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Synthesis and 3D crystal structure of new Ni(II)-ion-pair complex

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Abstract

The new Ni(II) ion-pair complex, [BzTPP][Ni(dto)$_2$] [(dto)$^{2-}$ = dithiooxalate and (BzTPP)$^+$= benzyltriphenylphosphonium] was synthesized and characterized by single crystal X-ray diffraction method. The crystal structure analysis indicates that complex crystallizes in the monoclinic space group P2$_1$/c and its asymmetric unit consists of discrete one [BzTPP]$^+$ organic cation and one-half of [Ni(dto)$_2$]$^{2-}$ complex anion. The nickel atom is four coordinate and square planar coordination geometry. In the crystal structure, the organic cations and inorganic anions are linked with the intermolecular C–H···O hydrogen bonds as well as C–H··· π and π−π interactions which form 3D crystal structures and ensure the lattice stability.

Keywords: *Ni(II) complex, crystal structure, dithiooxalate.*

Yeni Ni(II) iyon-çifti kompleksinin sentezlenmesi ve 3D kristal yapısı

Özet

Yeni Ni(II) iyon-çifti kompleksi, [BzTPP][Ni(dto)$_2$] [(dto)$^{2-}$ = ditiooksalat ve (BzTPP)$^+$= benziltrifenilfosfonyum] sentezlendi ve tek kristal X-ışını kırınımı yöntemi ile karakterize edildi. Kristal yapı analizi kompleksin monoklinik uzay grubu P2$_1$/c'de kristallendiğini ve asimetrik biriminde birbirinden ayrık olarak [BzTPP]$^+$ organik katyonu ve [Ni(dto)$_2$]$^{2-}$ kompleks anyonun yarısından oluştuğunu göstermektedir. Nikel atomu dört koordinatlıdır ve kare düzlem koordinasyon geometrisine sahiptir. Kristal yapıda, organik katyonlar ve inorganik anyonlar moleküller arası C–H···O hidrojen

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bağlarıyla ve C–H···π ve π−π etkileşimleriyle birbirlerine bağlanırlar, buda üç boyutlu kristal yapının oluşmasını ve kafes yapının kararlılığını sağlar.

Anahtar kelimeler: *Ni(II) kompleksi, kristal yapı, ditiooksalat.*

1. Introduction

Recently, the transition metal complexes with S donor ligands has attracted great interest among researchers since the applications of these complexes in catalysis, and bioinorganic chemistry [1–3]. One of these S donor ligands is the dithiooxalate dianion which is a multifunctional ligand which has unique coordination properties due to the presence of four donor atoms and the possibilities of charge delocalization on its atoms [4]. Besides that, Nickel(II) potassium-dithiooxalate, $K_2Ni(dto)_2$, complexes have been widely studied due to their highly delocalized extending system, extremely versatile set of structural properties and their various chemical and physical properties in catalysis, optics and magnetism [5,6]. We and others have previously reported some organic cations as counterions of $[M(dto)_2]^{2-}$ (M = Cu, Ni, Fe, Pd or Pt ion) anions as well as the use of the $[M(dto)_2]^{2-}$ dianionic tecton as a hydrogen bond acceptor [7–9]. These organic cations tunes the stacking pattern and overlapping mode of the $[M(dto)_2]^{2-}$ anions and obtains some molecular materials with unusual magnetic properties [8,10].

In view of this wide interest, and as a part of our research on complexes of the dithiooxalate ligand, in this paper, a new Ni(II) ion-pair complex, $[BzTPP][Ni(dto)_2]$ was synthesized and the single crystal x-ray structure was described in terms of C–H···O hydrogen bonds as well as C–H···π and π−π interactions observed in the crystal give rise to 3D structure. To the best of our knowledge, this Ni(II) ion-pair complex, $[BzTPP][Ni(dto)_2]$, is described here for the first time.

