

研究简报

配合物 [1-(4'-fluorobenzyl)pyridinium]₂[Ni(dto)₂]
(dto²⁻ = dithiooxalate dianion) 的合成及晶体结构刘玲^{1,2} 谢景力^{*1} 任小明¹ 孟庆金¹¹ 南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)² 云南师范大学化学化工学院, 昆明 650092)

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Synthesis and Crystal Structure of [1-(4'-fluorobenzyl)pyridinium]₂[Ni(dto)₂]
Complex (dto²⁻ = dithiooxalate dianion)LIU Ling^{1,2} XIE Jing-Li^{*1} REN Xiao-Ming¹ MENG Qing-Jin¹¹ State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093)² College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092)

The complex [1-(4'-fluorobenzyl)pyridinium]₂[Ni(dto)₂] (dto²⁻ means dithiooxalate dianion) has been prepared by reaction of Na₂[Ni(S₂C₂O₂)₂] and the 1-(4'-fluorobenzyl)pyridinium chloride salt. The crystallographic data for the title complex: triclinic $P\bar{1}$, $a = 8.5698(8) \text{ \AA}$, $b = 9.3461(9) \text{ \AA}$, $c = 10.5361(10) \text{ \AA}$, $\alpha = 67.177(2)^\circ$, $\beta = 67.398(2)^\circ$, $\gamma = 79.611(2)^\circ$, $V = 717.59(12) \text{ \AA}^3$, $Z = 1$. The [Ni(dto)₂]²⁻ anion with the Ni atom lying on an inversion center and exhibits a quasi-planar structure. An extensive hydrogen bond network of C-H...O is clearly observed. The nature and size of cation seems to play an important factor in the type of intermolecular interactions as well as the crystal packing in this kind of complexes.

Keywords: 1,2-dithiooxalato ligand nickelate(II) complex pyridinium cation crystal structure

0 Introduction

In the past two decades, efforts have been focused on the coordination chemistry of metal complexes with sulphur donor ligands for its application in analytical chemistry, catalysis and its relevance to bioinorganic systems^[1]. One of these sulphur donor ligands is the dithiooxalate dianion(dto²⁻) with unique coordination

properties for it have four donor atoms and the possibilities of charge delocalization on its atoms^[2]. Some groups have investigated this kind of complexes in detail because they show some interesting properties such as magnetic, conductivity and optical properties^[3]. Previous studies have shown that the nature and size of the counterions play an important role in the crystal

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packing of this kind of complexes^[4]. We present in this paper the synthesis and crystal structure of [1-(4'-fluorobenzyl) pyridinium]₂[Ni(dto)₂] with the aim of obtaining more information about the cation effects on the crystal packing and the strength of the intermolecular interactions in this type of complexes.

1 Experimental

1.1 Materials and Methods

4-fluorobenzyl chloride was purchased from Aldrich Chemical Co. and used as received. 1-(4'-fluorobenzyl) pyridinium chloride^[5], and the sodium salt of dithiooxalate (Na₂dto)^[6] were synthesized by a literature procedure. Elemental analyses were performed with a Perkin-Elmer 240 analytical instrument. IR spectrum was recorded on a 170SX Fourier Transform Infrared Spectrometer (KBr pellet).

1.2 Synthesis of [1-(4'-fluorobenzyl) pyridinium]₂[Ni(dto)₂]

The title complex was prepared by the direct combination of one molar equivalent of NiCl₂ · 6H₂O, two molar equivalent of 1-(4'-fluorobenzyl) pyridinium chloride and of Na₂dto in water at room temperature. A red precipitate was obtained by filtration, then washed by water and dried under vacuum. Good shaped red

single crystals suitable for X-ray analysis were obtained by dispersing ethyl ether into acetonitrile solution of complex and stood for about a week. Yield: 86%. Elemental analysis found (calc.): C, 49.28(49.79); H, 3.29(3.28); N, 4.22(4.15). Selected IR data (cm⁻¹): 1592vs, 1447m [ν(C=O)]; 1052vs [ν(C-C) + ν(C-S)]; 948s [δ(C-O) + ν_s(C-S)]; 563w, 543w [ν_s(C-S)].

