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Crystal structure and spectroscopic and magnetic properties of a novel *cis*-4,4′-bipyridine polymeric complex of Ni^{II}: *cis*-catena-(μ-4,4′-bipy) $[Ni(Et\text{-}XA)_2]\cdot 0.5EtOH\cdot CHCl_3$

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Abstract—The complex $[4,4'\text{-bipy-Ni(Et-XA)}_2\cdot 0.5EtOH\cdot CHCl_3]_n$ (where Et-XA = ethylcarbonadithiolate and 4,4′-bipy = 4,4′-bipyridine), has been synthesized and crystallographically characterized. It constitutes the first nickel(II) chain structure with 4,4′-bipyridine bridges having a *cis*-conformation. The magnetic susceptibility measurement for this compound shows simple Curie–Weiss law with $\theta = 1.3$ K in the temperature range of 5 K–300 K, which indicates no magnetic interaction between the nickel(II) ions through 4,4′-bipy bridges. © 1997 Elsevier Science Ltd

Keywords: nickel(II) complexes; polymeric complexes; inclusion complexes; ethylcarbonadithiolato-K^2,S,S′ complexes; crystal structures; magnetic susceptibility.

One dimension transition metal complexes bridged by bidentate π electron-containing ligands, such as pyrazine, 4,4′-bipyridine, azido and thiocyantao ligands continue to generate significant interest for their potential applications in organic conductors and magnetic materials [1]. Recently, the nickel(II) chain-structure with *cis* arrangement from end-to-end azido bridges has been explored [2]. Generally, the nickel(II) chain-structure with end on azido and 4,4′-bipy bridges should exhibit a *trans*-geometry [3–5]. However, as far as we are aware, none of nickel(II)-4,4′-bipy chains with a *cis*-conformation is known. Moreover, xanthate complexes are used as a host mainly due to their reversible and non-reversible inclusion ability [6]. As a consequence, the complex, *cis*-catena-poly{bis(ethylcarbonadithiolato-K^2,S,S′) nickel(II)-μ-(4,4′-bipyridine)-KN,KN′}0.5ethanol chloroform, $[4,4'\text{-bipy-Ni(Et-XA)}_2)\cdot 0.5EtOH\cdot CHCl_3]_n$ (**1**) which constitutes the first nickel(II) chain-structures with 4,4′-bipy bridges possessing a *cis* arrangement and reversible inclusion capacity has been prepared and characterized. Complex **1** shows simple paramagnetic behaviour.

EXPERIMENTAL

General procedures

Elemental analysis for C, H and N were performed on a Perkin 240 C analyzer. The infrared spectra from 4000 to 400 cm^{-1} and far-infrared spectra from 500 to 100 cm^{-1} in KBr pellets (Nujol mull modes) were obtained with a Nicolet 170 SX FT-IR spectrophotometer. Magnetic measurement were performed with Quantum Design SQUID (Superconducting Quantum Interference Device) with $Ni(en)_3S_2O_3$ as a standard at 1 T magnetic field. The resulting susceptibility was corrected for underlying diamagnetism. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VGES-CALAB MK-II spectrometer using Mg-K_α exciting radiation. Samples were in powder form on double-side sticky tape on a double-side silicon metal sample holder. Core level binding energy was measured for Ni, S, Cl,

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O, N and C atoms in the sample. Calibration was made using C_{1s} binding energy (284.3 eV).

Synthesis of $[4,4'\text{-bipy-Ni(Et-XA)}_2)\cdot 0.5\text{EtOH}\cdot \text{CHCl}_3]_n$ (**1**)

$Ni(Et\text{-}XA)_2$ was prepared according to the literature method [7]. 4,4′-bipyridine(analytic grade) was directly used without further purification. $Ni(Et\text{-}XA)_2$ (1 mmol) was dissolved in ethanol and $CHCl_3$, and excess of the solution containing 4,4′-bipy (2 mmol) was added until the colour of the solution changed from brown to green. The brown-black prismatic crystals of the title compound (product 62%) were obtained after the solution was left to evaporate at room temperature for a few weeks. Elemental analysis on $[4,4'\text{-(bipy)-Ni(Et-XA)}_2]$: Found: C, 42.0, H, 4.0, N, 6.8, Calc.: C, 42.0, H, 3.9, N, 6.1%. IR (cm^{-1}, KBr pellets) of a fine crystalline compound shows: 3434(b,w), 2973(m), 1605(s), 1532(w), 1474(w), 1407(m), 1181(s), 1123(s), 1043(s), 806(s), 757(s), 631(m), 471(s), 449(s), 395(w), 319(s), 225(sh,m), 241(s), 218(s), 195(w), 125(m) cm^{-1}.