2. Experimental

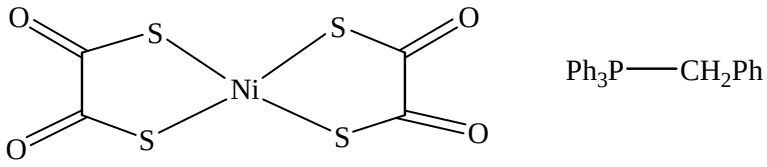
2.1. Materials and measurements

All chemical reagents and solvents were purchased from Aldrich and used without further purification. Elemental (C, H, N) analyses were run on a LECO, CHNS–932 analyzer with standard methods. Single crystal x-ray diffraction measurement was made on three-circle CCD diffractometers using graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å) at 273 K. The intensity data were integrated using the SAINT program [11]. Absorption, Lorentz and polarisation corrections were applied. The structures were solved by direct methods and refined using fullmatrix least-squares against F^2 using OLEX2 [12]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.2 times the U_{equiv} of their attached carbon atoms. Detail of the supramolecular π-interactions were calculated PLATON 1.17 program [13].

2.2. Synthesis of the complex

The salts $K_2[Ni(dto)_2]$ (dto = dithiooxalate) was synthesized according to the published procedure [14]. The complex was prepared by combination of $K_2[Ni(dto)_2]$ and benzyltriphenylphosphonium chloride ([BzTPP]Cl) in 1:1 molar ratio in water (20 ml).

The red crystals that formed was filtered off, washed with distilled water and dried air. The schematic view of the complex is outlined in Scheme 1. Yield: 79.8 %. Anal. Calcd (%) for $C_{54}H_{44}NiO_4P_2S_4$: C, 64.48; H, 4.41; Found: C, 64.72; H, 4.44.



Scheme 1. The schematic view of complex.

3. Result and discussion

3.1. Description of the Single Crystal Structure

The crystal data and refinement parameters are given in Table 1, whereas selected geometric parameters (Å, º) are listed in Table 2. Potential hydrogen Bonds (Å, °), short ring-interactions with Cg-Cg Distances and X-H···Cg (Pi-Ring) interactions are also given in Table 3. The molecular structure of **1** which crystallizes in the monoclinic space group $P2_1/c$ is depicted in Figure 1. The asymmetric unit of complex **1** consists of discrete one organic $[BzTPP]^+$ cation and one-half of $[Ni(dto)_2]^{2-}$ complex anion, with the nickel atom lying on a centre of symmetry. The coordination geometry about the nickel atom is four coordinate and square planar. All bond and angles are in good agreement with the literature data reported for various salts of $[Ni(dto)_2]^{2-}$ (Table 2) [2,4,5]. The $[Ni(dto)_2]^{2-}$ complex anion is almost planar and the dihedral angle between the strictly planar NiS_4 group and the $S_2C_2O_2$ ligand mean plane is 5.38°. This deviation is due to the C–H…O hydrogen bonds between three rings attached to P1 and the oxygen atoms O1 and O2 as well as the π-π interactions between the aromatic cations and the dithiooxalate groups (Table 3). In the crystal structure, the molecules are linked with intermolecular C–H···O hydrogen bonds which form 3D structure (Table 3, Fig. 2) as well as C–H···π and π−π interactions (Fig.3).

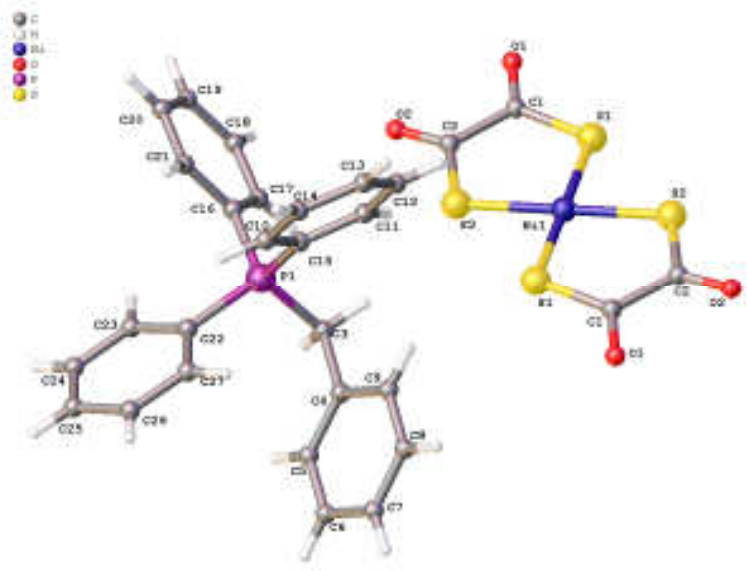


Figure 1. ORTEP plot showing the molecular structure of the complex.

