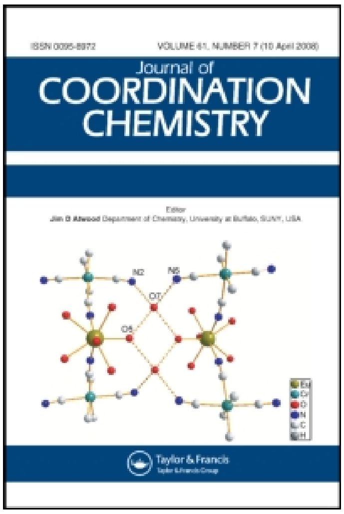

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A hydrogen-bonded, one-dimensional complex of cadmium(II) ions with 3,5-dinitrobenzoate and radicals: synthesis, characterization and crystal structure

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A novel one-dimensional complex, $[Cd(NIT4py)_2(DTB)_2(H_2O)_2]$ (**1**), (where NIT4py is 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and DTB is 3,5-dinitrobenzoate) has been synthesized and characterized by elemental analyses, IR and electronic spectra, single-crystal X-ray diffraction and magnetic measurements. The Cd(II) ion lies in a distorted octahedral environment with two nitrogen atoms from two NIT4py ligands and two oxygen atoms from two DTB molecules in the basal plane, and two oxygen atoms from two water molecules in axial positions. $[Cd(NIT4py)_2(DTB)_2(H_2O)_2]$ units are connected to form one-dimensional chains by intermolecular hydrogen bonds. The complex exhibits intramolecular antiferromagnetic interactions.

Keywords: Crystal structure; Nitronyl nitroxide radical; Cd(II) complex; Magnetism

1. Introduction

There has been much interest in the study of molecule-based magnetism in recent years [1, 2], Nitronyl nitroxide radicals (NITR), stable organic radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [3, 4], and magneto-structural correlations of complexes of nitronyl nitroxide radicals with paramagnetic metal ions have been extensively studied [5–7]. Meanwhile, investigation of diamagnetic metal complexes with radicals has also attracted great attention due to antiferro- or ferromagnetic interactions between the radicals through the diamagnetic metal ions [8–10].

In order to further understand magnetic exchange interactions between radicals through diamagnetic metal ions, we have used Cd(II) as a linking

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agent between radicals to synthesize a NIT4py–Cd–NIT4py complex (NIT4py is 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). Here, we present studies of such an octahedral complex.

2. Experimental

2.1. *General*

All reagents were purchased commercially and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Perkin–Elmer 240 instrument. IR spectra (KBr pellets) were recorded on a Shimadzu IR spectrophotometer model 408 in the 4000–600 $\mathrm{cm^{-1}}$ range. Electronic spectra were measured on a Shimadzu UV-12101 PC spectrophotometer. Variable-temperature magnetic susceptibilities were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated using the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2}$.

2.2. *[Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$]*

NIT4py was prepared according to a literature method [11, 12], The complex [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$] was synthesized by adding an aqueous solution (5 $\mathrm{cm^3}$) of potassium 3,5-dinitrobenzoate (0.101 g, 0.4 mmol) to a MeOH solution (15 $\mathrm{cm^3}$) obtained by mixing Cd(acetate)$_2\cdot$6H$_2$O (0.068 g, 0.2 mmol) and NIT4Py (0.094 g, 0.4 mmol). The mixture was stirred for 1 h and then filtered and the clear blue filtrate allowed to stand at room temperature for 3 days, after which blue crystals were obtained. Yield 0.133 g (64%). Anal. Calcd for $\mathrm{C_{38}H_{42}N_{10}O_{18}Cd}$ (%): C, 43.9; H, 4.1; N, 13.5. Found: C, 43.1; H, 3.9; N, 13.7.