X-ray photoelectron spectroscopy gave binding energies (eV) for Ni_{2p}(857.8), S_{2p}(165.7), Cl_{2p}(203.9), N_{1s}(402.9), O_{1s}(536.40) and C_{1s}(288.4). The presence of Ni_{2p} satellites indirectly confirms the octahedral stereochemistry of the complex (**1**), and that agrees with that of the other octahedral nickel(II) complex [7]. The EtOH and $CHCl_3$ solvate molecules began to escape at 368 K and were completely lost at 385 K, giving the green crystals of $[4,4'\text{-(bipy)-Ni(Et-XA)}_2]_n$. X-ray powder diffraction confirmed that **1** and $[4,4'\text{-(bipy)-Ni(Et-XA)}_2]_n$ exhibit the identical structure in the solid state; furthermore, 25.45% weight loss corresponded to the loss of C_2H_5OH and $CHCl_3$.

Crystallographic analysis

A brown-black prism single crystal with the approximate dimension 0.3 × 0.2 × 0.4 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. X-ray data were collected with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) at room temperature using the ω–2θ scan technique. Cell-parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range 9.25% $\leqslant 2\theta \leqslant 14.28°$. A total of 5221 independent reflections were measured in the range $0° \leqslant 2\theta \leqslant 50°$ ($h = 0, 19, k = 0, 14, l = -19, 19$), 2680 of which with $F_o^2 > 3.0\sigma(F_o^2)$, were used in the development and refinement of the structure. The slope of the least-squares line through a plot of intensity versus time

Table 1. Crystal data and experimental parameters for the crystal structure analysis of **1**

Empirical formula	$C_{36}H_{44}Cl_6N_4O_5S_8Ni_2$
Formula mass (g mol^{-1})	1199.43
Crystal system	Monoclinic
Space group	$P2_1/C$
a (Å)	16.024(3)
b (Å)	12.170(3)
c (Å)	16.038(4)
β (°)	119.45(2)
V (Å^3)	2723.6(8)
Z	2
Temperature (°C)	23
λ (Mo-K_α) (Å)	0.71073
D (g/cm^{-1})	1.46
μ (Mo-K_α) (cm^{-1})	13.3
$F(000)$	1228
Crystal dimensions (mm)	0.20 × 0.30 × 0.40
θ range (°)	$9.25 \leqslant \theta \leqslant 14.28$
Index ranges	$0 < h < 19, 0 < k < 14, -19 < l < 19$
No. of collected reflns	6021
No. of indep. reflns	5221
R_{int}	0.025
No. of reflns used	2680
No. of parameters	267
S	0.78
$R(F_o^2 > 3.0\sigma(F_o^2))$	0.057
R_W	0.071

$R = \Sigma|F_o - F_c|/\Sigma|F_o|$, $Rw = [\Sigma w(F_o - F_c)^2/wF_o^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.020F_o)^2 + 1.000]$

was -5 ± 1 counts/hour which corresponds to a total loss in intensity of 14.6%. The intensity data were corrected for Lorentz and polarization effects. An anisotropic decay correction was applied; the correction factors on I ranged from 1.000 to 1.259 with an average value of 1.130.

The structure was solved by direct methods with MULTAN-83 program. A total of 6 atoms were located from an E-map prepared from 32 phased E's of 319 reflections (minimum E of 1.75). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculation but their positions were not refined. All calculations were performed on a COMPAQ computer using MOLEN/PC [7]. The maximum and minimum peak values in the final difference Fourier map are 0.86 and -0.18 e/Å respectively. Crystal data and data collection parameters are summarized in Table 1, while selected bond distances and angles are listed in Table 2.

The atomic coordinates, thermal parameters and structure factors have been deposited with the editor as supplementary data.

