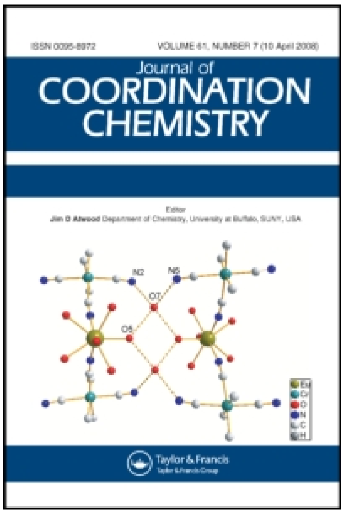

ISSN 0095-8972 VOLUME 61, NUMBER 7 (10 April 2008)
Journal of
COORDINATION
CHEMISTRY
Taylor & Francis

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Characterization and Molecular Structure of Bis(Isopropyl Xanthate) Bis(1,10-Phenanthroline) Nickel(II): [Ni(phen)$_2$(CH$_3$)$_2$CHOCSS](CH$_3$)$_2$CHOCSS

Kaijun Xu[a]; Weiping Ding[b]; Wei Meng[a]; Fang Hu[a]
[a] Physical Chemistry Laboratory, China Pharmaceutical University, Nanjing, P.R. China [b] Physical Chemistry Laboratory, Nanjing University, Nanjing, P.R. China

To cite this Article Xu, Kaijun , Ding, Weiping , Meng, Wei and Hu, Fang(2003) 'Characterization and Molecular Structure of Bis(Isopropyl Xanthate) Bis(1,10-Phenanthroline) Nickel(II): [Ni(phen)$_2$(CH$_3$)$_2$CHOCSS](CH$_3$)$_2$CHOCSS', Journal of Coordination Chemistry, 56: 9, 797 — 801

To link to this Article: DOI: 10.1080/0095897031000110673

URL: http://dx.doi.org/10.1080/0095897031000110673

J. Coord. Chem., Vol. 56, No. 9, 15 June 2003, pp. 797–801

Taylor & Francis
Taylor & Francis Group

CHARACTERIZATION AND MOLECULAR STRUCTURE OF BIS(ISOPROPYL XANTHATE) BIS(1,10-PHENANTHROLINE) NICKEL(II): $[Ni(phen)_2(CH_3)_2CHOCSS](CH_3)_2CHOCSS$

KAIJUN XU[a,]*, WEIPING DING[b], WEI MENG[a] and FANG HU[a]

[a]*Physical Chemistry Laboratory, China Pharmaceutical University, Nanjing, 210009, P.R. China;*
[b]*Physical Chemistry Laboratory, Nanjing University, Nanjing, 210008, P.R. China*

(Received 28 March 2002; Revised 2 August 2002; In final form 19 February 2003)

The crystal and molecular structure of the title compound, $[Ni(phen)_2(CH_3)_2CHOCSS](CH_3)_2CHOCSS$ has been determined by X-ray diffraction. The brown crystal is triclinic of space group $P\bar{1}$, with parameters $a = 11.790(2)$, $b = 12.410(3)$, $c = 12.680(3)$ Å, $\alpha = 92.49(3)$, $\beta = 96.54(3)$, $\gamma = 117.43(3)^\circ$ and $Z = 2$. The compound contains a six-coordinate cation and an isopropyl xanthate anion $(CH_3)_2CHOCSS^-$, the central Ni atom is chelated by four nitrogen atoms of two phenanthroline ligands and two sulfur atoms of an isopropyl xanthate ligand. The TG data indicate that it decomposed completely at 734°C.

Keywords: Nickel complex; 1,10-phenanthroline ligands; Xanthate

INTRODUCTION

Metal complexes of the type $[M(LL)_3]^n$, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [1,2]. The metal or ligands in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing easy access for understanding details involved in DNA-bond cleavage [3]. In this article, we select xanthate as the anion because of its ability to bind to various metals [4,5]. It forms a chelate with virtually all transition elements and has proved to be a versatile chelating agents for the separation and extraction of metals in analytical chemistry and mineral floating [6,7]. Salts, complexes, free acids, and esters as well as reactions of xanthate, peroxoxanthates, thioxanthates, and selenoxanthates have been discussed in detail [8]. Through the synthesis of the complex of isopropyl xanthate and phen with nickel(II), we report the structure of the title compound. Also IR, UV, and TG spectra of the title compound have been determined.

