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Metal String Complexes: Synthesis, Crystal Structures and Magnetic Properties of Heptanuclear Nickel(II) Complexes, $[Ni_7(\mu_7\text{-teptra})_4X_2]$ (teptra = tetrapyridyltriamido, X = Cl^-, NCS^-)

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The synthesis, crystal structures and magnetic properties of linear heptanuclear nickel(II) complexes $[Ni_7(\mu_7\text{-teptra})_4X_2]$, (teptra = tetrapyridyltriamido), with the axial ligand X = Cl^- (**1**), NCS^- (**2**), are reported. The hepta-nuclear metal chain is helically wrapped by four *syn-syn-syn-syn-syn-syn* $teptra^{3-}$ ligands. Both of the $[Ni_7(\mu_7\text{-teptra})_4]^{2+}$ moiety are isostructural involving a Ni_7 linear chain unit with all of the ∠Ni–Ni–Ni being 180°, terminated by two axial ligands. Three types of Ni–Ni distances are found in these complexes. The longest ones bonded with the axial ligands are 2.383(1), 2.374(2) and 2.375(2), 2.354(2), and the intermediate ones are 2.310(1), 2.304(1) and 2.300(2), 2.303(2) Å for (**1**) and (**2**), respectively. The innermost Ni–Ni distances are the shortest ones with the distances of 2.226(2), 2.214(2) and 2.194(2), 2.206(2) Å for (**1**) and (**2**), respectively. Two terminal Ni(II) ions bonded with the axial ligands are in a square-pyramidal (NiN_4X) environment and exhibit long Ni–N bonds (~2.10 Å) which are consistent with a high-spin Ni(II) configuration. The inner five Ni(II) ions displayed short Ni–N (~1.90 Å) bond distances which are consistent with a square-planar (NiN_4), diamagnetic arrangement of a low-spin Ni(II) configuration. The magnetic measurement of (**1**) shows an antiferromagnetic interaction of two terminal high-spin Ni(II) ions with the coupling constant J = -3.8 cm^{-1}. The Ni–Ni, Ni–N distances and magnetic behavior among tri-, penta-, and hepta-nickel(II) complexes are compared and discussed.

INTRODUCTION

Metal string complexes are highly interesting in the fundamental study of metal-metal interactions[1-11] and in their potential application as a molecular metal wire. Developing a new type of ligands, namely oligo-α-pyridylamino ligands, which might bind metal ions in a string[1,8-11] is our goal. In our past effort, the tri-nuclear metal $[M_3(dpa)_4X_2]$ (M = Cr,[2] Co,[3,4] Ni,[5] Cu,[6] Ru,[7] Rh[7]) complexes and pentanuclear metal $[M_5(tpda)_4X_2]$ (M = Cr,[8] Co,[9,10] Ni[9,10]) complexes have been successfully synthesized. The M–M distances obtained from structural analysis and bonding characterization obtained from qualitative molecular orbital analysis have provided a reasonable explanation on the relationship between bond order and d^n electrons of metal center in $[M_3(dpa)_4X_2]$ complexes. In order to extend the metal chain and study the M–M bonding, two heptanuclear nickel(II) complexes, $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$[11] and $[Ni_7(\mu_7\text{-teptra})_4(NCS)_2]$ were synthesized and characterized by structural analysis. The M–M, M–N bond distances and magnetic behavior among tri-, penta-, and heptanickel(II) complexes will also be compared and discussed in detail.