RESULTS AND DISCUSSION

Elemental analyses, IR and XPS have indicated that the reaction of $Ni(Et\text{-}XA)_2$ with the ligand 4,4′-bipyridine formed compound **1**. The room temperature magnetic moment (3.00 B.M.) of **1** is in the range normally found for octahedral coordinated nickel(II) complexes [8]. The magnetic susceptibility of **1** as a function of temperature is depicted in Fig. 1. The straight line is a least-squares fit to the data. The magnetic behaviour of **1** obeys the Curie–Weiss law with $\kappa_m = C/(T\text{-}\theta)$ ($C = 1.31$ and $\theta = 1.4$ K, derived from the straight line). Thus in the temperature range of 5 K–300 K, the magnetic behaviour of **1** exhibits no magnetic interaction between nickel(II) ions through 4,4′-bipy bridges, quite different from that of $[Ni(bipy)_2N_3]Y$ ($Y = ClO_4, PF_6$), probably due to azido bridges transferring π-electron very efficiently [2].

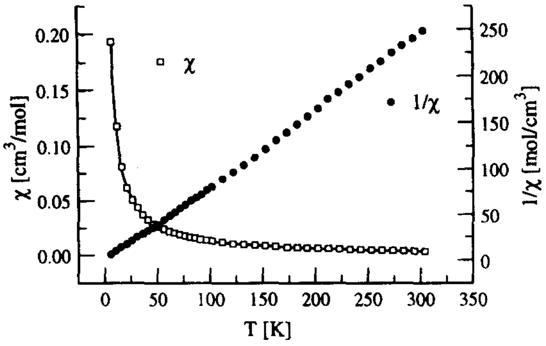

Fig. 1. The magnetic susceptibility [χ (□)] and reciprocal magnetic susceptibility [1/χ (●] of **1** as a function of temperature.

The local coordination geometry around the nickel(II) ions is a distorted octahedral *cis*-configuration (Fig. 2), in which $(Ni(Et\text{-}XA)_2$ units are linked by 4,4′-bipy in a zigzag fashion with a N(1)—Ni—N(2) angles of 88.4(2)° to form an infinite chain in the crystal (Fig. 3). The structural feature is quite different from that of $[Ni(Bu\text{-}XA)_2 \cdot (4,4'\text{-bipy}) \cdot 2CCl_2]_n$ (**2**) [4] in which the nickel(II) atom is an octahedral *trans*-environment. Another interesting feature is that the solvate molecules, C_2H_5OH and $CHCl_3$ may sit in open channels which are formed by the packing of the linear polymeric chains of the complex, suggesting that the solvate molecules can easily move along the channel and escape at the crystal surface thereby accounting for the reversible nature of adsorption/desorption behaviour found for this system [4]. To our knowledge, this is the first nickel(II)-4,4′-bipy chain structure with such an arrangement. The Ni—S bond distances are in good agreement with those found in **2** (2.4505(9)–2.4467(11) Å, [4], $Ni(Et\text{-}XA)_2 \cdot (ISQ)_2$ (**3**) (2.440(2)–2.464(2) Å) [9], $[Ni(Et\text{-}XA) \cdot (2,2'\text{-dpa}) \cdot C_6H_6]$ (**4**) (2.416(2)–2.520(2) Å) [4] and $[Ni(Et\text{-}XA)_2 \cdot (4,4'\text{-dm-}2,2'\text{-bipy})(CCl_4)_2]$ (**5**) (2.442(4)–2.456(3) Å) [6], while the Ni—N bond distances are

Table 2. Selected bond distances (Å) and angles (°) for **1**

Ni—S(1)	2.443(3)	Ni—S(2)	2.430(3)
Ni—S(3)	2.438(3)	Ni—S(4)	2.431(3)
Ni—N(1)	2.067(7)	Ni—N(2)	2.092(7)
S(1)—Ni—S(2)	73.4(1)	S(3)—Ni—S(4)	73.4(1)
N(1)—Ni—N(2)	88.4(3)	S(1)—Ni—S(3)	163.5(2)
S(1)—Ni—S(4)	94.4(1)	S(1)—Ni—N(1)	99.0(2)
S(1)—Ni—N(2)	94.5(3)	S(2)—Ni—S(3)	95.7(2)
S(2)—Ni—S(4)	92.9(2)	S(2)—Ni—N(1)	171.7(2)
S(2)—Ni—N(2)	89.0(3)	S(3)—Ni—N(1)	92.4(2)
S(3)—Ni—N(2)	97.7(3)	S(4)—Ni—(1)	90.9(3)
S(4)—Ni—(2)	171.0(2)		

