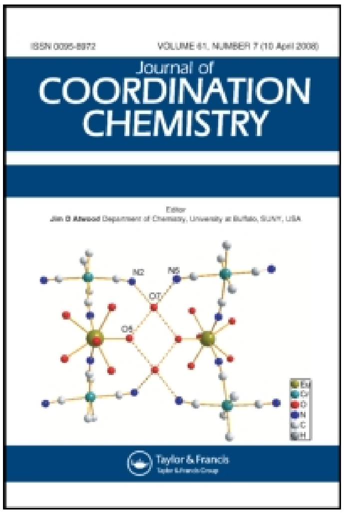

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Wen-Bo Wang[a]; Li-Xin Yang[a]; Liang-Cai Yu[b]; Chun-Xia Song[a]; Shu-Ying Wu[a]
[a] College of Chemistry, Xiangtan University, Xiangtan, China [b] School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, China

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Syntheses, crystal structures and characterizations of tetraazamacrocyclic complexes *meso*-[Ni(1,7-CT)]I_2 and *dl*-[Ni(1,7-CT)][$Fe(CN)_5NO$] · H_2O

WEN-BO WANG†, LI-XIN YANG*†, LIANG-CAI YU‡,
CHUN-XIA SONG† and SHU-YING WU†

†College of Chemistry, Xiangtan University, Xiangtan 411105, China
‡School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

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A centrosymmetric meso tetraazamacrocyclic nickel(II) complex *meso*-[Ni(1,7-CT)]I_2 (**1**) and a novel racemic ion-pair double complex *dl*-[Ni(1,7-CT)][$Fe(CN)_5NO$] · H_2O (**2**) (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene) have been synthesized and characterized by elemental analyses, single crystal X-ray diffraction, ^1H NMR, IR, UV-vis spectra and TG-DTA analyses. Results reveal that the structure of **1** consists of the overlapping *meso*-$[Ni(1,7\text{-CT})]^{2+}$ cation with the perfect square-planar NiN_4 chromophore and outer iodides. Compound **2** contains four kinds of structurally distinct ion-pairs **a**, **a′**, **b** and **b′** that are made up of distorted square *dl*-$[Ni(1,7\text{-CT})]^{2+}$ cations and distorted octahedral $[Fe(CN)_5NO]^{2-}$ anions, which are divided into two groups with an enantiotropic relationship between them in each group. They are linked by van der Waals forces and hydrogen bonds involving H_2O and arranged alternatively in adjacent layers, forming an orderly three-dimensional network structure.

Keywords: Tetraazamacrocyclic nickel(II) complex; Nitroprusside; Ion pairs; Crystal structures; Characterizations

1. Introduction

Tetraaza 14-membered macrocycles are a representative macrocyclic ligand, and research related to them has made remarkable progress [1–4]. The nickel(II) tetraazamacrocyclic complex cation, $[Ni(1,7\text{-CT})]^{2+}$ (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene), is easily synthesized in high yield and combines with different anions to form multiple kinds of ion-packing models [5–8] and center-bridging structures [9, 10]. In the same complex cation, the change of anion leads to the change of structure. The $[Ni(1,7\text{-CT})]^{2+}$ cation has meso and racemic isomers that can interconvert in aqueous solution, and shows quite interesting self-assembly behavior [11]. The $[Ni(1,7\text{-CT})]^{2+}$ cation reacts with mixed I^- and I_3^- anions, and $[Ni(CN)_4]^{2-}$ gives a Ni(II)–I–Ni(II) bridging-linkage dimer and

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*Corresponding author. Email: ylx@xtu.edu.cn

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a chain polymeric structure, respectively. However, crystal packing of even the simplest iodide reacting with the $[Ni(1,7\text{-}CT)]^{2+}$ cation is not clear, and a heterometallic complex anion reacting with $[Ni(1,7\text{-}CT)]^{2+}$ has not been reported. The nitroprusside anion is a useful counterion as a building block [12–15], and the reactive behavior of it and macrocyclic complex cations deserves to be explored. In the current work, we obtained the crystal structure of *meso*-$[Ni(1,7\text{-}CT)]I_2$ (**1**) by single crystal X-ray analysis. Through the assembly of $[Ni(1,7\text{-}CT)]I_2$ and nitroprusside, a novel ion-pair double complex containing racemic species, *dl*-$[Ni(1,7\text{-}CT)][Fe(CN)_5NO] \cdot H_2O$ (**2**), has been synthesized and structurally characterized. In the meantime, the ^1H NMR, IR, UV-vis spectra and TG-DTA analyses of **1** and **2** have also been determined and discussed.

2. Experimental

2.1. *Reagents and instruments*

All chemicals obtained commercially were of reagent grade and used without further purification. Elemental analyses for C, H and N were carried out using a PE-2400 II analyzer. The crystal structures were determined by a Bruker Smart APEX II CCD X-ray diffractometer. The ^1H NMR spectra were recorded at 400 MHz on a Bruker Avance-400 spectrometer with D_2O as solvent. The IR spectra were recorded on a PE FT-IR spectrometer as KBr pellets in 4000–400 cm^{-1} region. The UV-vis spectral measurements were performed on a PE Lambda 25 UV/vis spectrometer and the TG-DTA measurements were carried out with WCT-1A thermogravimeter (Peking, China) in air at a heating rate of $10°C\,min^{-1}$.