Table 1. Crystal data and refinement parameters

CCDC No	1816848
Chemical formula	$C_2Ni_{0.5}O_2S_2 \cdot C_{25}H_{22}P$
M_r	502.89
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	273
a, b, c (Å)	8.8517 (18), 16.759 (3), 15.608 (3)
β (°)	96.50 (3)
V (Å^3)	2300.5 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.72
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7392, 4344, 3490
R_{int}	0.023
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.073, 0.93
No. of reflections	4344
No. of parameters	295
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.39

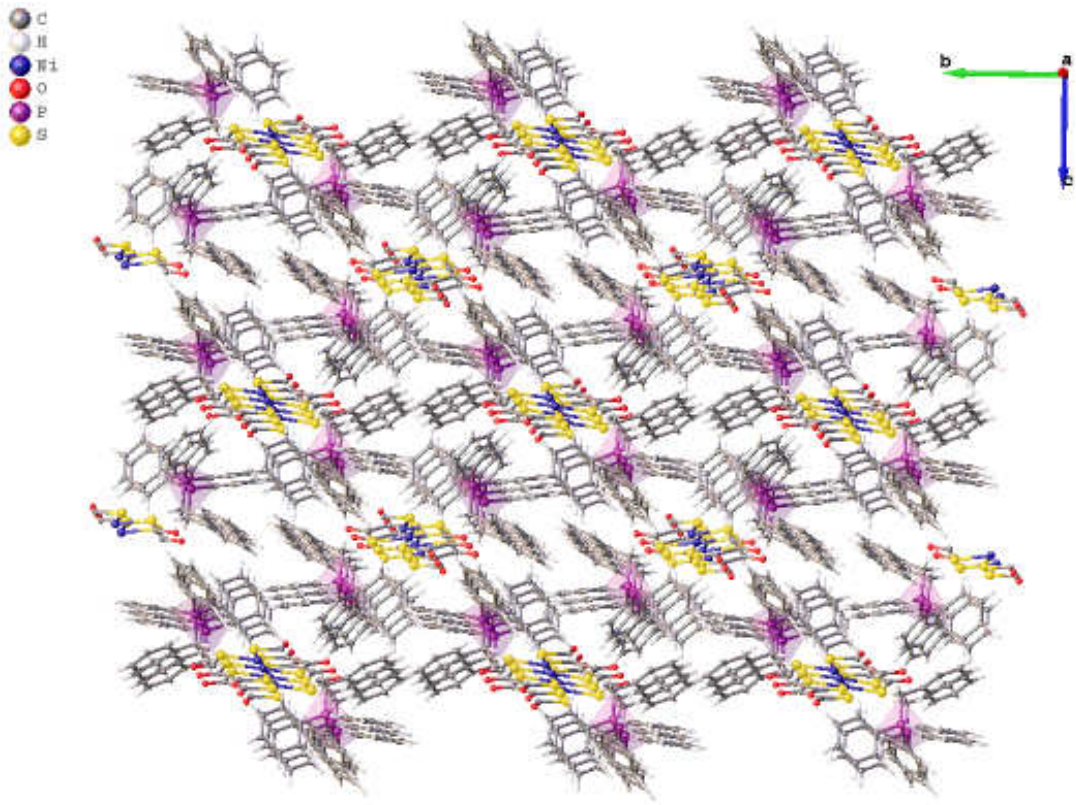


Figure 2**.** A view of 3D structure of complex.

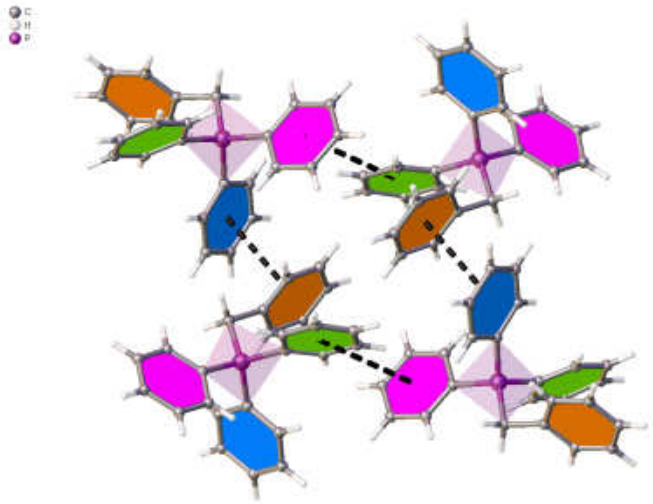


Figure 3. A view of π-π interaction in the crystal structure.