EXPERIMENTAL SECTION

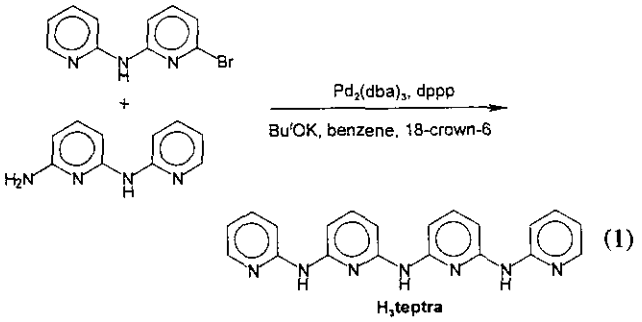
Spectroscopic Measurement

The infrared spectra were recorded on a Nicolet Fourier transform IR MAGNA-IR 500 spectrometer in the range of 500-4000 cm^{-1} using the KBr disk technique. UV-visible spectra were recorded on a Hewlett-Packard (HP) 8453 spectrophotometer; maxima are listed in the form λ_{max} (nm) (ε ($M^{-1}cm^{-1}$). The ^1H and ^{13}C NMR spectrum of H_3teptra was measured on a Brucker AMX 200 spectrometer. The temperature-dependent magnetic susceptibility was measured on the SQUID system with a 10,000 Gauss external magnetic field. Molar magnetic susceptibility was recorded every 5K in the range of 5-300K. Elemental analyses for $[Ni_7(teptra)_4Cl_2]$, (**1**) and $[Ni_7(teptra)_4(NCS)_2]$, (**2**) were satisfactory.

Preparation of Tetrapyridinrtriamine (H_3teptra) Ligand

The tetrapyridinetriamine (H_3teptra) ligand was synthesized by the palladium-catalyzed cross-coupling[12] of (6-bromo-2-pyridyl)(2′-pyridyl)amine and (6-amino-2-pyridyl)(2′-pyridyl)amine in the presence of catalyst $[Pd_2(dba)_3$,

dppp, Bu^{t}OK, and 18-crown-6] in refluxing benzene [Equation (1)]. The crude product was re-crystallized from propan-2-ol. H_3teptra was characterized on the basis of ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. IR (KBr): ν = 3190, 3069, 3019 (NH), 1595, 1576, 1517 (C=C) cm^{-1}. MS (FAB) [*m/z* (%)]: 356 (100), [M+1]$^+$. The ^{1}H NMR in $(CD_3)_2SO$ clearly shows two singlets (δ 9.33, 9.07), four doublets (δ 8.19, 7.88, 7.72, 7.10) and three triplets (δ 7.62, 7.50, 6.84) which are consistent with the structural assignment.



(1)

Preparation of [Ni$_7$(teptra)$_4$Cl$_2$] (1)

$NiCl_2 \cdot 6H_2O$ (1.659 g, 7 mmole) and H_3teptra (1.42 g, 4 mmole) were placed in an Erlemyer flask, to which naphthalene (7.2 g) was added. The mixture was heated (ca. 160-180 °C) for 10 minutes to remove water. Then *n*-butanol (3 mL) was added to the heated mixtures, and heating was continued until the *n*-butanol had almost completely evaporated. A solution of potassium *t*-butoxide (1.32 g, 12 mmole) in *t*-butanol (20 mL) was added dropwise. Heating was continued until the remaining *n*-butanol had evaporated completely. After the mixture had cooled, *n*-hexane was added to wash out the naphthalene. The remaining solid was extracted with CH_2Cl_2 and re-crystallized from $CHCl_3$/*n*-hexane. A deep purple crystal was then obtained (yield 10%). IR (KBr) ν = 1596, 1579, 1545 cm^{-1} (C=C). MS (FAB) [*m/z* (%)]: 1890 (90) [M]$^+$, 1855 (40) [M–Cl]$^+$. The electronic spectrum (CH_2Cl_2 solution, 5 × 10^{-5} M) shows maxima at λ = 268 nm (ε 1.06 × 10^5 M^{-1} cm^{-1}), 385 nm (ε 1.15 × 10^5 M^{-1} cm^{-1}), 550 nm (ε 1.05 × 10^4 M^{-1} cm^{-1}), 611 nm (ε 9.07 × 10^3 M^{-1} cm^{-1}).

Preparation of [Ni$_7$(teptra)$_4$(NCS)$_2$] (2)

NaSCN (45.36 mg, 0.56 mmol) was added to the deep purple solution of [Ni$_7$(teptra)$_4$Cl$_2$] (52.92 mg, 0.028 mmol) in an Erlemeyer flask (30 mL of THF). The solution was stirred about 48 hours and then 50 mL of water added to dissolve the unreacted NaSCN. The solution was extracted three times by 60 mL of CH_2Cl_2. Na_2SO_2 was added to the organic layer to remove the water. The solution was concentrated, and a deep purple powder was obtained. The powder was re-crystallized from a $CHCl_3$/*n*-hexane solution. Deep purple crystals were obtained (yield 20%). IR (KBr): ν = 1591, 1562, 1541 (C=C), 2057 (C≡N) cm^{-1}. MS (FAB) [*m/z* (%)]: 1935 (1), [M]$^+$; 1877 (1), [M–SCN]$^+$. The electronic spectrum (CH_2Cl_2 solution, 1.25 × 10^{-5} M) shows maxima at λ = 263 nm (ε 1.17 × 10^5 M^{-1} cm^{-1}), 341 nm (ε 7.08 × 10^4 M^{-1} cm^{-1}), 389 nm (ε 1.14 × 10^5 M^{-1} cm^{-1}), 548 nm (ε 1.11 × 10^4 M^{-1} cm^{-1}), 598 nm (ε 1.05 × 10^4 M^{-1} cm^{-1}).