2.2. *Single crystal growth of* meso-*$[Ni(1,7\text{-}CT)]I_2$*

The mononuclear tetraazamacrocyclic complex $[Ni(1,7\text{-}CT)]I_2$ was prepared by the literature method [16]. Isopropanol was slowly diffused into a solution of $[Ni(1,7\text{-}CT)]I_2$ dissolved in methanol, and two days later, yellow blocky single crystals of **1** suitable for X-ray structure analysis were obtained. Yield: 60%. Anal. Calcd for $C_{16}H_{32}N_4NiI_2$ (%): C, 32.41; H, 5.40; N, 9.45. Found: C, 32.42; H, 5.06; N, 9.32.

2.3. *Synthesis of* dl-*$[Ni(1,7\text{-}CT)][Fe(CN)_5NO] \cdot H_2O$*

A solution of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (0.5 mmol) in water (10 mL) was added dropwise to a yellow solution of $[Ni(1,7\text{-}CT)]I_2$ (0.5 mmol) in water/methanol (v/v = 1 : 1, 15 mL) with continuous stirring at room temperature. The resulting orange-yellow solution was filtered and the filtrate was allowed to stand at room temperature for two days; some orange-yellow crystals were isolated. These crystals were recrystallized from water; several days later well-developed blocky single crystals of **2** suitable for X-ray diffraction were obtained. Yield: 65%. Anal. Calcd for $C_{21}H_{34}N_{10}NiFeO_2$ (%): C, 44.01; H, 5.98; N, 24.44. Found: C, 43.82; H, 5.95; N, 23.96.

2.4. *Crystal structure determinations and refinements*

Selected single crystals of **1** ($0.45 \times 0.25 \times 0.10\,\text{mm}^3$) and **2** ($0.34 \times 0.20 \times 0.16\,\text{mm}^3$) were mounted on a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073\,\text{Å}$) by using the $\phi - \omega$ scan technique at 273(2) K. A total of 4435 for **1** and 44,898 for **2** were collected, of which 1873 for **1** and 10,836 for **2** were independent reflections with $R_{\text{int}} = 0.0794$ for **1** and 0.0439 for **2**. Multi-scan absorption corrections were applied using SADABS [17]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXTL-97 programs [18, 19]. All non-hydrogen atoms were refined anisotropically; all the hydrogen atoms attached to carbon atoms were placed in calculated positions and the water hydrogen atoms and amine hydrogen atoms were determined from a difference Fourier map. The final refinement converged to $R_1 = 0.0469$ for **1** and 0.0383 for **2**, $wR_2 = 0.1234$ for **1** and 0.0932 for 2 [$I > 2\sigma(I)$]. A summary of the crystallographic data for the two complexes is provided in table 1. Selected bond lengths and angles are listed in table 2. Hydrogen-bonding interactions in **2** are given in table 3.

3. Results and discussion

3.1. *Crystal structure of 1*

Structural analysis reveals that $[\text{Ni(1,7-CT)}]^{2+}$ has C_i symmetry, with secondary amine hydrogen atoms located in opposite directions, forming a meso isomer, as shown

Table 1. Crystallographic data for complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{16}H_{32}N_4NiI_2$	$C_{21}H_{34}N_{10}NiFeO_2$
Formula weight	592.95	573.12
Temperature (K)	273(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)		
a	6.7087(3)	15.0162(5)
b	8.7971(4)	17.6899(5)
c	9.9865(5)	20.9102(7)
α	100.8930(10)	90
β	93.4370(10)	96.650(2)
γ	110.1860(10)	90
Volume (Å^3)	538.17(4)	5517.1(3)
Absorption coefficient (mm^{-1})	3.774	1.245
θ range (°)	2.10–25.01	1.79–26.01
Z, calculated density (mg m^{-3})	1, 1.830	8, 1.380
$F(000)$	290	2400
Crystal shape/crystal colour	Block/yellow	Block/orange-yellow
Crystal size (mm^3)	$0.45 \times 0.25 \times 0.10$	$0.34 \times 0.20 \times 0.16$
Reflections collected/unique	4435/1873 [$R_{\text{int}} = 0.0794$]	44,898/10,836 [$R_{\text{int}} = 0.0439$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.093	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1234$	$R_1 = 0.0383$, $wR_2 = 0.0932$
R indices (all data)	$R_1 = 0.0487$, $wR_2 = 0.1259$	$R_1 = 0.0762$, $wR_2 = 0.1144$
Largest diff. peak and hole (e Å^{-3})	2.229 and −1.586	0.977 and −0.379

