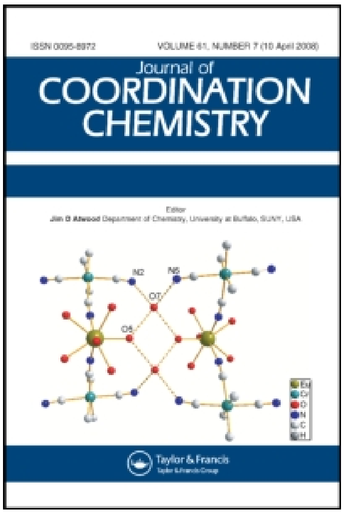

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Synthesis, structure and physical properties of nickel bis(dithiolene) complexes with different cations

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A series of new complexes of multi-sulfur 1,2-dithiolene ligands, $[Ru(bipy)_3][Ni(L)_2]_2$ (bipy = 2,2′-bipyridine; L = pddt (6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate), dddt (5,6-dihydro-1,4-dithiin-2,3-dithiolate)), have been synthesized and characterized. One typical complex, $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$ (**1**), crystallized in an acentric space group of $P2_12_12_1$, with the cell dimensions of $a = 8.634(1)$, $b = 14.560(1)$, $c = 49.889(5)$ Å, $\alpha = \beta = \gamma = 90°$, and $Z = 4$. It consists of alternating columns of cations and anions along the a direction. The structure was refined by full matrix least squares methods to $R_1 = 0.0340$, $wR_2 = 0.0670$. Magnetic studies on $[Ph_2Cr][Ni(dddt)_2]$ are also reported.

Keywords: Nickel complex; Crystal structure; Magnetic property; Dithiolene

1. Introduction

Nickel complexes of 1,2-dithiolene ligands have received attention in the area of new materials due to their unusual solid-state properties such as electrical and magnetic behavior and non-linear optical (NLO) effects [1–5]. The counter cations used in these complexes not only play a crucial role in the stacking mode of the anion complexes, but also make contributions to their properties [6, 7]. Efforts have been centered on developing new hybrid materials [8, 9], which could be formed from two or more molecular networks, such as anion/cation salts or host/guest solids. Ruthenium complexes with bipyridine ligands have attracted much attention from the viewpoint of luminescence and electrochemical properties while diphenyl chromium cations are used with the aim of achieving special magnetic properties [10–13]. It is expected that opto-electronic and magnetic properties can be enhanced or finely tuned through the coupling or interplay between cations and anions. In this article,

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we report the synthesis, and characterization of a series of bis(dithiolene) nickel complexes with tris-(2,2′-bipy)ruthenium(II) or diphenyl chromium as cations. The crystal structure of one typical complex, $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$ (**1**), is described and discussed. Complex (**3**), $[Ph_2Cr][Ni(dddt)_2]$ shows antiferromagnetic behavior.

2. Experimental

2.1. *Reagents*

All solvents were dried by standard techniques prior to use. $(Bu_4N)[Ni(dddt)_2]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) [14], $(Bu_4N)[Ni(pddt)_2]$ (pddt = 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate) [15], and $[Ph_2Cr]I$ were prepared by the literature method [16].

2.2. *Synthesis*

All reactions were carried out under nitrogen.

2.2.1. Synthesis of $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$ (1). An acetonitrile solution (20 mL) of $(Bu_4N)[Ni(pddt)_2]$ (34 mg, 0.05 mmol) was mixed with an acetonitrile solution (10 mL) of $[Ru(bipy)_3](ClO_4)_2 \cdot 2H_2O$ (20 mg, 0.025 mmol). After standing at room temperature for one week, black crystallized products were formed and collected by filtration. The crystals suitable for X-ray analysis were obtained by recrystallization from DMF/Et_2O. Anal. Calc. for $C_{50}H_{52}N_6Ni_2O_2RuS_{16}$: C, 40.02; H, 3.49; N, 5.60; Ni, 7.82. Found: C, 40.70; H, 3.50; N, 5.86; Ni, 7.92. Selected IR absorptions (cm^{-1}): 1417 (C=C), 1267 (C–S), 858, 460 (Ni–S).