Crystallographic Procedure

Data collection were carried out on a Siemens SMART diffractometer with a CCD detector with Mo radiation (λ = 0.71073 Å) at room temperature. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each; each frame corresponds to a 0.3° scan in 20 s, followed by spot integration and least-squares refinement. For each structure, data were measured using ω scans of 0.3° per frame for 20 s for (1) and 40 s for (2), respectively, until three runs of different Phi angles had been collected. The detector was put at the position of 4.0 cm. Cell parameters were retrived using SMART[13] software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT[14] software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[15] Detailed crystal data of (1) and (2) are listed in Table 1.

Crystal Data for (1)·3CHCl$_3$

A deep purple crystal of approximately the dimensions of 0.35 × 0.18 × 0.15 mm was mounted on a glass capillary. A total of 38984 reflections were collected with a final resolution of 0.75 Å and 16710 unique reflections (2θ < 55°, R_{int} = 0.063) were used in the refinement. Sadabs absorption correction (T_{min} = 0.61, T_{max} = 0.80) and full matrix least-squares refinement on F^2 converged to R_F = 0.151 (all data), 0.082 (I > 2σ(I)); R_{wF^2} = 0.302 (all data), 0.246 (I > 2σ(I)). The non-hydrogen atomic coordinates of (1)·3CHCl$_3$ are listed in Table 2.

Crystal Data for (2)·4CHCl$_3$

A deep purple crystal of approximately the dimensions of 0.2 × 0.2 × 0.03 mm was mounted on a glass capillary. A total of 37352 reflections were collected with a final resolution of 0.75 Å and 13502 unique reflections (2θ < 55°, R_{int} = 0.132) were used in the refinement. Sadabs absorption correction (T_{min} = 0.33, T_{max} = 0.80) and full matrix least-squares refinement on F^2 converged to R_F = 0.184 (all data), 0.092 (I > 2σ(I)); R_{wF^2} = 0.327 (all data), 0.264 (I > 2σ(I)).

Table 1. Crystal Data for Compounds (**1**) and (**2**)

Compound	(**1**)·3CHCl$_3$	(**2**)·4CHCl$_3$
Formula	$C_{83}H_{59}Cl_{11}N_{28}Ni_7$	$C_{86}H_{60}Cl_{12}N_{30}Ni_7S_2$
Formula weight	2249.50	2414.13
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 2$_1$/n	P 2$_1$/n
Color of crystal	deep purple	deep purple
a (Å)	19.7542(7)	24.4032(3)
b (Å)	16.9432(5)	16.3945(2)
c (Å)	28.5946(9)	24.4870(1)
β (°)	95.868(1)	106.381(1)
V (Å^3)	9520.4(5)	9399.0(2)
Z	4	4
Absorption Coefficient (mm^{-1})	1.722	1.822
F (000)	4544	4872
Crystal size (mm)	0.35 × 0.18 × 0.15	0.2 × 0.2 × 0.3
θ range for data collection (°)	1.20-25.03	1.04-23.26
Reflection collected	38984	37352
Independent reflections	16710 (R_{int} = 0.0626)	13502 (R_{int} = 0.1322)
Absorption correction	Sadabs	Sadabs
Max. and min. transmission	0.8017, 0.6062	0.8015, 0.3279
R_F, R_{wF^2} (all data)	0.1506, 0.3020	0.1839, 0.3265
R_F, R_{wF^2} ($I > 2\sigma(I)$)	0.0824, 0.2460	0.0916, 0.2638
GOF	1.072	1.004
Extinction coefficient	0.0012(2)	0.00016(10)

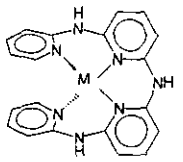
$R_F = \Sigma|F_o-F_c|/\Sigma|F_o|$; $R_{wF^2} = [\Sigma w|F_o^2-F_c^2|^2/\Sigma wF_o^4]^{1/2}$

The non-hydrogen atomic coordinates of (**2**)·4CHCl$_3$ are listed in Table 3.