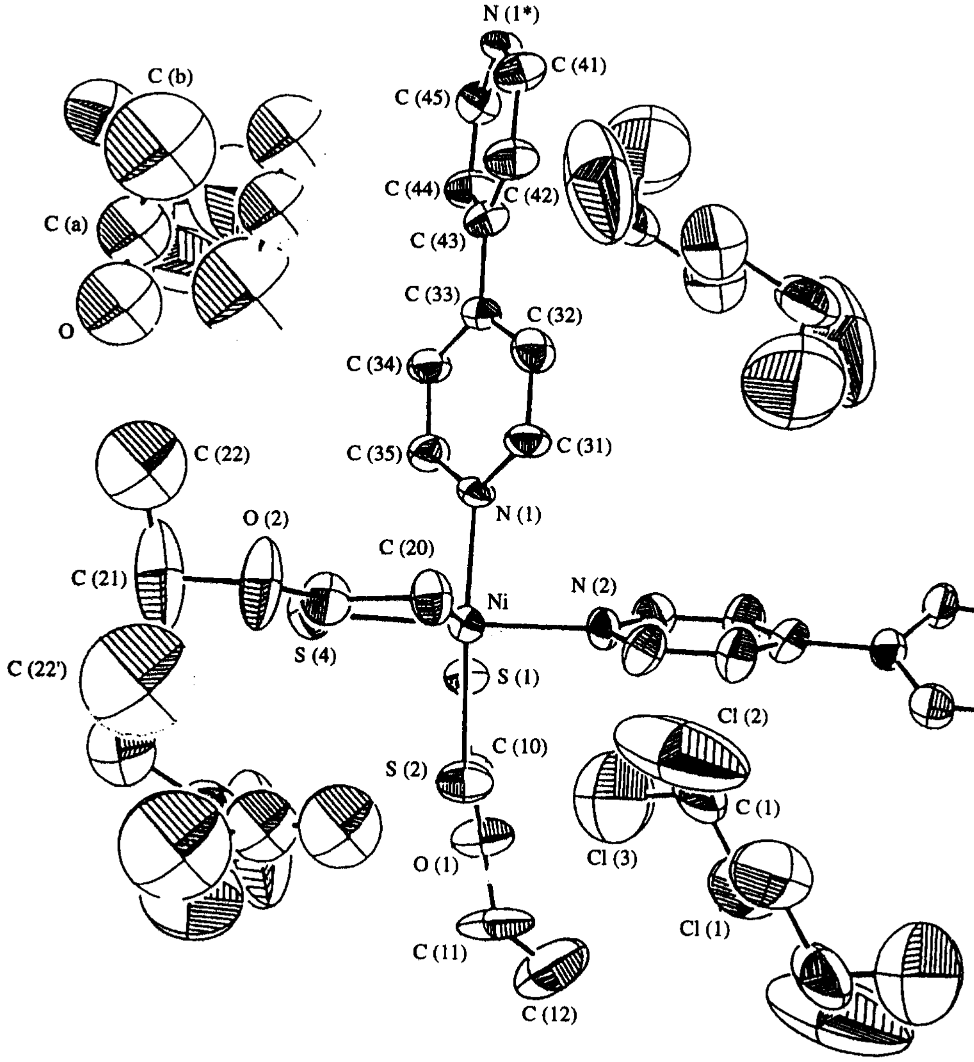

Fig. 2. ORTEP view of the 4,4′-bipy-Ni(Et-XA)$_2$ entities, which stack to generate the *cis*-bipyridine Ni(II) chains, together with the atom labeling.

in accord with those of **4** (2.067(5)–2.074(5) Å) [4] and **5** (2.068(8)–2.073(9) Å) [6], but slightly shorter than those found in **2** (2.106(7) Å) [4]. It is worth noting that the four Ni—S bond lengths in **1** are basically identical, but the Ni—S distances show much greater variation on the five-coordinate complexes $Ni(C_6H_{11}OCS_2)_2 \cdot P(Meph_2)$ (2.210(2)–2.722(4) Å) [10] and $Ni(C_2H_5OCS_2)_2 \cdot P(C_6H_5)_3$ (2.225(2)–2.654(3) Å) [11], probably due to the Ni atoms in the latter adopting a distorted square-pyramidal geometry in which four atoms, S(1), S(2), S(3) and P, describe an approximate basal plane and the apical position is occupied by the S(4) atom from a asymmetrically coordinating xanthate ligand. It should be pointed out that the C—C distances of 1.66(2) and 1.62(2) Å in the ethyl group are significantly greater than the typical C—C single-bond length (1.5 Å), probably a result of disorder, which is also apparent from the large displacement parameters of these atoms (see supplementary material), while the C—C, C—N, C—O and C—S bond distances are unexceptional. Surprisingly, the dihedral angle between the plane of N(1)C(31)C(32)C(33)C(34)C(35) and N(1)*C(41) C(42)C(43)C(44)C(45) is quite large (34.8°), showing that the conjugation effects between the two planes may be very weak, leading to very difficult π-electron transfer and therefore indicating paramagnetism is understandable [12].

