

Note

## Structure and magnetic properties of a novel chloro-bridged polymeric cadmium(II) complex with pyridyl-substituted nitronyl nitroxide

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### Abstract

A complex of 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-N-oxide (NIToPy) with Cd(II)Cl<sub>2</sub>·[(CdCl<sub>2</sub>)<sub>3</sub>·(NIToPy)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>], has been structurally and cryomagnetically characterized. The structure is based on a layered zigzagging polymeric chain along the (101) plane; the Cd(II) ions are linked into infinite chains by double chlorine bridges alternating between one CdCl<sub>2</sub>O<sub>2</sub> and two CdCl<sub>2</sub>NO octahedral coordination units. The temperature-dependence of the magnetic susceptibility reveals the presence of a Heisenberg antiferromagnetic exchange interaction of a two spin  $S = 1/2$  system, with  $J = -0.25 \text{ cm}^{-1}$  associated with the intermolecular interaction between the NO groups of two neighboring NIToPy radicals. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Crystal structures; Magnesium complexes; Cadmium complexes; Nitronyl nitroxide complexes; Polymeric complexes

### 1. Introduction

There has been an increasing interest in the coordination chemistry of cadmium in recent years due to the increased recognition of its role in biological organisms [1–5], as well as in molecular-based materials [6–8]. In the quest for molecular-based materials with interesting properties, much attention has been given to one-, two- and three-dimensional extended solids which involve cadmium [6–10].

Complexes of the type CdX<sub>2</sub> (X = Cl or Br) with organic bases (e.g. pyridine) typically form one- or two-dimensional halogen-bridged chain compounds with six-coordination octahedral cadmium(II) [10]. Pyridyl-substituted nitronyl nitroxide, 2-(2-pyridyl)4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-N-oxide (NIToPy), is a paramagnetic chelate ligand which can mediate a magnetic exchange interaction when bound to paramagnetic transition-metal halides such as NiCl<sub>2</sub>(NIToPy) and MnCl<sub>2</sub>(NIToPy) [11]. Nevertheless, no NIToPy compounds with diamagnetic metals have been reported.

The 2-pyridyl-substituted nitronyl nitroxide ligand is especially attractive because the position of the pyridyl nitrogen atom is such that it could enforce the coordination of the NO

group by the chelate effect. It is expected, therefore, that coordination will occur with a cadmium center. Our interest lies in the generation of polymeric structures in diamagnetic cadmium chloride with the paramagnetic chelate NIToPy ligand.

We describe here the structural characterization and the magnetic properties of the cadmium(II) chloride complex with 2-(2-pyridyl)4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-N-oxide (NIToPy) Scheme 1.

### 2. Experimental

#### 2.1. Synthesis

The 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-N-oxide (NIToPy) was prepared by following previously reported procedures [12].

##### 2.1.1. [(CdCl<sub>2</sub>)<sub>3</sub>(NIToPy)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>]

A solution of CdCl<sub>2</sub>·H<sub>2</sub>O (44.7 mg, 0.2 mmol) in ethanol (20 cm<sup>3</sup>) and a solution of NIToPy (46.8 mg, 0.2 mmol) in ethanol (10 cm<sup>3</sup>) were mixed at room temperature by stirring, and the resulting solution was slowly evaporated in air for

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several days to give crystals suitable for X-ray diffraction analysis. *Anal. Calc.* for  $C_{28}H_{42}N_6O_6Cl_6Cd_3$ : C, 30.32; H, 3.79; N, 7.58. *Found*: C, 30.36; H, 3.75; N, 7.56%. IR (KBr disc):  $\nu(NO)$ ,  $1361\text{ cm}^{-1}$ (s).

## 2.2. Physical measurements

The IR spectrum of the title compound was recorded on a Bio-Rad FTS-40FTIR spectrophotometer as KBr pellets in the  $4000\text{--}400\text{ cm}^{-1}$  region. X-band EPR spectra at 300 K for the complex in powder form were recorded on a Bruker ECS-106 spectrometer. Temperature-dependence of the magnetic susceptibilities of the polycrystalline sample was measured between 4 and 300 K at a field of 1 T using a Quantum Design model MPMS computer-controlled SQUID magnetometer. Corrections for the diamagnetism of the complex were estimated from Pascal's constants.