---

*Corresponding author. Tel.: 86 025 6636209. E-mail: xukaijun@public 1.ptt.js.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000110673

EXPERIMENTAL

Physical Measurements

Elemental analysis was performed on PE-240 elemental analyzer. IR spectra were measured in KBr discs using a Bruker Vector 22 spectrophotometer. Ultraviolet spectra were recorded on a Shimadzu UV-240 spectrophotometer. Thermal analyses were performed in nitrogen gas with a Shimadzu TGA-50 (20°C/min).

Preparation of the Title Compound

The title compound was synthesized by adding NaOH (0.40 g, 0.01 mol) powder gradually to a solution of isopropanol (10 mL) and CS_2 (1.4 mL) keeping the temperature around 15°C for half an hour. Light-yellow solid was obtained and dried *in vacuo* (90% yield). Dissolving the solid (0.005 mol) in water (10 mL) and adding $Ni(NO_3)_2$ (2.5 mmol) gave a greenish black precipitate which was filtered off, washed with water, and dried *in vacuo* over P_4O_{10} (98% yield). The precipitate (2.0 mmol) was solved in EtOH (20 mL) and 1,10-phenanthroline (4.0 mmol) was added to it. The mixture was refluxed at 60°C for 30 min till the solution changed red. The red solution was evaporated at room temperature and brown crystals were obtained a week later. Found: C, 55.56; H, 4.24; N, 8.28%. (Calcd.: C, 55.65; H, 4.35; N, 8.12%).

Crystallographic Data Collection and Solution of Structure

A summary of the key crystallographic information is given in Table I. The selected brown crystal of the title compound was mounted on a Bruker P4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 293 K using Mo-K_α radiation ($\lambda = 0.071073$ nm) with a graphite monochromator.

TABLE I Summary of crystallographic results for the title compound

Color/shape	Brown/prism
Empirical formula	$C_{19}H_{30}N_4NiO_2S_4$
Formula weight	689.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 11.790(2)$ Å, $b = 12.410(3)$ Å, $c = 12.680(3)$ Å $\alpha = 92.49(3)^\circ$, $\beta = 96.54(3)^\circ$, $\gamma = 117.43(3)^\circ$
Volume	1626.3(6) $Å^3$
Z, Calculated density	2, 1.408 mg/m^3
Absorption coefficient	0.889 mm^{-1}
$F(000)$	716
Crystal size	0.2 mm × 0.3 mm × 0.25 mm
Theta range for data collection	1.63 to 24.97°
Limiting indices	$0 < h \leq 14$, $-14 \leq k \leq 13$, $-15 \leq l \leq 14$
Reflections collected/unique	5974/5671 [R(int) = 0.0649]
Completeness to theta = 24.97	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5671/0/388
Goodness-of-fit on F^2	1.541
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0727$, $wR2 = 0.2328$
R indices (all data)	$R1 = 0.1259$, $wR2 = 0.3618$
Largest diff. peak and hole	0.851 and -1.377 e $Å^{-3}$

The technique used was ω-scan with θ limits of $1.63^\circ < \theta < 24.97^\circ$. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using SHELXTL5 [9]. The structure was solved by direct methods using SHELXS97 [10]. Nonhydrogen atoms were refined on F^2 anisotropically by full-matrix least-squares methods [11]. The hydrogen atoms were located from the difference map and refined isotropically. The final least-square cycle gave $R1 = 0.0727$ and $wR2 = 0.2328$ for 5671 reflections with $I > 2\sigma(I)$; the weighting scheme, $u = 1/[\sigma^2(F_o^2) - (0.2000P)^2]$, where $P = (F_o^2 - 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion correction were taken from the *International Table for X-ray Crystallography* [12]. The crystal structure for the title compound has been deposited at the CCDC and allocated the deposition number CCDC 174353.