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

***meso*-[Ni(1,7-CT)]I_2**					
Ni(1)–N(1)	1.915(4)	Ni(1)–N(2)	1.931(4)	C(2)–N(1)	1.276(6)
Ni(1)–N(1)a	1.915(4)	Ni(1)–N(2)a	1.931(4)	C(5)–N(2)	1.505(6)
N(1)–Ni(1)–N(1)a	180.000(1)	N(1)a–Ni(1)–N(2)	93.96(16)	N(1)a–Ni(1)–N(2)a	86.04(16)
N(1)–Ni(1)–N(2)	86.04(16)	N(1)–Ni(1)–N(2)a	93.96(16)	N(2)–Ni(1)–N(2)a	180.000(1)
***dl*-[Ni(1,7-CT)][Fe(CN)$_5$NO] · H_2O**					
Ni(1)–N(7)	1.899(2)	Fe(1)–C(3)	1.936(4)	C(5)–N(6)	1.138(4)
Ni(1)–N(8)	1.923(2)	Fe(1)–C(4)	1.934(3)	C(8)–N(8)	1.500(4)
Ni(1)–N(9)	1.894(2)	Fe(1)–C(5)	1.937(4)	C(12)–N(9)	1.289(4)
Ni(1)–N(10)	1.923(2)	C(1)–N(2)	1.135(4)	C(16)–N(10)	1.493(4)
Fe(1)–N(1)	1.663(3)	C(2)–N(3)	1.148(5)	C(20)–N(7)	1.278(4)
Fe(1)–C(1)	1.934(4)	C(3)–N(4)	1.152(4)	N(1)–O(1)	1.141(4)
Fe(1)–C(2)	1.928(4)	C(4)–N(5)	1.146(4)		
Ni(2)–N(17)	1.927(2)	Fe(2)–C(24)	1.935(3)	C(26)–N(16)	1.144(5)
Ni(2)–N(18)	1.900(2)	Fe(2)–C(25)	1.940(4)	C(29)–N(18)	1.281(4)
Ni(2)–N(19)	1.925(2)	Fe(2)–C(26)	1.895(4)	C(32)–N(19)	1.493(4)
Ni(2)–N(20)	1.889(2)	C(22)–N(12)	1.138(4)	C(37)–N(20)	1.287(4)
Fe(2)–N(11)	1.692(3)	C(23)–N(13)	1.139(4)	C(40)–N(17)	1.498(4)
Fe(2)–C(22)	1.927(4)	C(24)–N(14)	1.142(4)	N(11)–O(2)	1.143(4)
Fe(2)–C(23)	1.941(4)	C(25)–N(15)	1.141(4)		
N(7)–Ni(1)–N(8)	84.55(11)	C(4)–Fe(1)–N(1)	93.15(14)	C(3)–Fe(1)–C(4)	85.53(13)
N(7)–Ni(1)–N(10)	95.26(11)	C(5)–Fe(1)–N(1)	93.05(15)	C(3)–Fe(1)–C(5)	84.93(15)
N(8)–Ni(1)–N(10)	178.19(11)	C(1)–Fe(1)–C(2)	90.29(14)	C(4)–Fe(1)–C(5)	90.06(14)
N(9)–Ni(1)–N(7)	176.94(11)	C(1)–Fe(1)–C(3)	85.50(14)	Fe(1)–C(1)–N(2)	178.4(3)
N(9)–Ni(1)–N(8)	95.78(11)	C(1)–Fe(1)–C(4)	170.96(14)	Fe(1)–C(2)–N(3)	178.7(4)
N(9)–Ni(1)–N(10)	84.31(10)	C(1)–Fe(1)–C(5)	88.10(14)	Fe(1)–C(3)–N(4)	179.8(4)
C(1)–Fe(1)–N(1)	95.78(14)	C(2)–Fe(1)–C(3)	85.82(15)	Fe(1)–C(4)–N(5)	178.1(3)
C(2)–Fe(1)–N(1)	96.22(16)	C(2)–Fe(1)–C(4)	90.10(15)	Fe(1)–C(5)–N(6)	179.0(4)
C(3)–Fe(1)–N(1)	177.58(14)	C(2)–Fe(1)–C(5)	170.70(16)	Fe(1)–N(1)–O(1)	177.2(3)
N(18)–Ni(2)–N(17)	84.92(11)	C(25)–Fe(2)–N(11)	94.15(14)	C(24)–Fe(2)–C(25)	85.87(14)
N(18)–Ni(2)–N(19)	95.08(11)	C(26)–Fe(2)–N(11)	95.73(15)	C(24)–Fe(2)–C(26)	88.08(15)
N(19)–Ni(2)–N(17)	179.64(12)	C(22)–Fe(2)–C(23)	90.15(15)	C(25)–Fe(2)–C(26)	89.26(15)
N(20)–Ni(2)–N(18)	176.57(11)	C(22)–Fe(2)–C(24)	85.32(14)	Fe(2)–C(22)–N(12)	179.5(4)
N(20)–Ni(2)–N(17)	95.10(11)	C(22)–Fe(2)–C(25)	171.16(13)	Fe(2)–C(23)–N(13)	176.5(3)
N(20)–Ni(2)–N(19)	84.88(11)	C(22)–Fe(2)–C(26)	91.22(16)	Fe(2)–C(24)–N(14)	179.8(4)
C(22)–Fe(2)–N(11)	94.59(14)	C(23)–Fe(2)–C(24)	86.19(14)	Fe(2)–C(25)–N(15)	179.5(4)
C(23)–Fe(2)–N(11)	90.01(14)	C(23)–Fe(2)–C(25)	88.49(15)	Fe(2)–C(26)–N(16)	177.8(4)
C(24)–Fe(2)–N(11)	176.19(15)	C(23)–Fe(2)–C(26)	173.98(15)	Fe(2)–N(11)–O(2)	177.0(3)

Symmetry code: a = $-x+2$, $-y$, $-z+2$.

Table 3. Hydrogen bond lengths (Å) and bond angles (°) for complex **2**.

