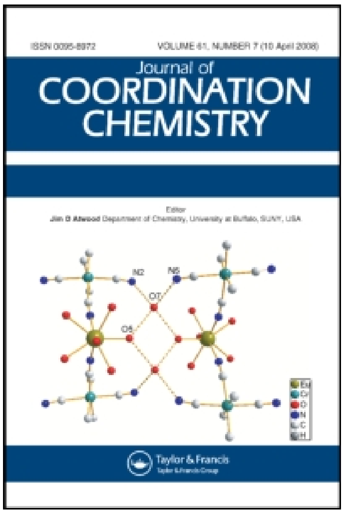

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A one-dimensional zigzag chain involving a cadmium(II)-imino nitroxide: structure and magnetic properties

Shu-Ping Wang[ab]; Dong-Zhao Gao[a]; Zhan-Quan Liu[a]; Zong-hui Jiang[a]; Shi-Ping Yan[a]; Dai-zheng liao[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China [b] Department of Chemistry, Hebei Normal University, Shijiazhuang 050016, P.R. China

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A one-dimensional zigzag chain involving a cadmium(II)-imino nitroxide: structure and magnetic properties

SHU-PING WANG†‡, DONG-ZHAO GAO†, ZHAN-QUAN LIU†, ZONG-HUI JIANG*†, SHI-PING YAN† and DAI-ZHENG LIAO†

†Department of Chemistry, Nankai University, Tianjin 300071, P.R. China
‡Department of Chemistry, Hebei Normal University,
Shijiazhuang 050016, P.R. China

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A novel one-dimensional complex salt with the formula $[Cd(IM2py)_2][Au(CN)_2]_2$ (IM2py = 2-(2′-pyridinyl)-4,4,5,5-tetramethylimidazoline-1-oxyl), has been synthesized and its structure was determined by single-crystal X-ray diffraction methods. The coordination geometry around Cd(II) ion is a distorted octahedral. IM2py coordinates to Cd(II) via pyridyl- and imino-N atoms to form a planar, five-membered chelate ring. $[Cd(IM2py)_2][Au(CN)_2]_2$ units are linked through weak Au$\cdots$Au interactions, generating an infinite 1D zigzag chain. Magnetic studies show weak antiferromagnetic coupling between two radicals through the diamagnetic Cd(II) ion.

Keywords: Aurophilic interaction; Cadmium(II); Imino nitroxide; Crystal structure; Magnetic properties

1. Introduction

Diamagnetic metal complexes of organic radicals form a particular group of compounds in the field of molecular-based magnetic materials. Several studies have shown that antiferro- or ferromagnetic interactions operate through the central metal ion, including Ti(IV), Cu(I), Ag(I), Hg(II), Zn(II) and Cd(II) [1–7]. In these complexes, the metal ion plays an active role in aiding exchange coupling between radicals. However, few reports dealing with polymers of diamagnetic metal radical complexes have appeared in the literature.

The design and synthesis of polymeric molecular-based magnetic materials is one of the major challenges in molecular materials research. Rigid or flexible bridges such as cyanide, azide, dicyanide, $[Ag(CN)_2]^-$, $[Au(CN)_2]^-$ and the terephthalate dianion have been used in the design of such species. A large number 1D [8–11], 2D [12] and 3D systems [13] have been reported. Here, a one-dimensional polymeric complex salt with an Au$\cdots$Au interaction, $[Cd(IM2py)_2][Au(CN)_2]_2$, is reported.

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*Corresponding author. Email: coord@nankai.edu.cn

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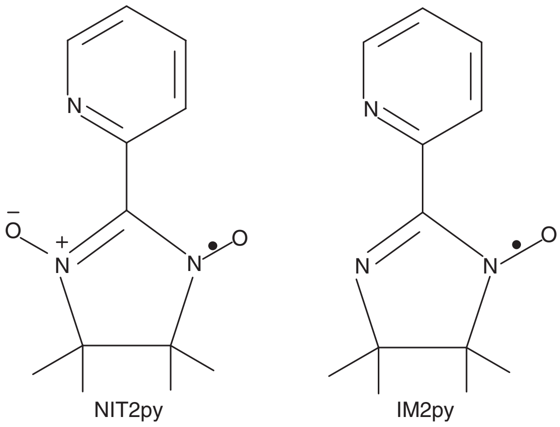

Scheme 1. The NIT2py radical and IM2py radical.