## 2.3. X-ray crystal structure analysis

Crystallographic data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation at  $25^\circ\text{C}$ . The unit cell parameters were determined from 25 reflections in the range  $20 \leq 2\theta \leq 32^\circ$ . The details of data collection, crystallographic data and data reduction are summarized in Table 1.

The structure was solved by the standard heavy-atom method and refined by full-matrix least-squares based on  $F$ . Reliability factors were defined as  $R_1 = \sum |F_o - F_c| / \sum |F_o|$  and the function minimized was  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ , where in the final least-squares calculation the weighting scheme  $1/\sigma^2(F_o)$  was used. Anisotropic thermal parameter refinement was performed, except for hydrogen atoms. All refinement calculations were performed using the NRCVAX computer program [13]. Selected positional parameters of the non-hydrogen atoms are listed in Table 2.

## 3. Results and discussion

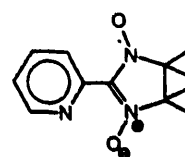
### 3.1. Description of the structure

The results of the X-ray crystal structure analysis for  $[(CdCl_2)_3(NIToPy)_2(C_2H_5OH)_2]$  is reproduced in Fig. 1. The selected bond distances and angles are given in Table 3.

The crystal structure has features of the monoclinic space group  $C2/c$ : twofold axes and symmetry centers. As illustrated in Figs. 1 and 2, the structure comprises an alternating polymeric chain layer along the (101) plane with monometallic  $Cd(1)Cl_4O_2$  moieties located at the centres, and  $[Cd(2)Cl_2NO]_2$  moieties. The Cd(II) ions of Cd(1) and Cd(2) are linked into an infinite chain by double chlorine bridges. The  $Cd(1) \cdots Cd(2)$  and  $Cd(2) \cdots Cd(2)'$  distances in the molecule are  $3.7634(11)$  and  $3.7723(14)$  Å, respectively. Cd(1), in  $CdCl_4O_2$ , is tetragonal as it is coordinated to four bridges of chlorine atoms, two Cl(3) and two Cl(4)

Table 1  
Crystallographic data for  $[(CdCl_2)_3(NIToPy)_2(C_2H_5OH)_2]$

Formula	$C_{28}H_{42}N_6O_6Cl_6Cd_3$
<i>M</i>	1108.2
Crystal system	monoclinic
Space group	$C2/c$
<i>a</i> (Å)	22.307(5)
<i>b</i> (Å)	10.481(3)
<i>c</i> (Å)	20.282(3)
$\beta$ ( $^\circ$ )	122.409(17)
<i>Z</i>	4
<i>D<sub>c</sub></i> ( $\text{g cm}^{-3}$ )	2.212
<i>F</i> (000)	2552
$\mu$ ( $\text{cm}^{-1}$ )	13.589
Crystal size (mm)	$0.40 \times 0.50 \times 0.60$
<i>R<sub>1</sub></i>	0.043
<i>R<sub>w</sub></i>	0.045



NIToPy  
Scheme 1.

Table 2  
Selected final atomic positional parameters and  $R_{eq}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$R_{eq}^a$
Cd(1)	1/4	1/4	0	3.39(4)
Cd(2)	-0.100067(24)	0.13229(5)	0.19491(3)	2.853(23)
Cl(1)	0	0.30023(23)	1/4	3.53(14)
Cl(2)	0	-0.04470(23)	1/4	3.53(14)
Cl(3)	-0.137547(10)	0.10902(21)	0.05305(9)	4.61(11)
Cl(4)	-0.20473(9)	0.29633(19)	0.14473(9)	3.96(10)
O(1)	-0.19178(22)	-0.0164(5)	0.16978(23)	3.7(3)
O(2)	-0.0709(3)	-0.2692(5)	0.3882(3)	5.9(4)
O(3)	-0.30116(25)	0.0601(5)	0.0139(3)	5.2(3)
N(1)	-0.08990(25)	0.1055(5)	0.3167(3)	2.6(3)
N(2)	-0.16763(25)	-0.1165(5)	0.2139(3)	2.9(3)
N(3)	-0.1107(3)	-0.2355(5)	0.3184(3)	3.5(3)