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	∠(DHA)
O(3)–H(3A) ··· N(3)a	0.76(3)	2.15(3)	2.900(5)	170(5)
O(4)–H(4A) ··· O(3)b	0.84(3)	1.94(3)	2.776(6)	174(7)
O(4)–H(4B) ··· N(2)c	0.85(3)	2.11(3)	2.954(5)	170(8)
O(3)–H(3B) ··· N(16)d	0.77(2)	2.14(3)	2.897(5)	166(4)
N(8)–H(8) ··· N(4)	0.83(2)	2.13(2)	2.952(4)	171(3)
N(10)–H(10) ··· N(5)	0.87(2)	2.13(2)	2.984(4)	168(3)
N(17)–H(17) ··· N(15)e	0.85(2)	2.12(2)	2.959(4)	171(3)
N(19)–H(19) ··· N(14)e	0.87(2)	2.12(2)	2.972(4)	170(3)
C(11)–H(11B) ··· N(6A)f	0.97	2.53	3.492	170
C(36)–H(36B) ··· N(12A)g	0.97	2.60	3.407	141

Symmetry codes: a = x, $-y+3/2$, $z+1/2$; b = x, $-y+3/2$, $z-1/2$; c = $-x+1$, $-y+1$, $-z$; d = $-x+1$, $y+1/2$, $-z+1/2$; e = $x-1$, y, z; f = $1-x$, $-1/2+y$, $1/2-z$; g = $-1+x$, $1/2-y$, $1/2+z$.

in figure 1. The structure of **1** is constructed by discrete *meso*-[Ni(1,7-CT)]$^{2+}$ and iodides. The nickel(II) is located at a crystallographic center of symmetry and coordinated by four nitrogen atoms from the 1,7-CT macrocycle. The Ni1–N1 and Ni1–N1A distances are equal (1.915(4) Å) and the distances of Ni1–N2 and Ni1–N2A are also identical with 1.931(4) Å, which indicate that the Ni–N bonds to the imines are slightly shorter than the Ni–N bonds to the secondary amines due to the different hybridization of nitrogen. The N1–Ni1–N1A and N2–Ni1–N2A angles are 180.000(1)°, exhibiting a perfect square-planar geometry of NiN_4. The maximum deviations from the NiN_4 plane are 0.1543 Å for C3, −0.1543 Å for C3A, −0.5301 Å for C4 and 0.5301 Å for C4A. The C2–N1 distance of 1.276(6) Å is slightly longer than the typical C=N bond length (1.21 Å) and the C5–N2 distance of 1.505(6) Å is close to the normal C–N bond length (1.46 Å) [20]. The crystal packing of **1** is shown in figure 2. Because there is no influence of complicated anions, the tetraazamacrocyclic complex takes a perfect overlapping arrangement. The iodides alternating with *meso*-[Ni(1,7-CT)]$^{2+}$ in the structure present short contacts with the methyl hydrogen atoms (H1A and H6C) from adjacent macrocycles, and simultaneously form hydrogen bonds with secondary amine hydrogen atoms, the shortest distances of I ··· H1A, I ··· H6C and N ··· I being 3.165, 3.173 and 3.578(4) Å, respectively, and the N–H ··· I angle being 174(6)°.

3.2. *Crystal structure of 2*

Single crystal X-ray analysis shows that the crystal structure of **2** exhibits four kinds of structurally distinct ion-pairs that are made up of distorted square *dl*-[Ni(1,7-CT)]$^{2+}$

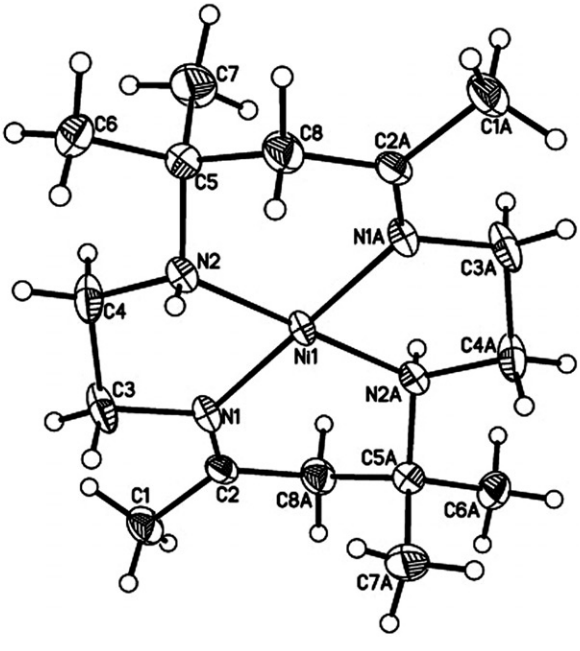


Figure 1. Structure of the *meso*-[Ni(1,7-CT)]$^{2+}$ cation with the atom numbering scheme and thermal ellipsoids drawn at 30% probability. Symmetry code: A = $-x+2$, $-y$, $-z+2$.

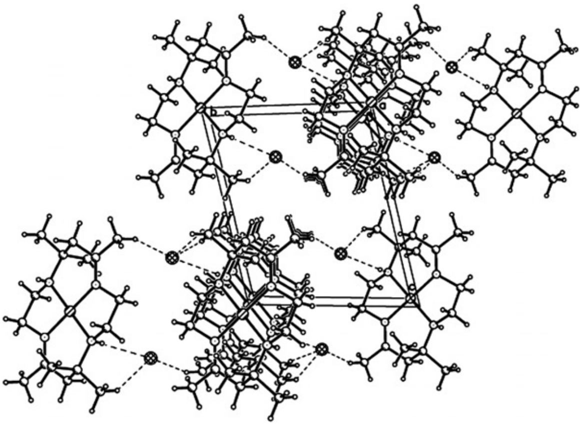


Figure 2. Macrocyclic packing arrangement of **1** along the *a* axis showing the weak short-contact interactions between iodide and hydrogen atoms which are indicated by dashed lines.