2.3. *Crystal structure determination*

A blue single crystal of the complex of approximate dimensions 0.48 × 0.40 × 0.20 mm, was mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the ω–ϕ scan technique in the range $1.94 \le \theta \le 25.03^\circ$ with index ranges $-9 \le h \le 12$, $-12 \le k \le 12$, $-11 \le l \le 12$. A total of 6080 reflections was collected, of which 3886 were independent ($R_{\mathrm{int}} = 0.0133$). A summary of crystallographic data is given in table 1. The structure was solved by direct methods SHELXS-97 [13], H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical constraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [13]. Final agreement factors are $R_1 = 0.0238$, $wR_2 = 0.0622$ ($I > 2\sigma(I)$); $R_1 = \sum(||F_{\mathrm{o}}| - |F_{\mathrm{c}}||)/\sum|F_{\mathrm{o}}|$, $wR_2 = (\sum w(|F_{\mathrm{o}}|^2 - |F_{\mathrm{c}}|^2)^2/\sum w|F_{\mathrm{o}}|^2)^2$, $w = 1/[\sigma^2(F_{\mathrm{o}}^2) + (0.0341P)^2 + 0.3522P]$, where $P = (F_{\mathrm{o}}^2 + 2F_{\mathrm{c}}^2)/3$. Positional parameters and selected bond distances and angles are given in tables 2 and 3, respectively.

Table 1. Crystallographic data and processing parameters for the complex.

Empirical formula	$C_{38}H_{42}N_{10}O_{18}Cd$
Formula weight	1039.22
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.132(4)$ Å, $\alpha = 78.779(5)^\circ$
	$b = 10.470(4)$ Å, $\beta = 88.472(5)^\circ$
	$c = 10.705(5)$ Å, $\gamma = 86.844(5)^\circ$
Volume, Z	1112.1(8) Å^3, 1
Calculated density (g cm^{-3})	1.552
Absorption coefficient (mm^{-1})	0.578
$F(000)$	532
Crystal size (mm)	0.48 × 0.40 × 0.20
θ Range for data collection (°)	1.94 ~ 25.03
Limiting indices	$-9 \leq h \leq 12$, $-12 \leq k \leq 12$, $-11 \leq l \leq 12$
Reflections collected	6080
Independent reflection	3886 [R(int) = 0.0133]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3886/3/08
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0238$, $wR2 = 0.0622$
R indices (all data)	$R1 = 0.0248$, $wR2 = 0.0627$
Largest diff. peak and hole	0.319 and −0.453 e Å^{-3}

3. Results and discussion

3.1. *Crystal structure of [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$]*

An ORTEP drawing of [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$] is shown in figure 1. The Cd(II) ion is six-coordinate and lies in a distorted octahedral CdN_2O_4 environment. The equatorial plane is formed by N(1) and N(1A) from two NIT4py ligands, and O(3) and O(3A) from two DTB molecules. Cd–O and Cd–N bond lengths in the basal plane are 2.2667(16) and 2.3251(17) Å, respectively. The dihedral angle between the pyridyl ring and the ON–C–NO moieties is 5.6°. The axial positions are occupied by oxygen atoms of two water molecules with Cd–O equal to 2.2978(17) Å. A sketch of the intermolecular hydrogen bonds in the complex is shown in figure 2. Hydrogen bonds are between one oxygen atom of NIT4py and a neighbouring oxygen atom of coordinated water (2.773 Å for O(2AD)···O(9AB)). [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$] units are thus connected into a one-dimensional chain.

3.2. *Spectroscopic properties*

FT-IR spectra of **1** show characteristic bands of the carboxyl groups at 1624 cm^{-1} for the antisymmetrical stretch and at 1344 cm^{-1} for the symmetrical stretch. The separation between ν_{asym} and ν_{sym} indicate the monodentate coordination mode, consistent with the crystal structure. A strong broad band centered around 3386 cm^{-1} is assigned to ν(H–O) of the water molecular. The ν(N–O) band at 1374 cm^{-1} is near to the value (1372 cm^{-1}) of free NIT4Py, indicating that the oxygen atom of NIT4Py is not coordinated to Cd(II).

The electronic spectrum of [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$] in methanol displays a strong bond at 324 nm assigned to the $\pi \rightarrow \pi^*$ transition of the conjugated ONCNO