RESULTS AND DISCUSSION

Spectroscopic Properties

IR and UV–Vis data are collected in Table II. The IR spectrum of the compound exhibits characteristic strong bands at 1241.2, and 1190 cm^{-1} for ν(C–O–R). The band at 1040 cm^{-1} is the characteristic absorption of ν(C=S). The bands at 1580($\nu_{C=N}$), 1514, and 1425 cm^{-1} ($\nu_{C=C}$) belong to the coordinated phen ligands [13]. The solution ultraviolet spectrum of the complex in EtOH exhibits two bands at 214 and 269 nm which belong to π–π* and *n*–π* orbital transition of triphenylphosphine ligand (at 216 and 262 nm for the free ligand). The band at 450 nm might be the charge-transfer absorption of six-coordinated Nickel(II) complexes. The *d*–*d* bands at 598 and 661 nm of the complex are also observed.

Thermal Gravimetric Analysis

In order to examine the thermal stability of the title compound, thermal gravimetric analysis was carried out from 20°C to 800°C in nitrogen gas. The TGA curve of the title compound is shown in Fig. 1. The complex first decomposes at temperatures ranging from 19 to 108°C and loses a molecule of isopropanol [$(CH_3)_2CHO$] (Found: 7.8%. Calcd.: 8.5%). With the increase of the temperature, the complex loses weight slowly at temperatures ranging from 109 to 455°C, and the lost weight is 52.1%, which indicates loss of two molecules of phenanthroline (Calcd.: 52.2%). At last, the complex decomposes at temperatures ranging from 455 to 734°C and loses a molecule of isopropyl xanthate [$(CH_3)_2CHOCSS$] and carbon disulfide [CS_2], leaving nickel metal (Found: 32.4%, Calcd.: 31.0%).

TABLE II IR and UV–Vis spectroscopic data for the title compound

IR (cm^{-1})			
ν(C–O–R)	*ν(C=S)*	*ν(C=N)*	*ν(C=C)*
1241, 1190	1040	1580	1514, 1425
UV–Vis [λ (nm)]			
π–π*	*n*–π^*	*Charge-transfer*	*d–d*
214	269	450	589, 661

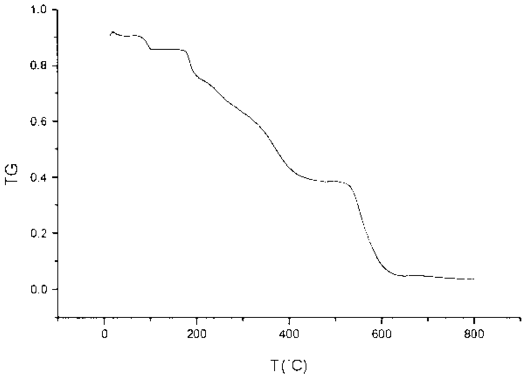

FIGURE 1 TG diagram of the title compound.

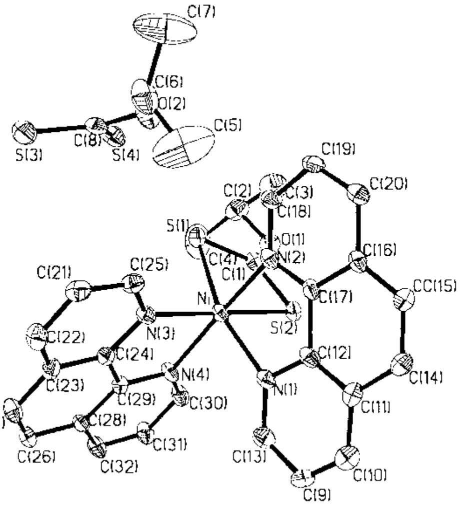

FIGURE 2 Molecular structure of the title compound (displacement ellipsoids are at the 50% probability level).

Description of the Title Compound Structure

Figure 2 shows a diagram of the molecular structure of the title compound. Selected bond distances and angles are listed in Table III. The solid-state structure consists of six-coordinate $[Ni(phen)_2(CH_3)_2CHOCSS]^+$ cations and $(CH_3)_2CHOCSS^-$ anions. In the cation, due to the small bite (73.01°) of the xanthate ligand, the nickel atom exhibits a distorted octahedral geometry in which Ni is coordinated to four nitrogen atoms from two phenanthroline molecules and two sulfur atoms from the bidentate isopropyl xanthate ligand. The Ni atom is 0.017, 0.023, 0.037 Å out of Plane 1 defined by C1, S1, S2, Plane 2 by N3, N4, C24, and the Plane 3 by N1, N2, C17, respectively. The dihedral angles between three planes are 88.37° (1 and 2), 85.68° (2 and 3), and 89.70° (1 and 3), respectively. The Ni–N distances normal range from 2.070(6) to 2.093(7) Å in good agreement with a previously reported structure [13]. The Ni–S distance are in the range of 2.436(3)–2.469(3) Å, similar to those found in related systems [14].

