

Synthesis and Determination of Crystal and Molecular Structure of {Bispyridine-bis[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]}nickel(II)

Ertuğrul Gazi SAĞLAM,[†] Ömer ÇELİK,^{**} Semra İDE,^{***} and Hamza YILMAZ^{**}

^{*}Department of Chemistry, Science Faculty, Ankara University, Ankara, Turkey

^{**}Department of Physics, Science and Art Faculty, Harran University, Şanlıurfa, Turkey

^{***}Department of Physics Eng., Faculty of Engineering, Hacettepe University, Ankara, Turkey

The addition of *trans*-bis[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]nickel(II) with pyridine (py) gave the {bispyridine-bis[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]}nickel(II) [Ni(Py)₂(L)₂] complex. The structure of the complex has been characterized by X-ray diffraction. Ni(II)dithiophosphinato complex was reported¹ to be of square-planar geometry while the latter compound was of an octahedral coordination geometry. It crystallizes in monoclinic system, space group *P*2₁/*n*, with lattice parameters *a* = 12.4968(12)Å, *b* = 9.7051(10)Å, *c* = 16.0975(17)Å, (*β* = 101.734(8)°, *Z* = 2, (*μ* = 0.84 mm⁻¹, *S* = 1.003, *R* = 0.0437 and *wR* = 0.1017 for 3562 observed reflections. The structure was solved by direct methods using the SHELX-97 program and refined on *F*².

(Received January 26, 2011; Accepted March 26, 2011; Published on web May 10, 2011)

The dithiophosphinate (DTP) anions [R₂PS₂]⁻ can act as bidentate ligands with many transition metals to form stable chelate complexes; consequently, these sulfur ligands are suitable for solvent extraction of metals. An example of such dithiophosphinates, known as CYANEX 301, has found use in industry for metal extraction.^{2,3} Some of these complexes have antitumor activity and are therefore the subject of chemotherapy studies.⁴

A solution of *trans*-bis[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]nickel(II) in mixed chloroform-ethanol (1:1) was heated. Exceed pyridine was added dropwise to this solution with stirring. The color of the mixture changed rapidly from dark blue to light brown. After two days, the green complex was filtered and recrystallized from ethanol. The solution was left to stand overnight to obtain crystals. Pyridine complexes are unstable and additional ligands can be lost with regeneration of the original complex. In order to prevent decomposition, the green complex was isolated in a vacuum desiccator. Yield: 0.18 g (% 90). M.P. 188 – 190°C. *Anal.* Calcd. for C₃₄H₄₆N₂NiO₂P₂S₄ (763.64 g/mol): C, 53.5; H, 6.1; N, 3.8; S, 16.8; found: C, 53.4; H, 6.1; N, 3.7; S, 16.6. Fig 1 is given the chemical scheme of the compound.

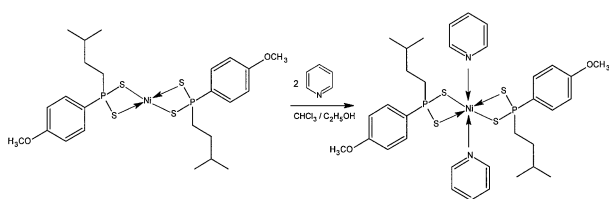


Fig. 1 Chemical diagram of [Ni(Py)₂(L)₂].

Single crystals of size 0.30 × 0.20 × 0.15 mm were selected for X-ray diffraction. The unit cell dimensions were found to be on the basis of twenty-five preliminary reflections in the *θ* range of 10.47° – 18.06°. Crystal data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo *K*_α radiation (*λ* = 0.71073 Å). The intensity data were collected by the *ω*-2*θ* scan mode within the 5.16° ≤ 2*θ* ≤ 52.58°

Table 1 Crystal data and structure refinement parameters of [Ni(Py)₂(L)₂]