1.3 Data Collection, Structure Solution, and Refinement

The red single crystal of the title complex, has approximate dimensions 0.52 × 0.30 × 0.10mm was selected for X-ray structure measurement. Data were collected on a Siemens Smart CCD area diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073Å) by ω scans mode within the angular range 2.24° < θ < 25.05°. Space group, lattice parameters, and other relevant information are listed in Table 1. The structure was solved by direct methods and refined on F² by full-matrix least-square using the SHELXL-97^[7]. All nonhydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions (C-H 0.93, 0.97Å), assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached

Table 1 Crystal Data and Structure Refinement

color/shape	red/block
chemical formula	C ₂₈ H ₂₂ F ₂ N ₂ NiO ₄ S ₄
formula weight	675.43
temperature, K	293(2)
wavelength	0.71073Å
crystal system	triclinic
space group	P $\bar{1}$
unit cell dimensions	a = 8.5698(8)Å α = 67.177(2)Å b = 9.3461(9)Å β = 67.398(2)Å c = 10.5361(10)Å γ = 79.611(2)Å
volume/Å ³	717.59(12)
Z	1
density (calculated)	1.563mg · m ⁻³
absorption coefficient	1.018mm ⁻¹
F(000)	346
reflections collected	3752
independent reflections	2520 (R _{int} = 0.0171)
data/restraints/parameters	2520/0/187
goodness of fit on F ²	1.090
final R indices [I > 2σ(I)]	R ₁ = 0.0399, wR ₂ = 0.0970
R indices (all data)	R ₁ = 0.0539, wR ₂ = 0.1104
largest diffraction peak and hole	0.339 and -0.271e · Å ⁻³

atom, and allowed to ride on their respective parent atoms.

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2 Results and Discussion

As for the title complex, it crystallizes in the triclinic space group $P\bar{1}$. The atom arrangements and the numbering system for it are shown in Fig. 1. Fractional atomic coordinates and equivalent isotropic displacement parameters of the complex are listed in Table 2. Selected bond lengths, angles and the hydrogen con-

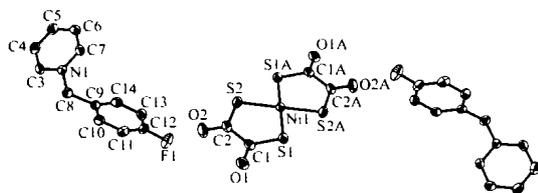


Fig. 1 ORTEP plot (30% probability ellipsoids) showing the molecular structure of [1-(4'-fluorobenzyl)pyridinium]₂[Ni(dto)₂]

tacts are listed in Table 3.

The [Ni(dto)₂]²⁻ anion has a center of symmetry at the nickel atom and two [1-(4'-fluorobenzyl)pyridinium]⁺ ions are related to each other by the symmetry center. The nickel atom is coordinated to four sulfur atoms, and exhibits square-planar coordination geometry. The average S-Ni-S bond angle within the five-membered ring is 92.2°, and the average Ni-S bond distance is 2.18 Å, these values are in agreement with that of [Ni(dto)₂]²⁻ complexes reported^[46]. The average C-S bond distances of 1.72 Å and the average C=O bond distance of 1.22 Å are due to there exists the delocalization throughout S-C-O units in the dianion, and the average single C-C bond is 1.53 Å. The complex [Ni(dto)₂]²⁻ dianion, is not completely planar with the deviation of O(1) atom from NiS₄ plane is 0.289(3) Å, O(2) atom from NiS₄ plane is 0.232(3) Å. There exists a dihedral angle of 5.77° between the planar NiS₄ group and the O(1)C(1)S(1)O(2)C(2)S(2) (dto²⁻) mean plane so as to show a chair confor-

