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A novel molecular channel: thermal analyses and X-ray structure of [Ni(Et-XA)$_2$ · phen] · 3H$_2$O (Et-XA = ethylcarbonodithiolato-*S*,*S*′, phen = phenanthroline)

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Abstract—The crystal structural determination reveals that bis(o-ethylcarbonodithiolato-*S*,*S*′)(1,10-phenanthroline-N^1,N^{10})nickel(II) ([Ni(Et-XA)$_2$ · phen] · 3H$_2$O) forms a lattice inclusion compound with water molecules trapped in channels and grouped into triplets, within which exist very strong hydrogen bonds. The thermal analyses further confirms that the structure appears to be very stable and release of water molecules can be achieved only by the rupture of structure. © 1997 Elsevier Science Ltd

Keywords: nickel(II) complex; crystal structure; inclusion compound; 1,10-phenanthroline-N1; 10-complex; ethylcarbonodithiolato-S; thermal analyses.

Molecular recognition between host and guest molecules, inclusion phenomena and noncovalent molecular interaction are fundamental problems at the frontiers of both organic and inorganic chemistry [1]. Inclusion compounds with the special cavities, windows and channels have received increasing attention in recent years due in part to them being useful as molecular sieves and in catalysts [2]. Furthermore, inclusion formation affects both the physicochemical properties of the guest and chemical reaction [3]. Also, the inclusion compounds derived from the adduct of Ni(XA)$_2$ with neutral nitrogen bases have been extensively studied recently [4–5]. Gable and coworkers reported inclusion compounds [Ni(Et-XA)$_2$ · (2′, 2′-dpa) · C$_6$H$_6$] and [Ni(Bt-XA)$_2$ · (4, 4′-bipy) · 2CCl$_4$] in which the guest molecules are respectively encaged in the host lattice and channels [4]. Pang and coworkers also investigated the clathrate ability of Ni(Et-XA)$_2$ · phen for CCl$_4$ by ^{35}Cl NQR techniques [5]. We report herein the thermal analyses and structure of bis(o-ethylcarbonodithiolato-*S*, *S*′) (1,10-phenthroline-*N*^{1},*N*^{10})nickel(II) inclusion compounds with water molecules. This is the first crystallographic structure of the inclusion of water molecules with very strong hydrogen bonding to one another in the Ni(Et-XA)$_2$ channel.

EXPERIMENTAL

Synthesis and thermal analyses

To a chloroform (10 cm^3) and ethanol (95%, 20 cm^3) solution (30 cm^3) containing 1 mmol of Ni(Et-XA)$_2$ was added 1 mmol phenathroline. After stirring in air for about half an hour, the brown solution was filtered; the transparent solution evaporated for a few weeks at ambient temperature to yield the black crystals (yield 85%, based on Ni(Et-XA)$_2$). Its IR spectrum shows all the features of Ni(Et-Et)$_2$ and phen, and also exhibits a broad absorption band of uncoordinated water at 3503–3405 cm^{-1}.

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Thermogravimetric and difference thermal analyses were performed on a Perkin-Elmer thermal analyzer under flowing N_2 with a heating rate of $10°C/min^{-1}$.

Structure determination

A crystal with dimensions of $0.50 \times 0.38 \times 0.34$ mm was employed for structural analysis on a Siemens P4 four-circle diffractometer with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$Å). Unit-cell parameters were determined by the least-squares method based on the setting angles of 50 reflections. Intensity data were measure using $\theta/2\theta$ scan technique with variable scan speed, the 4471 independent reflections in the range $1.04 < \theta < 25.01°$, 4470 with $I > 2\sigma(I)$ were used to calculated the conventional R_F factor. Intensity data were corrected for Lorentz polarization effects and absorption based on ψ-scan data [8].