Chemical Formula: C ₃₄ H ₄₆ N ₂ NiO ₂ P ₂ S ₄	
Formula weight = 763.62	
<i>T</i> = 293 K	
Crystal system: monoclinic	Space group (no): <i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> = 12.4968(12)Å	
<i>b</i> = 9.7051(10)Å	<i>β</i> = 101.734(8)°
<i>c</i> = 16.0975(17)Å	
<i>V</i> = 1911.5(3)Å ³	<i>Z</i> = 2
<i>D</i> _x = 0.399 g/cm ³	
Radiation: Mo <i>K</i> _α (<i>λ</i> = 0.71073 Å)	
<i>μ</i> (Mo <i>K</i> _α) = 0.841 mm ⁻¹	<i>F</i> (0 0 0) = 804
Crystal sizes = 0.30 × 0.20 × 0.15 mm ³	
No. of reflections collected = 3738	
No. of independent reflections = 3570	
<i>θ</i> range for data collection: 2.58 – 26.29°	
Data/Restraints/Parameters = 3738/0/205	
Goodness-of-fit on <i>F</i> ² = 1.002	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>): <i>R</i> 1 = 0.0441, <i>wR</i> 2 = 0.1031	
<i>R</i> indices (all data): <i>R</i> 1 = 0.0973, <i>wR</i> 2 = 0.1205	
(Δσ) _{max} = 0.000	
(Δρ) _{max} = 0.527 eÅ ⁻³	(Δρ) _{min} = -0.349 eÅ ⁻³
Measurement: Enraf-Nonius CAD4	
Program system: Enraf-Nonius CAD4 Express	
Structure determination: WinGX (SHELXL and SHELXS)	
Refinement: full matrix	
CCDC deposit number: 264281	

[†] To whom correspondence should be addressed.
E-mail: celiko21@yahoo.com

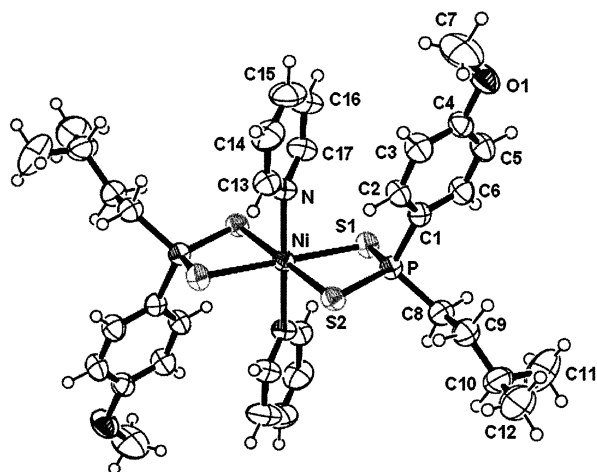


Fig. 2 ORTEP III diagram of $[\text{Ni}(\text{Py})_2(\text{L})_2]$, showing the molecular numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms, except for H, for which they have been set to be artificially small.

Table 2 Hydrogen bonding geometry (\AA , $^\circ$)

$D\text{-H}\cdots A$	$D\text{-H}$	$H\cdots A$	$D\cdots A$	$D\text{-H}\cdots A$
$\text{C}2\text{-H}2\cdots\text{S}2^i$	0.898	2.876	3.350(4)	114
$\text{C}17\text{-H}17\cdots\text{S}1^i$	1.023	2.819	3.378(4)	114
$\text{C}6\text{-H}6\cdots\text{O}^{ii}$	0.970	2.517	3.466(5)	166
$\text{C}13\text{-H}13\cdots\text{S}1^{iii}$	0.930	2.814	3.353(4)	116

Symmetry codes: (i) x, y, z ; (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $-x+1, -y+1, -z+1$.

range with $-15 \leq h \leq 0$, $-12 \leq k \leq 0$ and $-19 \leq l \leq 20$ in the monoclinic crystal system. Out of 3738 unique reflections, 2363 with $I > 2\sigma(I)$ were used for the structure solution and refinement. Data were corrected for Lorentz and polarization effects. The structure was solved in monoclinic space group $P2_1/n$ by the combination of direct and Fourier techniques, and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms with a riding model. An absorption correction was made to the data using psi-scan after obtaining the complete structural model. The final refinement was converged to $R = 0.0441$, $wR_2 = 0.1031$ using 205 parameters and 3570 data. The goodness-of-fit on F^2 was 1.002 and the maximum shift/e.s.d was 0.000. The WinGX package program and ORTEPIII were used to solve and refine the structure and for molecular graphics. Crystal data and structure refinement parameters of the compound are given in Table 1.

The coordination environment of the $[\text{Ni}(\text{Py})_2(\text{L})_2]$ was found to have an octahedral geometry. The complex is paramagnetic and the ambient temperature NMR spectrum is so complex as to make it awkward to comment on. The magnetic susceptibility of the complex is compatible with the theoretical value (calcd. $\mu_{\text{eff}} = 2.82 \mu\text{B}$; found $\mu_{\text{eff}} = 2.79 \mu\text{B}$). The characteristic asymmetric and symmetric P=S bands for $[\text{Ni}(\text{Py})_2(\text{L})_2]$ were observed at 619 cm^{-1} and 546 cm^{-1} , respectively.