Table 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Title Complex

atom	x	y	z	$U(\text{eq})$	atom	x	y	z	$U(\text{eq})$
Ni(1)	0	0	0	43(1)	S(1)	257(1)	2289(1)	-1715(1)	54(1)
S(2)	2727(1)	-412(1)	-627(1)	60(1)	F(1)	6695(3)	-1639(3)	-3974(3)	89(1)
O(1)	2980(3)	3568(3)	-3845(3)	64(1)	O(2)	5104(3)	1278(3)	-2872(3)	79(1)
N(1)	13407(3)	-3802(3)	-2384(3)	43(1)	C(1)	2384(4)	2464(4)	-2727(4)	48(1)
C(2)	3593(4)	1154(4)	-2186(4)	52(1)	C(3)	14756(4)	-4728(4)	-2741(4)	51(1)
C(4)	15074(5)	-6046(4)	-1676(4)	62(1)	C(5)	13990(5)	-6424(4)	-266(4)	64(1)
C(6)	12605(5)	-5465(5)	84(4)	61(1)	C(7)	12338(4)	-4153(4)	-987(4)	53(1)
C(8)	13102(4)	-2330(4)	-3530(4)	55(1)	C(9)	11350(4)	-2197(4)	-3584(3)	44(1)
C(10)	10949(4)	-3050(4)	-4226(4)	53(1)	C(11)	9365(5)	-2885(4)	-4340(4)	58(1)
C(12)	8235(4)	-1835(4)	-3817(4)	54(1)	C(13)	8571(4)	-985(4)	-3167(4)	52(1)
C(14)	10146(4)	-1172(4)	-3056(3)	47(1)					

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected Bond Lengths (\AA), Bond Angles ($^\circ$) and Hydrogen Contacts

Ni(1)-S(1)	2.1802(8)	Ni(1)-S(2)	2.1753(9)	S(1)-C(1)	1.722(3)
S(2)-C(2)	1.726(4)	O(1)-C(1)	1.223(4)	O(2)-C(2)	1.217(4)
C(1)-C(2)	1.534(5)				
S(2)-Ni(1)-S(1)	92.25(3)	O(1)-C(1)-C(2)	118.5(3)	C(1)-S(1)-Ni(1)	105.98(12)
O(1)-C(1)-S(1)	123.9(3)	C(2)-S(2)-Ni(1)	105.88(12)		
	X-H	X...O	H...O	\angle X-H...O	
C(3)-H(3A)-O(1')	0.93	3.201	2.278	171.9	
C(8)-H(8A)-O(2')	0.97	3.298	2.411	151.8	
C(10)-H(10A)-O(1')	0.93	3.279	2.488	143.0	
C(13)-H(13A)-O(2')	0.93	3.306	2.487	147.0	

Symmetry codes: $i = 2 - x, -y, -z - 1$; $j = x + 1, y - 1, z$

mation. This angle is much larger than those observed in analogous $[\text{Ni}(\text{dto})_2]^{2-}$ complexes containing aromatic cations^[4b]. Some factors have effect on the value of angle, among them, one factor is the hydrogen contacts between the hydrogen atoms of cations and the oxygen atoms of dto^{2-} which will be known below^[8]. In the 1-(4-fluorobenzyl) pyridinium cation, the dihedral angles with the N(1)-C(8)-C(9) reference plane are $74.4(2)^\circ$ for phenyl ring, $53.1(2)^\circ$ for pyridine ring, respectively.

The view of the unit cell of the title complex together with the hydrogen bond interactions between the cations and anions are shown in Fig. 2 (dotted lines). One hydrogen bond pair is between C(3) atom on pyridine ring and O(1') atom on $[\text{Ni}(\text{dto})_2]^{2-}$ anion ($i = 2 - x, -y, -z - 1$), C(10) atom on phenyl ring and O(1') atom ($j = x + 1, y - 1, z$); another hydrogen bond pair between C(8) atom on methylene and O(2') atom on $[\text{Ni}(\text{dto})_2]^{2-}$ anion ($i = 2 - x, -y, -z - 1$), as well as C(13) atom on phenyl ring and O(2) atom. The corresponding hydrogen bond contacts and angles are given in Table 3. As could be noted, the neighbouring cations and anions form channels by means of these hydrogen bond pairs (Fig. 3). In the title complex, there is no evidence of π - π interaction between dithiooxalate groups belonging to neighbor anions, which have been found previously^[4a].