Table 2. Selected geometric parameters (Å, º)

Ni1—S1	2.1712 (7)	O2—C2	1.224 (2)
Ni1—S2	2.1708 (8)	P1—C3	1.803 (2)
S1—C1	1.730 (2)	P1—C10	1.798 (2)
S2—C2	1.726 (2)	P1—C16	1.789 (2)
O1—C1	1.223 (3)	P1—C22	1.793 (2)
$S1^{i}$—Ni1—S1	180.0	C16—P1—C3	111.49 (10)
$S2^{i}$—Ni1—S1	92.00 (2)	C16—P1—C10	107.67 (9)
S2—Ni1—S1	88.00 (2)	C16—P1—C22	107.97 (10)
C1—S1—Ni1	106.42 (9)	C22—P1—C3	109.15 (10)
O1—C1—S1	124.08 (18)	C22—P1—C10	111.78 (10)
C10—P1—C3	108.81 (9)		
Ni1—S1—C1—O1	−172.91 (16)	P1—C10—C11—C12	179.20 (16)
Ni1—S1—C1—$C2^{i}$	8.76 (16)	P1—C10—C15—C14	−179.76 (16)
Ni1—S2—C2—O2	177.15 (16)	P1—C16—C17—C18	−179.85 (15)
Ni1—S2—C2—$C1^{i}$	−1.14 (16)	P1—C16—C21—C20	178.96 (15)
P1—C3—C4—C5	98.2 (2)	P1—C22—C23—C24	179.75 (18)
P1—C3—C4—C9	−82.5 (2)	P1—C22—C27—C26	179.46 (15)

Symmetry code: (i) −x+1, −y, −z+2.

Table 3. Potential hydrogen Bonds (Å, °), short ring-interactions with Cg-Cg Distances and C-H...Cg (Pi-Ring) interactions.

D–H…A*	**D–H**	**H…A**	**D…A**	**D–H…A**	**Symmetry Code**
C3–H3A…O1	0.97	2.39	3.347(3)	168	-1+x,y,z
C15–H15…O2	0.93	2.31	3.163(3)	151	-x,1/2+y,3/2-z
C21–H21…O1	0.93	2.57	3.438(3)	155	-1+x,1/2-y,-1/2+z
C26–H26…Cg(3)	0.93	2.98	3.719(3)	138	-x,1/2+y,3/2-z
Cg(I)…Cg(J)					
Cg(1)…Cg(2)			3.776(1)		x,1/2-y,1/2+z
Cg(2)…Cg(1)			3.776(1)		x,1/2-y,-1/2+z
Cg(1)…Cg(4)			4.710(2)		x,y,z
Cg(3)…Cg(4)			4.945(2)		-x,1/2+y,3/2-z
Cg(4)…Cg(1)			4.712(2)		x,y,z

D: Donor, A: Acceptor, Cg(I): Plane number I (=ring number in () above), Cg(1): C4-C5-C6-C7-C8-C9, Cg(2): C10-C11-C12-C13-C14-C15, Cg(3): C16-C17-C18-C19-C20-C21, Cg(4): C22-C23-C24-C25-C26-C27.

4. Conclusion

A new Ni(II) ion-pair complex, [BzTPP][Ni(dto)$_2$] is discovered and characterized in the solid state. The asymmetric unit of complex **1** consists of discrete one organic [BzTPP]$^+$ cation and one-half of [Ni(dto)$_2$]$^{2-}$ complex anion. The [Ni(dto)$_2$]$^{2-}$ complex anion is almost planar and the nickel atom is square planar geometry. In the crystal structure, there are an extended hydrogen bonds network of the type C–H···O between the hydrogen atoms of C3, C15 and C21 of the benzyltriphenylphosphonium cation and two oxygen atoms of the same dithiooxalate anion. The ions are also linked by means of strong C–H···π and π−π interactions (3.776 - 4.955 Å).

5. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.uk; www: http://www.ccdc.cam.ac.uk; fax: +44 1223 336033) and are available free of charge on request, quoting the Deposition No. CCDC 1816848.

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