cations and distorted octahedral $[Fe(CN)_5NO]^{2-}$ anions, which are labeled as **a**, **a**′, **b** and **b**′, as shown in figure 3. The obvious enantiotropic relationship can be found between **a** and **a**′ as well as between **b** and **b**′ as racemates. The two secondary amine hydrogen atoms are arranged in the same direction, the *dl*-$[Ni(1,7\text{-}CT)]^{2+}$ diastereoisomers have C_2 symmetry as free ions and $[Fe(CN)_5NO]^{2-}$ in ion-pairs **a** and **b** or **a**′ and **b**′ assume two different paired styles. The ion-pairs **a**, **a**′, **b** and **b**′ are linked by oriented van der Waals forces and hydrogen bonds that involve H_2O and alternatively arrange in the crystal, creating a stable three-dimensional network structure. In **2**, the nickel(II) is coordinated with 1,7-CT ligand and the Ni–N distances are not identical, ranging from 1.894(2) to 1.923(2) Å for **a** or **a**′ and from 1.889(2) to 1.927(2) Å for **b** or **b**′; these bond lengths are obviously shorter than the corresponding values observed in **1**. The four bond angles of N7–Ni1–N9, N8–Ni1–N10, N17–Ni2–N19 and N18–Ni2–N20 are 176.94(11), 178.19(11), 179.64(12) and 176.57(11)°, respectively, indicating that nickel(II) is not located at a crystallographic center of symmetry in forming the ion-pair complex.

The Fe sites present a slightly distorted octahedral geometry similar to those in other nitroprusside compounds [14, 21]. The equatorial planes of the distorted octahedral $[Fe(CN)_5NO]^{2-}$ anions are defined by cyano carbon atoms with C2–Fe1–C5 angle of 170.70(16)°, C3–Fe1–N1 angle of 177.58(14)°, C22–Fe2–C25 angle of 171.16(13)° and C23–Fe2–C26 angle of 173.98(15)°. The two axial positions are occupied by a cyano carbon and a nitrosyl nitrogen with the C1–Fe1–C4 angle of 170.96(14)° and the N11–Fe2–C24 angle of 176.19(15)°. The mean Fe–C and C–N bond lengths are 1.934 and 1.144 Å for **a** or **a**′, 1.928 and 1.141 Å for **b** or **b**′, respectively. The Fe1–N1 bond length of 1.663(3) Å is shorter than Fe2–N11 bond length of 1.692(3) Å, and N1–O1 distance of 1.141(4) Å is very close to N11–O2 length of 1.143(4) Å, yet these values are all longer than the previously reported values in $[Ni(bpy)_3][Fe(CN)_5NO] \cdot 3H_2O$ [22]. The Fe–N distances are significantly shorter than the Fe–C distances, all N–Fe–C angles are larger than 90°, and the Fe–N–O and Fe–C–N bond angles are nearly linear.

In the packing diagram of **2**, the two cyano nitrogen atoms of $[Fe(CN)_5NO]^{2-}$ and their adjacent secondary amine hydrogen atoms of *dl*-$[Ni(1,7\text{-}CT)]^{2+}$ form strong intra-ion-pair N–H $\cdots$ N hydrogen bonds with N $\cdots$ N distances of 2.952(4) Å