We have observed a complex of nickel dithiooxalate described above. The topology and size of the aromatic cation has related to its molecular conforma-

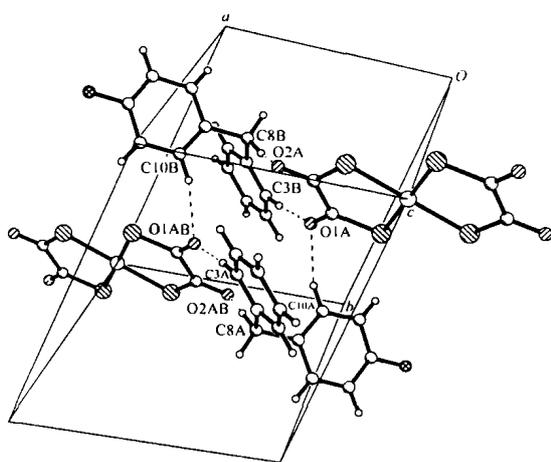


Fig. 2 Packing of the title complex together with network of hydrogen bond

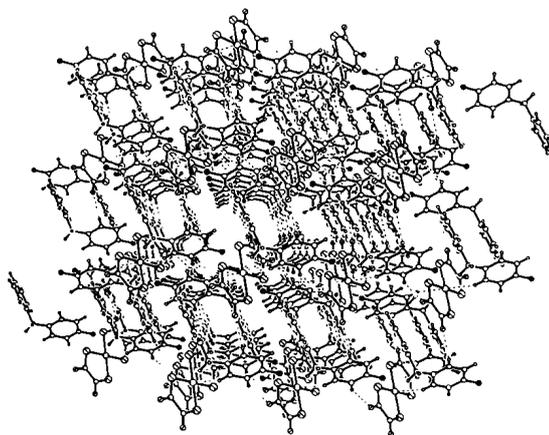


Fig. 3 Channel formed by hydrogen bond in title complex. Furthermore, the crystal packing of this kind of complexes could be influenced.

References

- [1] (a) Muller A. *Polyhedron*, **1986**, *5*, 323;
(b) Wilkinson G., Gillard R. D., McCleverty J. A. *Comprehensive Coordination Chemistry*, Pergamon Press: New York, **1987**, Vol. 6, Edited by McCleverty J. A., p541;
(c) Holm R. H. *Accs. Chem. Res.*, **1977**, *10*, 427.
- [2] Coucouvanis D., Baezinger N. C., Johnson S. M. *J. Am. Chem. Soc.*, **1973**, *95*, 3875.
- [3] (a) Dietzsch W., Strauch P., Hoyer E. *Coord. Chem. Rev.*, **1992**, *121*, 43;
(b) Kojima N., Aoki W., Itoi M., Ono Y., Seto M., Kobayashi Y., Maeda Yu. *Solid State Comm.*, **2001**, *120*, 165;
(c) Hass P., Griesshaber E., Gorshunov B., Schweitzer D., Dressel M., Klaus T., Strunz W., Assaad F. F., *Phys. R. B. Condens. Matter. Mater. Phys.*, **2000**, *62*, R14673.
(d) Saito G., Izukashi H., Shibata M., Yoshida K., Kusch L. A., Konda T., Yamochi H., Drozdova O. O., Matsumoto K., Kusunoki M., Sakaguchi K. I., Kojima N., Yagubskii E. B. *J. Mater. Chem.*, **2000**, *10*, 893.
- [4] (a) Roman P., Luque A., Beitia J. I., Guzman-Miralles C. *Polyhedron*, **1992**, *11*, 1883;
(b) Roman P., Beitia J. I., Luque A., Aranzabe A. *Polyhedron*, **1993**, *12*, 1345.
- [5] Bulgarevich S. B., Bren D. V., Movshovic D. Y., Finocchiaro P., Failla S. *J. Mol. Struct.*, **1994**, *317*, 147.
- [6] Cox E. G., Wardlaw W., Webster K. C. *J. Chem. Soc.*, **1935**, 1475.
- [7] *SHELXTL, Version 5.10. Structure Determination Software Programs*, Bruker Analytical X-ray Systems Inc. Madison, Wisconsin, USA.
- [8] Roman P., Gutierrez-Zorrilla J. M., Luque A., Beitia J. I., Guzman-Miralles C. *Acta Cryst.*, **1991**, *C47*, 48.