2.2.2. Synthesis of $[Ru(bipy)_3][Ni(dddt)_2]_2 \cdot 2H_2O$ (2). $[Ru(bipy)_3][Ni(dddt)_2]_2$ was prepared by a similar method using $(Bu_4N)[Ni(dddt)_2]$ instead of $(Bu_4N)[Ni(pddt)_2]$. Anal. Calc. for $C_{46}H_{44}N_6Ni_2O_2RuS_{16}$: C, 38.06; H, 3.03; N, 5.79. Found: C, 38.50; H, 3.10; N, 5.86.

2.2.3. Synthesis of $[Ph_2Cr][Ni(dddt)_2]$ (3). $Na_2[Ni(dddt)_2]$ was prepared *in situ* from $Na_2(dddt)$ (0.240 g, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (0.012 g, 0.5 mmol) in ethanol (30 mL). The reaction mixture was stirred for 50 min and then exposed to air for 10 min. After filtration, $[Ph_2Cr]I$ (0.168 g, 0.5 mmol) in 10 mL of ethanol was added to the filtrate. The dark green precipitate was collected by filtration and dried *in vacuo*. Anal. Calc. for $C_{20}H_{20}CrNiS_8$: C, 38.27; H, 3.20. Found: C, 38.68; H, 3.47. IR absorptions (cm^{-1}): 1428 (C=C), 1279 (C–S), 859, 463 (Ni–S).

2.3. *General methods*

Elemental analyses were performed using a Perkin–Elmer 240C analytical instrument. Ni analysis was measured on a Jarrell-ash ICP quantimeter. IR spectra were collected on a Shimadzu 440 spectrometer with KBr pellets. UV-VIS spectra were recorded on a UV-3100 spectrophotometer. The ESR spectra were recorded on a Bruker ER 200-D-SRC spectrometer. Variable-temperature magnetic susceptibility data were collected in the temperature range of 2–300 K using a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

2.4. *X-ray structure determination*

The crystal structure of **1** was measured on a CCD area detector equipped with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation at 293(2) K. A summary of the crystal data collection and refinement parameters is given in table 1.

The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL [17]. All H atoms were geometrically fixed and allowed to ride on their attached atoms. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 251551. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$ with the atom numbering scheme is shown in figure 1. The selected bond distances and angles of the anions are listed in table 2. The asymmetric unit consists of one unit of $[Ru(bipy)_3]^{2+}$ and two $[Ni(pddt)_2]^-$ anions which are situated on either side of the cation. In one unit

Table 1. Crystallographic data for complex **1**.

Formula	$C_{50}H_{52}N_6Ni_2O_2RuS_{16}$
Formula weight	1500.43
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.634(1)
b (Å)	14.560(1)
c (Å)	49.889(5)
V (Å^3)	6271.8(11)
Z	4
Density (calculated) (g cm^{-3})	1.589
Absorption coefficient (mm^{-1})	1.408
F(000)	3064
Crystal size (mm)	0.28 × 0.18 × 0.10
Theta range for data collection (°)	0.82, 26.00
Limiting indices	$-10 \le h \le 10$, $-17 \le k \le 12$, $-61 \le l \le 61$
Reflections collected/unique (R$_{int}$)	39290, 12309, 0.0343
Max. and min. transmission	0.77 and 0.74
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12309/0/694
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0340$, $wR_2 = 0.0670$
All data	$R_1 = 0.0399$, $wR_2 = 0.0680$
Absolute structure parameter	0.022(10)
Largest diff. peak and hole	0.342 and $-0.473\,e^{-3}$