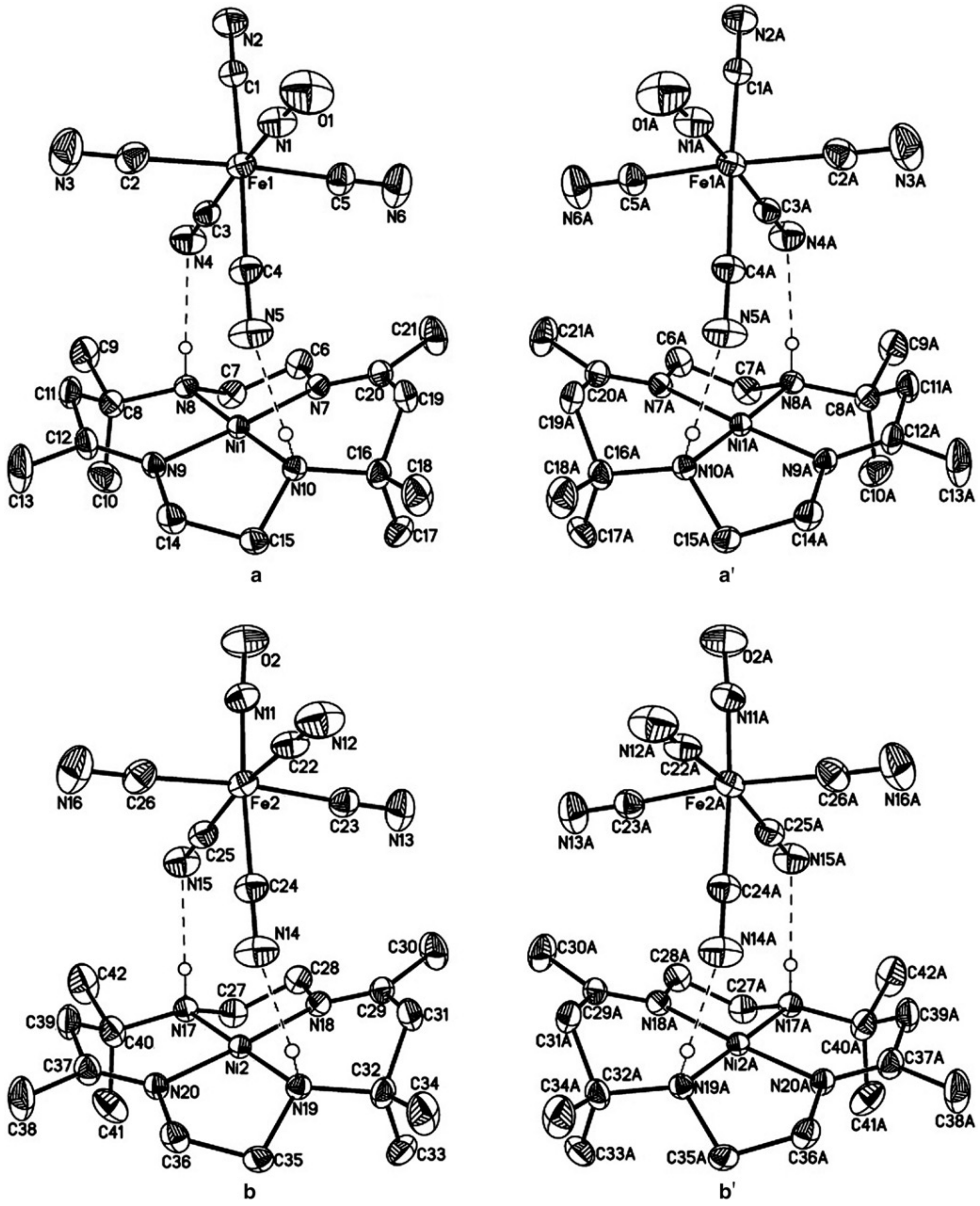
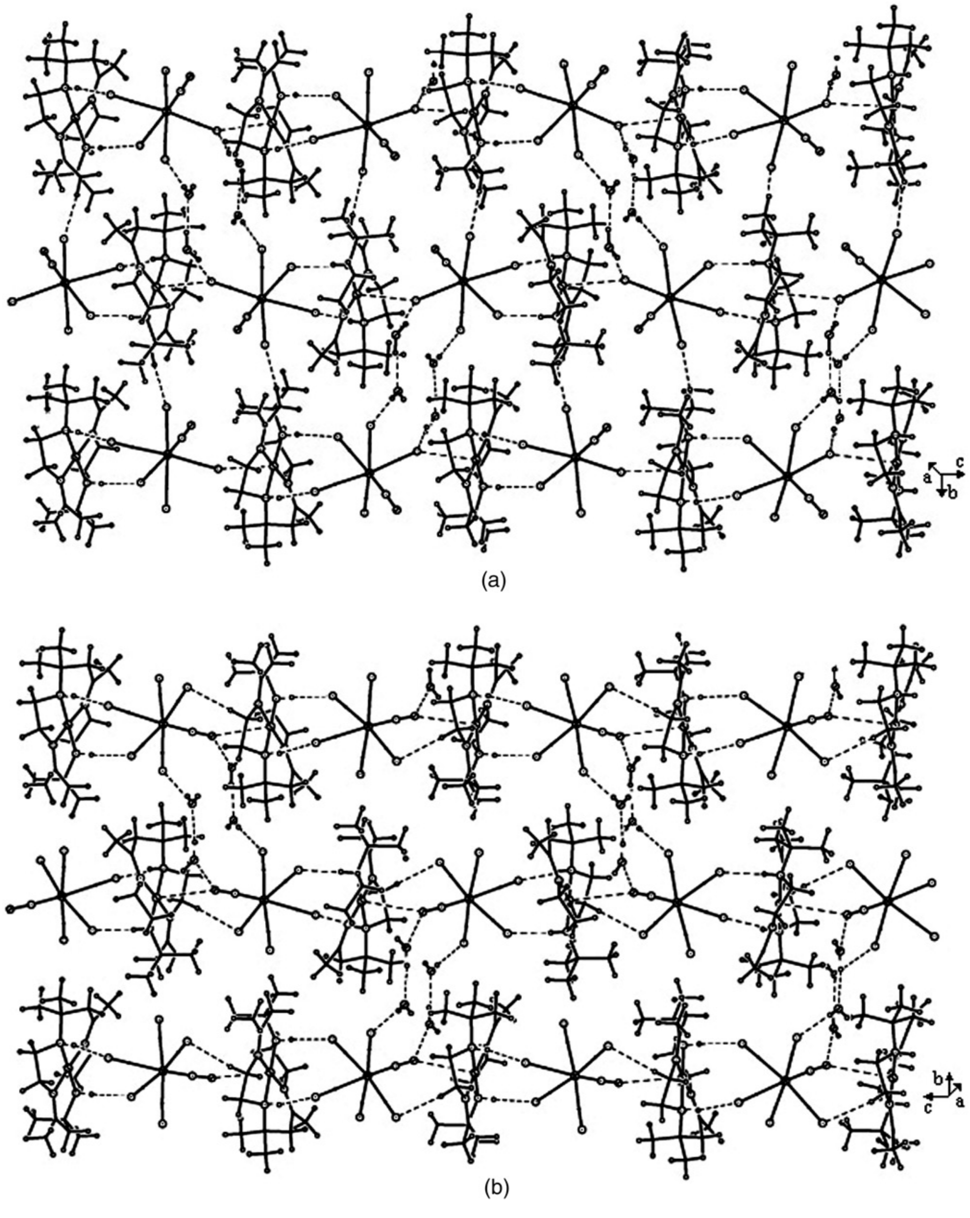


Figure 3. Structures of the four different ion-pairs **a**, **a′**, **b** and **b′** observed in **2** with the atom numbering and thermal ellipsoids drawn at 30% probability. The hydrogen atoms, except for the two amine hydrogen atoms, are omitted for clarity. The capital A in labels denotes corresponding mirror atoms.