The structure was solved by the direct methods using SHELX86 [8], and refined using SHELXL93 [9]. The coordinates and the anisotropic thermal parameters for the non-hydrogen atoms were refined by full-matrix least-squares. All the H atoms were generated geometrically, allowed to ride on the atoms to which they are attached and refined isotropically. All calculations were carried out on a PC. The refinement was based on F^2, where $w = 1/[\sigma^2(Fo^2) + (0.0945P)^2]$ and $P = (Fo^2 + 2Fc^2)/3$. A summary of crystallographic data and additional data collection parameters is given in Table 1. Selected bond distance and angles are listed in 2.

Complete tables of atomic coordinates and thermal parameters, together with structure factors have been deposited at the Cambridge Crystallographic Data Centre, from whom copies are available on request.

Table 1. Data collection and processing parameters

Molecular formula	$C_{18}H_{18}N_2O_2S_4Ni \cdot 3H_2O$
Molecular weight	535.34
Crystal system	trigonal (on hexagonal axes)
Space group	$R\bar{3}$
Unit cell parameters	
a (Å)	39.205(3)
b (Å)	39.205(3)
c (Å)	8.583(1)
γ (°)	120
V (Å^3)	11425(2)
D_c (gcm^{-3})	1.401
Z	18
μ (mm^{-1})	1.122
F(000)	5004
h, k, l range	$-46,46$; $-46,46$; $-10,1$
Reflections collected	15291
Independent reflections	4471[R(int) = 0.0608]
Data/restraints/parameters	4470/0/274
$R[I > 2\sigma(I)]$	0.0669
Rw	0.2040
S	1.031

RESULTS AND DISCUSSION

Thermal analysis

Thermogravimetric analysis (TGA) of [Ni(Et-XA)$_2$·phen]·3H$_2$O reveals that the decomposition events mainly take place at 143, 155 and 177°C, respectively. On the base of weight changes, the first process of the weight loss (32.47%) corresponds to the loss of phen (found. 32.5% calc.: 33.6%), with an *endo* thermal phenomenon, the second event of the weight loss may be related to the loss of water (found: 12.3%, calc.: 10.9%) with an exothermal peak. Finally, at more than 177°C, Ni(Et-XA)$_2$ begins to decompose. It is interesting to note that at 143°C the release of phen molecule takes place first, suggesting that the water molecules are firmly clathrated in the channel leading to very strong hydrogen bonding confirmed by the X-ray crystal structural determination described later.

Crystal structural description

Figure 1 shows the structure of the Ni(Et-XA)$_2$ clathrate with three water molecules. The nickel atom is in a distorted octahedral environment surrounded by two chelating xanthate anions and one chelating phenanthroline ligand. The guest water molecules are very strongly hydrogen bonded to each other to form an almost equilateral triangle. The shortness of the three hydrogen bonds in this neutral cluster is the most unexpected feature. The average (O···O) distance is 2.56Å, which is 0.20Å and 0.29Å, shorter than that of ice (2.76Å) and pure water (2.83Å), respectively [5]. It is noteworthy that the value falls into the range of hydrogen bonds found in $HSbCl_6 \cdot 3H_2O$ ($r_{ave} = 2.53$Å) [5]. Consequently, the hydrogen bonds, among those involving neutral water molecules, are among the shortest known [6]. Figure 2 illustrates a channel in which six host molecules are depicted. The channel measures nearly 10.3 Å in diameter. The eighteen water molecules existed in six triplets. This structure seems to be very stable energetically. Release of the water molecules can be achieved only by the rupture of the structure as confirmed by thermal analyses. The Ni—S bond lengths in [Ni(Et-XA)$_2$·phen]·3H$_2$O are in good agreement with those found in [Ni(S$_2$COBu)$_2$·(4,4′-bipy). 2CCl$_4$]$_n$ (2.4505(9)–2.4407(11) Å), Ni(Et-XA)$_2$·(ISQ)$_2$ (2.440(2)–2.466(2) Å), Ni(Et-XA)$_2$·phen-*o* (2.3882(7)–2.4330(8) Å) and Ni(Et-XA)$_2$·Me$_2$-phen(2.376(2)–2.522(2) Å), respectively [4,10], and differ from those of the apical Ni—S bond length in Ni(Et-XA)$_2$·pph$_3$(2.654(2) Å) and Ni(Cy-XA)$_2$·P-Meph$_2$ (2.722(4) Å) where the Ni atoms adopt a distorted square-pyramidal geometry with S(1), S(2), S(3) and P in the basal plane and S(4) apical [11]. Moreover, the Ni—N bond lengths in [Ni(Et-XA)$_2$·phen]·3H$_2$O are somewhat shorter than those