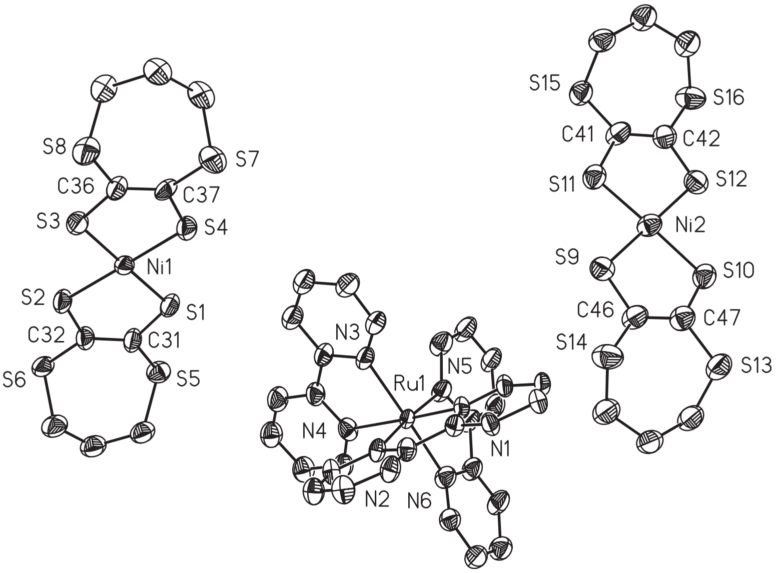

Figure 1. Molecular structure of $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$ (**1**) (ORTEP, 50% ellipsoids). Hydrogen atoms and water molecules are omitted for clarity.

of anion including the Ni(1) atom, four sulfur atoms around the nickel atom yield a square–planar environment with the Ni–S bond lengths of 2.112(1), 2.118(1), 2.120(1) and 2.111(1) Å, which differ very slightly from those of other $[Ni(pddt)_2]^-$ anion complexes [15, 18]. The S–Ni–S angles are nearly the same. There is a little distortion in the Ni(2) unit for the Ni(2)–S(10) bond distance is a little longer than the other three bonds.

1 crystallized in an acentric space group: $P2_12_12_1$. Figure 2 shows the packing diagram of the unit cell looking along the *a* axis. The anions form two alternating stacks along the *a* direction. The shortest intermolecular $S \cdots S$ contact among the $[Ni(pddt)_2]^-$ anions is 3.527(3) Å, occurring between S5 and S16, which is less than the sum of the van der Waals radii of S atom (3.70 Å) [19]. The $[Ni(pddt)_2]^-$ anions are well separated by the large $[Ru(bipy)_3]^{2+}$ cations.

3.2. *ESR, UV and emission spectra*

The ESR spectrum of complex **1** in DMF at 110 K shows three peaks with $g_1 = 2.104$, $g_2 = 2.047$, $g_3 = 2.022$, slightly different from the corresponding values in $(Bu_4N)[Ni(pddt)_2]$ ($g_1 = 2.156, g_2 = 2.070, g_3 = 2.013$). Complex **3** shows only one broad peak at $g = 2.012$, which could be ascribed to the strong signal of Cr^I ions $(S = 1/2)$.

The optical absorption spectra of the complexes show quite a number of bands. The strong broad absorption at 930 nm of complex **1** is assigned to a $\pi \rightarrow \pi^*$ transition ($2b_{1u} \rightarrow 3b_{2g}$) of the anion [20]. Generally, the electronic transitions in Ru(II) tris-bipyridine complexes can be classified as metal centered (MC, d–d), ligand centered (LC, π–π^*) and metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT). The peak at 451 nm is assigned to a d–π (MLCT) transition [12].

Table 2. Selected bond distances (Å) and angles (°) in $[Ru(bipy)_3][Ni(pddt)_2]_2 \cdot 2H_2O$.