(N4 ··· N8), 2.984(4) Å (N5 ··· N10), 2.972(4) Å (N14 ··· N19) and 2.959(4) Å (N15 ··· N17). The ion-pairs **a** and **a′** are linked by equivalent inter-ion-pair N2 ··· Ni1A and N2A ··· Ni1 short contacts to form one-dimensional extended chains, then these individual chains are further held together by C11–H11B ··· N6A and C11A–H11AB ··· N6 hydrogen bonds with the C ··· N distance 3.492 Å and the



(a)

(b)

Figure 4. Packing diagram of **2** along the *bc* plane showing the two-dimensional layers constructed by van der Waals forces and hydrogen-bond interactions: (a) a two-dimensional layer formed by ion-pairs **a** and **a**′; (b) a two-dimensional layer formed by ion-pairs **b** and **b**′.

C–H $\cdots$ N angle 170°, and water dimer bridges between the cyano nitrogen atoms from nitroprusside anions in adjacent chains. Thus, an extended two-dimensional layer (a) is constructed along the *bc* plane, as shown in figure 4(a). While the ion-pairs **b** and **b**′ also form chains by O2 $\cdots$ Ni2A and O2A $\cdots$ Ni2 short contacts and inter-ion-pair hydrogen bonds C36–H36B $\cdots$ N12A and C36A–H36AB $\cdots$ N12 with the C $\cdots$ N distance of 3.407 Å and the C–H $\cdots$ N angle of 141°, and then these chains are further constructed into two-dimensional layer (b) along the *bc* plane by water dimer bridges, as shown in figure 4(b). Layer (a) and layer (b) alternately arrange to form a three-dimensional framework.

3.3. ^{1}*H NMR spectra*

The ^{1}H NMR spectra of **1** and **2** are identical when using neutral D_2O as solvent, consisting of the mixed spectra of *meso*-$[Ni(1,7\text{-}CT)]^{2+}$ and *dl*-$[Ni(1,7\text{-}CT)]^{2+}$ racemates as a main part. This reveals that there is a rapid transformation and equilibrium between *meso*- and *dl*-isomers in neutral environment. However, in acidic D_2O (pD $\approx$ 2, HCl added), the ^{1}H NMR spectra of pure *meso*- and *dl*-isomers can be obtained, proving that the isomers are kinetically stable and their equilibrium is inhibited in acidic aqueous solution at room temperature. Because of the complete dissociation of **2** in aqueous solution, $[Fe(CN)_5NO]^{2-}$ has no influence on the ^{1}H NMR of the macrocyclic cation. Their ^{1}H NMR spectra are shown in figure 5. The sharp singlets at 1.17, 1.63 and 2.12 ppm for **1** and at 1.16, 1.95 and 2.06 ppm for **2** correspond to the equatorial methyl group of the geminal pair, the axial geminal methyl group and the imine methyl group, respectively. The coupling of three kinds of methylene protons on the macrocycles is complicated. The multiplets assumed four obvious splitting peaks at 2.64–2.83 ppm region for **1** and 2.62–2.86 ppm region for **2** as compressed AB patterns, the quartets at 3.56 ppm for **1** and 3.48 ppm for **2** and the multiplets at 2.52 ppm for **1** and 2.47 ppm for **2** are attributed to the methylene protons adjacent to two carbon groups, the imine dimethylene protons and amine dimethylene protons, respectively. However, the above chemical shift values are all smaller than the corresponding values calibrated from external TMS in literature [23], while the peak positions in figure 5(a2), (b2) are close to the corresponding peak values of mixed isomers reported in the literature [16]. Figure 5(a1), (b1) can act as the ^{1}H NMR standard spectra of *meso*-$[Ni(1,7\text{-}CT)]^{2+}$ and *dl*-$[Ni(1,7\text{-}CT)]^{2+}$ racemates, respectively.

3.4. *IR spectra*

The IR spectrum of **2** shows the presence of crystalline water (3413–3529 cm^{-1}). The most significant difference between the IR spectra of **1** and **2** is the appearance of two sharp and strong absorption peaks at 1900 and 2138 cm^{-1} in the spectrum of the latter. The strong single absorption peak at 1900 cm^{-1} is reasonably assigned to the N=O stretching vibration, which is lower than 1946 cm^{-1} of nitroprusside anion, and the single peak at 2138 cm^{-1} is ascribed to the C$\equiv$N stretching vibration, which is slightly smaller than the corresponding values (2144, 2158 and 2174 cm^{-1}) in $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ [24]. The strong C=N stretching vibrations at 1653 cm^{-1} for **1** and 1650 cm^{-1} for **2**, and the C–N stretching vibrations at 1129, 1168 and 1184 cm^{-1} for **1** and 1130, 1175 cm^{-1} for **2** can be clearly observed, indicating that there are two different bonding nitrogen atoms in $[Ni(1,7\text{-}CT)]^{2+}$ cations.