Table 2. Final 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)
Cd(1)	5000	0	5000	34(1)
O(1)	9122(2)	3400(2)	−211(2)	68(1)
O(2)	11754(2)	215(2)	2286(2)	62(1)
O(3)	4222(2)	2105(1)	4499(1)	49(1)
O(4)	4042(2)	2626(2)	6436(1)	56(1)
O(5)	323(2)	6076(2)	6277(2)	81(1)
O(6)	198(2)	7624(2)	4670(2)	81(1)
O(7)	3473(2)	7754(2)	1243(2)	70(1)
O(8)	4450(3)	5947(2)	1014(2)	91(1)
O(9)	4327(2)	−420(2)	3094(2)	56(1)
N(1)	6879(2)	691(2)	3823(2)	42(1)
N(2)	10115(2)	2685(2)	245(2)	40(1)
N(3)	11370(2)	1194(2)	1433(2)	38(1)
N(4)	709(2)	6617(2)	5239(2)	51(1)
N(5)	3765(2)	6609(2)	1612(2)	54(1)
C(1)	9169(2)	487(2)	3301(2)	41(1)
C(2)	8085(2)	164(2)	4077(2)	43(1)
C(3)	6743(2)	1576(2)	2747(2)	60(1)
C(4)	7761(2)	1952(2)	1911(2)	55(1)
C(5)	9023(2)	1400(2)	2180(2)	34(1)
C(6)	10140(2)	1750(2)	1315(2)	34(1)
C(7)	12336(2)	1957(2)	529(2)	40(1)
C(8)	13390(2)	1068(3)	68(2)	64(1)
C(9)	12939(3)	2854(3)	1296(2)	66(1)
C(10)	11384(2)	2669(2)	−508(2)	42(1)
C(11)	11137(3)	1893(3)	−1533(2)	74(1)
C(12)	11739(3)	4047(3)	−1099(3)	70(1)
C(13)	3927(2)	2855(2)	5262(2)	40(1)
C(14)	3356(2)	4187(2)	4637(2)	37(1)
C(15)	2374(2)	4820(2)	5243(2)	40(1)
C(16)	1829(2)	6007(2)	4629(2)	40(1)
C(17)	2271(2)	6631(2)	3446(2)	43(1)
C(18)	3263(2)	5983(2)	2880(2)	41(1)
C(19)	3795(2)	4770(2)	3430(2)	41(1)

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

Bond lengths			
Cd(1)–O(3)	2.2667(16)	O(7)–N(5)	1.210(3)
Cd(1)–O(9)	2.2978(17)	O(8)–N(5)	1.211(3)
Cd(1)–N(1)	2.3251(17)	O(5)–N(4)	1.210(3)
O(1)–N(2)	1.269(2)	O(6)–N(4)	1.206(2)
O(2)–N(3)	1.284(2)		
Bond angles			
O(3)#1–Cd(1)–O(3)	180.0	C(3)–N(1)–Cd(1)	119.05(13)
O(3)#1–Cd(1)–O(9)	88.04(6)	O(7)–N(5)–O(8)	124.3(2)
O(3)–Cd(1)–O(9)	91.96(6)	O(6)–N(4)–O(5)	122.8(2)
O(3)–Cd(1)–N(1)	86.16(6)	O(1)–N(2)–C(6)	126.91(17)
O(3)–Cd(1)–N(1)#1	93.84(6)	O(1)–N(2)–C(10)	120.63(16)
O(9)–Cd(1)–N(1)#1	96.68(7)	O(2)–N(3)–C(6)	126.11(15)
O(9)–Cd(1)–N(1)	83.32(7)	O(2)–N(3)–C(7)	121.53(15)
C(2)–N(1)–Cd(1)	123.96(13)	O(6)–N(4)–C(16)	118.48(19)

Symmetry transformation used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z+1$.

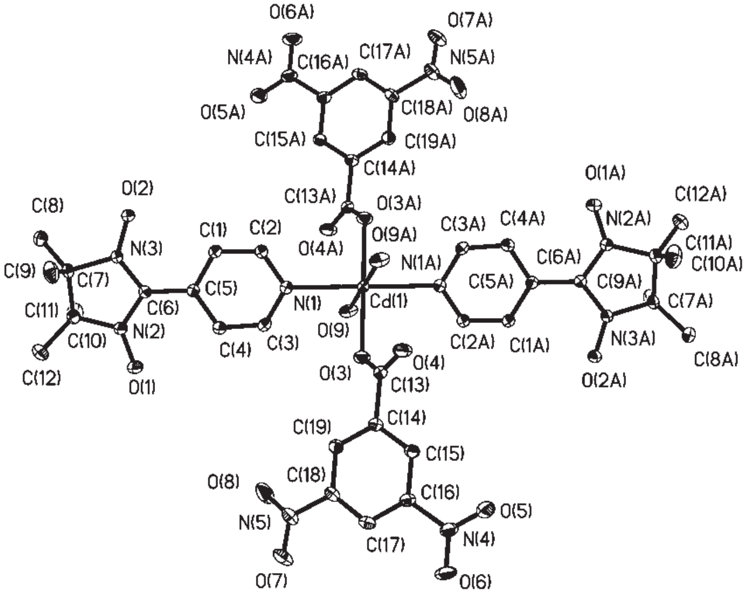

Figure 1. ORTEP drawing of the complex showing the atom labelling scheme.