Ru(1)–N(1)	2.028(3)	Ru(1)–N(2)	2.035(3)
Ru(1)–N(3)	2.068(3)	Ru(1)–N(4)	2.048(3)
Ru(1)–N(5)	2.022(3)	Ru(1)–N(6)	2.032(3)
Ni(1)–S(1)	2.112(1)	Ni(1)–S(2)	2.118(1)
Ni(1)–S(3)	2.120(1)	Ni(1)–S(4)	2.111(1)
Ni(2)–S(10)	2.146(1)	Ni(2)–S(11)	2.116(1)
Ni(2)–S(9)	2.111(1)	Ni(2)–S(12)	2.105 (1)
S(1)–C(31)	1.711(4)	S(2)–C(32)	1.700(4)
S(3)–C(36)	1.684(4)	S(4)–C(37)	1.718(4)
S(5)–C(35)	1.818(4)	S(5)–C(31)	1.729(4)
S(6)–C(32)	1.759(4)	S(6)–C(33)	1.734(4)
S(7)–C(38)	1.760(4)	S(8)–C(36)	1.773(4)
S(10)–C(47)	1.649(4)	S(9)–C(46)	1.710(4)
S(12)–C(42)	1.667(4)	S(11)–C(41)	1.701(4)
S(13)–C(48)	1.823(5)	S(13)–C(47)	1.743(5)
S(14)–C(46)	1.741(4)	S(14)–C(50)	1.845(5)
S(15)–C(45)	1.750(4)	S(15)–C(41)	1.724(4)
S(16)–C(42)	1.765(4)	S(16)–C(43)	1.800(5)
C(31)–C(32)	1.353(5)	C(36)–C(37)	1.319(5)
C(41)–C(42)	1.384(6)	C(46)–C(47)	1.386(6)
S(1)–Ni(1)–S(2)	91.03(4)	S(1)–Ni(1)–S(4)	88.99(4)
S(2)–Ni(1)–S(3)	89.27(4)	S(3)–Ni(1)–S(4)	90.70(4)
S(9)–Ni(2)–S(10)	90.72(5)	S(9)–Ni(2)–S(11)	88.55(5)
S(10)–Ni(2)–S(12)	89.16(5)	S(11)–Ni(2)–S(12)	91.62(5)
Ni(1)–S(2)–C(32)	104.76(15)	Ni(1)–S(3)–C(36)	103.97(13)
Ni(1)–S(4)–C(37)	105.40(13)	Ni(1)–S(1)–C(31)	105.70(13)
Ni(2)–S(9)–C(46)	105.54(15)	Ni(2)–S(10)–C(47)	104.91(16)
Ni(2)–S(11)–C(41)	105.12(15)	Ni(2)–S(12)–C(42)	104.81(15)
S(1)–C(31)–C(32)	118.0(3)	S(1)–C(31)–S(5)	116.6(2)
S(2)–C(32)–S(6)	115.5(2)	S(6)–C(32)–C(31)	123.7(3)
S(8)–C(36)–C(37)	124.1(3)	S(3)–C(36)–C(37)	122.5(3)
S(7)–C(37)–C(36)	127.5(3)	S(4)–C(37)–C(36)	117.2(3)
S(9)–C(46)–S(14)	116.0(2)	S(9)–C(46)–C(47)	117.5(3)
S(10)–C(47)–C(46)	121.0(3)	S(10)–C(47)–S(13)	118.8(2)
S(11)–C(41)–C(42)	117.3(3)	S(11)–C(41)–S(15)	116.7(2)
S(12)–C(42)–S(16)	117.0(2)	S(12)–C(42)–C(41)	121.1(3)
S(13)–C(47)–C(46)	120.1(3)	S(14)–C(46)–C(47)	125.7(3)
S(15)–C(41)–C(42)	125.6(3)	S(16)–C(42)–C(41)	121.5(3)

Figure 3 shows the excitation and the emission spectra of the complex **1**. Upon excitation at 478 nm, it shows a broadened emission peak at 617 nm, which is assigned to the d → (bipy)π^* transition of the cation, $[Ru(bipy)_3]^{2+}$ [11].

Complex **2**, $[Ru(bipy)_3][Ni(dddt)_2] \cdot 2H_2O$, exhibits similar results, suggesting that counter ions have small effects on the luminescence property of $[Ru(bipy)_3]^{2+}$.

3.3. *Magnetic susceptibility of complex 3*

The temperature dependence of the molar magnetic susceptibility (χ_M) and $\chi_M T$ measured for complex **3** is shown in figure 4. The value of $\chi_M T$ at room temperature is $0.574\,\mathrm{K\,emu\,mol^{-1}}$ ($2.14\mu_B$), which is smaller than the value of $0.75\,\mathrm{K\,emu\,mol^{-1}}$ in this anion/cation system with the magnetically isolated Cr(I) (S = 1/2) and Ni(III) (S = 1/2) ions. As the temperature is lowered, $\chi_M T$ decreases steadily until it reaches a value of $0.117\,\mathrm{K\,emu\,mol^{-1}}$ at 2 K, indicating a weak antiferromagnetic interaction between the Cr(I) and Ni(III) ions. Furthermore, in the temperature range from 2 to 300 K, the observed data are well described by the Curie–Weiss law