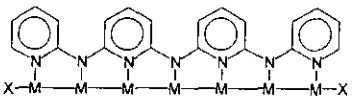
RESULTS AND DISCUSSION

Synthesis of All-*Anti* Form and All-*Syn* Form Complexes

The coordination chemistry of the H$_3$teptra ligand can be divided into two types of bonding modes. One is the all-*anti* form **I**, the other is the all-*syn* form **II**.



Form I (all-*anti*)



Form II (all-*syn*)

The mononuclear metal complexes as in form **I** can be synthesized by a conventional method with equimolar amounts of M(ClO$_4$)$_2$·nH$_2$O with an H$_3$teptra ligand.[1] The H$_3$teptra can act as a tetra-dentate ligand binding with the metal ions through the nitrogen atoms of pyridine moieties. The metal ions can bind with one H$_3$teptra ligand to form three types of metal complexes of [M(teptra)](ClO$_4$)$_2$ (M = Fe[16], Cu[1]), [M(teptra)L](ClO$_4$)$_2$ (M = Co, L = Cl$^-$; M = Zn, L = CH$_3$CN)[16], and [M(teptra)L$_1$L$_2$](ClO$_4$)$_2$ (M = Mn, L$_1$ = H$_2$O, L$_2$ = CH$_3$OH; M = Fe, Co, Ni, L$_1$ = H$_2$O, L$_2$ = CH$_3$CN)[16].

The all-*syn* form hepta-nuclear nickel(II) complexes of **II** can be obtained by a specific synthetic method in which the Bu^{t}OK is used to deprotonate the H$_3$teptra ligand under heating with naphthalene.[11] The teptra^{3-} ligand acts as a heptadentate ligand to bind with seven Ni ions. Both of the infrared spectra of (**1**) and (**2**) compounds are similar except for the axial ligand's vibration. The N–H stretching bands of H$_3$teptra in the 3190 cm^{-1} region are completely absent, and the C–C vibrational modes of the pyridine ring are shown in the range of 1200-1600 cm^{-1}. The MS (FAB) of parent peaks of [Ni$_7$(teptra)$_4$Cl$_2$] and [Ni$_7$(teptra)$_4$(NCS)$_2$] are observed at *m/z* 1890 and 1935, respectively, and are consistent with the simulated patterns.

Structural Results

Both the space group of complex (**1**) and (**2**) is P 2$_1$/n with a whole molecule and three CHCl$_3$ molecules for (**1**)