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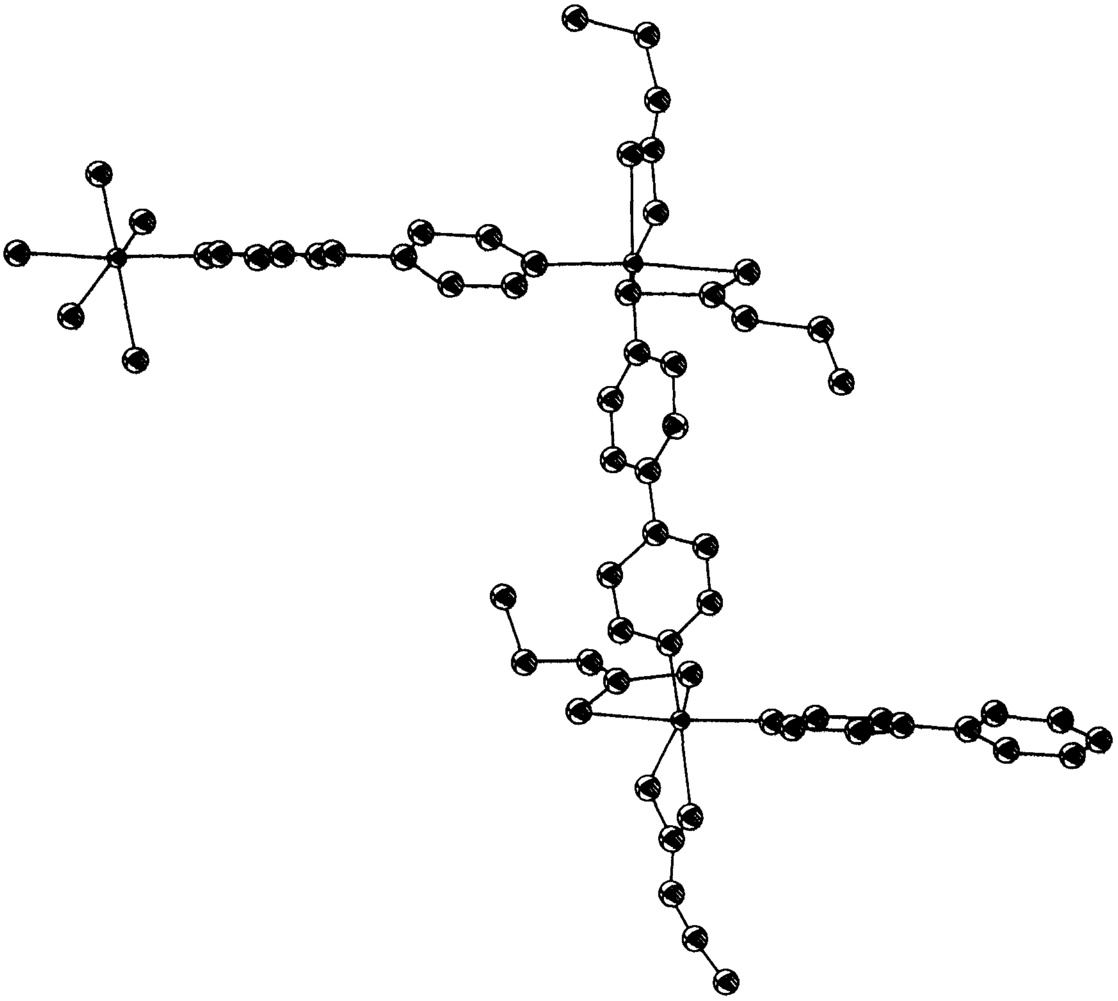

Fig. 3. The perspective view of the chain propagation of 1. Solvates are omitted for clarity.

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