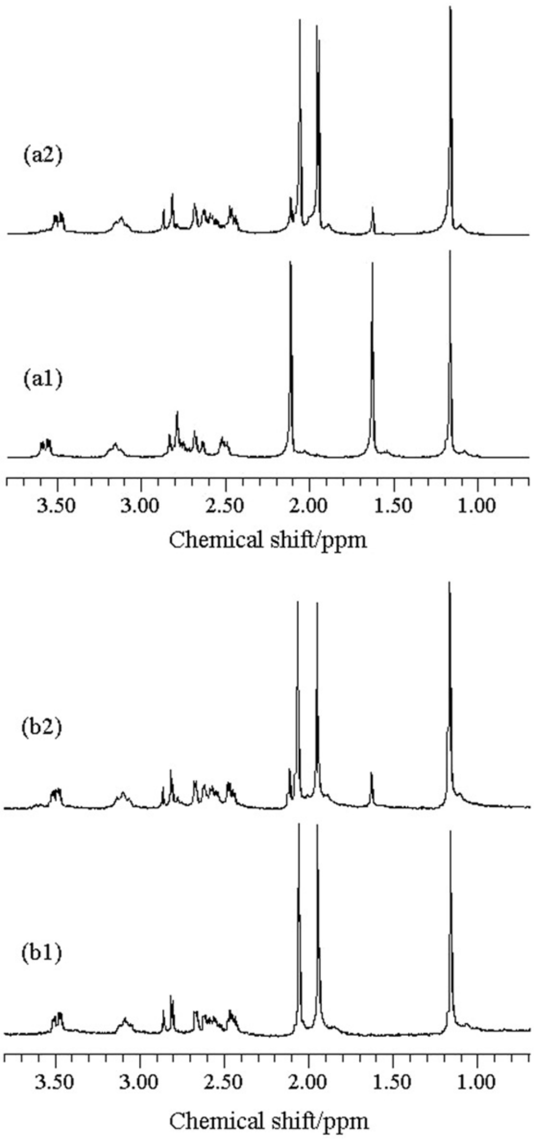


Figure 5. ^{1}H NMR spectra of pure meso and racemic macrocyclic isomers in aqueous solutions: (a1) **1** at pD ≈ 2, (a2) **1** in neutral D_2O; (b1) **2** at pD ≈ 2, (b2) **2** in neutral D_2O.

3.5. *UV-vis spectra*

The UV-vis spectra of **1** and **2** were determined in HCl aqueous solution at pH ~2. In **1**, the sharp absorption band at 226 nm can be assigned to the charge transfer ($L \rightarrow Ni^{2+}$) and the absorption band at 283 nm is associated with a $\pi \rightarrow \pi^*$ electronic transition of the imine group. The UV-vis spectrum of **2** shows a charge transfer band ($L \rightarrow Ni^{2+}$) at 202 nm and a $\pi \rightarrow \pi^*$ electronic transition of the imine group at 278 nm,

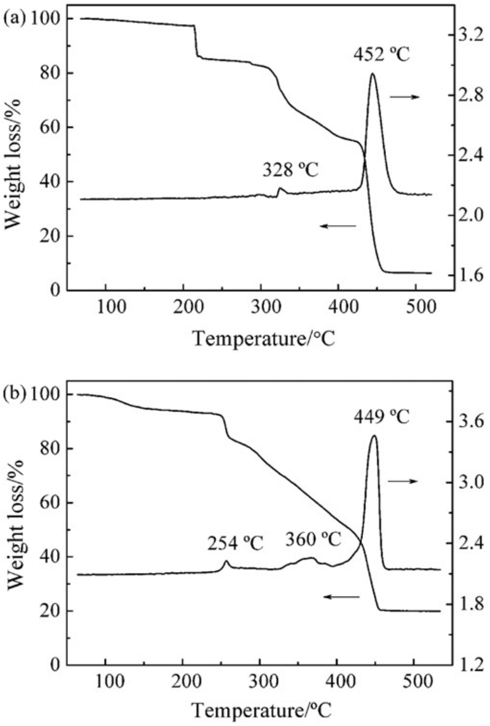


Figure 6. TG and DTA curves of: (a) complex **1**; (b) complex **2**.

shifted to short wavelength relative to **1**; this may be a result of strong absorption of $[Fe(CN)_5NO]^{2-}$ in ultraviolet region. The absorption band of **2** in visible region at 431 nm ($\varepsilon_{max} = 95$) has no obvious change in contrast to that of **1** at 432 nm ($\varepsilon_{max} = 86$), both extinction coefficients approach 90, which indicates that the Ni(II) center retains four-coordinate square configuration after forming the bimetallic ion-pair complex.

3.6. *TG-DTA analyses*

The TG-DTA patterns of **1** and **2** are shown in figure 6. In the TG curves, the rapid continuous weight losses of about 43.27% between 433 and 458°C for **1** and about 28.54% between 422 and 453°C for **2** can be observed and ascribed to the removal of I^- ions and the cyano and nitrosyl groups of $[Fe(CN)_5(NO)]^{2-}$; the corresponding strong exothermic peaks in the DTA curves are at 452°C for **1** and 449°C for **2**. Likewise, the successive weight losses of about 47.76% between 213 and 433°C for **1** and about 49.27% from 244 to 422°C for **2** represent decomposition of the macrocyclic ligand, and the successive weight loss of **2** between 93 and 149°C (~5.13%) corresponds with the release of water.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 609932 and 610094 for **1** and **2**, respectively. Copies of this information may be obtained from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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