$$^a R_{eq} = (8\pi^2/3) \sum_i U_{ii} a_i^* a_i$$

atoms, and two oxygen atoms from two  $C_2H_5OH$  ligands. The bond lengths of  $Cd(1)\text{--}Cl(3)$ ,  $Cd(1)\text{--}Cl(4)$  and  $Cd(1)\text{--}O(3)$  are  $2.5966(18)$ ,  $2.5875(17)$ , and  $2.385(5)$  Å, respectively. The intramolecular hydrogen bond  $[O(3)\text{--}H \cdots O(1)$ ,  $1.82(4)$  Å] exists between the OH group of ethanol ligands and the oxygen atom of the NO group. The  $Cd(1)\text{--}O(3)\text{--}C(13)$  bond angle is of  $121.5(7)^\circ$ .

In the bimetallic  $[Cd(2)Cl_2NO]_2$  moiety, the Cd(2) ions are coordinated by the four bridging chlorine atoms, and chelated by one nitrogen atom and one oxygen atom from the NIToPy ligands. The mean bond distance of Cd–Cl is  $2.598$  Å. Two  $Cd(2) \cdots Cd(2)'$  atoms are linked by a pair of bridging Cl(1) and Cl(2) atoms, and separated by  $3.7723(4)$  Å.

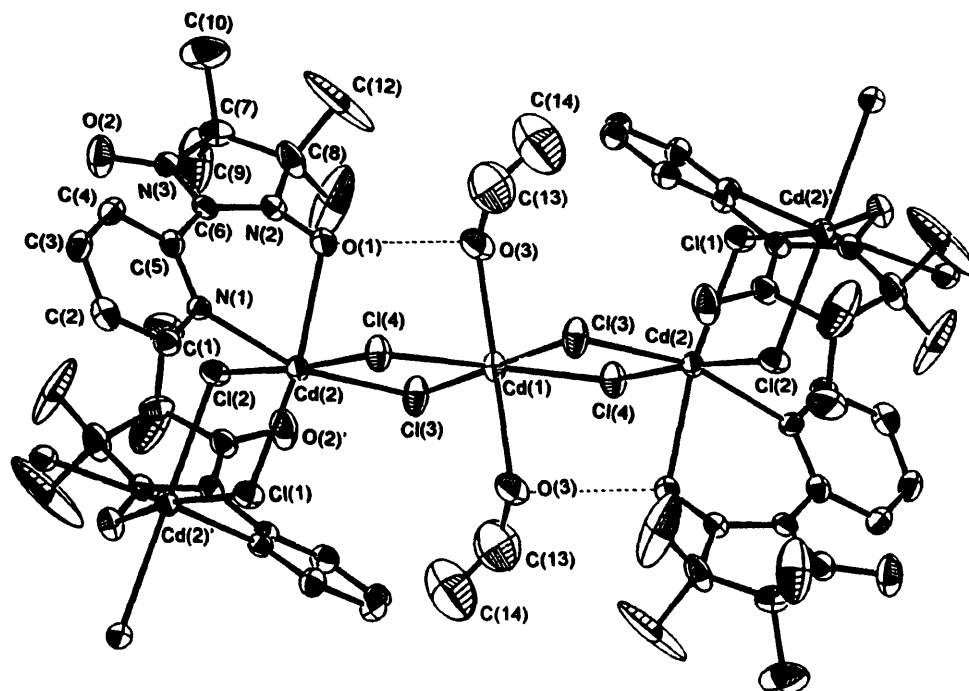


Fig. 1. Structure of the  $[(\text{CdCl}_2)_3(\text{NIToPy})_2(\text{C}_2\text{H}_5\text{OH})_2]$  showing the atom-labelling scheme and 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. The broken lines indicate the hydrogen bonds.