Table 1 gives crystal data and on structure refinement and Fig. 2 is the ortep diagram created there for the molecular structure

Table 3 Selected geometric parameters (\AA , $^\circ$)

Ni-N	2.137 (3)	P-S1	2.0050 (13)
Ni-S1	2.4846 (9)	P-S2	2.0059 (12)
Ni-S2	2.5044 (9)	C4-O	1.367 (4)
P-C1	1.809 (3)	O-C7	1.413 (5)
P-C8	1.809 (3)		
N-Ni-S1	90.82 (8)	C8-P-S2	110.50 (12)
N-Ni-S2	89.76 (8)	S1-P-S2	110.09 (5)
S1-Ni-S2	82.43 (3)	C13-N-Ni	121.8 (2)
C1-P-C8	105.64 (16)	C17-N-Ni	121.1 (3)
C1-P-S1	109.43 (11)	P-S1-Ni	83.21 (4)
C8-P-S1	109.53 (13)	P-S2-Ni	82.68 (4)
C1-P-S2	111.54 (12)		
C1-P-S1-Ni	-111.93 (12)	C1-P-S2-Ni	110.76 (12)
C8-P-S1-Ni	132.70 (13)	C8-P-S2-Ni	-132.04 (13)
S2-P-S1-Ni	11.00 (5)	S1-P-S2-Ni	-10.92 (5)
N-Ni-S1-P	81.33 (8)	N-Ni-S2-P	-82.53 (8)
S2-Ni-S1-P	-8.32 (4)	S1-Ni-S2-P	8.33 (4)

of $[\text{Ni}(\text{Py})_2(\text{L})_2]$. The Ni atom lies on a crystallographic centre of symmetry, and has a slightly distorted octahedral coordination with four-S atoms at the corners of a square and two *trans*-configured pyridine rings. The angle between the planes Ni-S1-S2 and P-S1-S2 was measured to be $165.47(7)^\circ$, indicating a 14.53° buckling. Again, Ni-S1-P and Ni-S2-P are not coplanar and the four-membered ring Ni-S1-P-S2 can conveniently be called twisted chair. The ring Ni-S1-P-S2 was calculated to have a total wrinkle of $-0.1802(9)\text{\AA}$.⁵

The Ni-S1 and Ni-S2 bond lengths are 2.4845(1) and 2.5049(9) \AA ; S1-S2 and S1-S2 are 3.287 and 3.753 \AA , respectively. The internal angles of the square formed by the four S atoms are all close to 90° , the deviations being less than a degree. This indicated that the overall coordination geometry is pretty close to octahedral. Ni atoms are located in the above mentioned Resulty and the deviation is noteworthy. The P-S1, P-S2, P-C1 and P-C8 bond lengths are 2.005(1), 2.006(1), 1.808(3) and 1.809(3) \AA , respectively. The data reported for similar structures¹ are consistent with ours.

The dihedral angles between the plane formed by sulfur and nickel atoms and the pyridine ring is $95.12(9)^\circ$. The same central square forms another dihedral angle of $105.92(7)^\circ$ with the phenyl ring. The angle between the pyridine and the phenyl rings is measured to be $31.64(13)^\circ$.

The hydrogen bonding geometry is given in Table 2. In the crystal form of the complex there involves two intramolecular and two intermolecular hydrogen bonds of types C-H \cdots S and C-H \cdots O. The intramolecular interactions, the donor-acceptor distances, namely C2 \cdots S2, C17 \cdots S1, C6 \cdots O1 and C13 \cdots S1, are 3.349(4), 3.379(4), 3.466(5) and 3.352(4) \AA , respectively.

References

1. E. G. Sađlam, Ö. Çelik, H. Yılmaz, and S. İde, *Trans. Metal. Chem.*, **2010**, 35, 399.
2. G. Bina and I. Z. Begum, *Sep. Purif. Technol.*, **2008**, 63, 77.
3. R. Singh, A. R. Khwaja, B. Gupta, and N. S. Tandon, *Solvent Extr. Ion Exch.*, **1999**, 17, 367.
4. A. C. Bara, C. Silvestru, and I. Haiduc, *Anticancer Res.*, **1991**, 11, 1651.
5. D. Cremer and J. A. Pople, *J. Amer. Chem. Soc.*, **1975**, 97, 1354.