Weak antiferromagnetic coupling between two IM2py radicals (scheme 1) through Cd(II) is observed in the complex salt.

2. Experimental

2.1. *Physical measurements*

Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240 system. IR spectra (KBr pellets) were measured on a Bruker Tensor 27 FTIR spectrophotometer in the 4000–400 cm^{-1} range. Variable temperature magnetic susceptibility measurements were carried out with a MPMS XL7 SQUID magnetometer in the temperature range 2.0–300 K at a magnetic field of 2000 G. Molar susceptibilities were corrected for the sample holder and diamagnetic contributions of all constituent atoms using Pascal's constants.

2.2. *Synthesis*

All starting materials were of analytical grade and used as purchased without further purification. The ligand 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (IM2py) was prepared according to a literature method [14]. For the complex salt, $Cd(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) and IM2py (0.2 mmol) were dissolved in 10 cm^3 of methanol. Then 5 cm^3 of an aqueous solution of $K[Au(CN)_2]$ (0.2 mmol) was added dropwise with stirring at room temperature. The mixture was stirred for 4 h and then filtered. Deep red single crystals suitable for X-ray structure analysis were grown by slow evaporation of the filtrate.

Caution! Cyanide salts are toxic and should be handled with care! *Anal.* Calcd for $C_{28}H_{32}N_{10}O_2Au_2Cd$ (%): C, 32.15; H, 2.97; N, 13.38. Found: C, 32.12; H, 3.08; N, 13.38.

Table 1. Crystallographic data and structure refinement parameters for the complex.

Empirical formula	$C_{28}H_{32}N_{10}O_2Au_2Cd$
Formula weight	1046.97
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, Space group	Orthorhombic, *Pbcn*
Unit cell dimensions (Å, °)	
a	8.323(2)
b	18.830(5)
c	20.465(5)
Volume ($Å^3$)	3207(2)
Z, Calculated density ($g\,cm^{-3}$)	4, 2.168
Absorption coefficient (mm^{-1})	9.826
F(000)	1968
Crystal size (mm^3)	$0.18 \times 0.16 \times 0.14$
θ range for data collection (°)	1.99–26.42
Limiting indices	$-9 \le h \le 10$, $-23 \le k \le 17$, $-25 \le l \le 24$
Reflections collected/unique	17,404/3305 [$R_{int} = 0.0536$]
Completeness to $\theta = 26.42°$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.696
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3305/0/199
Goodness-of-fit on F^2	1.175
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0371$, $wR_2 = 0.0655$
R indices (all data)	$R_1 = 0.0576$, $wR_2 = 0.0697$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.147 and −1.122

2.3. *X-ray crystallography*

A single crystal of the complex was mounted on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the $\phi-\omega$ scan mode. Unit cell parameters were determined from reflections with $1.99° \le \theta \le 26.42°$. Details of data collection, crystallographic data and structure refinement parameters are summarized in table 1. The structure was solved by direct methods using SHELXS-97 [15]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [16]. Reliability factors were defined as $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$, and the function minimized was $wR_2 = (\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^{1/2}$, where unit weights were used. All non-hydrogen atoms were refined anisotropically. Final atomic coordinates for the non-hydrogen atoms and equivalent istropic thermal parameters are listed in table 2; selected bond distances and angles are listed in table 3.

3. Results and discussion

In the IR, the complex shows two sharp ν_{CN} bands at about 2145 and 2174 cm^{-1}. The splitting indicates the presences of two different coordination modes

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex.