Table 2. Selected bond lengths (Å), possible hydrogen bonds (Å) and angles (°) for $[Ni(Et\text{-}X)_2 \cdot phen] \cdot 3H_2O$ with e.s.d.s in parentheses

Ni—N(1)	2.074(4)	Ni—N(2)	2.076(4)
Ni—S(1)	2.438(2)	Ni—S(2)	2.443(2)
Ni—S(3)	2.438(2)	Ni—S(4)	2.476(2)
O1w···O2w	2.50(2)	O1w···O3w	2.61(4)
O2w···O3w	2.57(4)		

N(1)—Ni—N(2)	80.0(2)	S(1)—Ni—S(2)	73.16(6)
S(3)—Ni—S(4)	72.68(5)	N(1)—Ni—S(1)	96.34(13)
N(1)—Ni—S(2)	96.75(14)	N(1)—Ni—S(3)	92.66(13)
N(1)—Ni—S(4)	163.85(13)	N(2)—Ni—S(1)	91.41(13)
N(2)—Ni—S(2)	163.87(13)	N(2)—Ni—S(3)	98.86(13)
N(2)—Ni—S(4)	95.31(13)	S(1)—Ni—S(3)	167.39(6)
S(1)—Ni—S(4)	99.23(6)	S(2)—Ni—S(3)	97.06(6)
S(2)—Ni—S(4)	91.87(7)		