Table 2. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^{31}$] for **1**. U(eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	U(eq)
Ni(1)	8362(1)	8469(1)	-2230(1)	46(1)
Ni(2)	8395(1)	8091(1)	-1425(1)	37(1)
Ni(3)	8417(1)	7715(1)	-648(1)	33(1)
Ni(4)	8437(1)	7358(1)	102(1)	50(1)
Ni(5)	8434(1)	7007(1)	849(1)	34(1)
Ni(6)	8436(1)	6641(1)	1625(1)	39(1)
Ni(7)	8449(1)	6248(1)	2422(1)	52(1)
Cl(1)	8308(2)	8834(2)	-3033(1)	71(1)
Cl(2)	8453(2)	5837(2)	3210(1)	83(1)
N(1)	7797(4)	9441(4)	-1993(2)	47(2)
N(2)	8210(4)	9129(4)	-1232(2)	47(2)
N(3)	8570(4)	8795(4)	-454(2)	39(2)
N(4)	8893(4)	8310(4)	287(2)	41(2)
N(5)	9157(4)	7726(4)	1019(2)	37(2)
N(6)	9336(4)	7033(4)	1726(2)	46(2)
N(7)	9510(5)	6300(5)	2409(2)	56(2)
N(8)	8950(4)	7435(5)	-2275(2)	46(2)
N(9)	8579(4)	7014(4)	-1567(2)	45(2)
N(10)	8268(4)	6642(4)	-834(2)	40(2)
N(11)	7977(4)	6390(4)	-88(2)	41(2)
N(12)	7711(4)	6279(4)	676(2)	42(2)
N(13)	7546(4)	6264(4)	1474(3)	48(2)
N(14)	7391(5)	6301(5)	2262(3)	58(2)
N(15)	7489(4)	7749(4)	-2296(2)	48(2)
N(16)	7449(4)	7862(5)	-1495(2)	47(2)
N(17)	7451(3)	7875(4)	-680(2)	40(2)
N(18)	7574(4)	7876(5)	137(3)	48(2)
N(19)	7789(4)	7821(4)	941(2)	41(2)
N(20)	8095(4)	7665(4)	1745(3)	48(2)
N(21)	8449(5)	7477(5)	2529(3)	58(2)
N(22)	9266(4)	9049(4)	-1990(2)	45(2)
N(23)	9350(4)	8283(4)	-1310(2)	42(2)
N(24)	9379(3)	7549(4)	-619(2)	34(2)
N(25)	9311(4)	6853(4)	68(2)	41(2)
N(26)	9099(4)	6220(4)	758(2)	38(2)
N(27)	8784(4)	5667(4)	1451(2)	49(2)
N(28)	8447(4)	5107(4)	2122(3)	51(2)
C(1)	7426(5)	9888(6)	-2305(3)	55(3)
C(2)	6992(6)	10478(7)	-2185(4)	68(3)
C(3)	6935(6)	10603(6)	-1721(4)	69(3)
C(4)	7347(5)	10155(6)	-1389(3)	59(3)
C(5)	7791(5)	9599(6)	-1533(3)	49(2)
C(6)	8415(4)	9367(5)	-779(3)	39(2)
C(7)	8530(5)	10169(5)	-637(3)	54(3)
C(8)	8747(5)	10328(5)	-182(3)	52(2)
C(9)	8880(5)	9738(5)	146(3)	50(2)
C(10)	8816(4)	8945(5)	1(3)	37(2)
C(11)	9314(4)	8307(5)	704(3)	42(2)
C(12)	9890(5)	8777(5)	817(3)	47(2)
C(13)	10269(5)	8685(6)	1235(3)	53(2)
C(14)	10086(5)	8137(6)	1555(3)	55(3)
C(15)	9547(5)	7630(5)	1437(3)	39(2)
C(16)	9796(6)	6651(6)	2042(3)	52(2)
C(17)	10491(6)	6573(6)	2001(4)	63(3)