Table 3  
Selected bond distances (Å) and angles (°)

Cd(1)–Cl(3)	2.5966(18)	Cd(1)–Cl(4)	2.5875(17)
Cd(1)–O(3)	2.385(5)	Cd(2)–Cl(1)	2.5798(18)
Cd(2)–Cl(2)	2.6455(19)	Cd(2)–Cl(3)	2.5416(18)
Cd(2)–Cl(4)	2.6260(19)	Cd(2)–O(1)	2.400(4)
Cd(2)–N(1)	2.373(5)	N(2)–O(1)	1.294(7)
N(3)–O(2)	1.254(7)	C(6)–N(2)	1.334(7)
C(6)–N(3)	1.353(9)	Cd(2)···Cd(2)'	3.7723(14)
Cd(1)···Cd(2)	3.7634(11)		
Cl(3)–Cd(1)–Cl(3)	179.9	Cl(4)–Cd(1)–Cl(4)	180
Cl(3)–Cd(1)–Cl(4)	93.80(6)	O(3)–Cd(1)–O(3)	179.9
Cd(1)–O(3)–C(13)	121.5(7)	O(3)–C(13)–C(14)	121.8(12)
Cd(1)–Cl(3)–Cd(2)	94.18(6)	Cd(1)–Cl(4)–Cd(2)	92.41(6)
Cl(3)–Cd(2)–N(1)	163.16(13)	O(1)–Cd(2)–Cl(1)	167.56(11)
Cd(2)–Cl(2)–Cd(2)'	90.95(8)	Cd(2)–Cl(1)–Cd(2)'	93.96(8)
N(1)–Cd(2)–O(1)	74.88(16)	Cd(2)–O(1)–N(2)	112.8(3)
C(6)–N(2)–O(1)	124.8(5)	Cd(2)–N(1)–C(5)	125.9(4)
Cd(2)–N(1)–C(1)	115.9(4)		

The Cd(2)–N(1) (pyridine) and Cd(2)–O(1) (nitroxide) bond distances are 2.373(5) and 2.400(4) Å, respectively.

The nitronyl nitroxide fragment O(1)–N(2)–C(6)–N(3)–O(2) in the NIToPy is almost coplanar, but makes a dihedral angle of 34.1(2)° with the pyridyl ring, suggesting some resonance interactions between the pyridyl ring  $\pi$  system and the N-oxide-N-oxyl system. The shortest intermolecular space between two non-bonding O(2)···O(2)' atoms of NO groups, which belong to two different NIToPy radicals, is 6.426(8) Å. This intermolecular contact is large, thus the direct magnetic exchange interactions between two neighboring NO groups is negligible in the crystal lattice.

### 3.2. Magnetic properties

The EPR (at 9.80 GHz) spectra at 300 K of  $[(\text{CdCl}_2)_3(\text{NIToPy})_2(\text{C}_2\text{H}_5\text{OH})_2]$  in benzene solution shows five major narrow lines in the ratio of 1:2:3:2:1, as expected for coupling with two identical nitrogens of NO groups of NIToPy ligands. The  $g$  value and the nitrogen hyperfine coupling constant  $a^{\text{N}}$  are 2.01 and 7.4 G, respectively.

$\chi_m$  and  $\chi_m T$  versus  $T$  plots for the complex are depicted in Fig. 3, where  $\chi_m$  is the molar magnetic susceptibility. The  $\chi_m T$  value, 0.75 cm<sup>3</sup> mol<sup>-1</sup> K, at 300 K is in good agreement with the value expected for two uncorrelated spin,  $S = 1/2$ ,

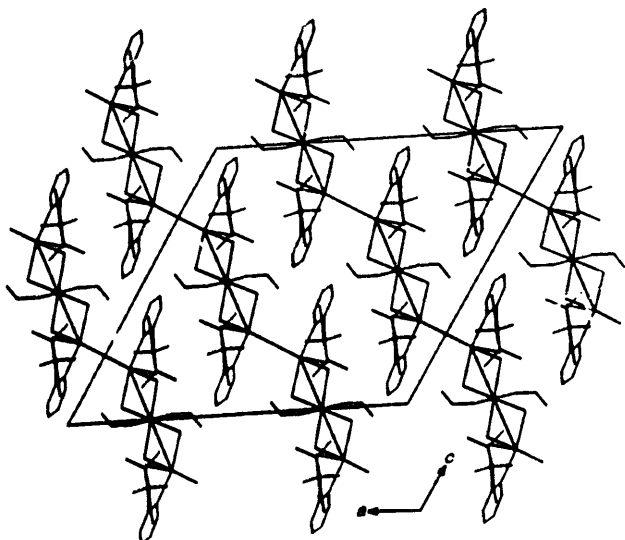


Fig. 2. View of a two-dimensional polymeric structure layer along the (101) plane.