	x/*a*	*y*/*b*	*z*/*c*	*U* (eq)
Au(1)	645(1)	11,329(1)	6773(1)	38(1)
Cd(1)	5000	9341(1)	7500	28(1)
O(1)	5179(7)	8621(3)	4917(2)	56(1)
N(1)	3246(7)	10201(3)	7132(3)	42(1)
N(2)	−2097(9)	12,366(4)	6358(4)	76(2)
N(3)	3500(6)	8484(2)	6895(2)	31(1)
N(4)	6146(6)	9192(2)	6458(2)	29(1)
N(5)	5827(6)	8884(3)	5418(2)	37(1)
C(1)	2337(8)	10,618(3)	6996(3)	36(2)
C(2)	−1099(9)	11,993(4)	6507(4)	51(2)
C(3)	2310(8)	8094(3)	7136(3)	42(2)
C(4)	1368(8)	7663(4)	6738(4)	49(2)
C(5)	1661(8)	7634(3)	6087(4)	49(2)
C(6)	2913(8)	8032(3)	5833(3)	43(2)
C(7)	3813(7)	8437(3)	6249(3)	31(1)
C(8)	5250(7)	8846(3)	6057(3)	27(1)
C(9)	7434(8)	9235(3)	5407(3)	36(1)
C(10)	7484(9)	9766(4)	4844(3)	54(2)
C(11)	8647(9)	8645(4)	5281(4)	50(2)
C(12)	7462(7)	9563(3)	6106(3)	31(1)
C(13)	9011(8)	9438(4)	6470(3)	50(2)
C(14)	7022(9)	10,344(3)	6118(3)	47(2)

Table 3. Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths		Bond angles	
Au(1)–C(1)	1.995(7)	C(2)–Au(1)–C(1)	176.2(3)
Au(1)–C(2)	1.992(8)	C(1)–Au(1)–Au(1)#1	91.44(17)
Au(1)–Au(1)#1	3.1622(9)	N(4)–Cd(1)–N(4)#2	166.3(2)
Cd(1)–N(4)	2.352(5)	N(1)#2–Cd(1)–N(4)	97.07(18)
Cd(1)–N(1)	2.307(6)	N(1)–Cd(1)–N(3)	88.53(18)
Cd(1)–N(3)	2.387(5)	N(4)#2–Cd(1)–N(3)	100.24(17)
N(1)–C(1)	1.125(8)	C(2)–Au(1)–Au(1)#1	90.6(2)
N(2)–C(2)	1.130(9)	N(1)#2–Cd(1)–N(3)	167.22(18)
N(3)–C(3)	1.327(7)	N(1)#2–Cd(1)–N(1)	90.8(3)
N(3)–C(7)	1.349(7)	N(1)–Cd(1)–N(4)	92.51(18)
N(4)–C(8)	1.286(7)	N(4)–Cd(1)–N(3)	70.22(16)
N(4)–C(12)	1.486(7)	N(3)–Cd(1)–N(3)#2	94.9(2)
O(1)–N(5)	1.260(6)		
N(5)–C(8)	1.395(7)		
N(5)–C(9)	1.491(8)		

Symmetry transformations used to generate equivalent atoms are: #1: $-x, y, -z+3/2$; #2: $-x+1, y, -z+3/2$.

(terminal and bridging). It is well known that the formation of a cyanide bridge shifts ν_{CN} toward higher frequencies [17]. The strong band at 2174 cm^{-1} may therefore be attributed to ν_{CN} of the bridging cyanide and that at 2145 cm^{-1} to the terminal one. The characteristic ν_{NO} vibration of IM2py was found at 1373 cm^{-1}.

Crystallization of the complex from methanol-water gave single crystals of formula $[Cd(IM2py)_2][Au(CN)_2]_2$, which are orthorhombic, space group *Pbcn*, with $Z = 4$. The $[Cd(IM2py)_2][Au(CN)_2]_2$ dimer is shown in figure 1. The Cd(II) ion is bonded to six nitrogen atoms with distorted octahedral geometry, and the complex can be described as being the *trans*(im)–*cis*(py) isomer (im denotes the imino nitroxide moiety).