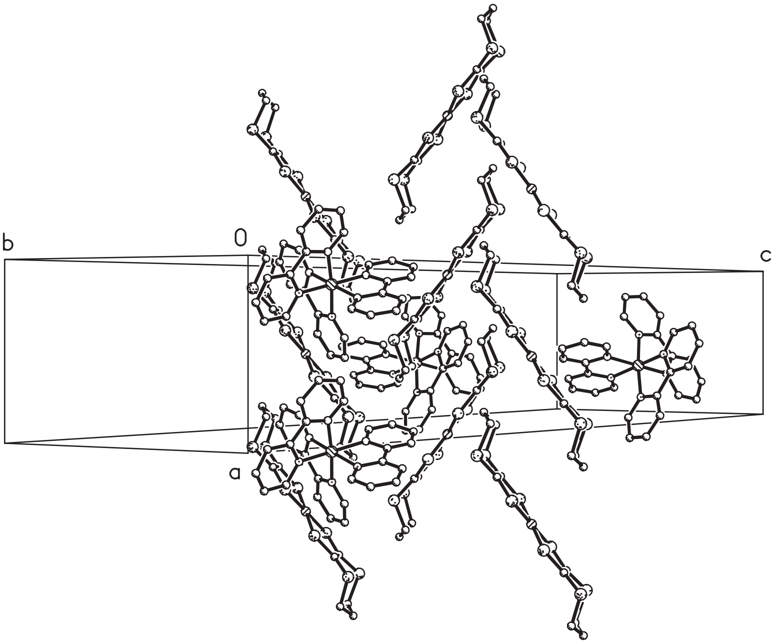

Figure 2. Packing diagram of the unit cell of **1** looking down the *a* axis.

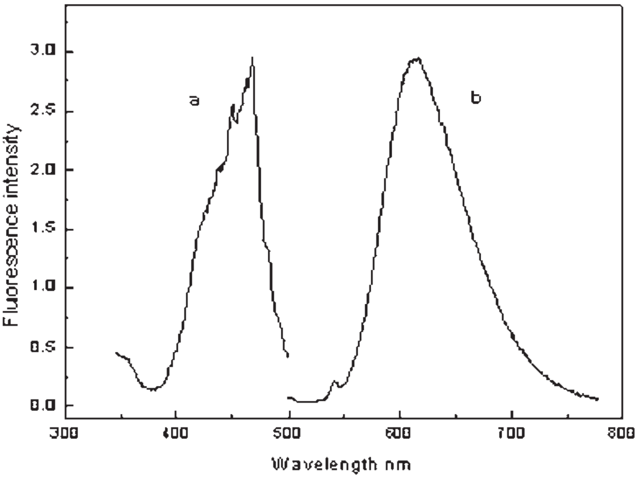

Figure 3. The excitation (a) and the emission (b) spectra of complex **1** in DMF (Concentration 10^{-5} mol L^{-1}), $\lambda_{ex} = 478$ nm.

with a Curie constant of 0.617 K emu mol^{-1} and a Weiss constant of -20.63 K. The magnetic antiferromagnetic coupling is ascribed to the intermolecular interactions between $[Ni(dddt)_2]^-$ anions or between the $[Ph_2Cr]^+$ cations and anions, since we can observe the overlap between the neighboring anions in the solid structure of complex **1**.

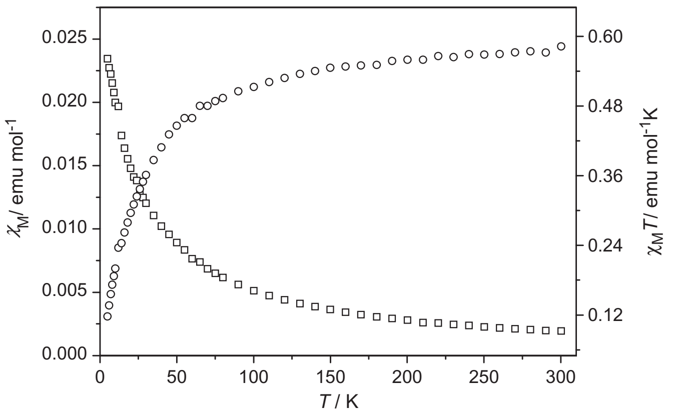

Figure 4. Temperature dependence of χ_M (open squares) and $\chi_M T$ (open circles) for complex **3**.

Further characterization of the above complexes, such as the experiments for non-linear optical (NLO) effects, is in progress in our laboratory. We are trying to develop a new approach for achieving new hybrid molecular materials.

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