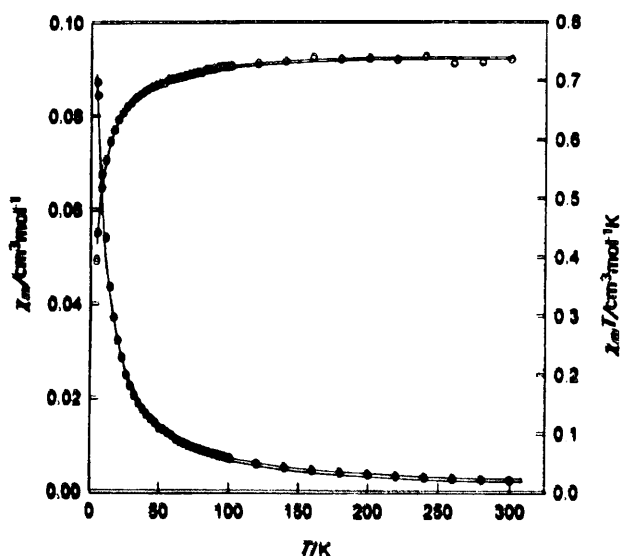


Fig. 3. Temperature-dependence of  $\chi_m$  (●) and  $\chi_m T$  (○) for  $[(\text{CdCl}_2)_2(\text{NIToPy})_2(\text{C}_2\text{H}_5\text{OH})_2]$ . The solid lines represent the values calculated with the parameters of the text.

systems ( $0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ). On lowering the temperature,  $\chi_m T$  decreases down to  $0.39 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 4 K, clearly indicating the existence of weak intrachain antiferromagnetic exchange interactions between two NO radicals in the solid.

As described in Section 3.1, the shortest intermolecular contact between the paramagnetic centers of NO groups,  $\text{O}(2) \cdots \text{O}(2)'$ , is  $6.426(4) \text{ \AA}$ . This large separation suggests that direct magnetic coupling between two spins of NO groups is extremely difficult. Anticipating this result, we explain these data by considering only a bimetallic  $[(\text{CdCl}_2)_2(\text{NIToPy})_2]$  moiety in the polymer chain with nearest-neighbor interactions between NO groups. From the structural features, there are two reliable superexchange pathways following the  $\text{NO}(1)-\text{Cd}(2)-\text{Cl}(1)-\text{Cd}(2)'$ - $\text{O}(1)\text{N}'$  and  $\text{NO}(1)-\text{Cd}(2)-\text{Cl}(2)-\text{Cd}(2)'$ - $\text{O}(1)\text{N}'$

bonds. Although exchange interactions by these pathways are expected to be weak, it is instructive to examine the results one gets by fitting a simple two spin  $S = 1/2$  model to our data by using the Bleaney–Bowers expression (Eq. (1)) [14]:

$$\chi_m = 2Ng^2\beta^2/k(T-\theta)[3 + \exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

This results from considering the eigenvalues of the Heisenberg exchange Hamiltonian,  $H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$ . A very close agreement with the experiment is obtained with  $J = -0.25 \text{ cm}^{-1}$ ,  $\theta = -0.05 \text{ K}$ ,  $g = 2.01$  (from EPR),  $N\alpha = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  and the disagreement factor  $R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum\chi_{\text{obs}}^2]^{1/2} = 6 \times 10^{-5}$ .

Finally, diamagnetic metal ions are believed not to mediate magnetic interactions. Recently however, several diamagnetic metal complexes with organic radicals as ligands showed that antiferro- or ferromagnetic interactions were possible through diamagnetic metal ions such as alkali metals [15,16], Ga(III) [17], Ti(IV) [18] and Cu(I) [19]. In the present paper, the cadmium ions appear to play an important role in the coupling pathways. Although only a weak antiferromagnetic interaction was observed between NIToPy radicals in this polymer chain, this is a new example of a polymeric diamagnetic cadmium compound with paramagnetic nitronyl nitroxide ligands. Further investigations will probe the nature of the interactions to find a strong ferromagnetic interaction of the cadmium ions with the other radical chelate ligands.

#### 4. Supplementary material

Tables containing complete atomic positions, anisotropic thermal parameters, hydrogen atom locations, and bond distances and angles are available from the authors on request.

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