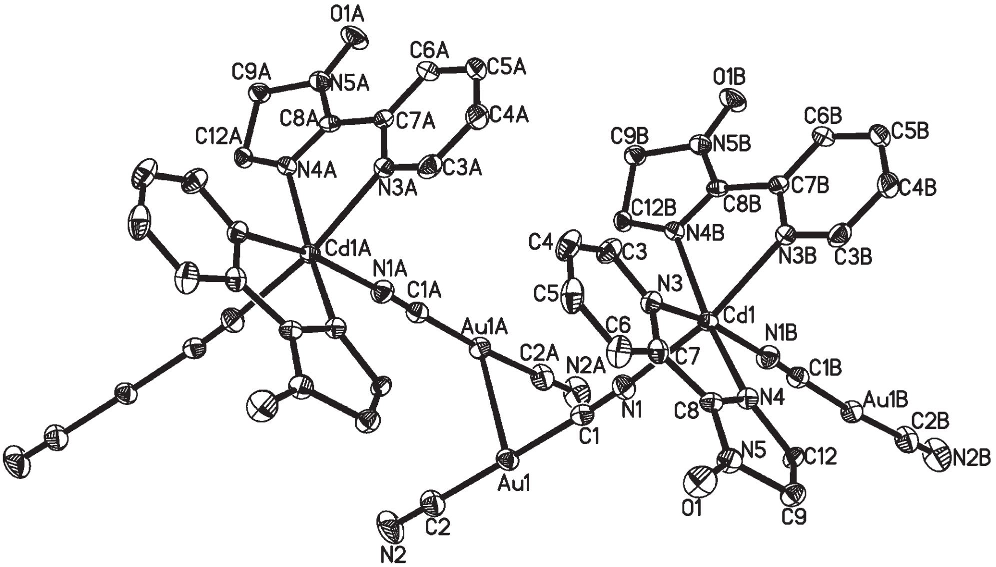

Figure 1. The $[Cd(IM2py)_2][Au(CN)_2]_2$ dimer drawn with 30% probability thermal ellipsoids. Methyl groups of IM2-py are omitted for clarity.

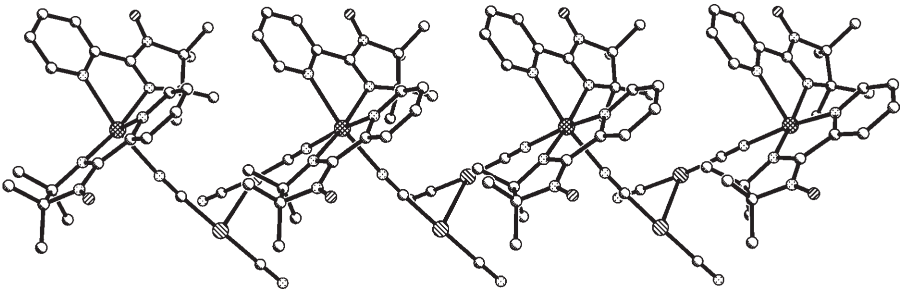

Figure 2. The one-dimensional chain in the $[Cd(IM2py)_2][Au(CN)_2]_2$ salt.

IM2py coordinates to Cd(II) via the pyridyl- and imino-N atoms to form a planar, five-membered chelate ring as found in $[MCl_2(IM2py)_2]$ (M=Mn, Co, Ni, Zn) [5b]. The chelate ring is almost coplanar with the pyridyl ring and the imino nitroxide moiety. The dihedral angle between the two N–C–NO moieties in one $[Cd(IM2py)_2][Au(CN)_2]_2$ fragment is 67.8°. Two $[Au(CN)_2]^-$ anions link to $[Cd(IM2py)_2]^{2+}$ in the *cis*-configuration. In each $[Au(CN)_2]^-$ anion, one CN^- group is used as a bridging ligand between Cd(II) and Au(I) ions, and the other is terminal on Au(I), consistent with the IR results. The shortest intermolecular Au $\cdots$ Au distance is 3.1622(9) Å, much shorter than the sum of the van der Waals radii (3.60 Å). Thus, $[Cd(IM2py)_2][Au(CN)_2]_2$ units are linked to generate an infinite 1D zigzag chain (figure 2), $\{[Cd(IM2py)_2][Au(CN)_2]_2\}_n$. The shortest N–O $\cdots$ O–N contact observed between two imino nitroxide moieties on adjacent zigzag chains is 5.512 Å. In the 1D chain, the distance between the neighbouring Cd(II) ions is 8.323 Å, corresponding to the *a* cell length. The shortest interchain Cd(II) $\cdots$ Cd(II) separation is 10.294 Å.