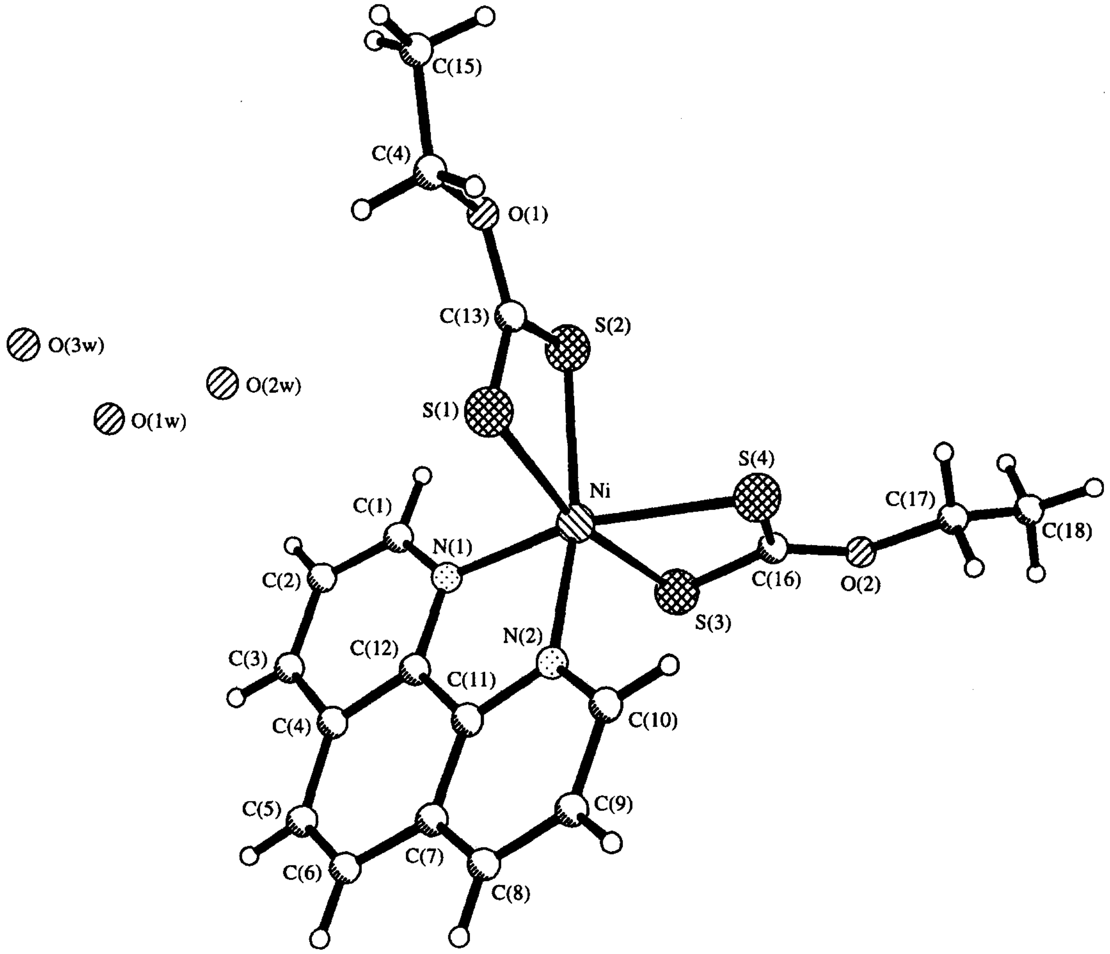

Fig. 1.

of $Ni(Et\text{-}XA)_2 \cdot$phen-*o* (2.151(2)–2.182(2) Å), $Ni(Et\text{-}XA)_2 \cdot Me_2$-phen (2.107(4)–2.153(3) Å) and in accord with those found in $Ni(Et\text{-}XA)_2 \cdot$(4,4′-dm-2,2′-bpy)$\cdot 2CCl_4$ (2.068(8)–2.073(9)Å) [4] and $Ni(Et\text{-}XA)_2 \cdot$(2,2′-dpa)$\cdot C_6H_6$ (2.067(5)–2.074(5) Å) [3], suggesting that the inclusion formation enhances the adduct stability.

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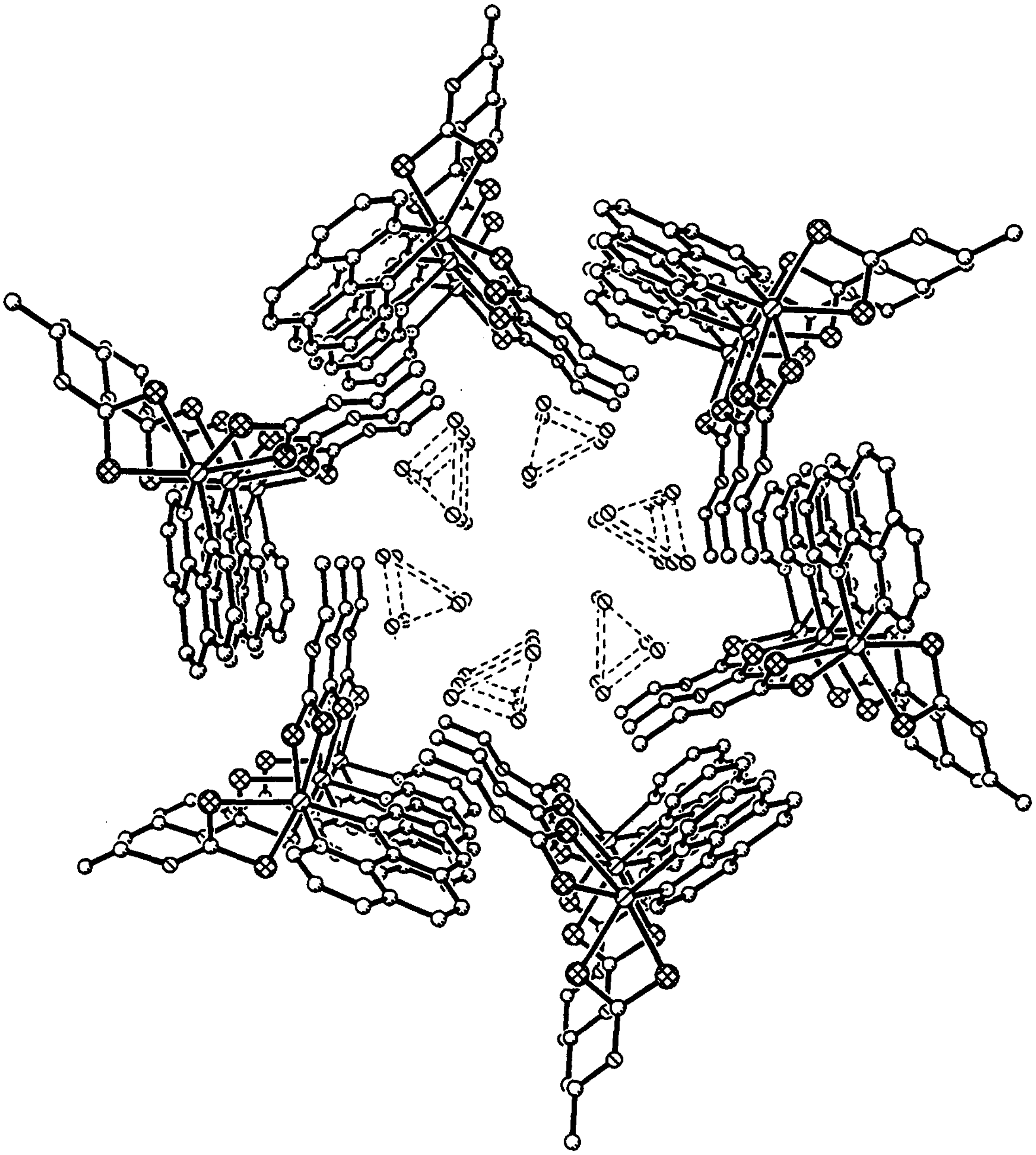