TABLE III Selected bond lengths [Å] and angles [°] for the title compound

Ni–N(1)	2.087(7)	Ni–N(3)	2.087(7)
Ni–N(2)	2.070(6)	O(2)–C(8)	1.354(12)
Ni–N(4)	2.093(7)	O(2)–C(6)	1.456(14)
Ni–S(2)	2.436(2)	C(8)–S(3)	1.678(10)
Ni–S(1)	2.469(3)	C(8)–S(4)	1.682(11)
S(2)–C(1)	1.686(9)	O(1)–C(1)	1.335(9)
S(1)–C(1)	1.697(8)	O(1)–C(2)	1.443(12)
N(2)–Ni–N(1)	79.9(3)	N(2)–Ni–N(4)	170.7(3)
N(3)–Ni–N(4)	79.8(3)	N(1)–Ni–N(4)	93.7(3)
N(3)–Ni–S(2)	173.40(19)	N(1)–Ni–S(1)	163.09(18)
S(2)–Ni–S(1)	73.01(8)	S(3)–C(8)–S(4)	125.4(6)
S(2)–C(1)–S(1)	119.2(5)		

The S_2CO groups are approximately planar. The mean values for S–C and C–O in these S_2CO groups of the xanthate ligands are 1.686 and 1.345 Å, respectively, and compare well with the corresponding values of previously reported xanthate complexes [15,16]. These values indicate partial double-bond character in the S_2CO groups.

That all bond angles and lengths of xanthate ligands coordinated to Ni atom are different from those of xanthate in the anion confirms their different chemical circumstances.

References

[1] J.K. Barton, *Science* **233**, 727 (1986).
[2] K. Naing, M. Takashani, M. Taniguichi and A. Yamagishi, *Inorg. Chem.* **34**, 350 (1995).
[3] P.C. Sammes and G. Yahioglu, *Chem. Soc. Rev.* 327 (1994).
[4] J. Formanek, H. Holeckova, W. Charewicz, W. Walkowiak and T. Gendolla, *Przem. Chem.* **64**, 98 (1985).
[5] D.G. Kotlyar and W.K. Tolley, *Min. Eng.* **11**, 1033 (1995).
[6] M.C. Gimeno, E. Jambrina, A. Laguna, M. Laguna, H.H. Murray and R. Terroba, *Inorg. Chem. Acta* **249**, 69 (1996).
[7] F.H. Allen and O. Kennard, *Chem. Des. Autom. News* **8**, 31 (1993).
[8] G. Gerhard, *Sulfur Rep.* **14**, 1 (1993).
[9] G.M. Sheldrick, SHELXTL 5: The Complete Software Package for Single Crystal Structure Determination (Siemens, AG, Analytical Systems Aut37, D76181 Karlsruhe 21, Germany, 1997).
[10] G.M. Sheldrick, *Acta Cryst.* **A46**, 467 (1969).
[11] G.M. Sheldrick, SHELXTL 93: Program for Crystal Structure Refinement (University of Gottyingen, Germany, 1993).
[12] A.J. Wilson, International Table for X-ray Crystallography (Kluwer Academic Publishers, Dordecht, 1992), Vol. C, Tables 6.1.1.4, pp. 500–502 and 4.2.6.8, pp. 219–222, respectively.
[13] Q.F. Han, F.F. Jian, L.D. Lu, X.J. Yang and X. Wang, *J. Coord. Chem.* **55**(6), 633 (2002).
[14] L. Ballester, A. Gutierrez and M.F. Peroinan, *Polyhedron* **15**(7), 1103 (1996).
[15] G.A. Stergioudis, P.C. Christidis and P.J. Rentzeperis, *Acta Cryst.* **B35**, 616 (1979).
[16] P.C. Christidis and P.J. Rentzeperis, *Acta Cryst.* **B34**, 2141 (1978).