C(18)	10896(6)	6189(7)	2347(4)	74(3)
C(19)	10609(7)	5857(7)	2725(4)	75(3)
C(20)	9937(7)	5916(7)	2738(4)	69(3)
C(21)	9325(6)	7356(6)	-2624(3)	60(3)
C(22)	9766(6)	6734(8)	-2659(4)	75(3)
C(23)	9807(6)	6162(7)	-2308(4)	68(3)
C(24)	9402(5)	6237(6)	-1950(3)	58(3)
C(25)	8968(5)	6877(5)	-1931(3)	45(2)
C(26)	8373(5)	6425(5)	-1292(3)	43(2)
C(27)	8221(6)	5662(6)	-1442(3)	63(3)
C(28)	8025(6)	5108(6)	-1129(4)	72(3)
C(29)	7967(5)	5332(6)	-671(3)	58(3)
C(30)	8045(5)	6097(5)	-527(3)	43(2)
C(31)	7574(4)	6048(5)	224(3)	40(2)
C(32)	7046(6)	5536(7)	109(4)	71(3)
C(33)	6682(6)	5229(8)	454(4)	81(4)
C(34)	6840(6)	5436(7)	916(4)	69(3)
C(35)	7348(5)	5986(6)	1025(3)	48(2)
C(36)	7100(5)	6311(6)	1805(4)	56(3)
C(37)	6389(6)	6415(8)	1705(4)	81(4)
C(38)	5980(7)	6513(8)	2074(6)	92(4)
C(39)	6294(8)	6516(7)	2536(5)	83(4)
C(40)	6967(7)	6417(7)	2604(4)	71(3)
C(41)	7278(6)	7408(7)	-2711(4)	69(3)
C(42)	6784(6)	6878(8)	-2776(4)	79(4)
C(43)	6451(6)	6616(7)	-2376(4)	70(3)
C(44)	6670(6)	6953(6)	-1954(4)	66(3)
C(45)	7186(5)	7543(6)	-1918(3)	49(2)
C(46)	7086(4)	7917(6)	-1113(3)	46(2)
C(47)	6388(5)	8044(7)	-1142(4)	67(3)
C(48)	6072(5)	8080(8)	-732(4)	75(3)
C(49)	6431(5)	8016(7)	-299(4)	68(3)
C(50)	7140(5)	7931(6)	-274(3)	49(2)
C(51)	7430(5)	8165(5)	570(3)	45(2)
C(52)	6993(6)	8774(6)	628(4)	62(3)
C(53)	6874(7)	8994(7)	1082(4)	78(4)
C(54)	7214(5)	8608(6)	1453(4)	61(3)
C(55)	7703(5)	8046(5)	1392(3)	46(2)
C(56)	8271(5)	7994(6)	2177(3)	51(2)
C(57)	8324(5)	8808(6)	2267(3)	54(3)
C(58)	8511(6)	9096(7)	2691(4)	71(3)
C(59)	8673(7)	8575(8)	3062(4)	87(4)
C(60)	8662(7)	7780(7)	2958(4)	75(3)
C(61)	9499(6)	9614(6)	-2255(4)	62(3)
C(62)	10080(6)	10035(7)	-2127(4)	66(3)
C(63)	10444(6)	9879(6)	-1692(4)	63(3)
C(64)	10200(5)	9302(6)	-1413(3)	55(3)
C(65)	9627(5)	8874(5)	-1570(3)	48(2)
C(66)	9735(5)	7867(5)	-969(3)	42(2)
C(67)	10415(5)	7713(6)	-969(3)	50(2)
C(68)	10770(5)	7362(6)	-577(4)	59(3)
C(69)	10431(5)	7097(6)	-209(3)	51(2)
C(70)	9726(4)	7150(5)	-248(3)	36(2)
C(71)	9519(5)	6268(5)	397(3)	43(2)
C(72)	10028(5)	5722(5)	368(3)	52(2)
C(73)	10132(5)	5130(6)	698(4)	58(3)
C(74)	9718(5)	5080(6)	1067(3)	58(3)
C(75)	9200(5)	5619(5)	1093(3)	45(2)

