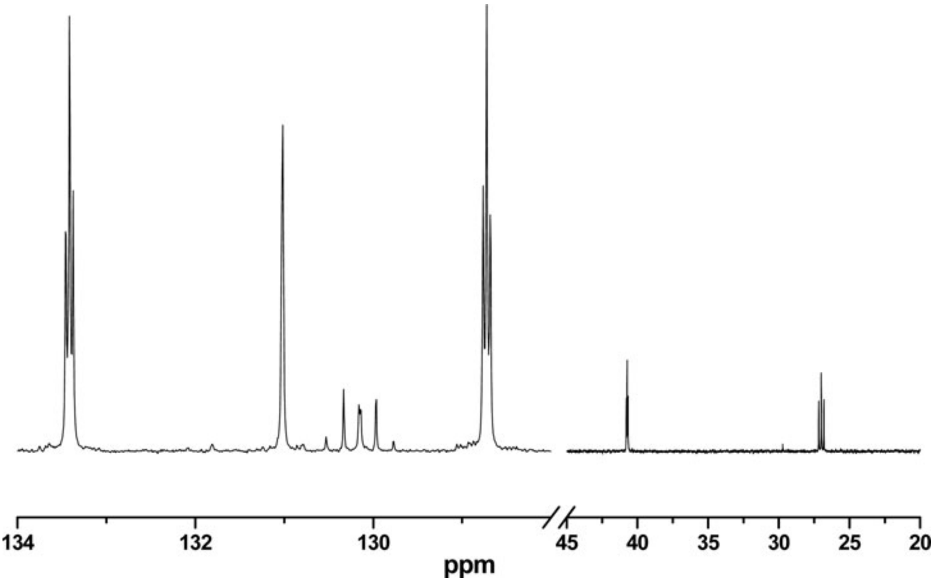


Figure 2. $^{13}C\{^1H\}$ NMR spectra of the title complex.

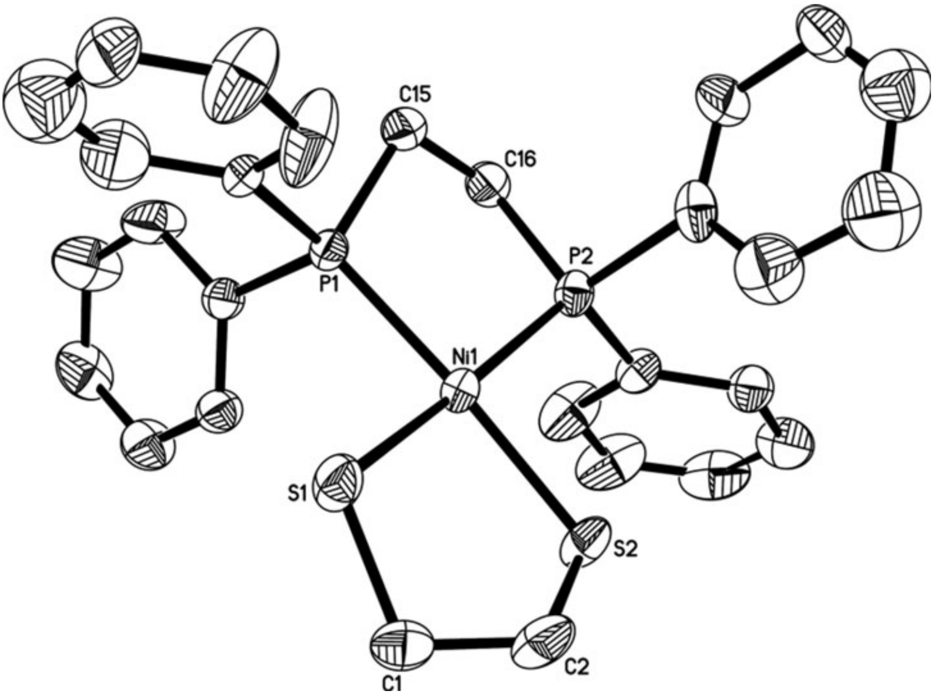


Figure 3. ORTEP view of the title complex with 30% probability level ellipsoids.

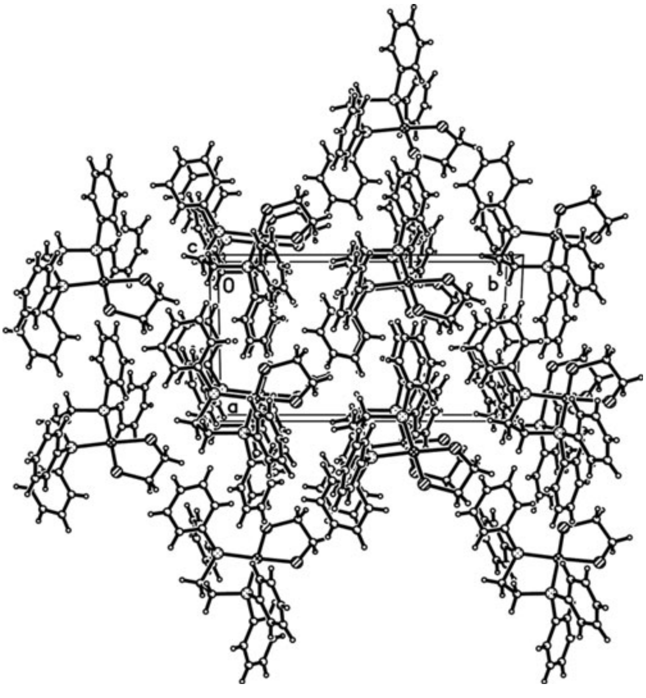


Figure 4. Crystal packing diagram of the title complex.

Table 2. Selected bond lengths (Å) and angles (°)

Ni(1)-P(2)	2.1505(1)	S(1)-C(1)	1.820(5)
Ni(1)-P(1)	2.1619(1)	S(2)-C(2)	1.803(6)
Ni(1)-S(2)	2.1722(1)	C(1)-C(2)	1.474(8)
Ni(1)-S(1)	2.1773(1)	C(15)-C(16)	1.531(6)
P(2)-Ni(1)-P(1)	87.83(4)	S(2)-Ni(1)-S(1)	92.81(5)
P(2)-Ni(1)-S(2)	89.78(5)	C(15)-P(1)-Ni(1)	108.55(2)
P(1)-Ni(1)-S(2)	170.55(5)	C(16)-P(2)-Ni(1)	108.34(2)
P(2)-Ni(1)-S(1)	173.42(5)	C(1)-S(1)-Ni(1)	101.54(2)
P(1)-Ni(1)-S(1)	90.55(5)	C(2)-S(2)-Ni(1)	101.78(2)

As shown in Fig. 4, there are no noncovalent interactions in the crystal packing diagram and the crystal structure is stabilized by van der Waals' interactions.

Conclusions

In summary, the mononuclear nickel complex has been synthesized and structurally characterized by NMR and MS spectra. Particularly, the molecular structure was determined by X-ray crystallography.

Acknowledgments

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Supplemental materials

Supplemental materials are available for this article. Go to the publisher's online edition of *Molecular Crystals and Liquid Crystals* to view the free supplemental file: Crystallographic data for the structural analysis have been depositedwith the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1017805 for the title complex. Copies of the data can be obtained free of charge at 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) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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