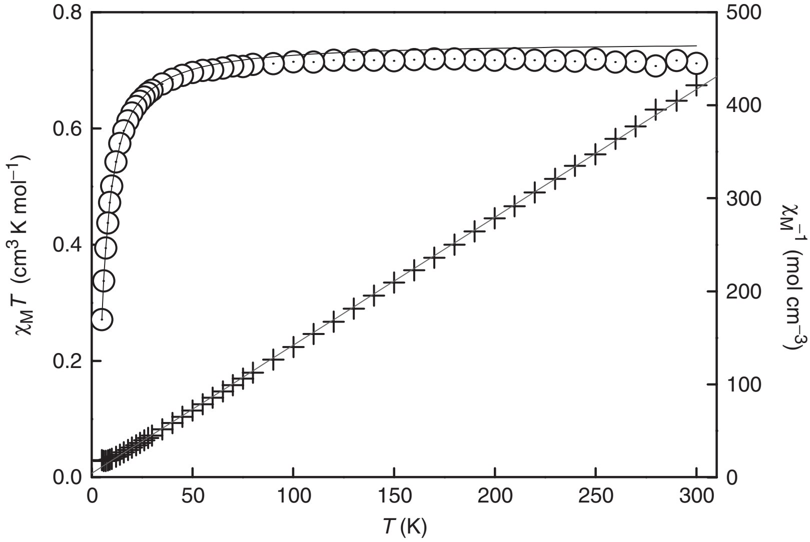

Figure 3. Plots of $\chi_M T$ (○) and χ_M^{-1} (+) *vs.* T for [Cd(IM2py)$_2$][Au(CN)$_2$]$_2$. The solid lines correspond to best theoretical fits.

Plots of $\chi_M T$ and χ_M^{-1} *versus* T are shown in figure 3, where χ_M is the magnetic susceptibility per [Cd(IM2py)$_2$][Au(CN)$_2$]$_2$ unit. The $\chi_M T$ value at room temperature is 0.71 cm^3 K mol^{-1}, which is slightly lower than that expected for independent spins (0.75 cm^3 K mol^{-1} for two $S_R = 1/2$). As temperature is lowered, the $\chi_M T$ value decreases slowly and reaches 0.70 cm^3 K mol^{-1} at 50 K. Then, $\chi_M T$ decreases rapidly and reaches 0.27 cm^3 K mol^{-1} at 5 K. The trace of χ_M^{-1} against T obeys the Curie–Weiss law in the range 10–300 K with a Curie constant of 0.723 cm^3 K mol^{-1} and a Weiss temperature (θ) of -2.30 K, indicating that the solid-state magnetic behaviour is governed by an overall antiferromagnetic interaction in the complex.

Based on the structure, the shortest intermolecular contact between the paramagnetic centers of NO groups is 5.512 Å. This separation suggests that direct magnetic coupling between two spins of NO groups is extremely difficult. However, two imino units are directly coordinated to Cd(II) ion in each [Cd(IM2py)$_2$][Au(CN)$_2$]$_2$ fragement, so the Cd(II) ion may transmit the magnetic interaction. In other words, the Cd(II) ion may provide a superexchange pathway along N(4)–Cd(1)–N(4B), although this interaction is expected to be weak. To evaluate the exchange coupling constants, the system was treated as a biradical system (two spins, $S = 1/2$) [5a], while the average magnetic interactions of the nearest radicals through space were treated as a molecular field approximation. The Hamitonian for the biradical system can be written as $\hat{H} = -2J\hat{S}_1\hat{S}_2$, and the magnetic susceptibility can be expressed as $\chi = (2Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1}$; the total magnetic susceptibility is $\chi_M = \chi/[1 - \chi(2\,zJ'/Ng^2\beta^2)]$. Least-squares analysis of magnetic susceptibilities (data in the range $5 \sim 300$ K) led to $g = 2.00$ (fixed), $J = -3.51$ cm^{-1}, $zJ' = -0.46$ cm^{-1}. The agreement factor R (defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{Calcd}]^2/\Sigma[(\chi_M)_{obs}]^2$) is equal to 2.22×10^{-5}. Fitted magnetic data provide evidence for a weak antiferromagnetic interaction between radicals through an N(4)–Cd(1)–N(4B) superexchange pathway.

The Cd(II)-radical complexes [$Cd_4Cl_8(NIT2py)_4$] (**1**) and [$(CdCl_2)_3(NIT2py)_2(C_2H_5OH)_2$] (**2**) also show weak intramolecular exchange interactions between the paramagnetic ligands. The coupling constants between two NIT2py ligands were 1.12 and $-0.25\,cm^{-1}$, respectively [7, 18]. In **1**, **2** and the present complex, the spin-bearing aminoxyl (or imino-N) units are directly coordinated to the central Cd(II) ion, so as the diamagnetic metal mediates the intramolecular exchange, only weak interactions are observed.

Supplementary material

CCDC 226022 contains supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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