Fig. 2.

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REFERENCES

1. Stang, P. J. and Cao, D. H., *J. Am. Chem. Soc.*, 1994, **116,** 4981.
2. Kim, J., Whang, D., Lee, J. I. and Kim, K., *J. Chem. Soc., Chem. Commun.*, 1993, 1400.
3. Harata, K., *J. Chem. Soc., Chem. Commun.*, 1993, 546.
4. Gable, R. W., Hoskins, B. F. and Winter, G., *Inorg. Chim. Acta*, 1985, **96,** 151.
5. Pang, L., Lucken, E. A. C. and Bernardinelli, G., *J. Am. Chem. Soc.* 1990, **112,** 8754.
6. Mak, T. C. W. and Zhou, G.-D., *Crystallography in Modern Chemistry*, John Wiley and Sons, Inc., New York, 1992.
7. Emsley, J., Arif, M., Bates, P. A. and Hursthouse, M. B., *J. Chem. Soc., Chem. Commun.*, 1988, 1387.

8. Sheldrick, G. M., *Acta Cryst.* 1990, **A46** 467.
9. Sheldrick, G. M. SHELXL93. Program for crystal structure refinement, University of Goettingen, Germany, 1993.
10. Xiong, R.-G., Zuo, J.-L., You, X.-Z. and Huang, X.-Y., *Acta. Cryst.* 1996 C52, 1157, 521; Xiong, R.-G., Zuo, J.-L., You, X.-Z. and Huang, X.-Y., *Acta Cryst.* 1996 C52, in press; Guo, Y.-H., Xue, Y.-Q., Xiong, R.-G., Zuo, J.-L., You, X.-Z. and Huang, X.-Y., *Acta Cryst.* 1996 C52, 1157, 523.
11. Tiekink, E. R. T. and Winter, G., *Aust. J. Chem.*, 1986, **39,** 813; Ballester, L., Gutierrez-Alonso, A., Perpinan, M. F., Gutierrez-Puebla, E. and Ruiz-Valero, C., *Polyhedron*, 1990, **9,** 1341.