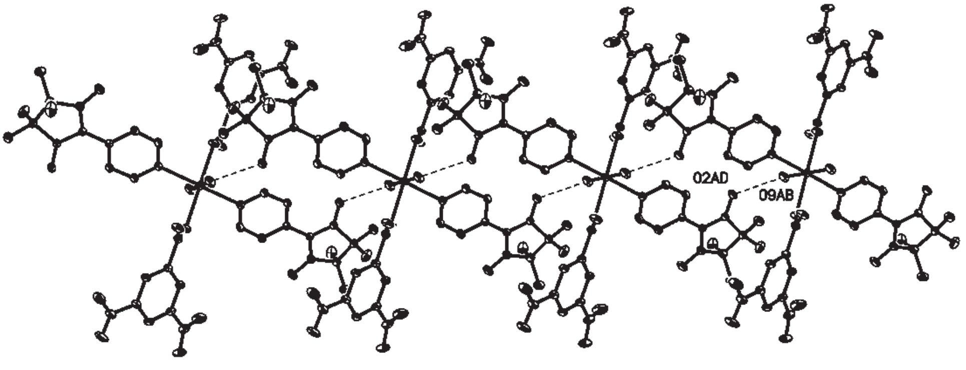

Figure 2. A sketch of the intermolecular hydrogen bonding in the complex.

group of NIT4Py. A band at 260 nm is assigned to the $\pi \rightarrow \pi^*$ transition of the pyridine ring. There is a broad band maximum at 590 nm, attributed to the $n \rightarrow \pi^*$ transition. The EPR spectrum of powdered [Cd(NIT4py)$_2$(DTB)$_2$(H$_2$O)$_2$] at room temperature was measured. A symmetrical, broad band was observed at $g = 2.01$, corresponding to the magnetic analysis.

3.3. *Magnetic properties*

Magnetic susceptibilities, χ_M, of the complex were measured in the 5–300 K range at 10 000 G. A plot of μ_{eff} and χ_M versus T is shown in figure 3. The μ_{eff} value at room temperature is $2.43\mu_B$, which is close to the spin-only value expected for two $S = 1/2$ uncoupled spin systems ($2.45\mu_B$). As the sample is cooled, the μ_{eff} value decreases,

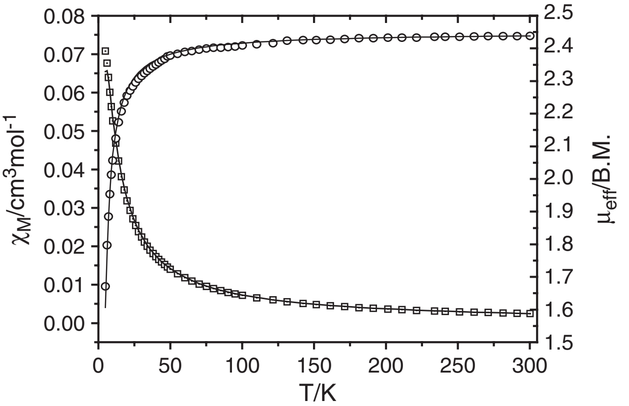

Figure 3. Temperature dependence of the molar magnetic susceptibility χ_M (□) and μ_{eff} (○) for the complex.

implying the existence of weak antiferromagnetic spin exchange between NIT4py ligands. For the NIT4py–Cd–NIT4py complex, the two paramagnetic centres are linked by a diamagnetic metal ion and analysis of magnetic properties was performed using the Bleany–Bowers (dimer) model [14], Magnetic data were fitted to the theoretical expression of the magnetic susceptibility in line with the Heisenberg Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where J is the interaction parameter between two paramagnetic centres.

$$\chi_M = \frac{2Ng^2\beta^2}{KT}[3 + \exp(-2J/KT)]^{-1}.$$

The best-fit parameters were $J = -3.56\,\mathrm{cm}^{-1}$, $g = 2.00$ with $R = 2.56 \times 10^{-5}$, where R is defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum(\chi_M)^2_{obs}$.

The results indicate that the diamagnetic metal ion provides an orbital pathway for inter-radical exchange. Antiferromagnetic exchange between radicals through Cd(II) is weak.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 269100. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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