C(76)	8622(5)	4991(5)	1689(3)	48(2)
C(77)	8589(6)	4226(6)	1492(4)	62(3)
C(78)	8421(6)	3600(6)	1753(4)	71(3)
C(79)	8263(7)	3716(7)	2192(4)	80(4)
C(80)	8287(6)	4490(6)	2359(4)	67(3)
C(81)	7138(15)	1417(17)	761(10)	193(10)
C(82)	7445(12)	12865(14)	-868(8)	163(8)
C(83)	3896(22)	4908(26)	1194(14)	310(19)
Cl(3)	7130(6)	2471(8)	845(3)	302(5)
Cl(4)	6948(9)	1090(8)	289(4)	415(11)
Cl(5)	7937(7)	1124(9)	936(5)	398(8)
Cl(6)	7417(6)	13355(4)	-344(2)	261(5)
Cl(7)	8262(5)	12671(7)	-950(3)	288(5)
Cl(8)	6944(9)	12075(6)	-870(4)	394(9)
Cl(9)	4938(11)	4908(13)	1520(7)	499(10)
Cl(10)	4154(11)	4148(14)	947(7)	505(12)
Cl(11)	4387(14)	5630(15)	748(8)	595(14)

and four $CHCl_3$ molecules for (**2**) in the asymmetric unit. Due to the free vibration of the S atom in the NCS^- ligand, the sulfur atoms in compound (**2**) are disordered with 50% of S atoms in one site and 50% of S atoms in the other site. The crystal structures of heptanickel(II) complexes $[Ni_7(\mu_7\text{-teptra})_4X_2]$ are shown in Figs. 1 and 2 for (**1**) and (**2**), respectively. Similar to the geometric conformations of $[Ni_3(\mu_3\text{-dpa})_4X_2]$[5] and $[Ni_5(\mu_5\text{-tpda})_4X_2]$[8,9] complexes, the heptanickel chain is helically wrapped by four *syn-syn-syn-syn-syn-syn* type $teptra^{3-}$ ligands. The complex exhibits approximate D_4 symmetry. The seven Ni(II) ions are collinear. Three values of Ni-Ni distances listed in Table 4 are both found in these two complexes. The longest ones correspond with one Ni ion connected with the axial ligand X^- are 2.383(1), 2.374(2) Å for (**1**) and 2.375(2), 2.354(2) Å for (**2**). They are shorter than those of 2.443(1) and 2.4258(9) Å in $[Ni_3(\mu_3\text{-dpa})_4Cl_2]$[5] and $[Ni_3(\mu_3\text{-dpa})_4(NCS)_2]$, respectively, but are comparable to the outer Ni-Ni distance of 2.385(2) and 2.369(2) Å in $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$ and $[Ni_5(\mu_5\text{-tpda})_4(NCS)_2]$ complexes.[9,10] The intermediate ones are 2.310(1), 2.304(1) Å for (**1**) and 2.300(2), 2.303(2) Å for (**2**), which are comparable to the inner Ni-Ni distance of 2.306(1) and 2.296(2) Å in $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$ and $[Ni_5(\mu_5\text{-tpda})_4(NCS)_2]$ complexes.[9,10] The Ni-Ni distances of the innermost Ni ions are 2.226(2), 2.214(2) Å for (**1**) and 2.194(2), 2.206(2) Å for (**2**), which are the shortest known Ni-Ni distances in any nickel(II) complexes. The comparisons of Ni-Ni distances among tri-, penta-, and heptanickel(II) complexes are clearly shown in Fig. 4. If the Ni-Ni distances are ignored, the inner five Ni ions in both complexes are four-coordinated, square planar conformations. All of the average Ni_{inner}-N bond distances of 1.89-1.92 Å are short, consistent with a low-spin (S = 1), diamagnetic ar-

Table 3. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^3$] for **2**. U(eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	U(eq)
Ni(1)	8313(1)	1869(1)	4304(1)	46(1)
Ni(2)	7387(1)	1312(1)	3907(1)	37(1)
Ni(3)	6491(1)	768(1)	3533(1)	32(1)
Ni(4)	5634(1)	254(1)	3175(1)	59(1)
Ni(5)	4777(1)	-264(1)	2796(1)	29(1)
Ni(6)	3880(1)	-803(1)	2400(1)	32(1)
Ni(7)	2966(1)	-1361(1)	2000(1)	40(1)
S(1)	10174(7)	2952(12)	5145(9)	123(8)
S(2)	1185(16)	-2537(28)	902(12)	87(8)
S(1')	10023(9)	3051(18)	5394(10)	207(16)
S(2')	1180(18)	-2456(26)	1081(12)	97(10)
N(1)	8098(4)	1763(7)	5067(4)	42(3)
N(2)	7388(4)	867(7)	4619(4)	43(3)
N(3)	6640(4)	-13(7)	4154(4)	36(3)
N(4)	5856(4)	-747(6)	3591(4)	34(2)
N(5)	5067(4)	-1346(6)	2992(4)	33(3)
N(6)	4238(4)	-1795(7)	2325(4)	41(3)
N(7)	3430(4)	-2186(7)	1635(4)	43(3)
N(8)	8551(4)	646(7)	4366(4)	48(3)
N(9)	7692(4)	340(7)	3704(4)	40(3)
N(10)	6807(4)	18(6)	3094(4)	33(2)
N(11)	5877(4)	-202(7)	2546(4)	37(3)
N(12)	4919(4)	-336(7)	2056(4)	35(3)
N(13)	3935(4)	-444(7)	1676(4)	40(3)
N(14)	2953(4)	-518(7)	1356(4)	42(3)
N(15)	7859(5)	2976(8)	4149(4)	49(3)
N(16)	7028(4)	2263(7)	4077(4)	46(3)
N(17)	6168(4)	1535(6)	3963(4)	37(3)
N(18)	5384(4)	722(6)	3805(4)	36(3)
N(19)	4615(4)	-176(6)	3528(4)	31(2)
N(20)	3886(4)	-1118(7)	3155(4)	38(3)
N(21)	3196(4)	-2063(7)	2761(4)	38(3)
N(22)	8318(4)	1867(8)	3442(4)	49(3)
N(23)	7348(4)	1706(7)	3165(4)	43(3)
N(24)	6357(4)	1518(6)	2916(4)	35(3)
N(25)	5407(4)	1217(7)	2746(4)	38(3)
N(26)	4464(4)	795(6)	2613(4)	30(2)
N(27)	3569(4)	237(7)	2508(4)	37(3)
N(28)	2733(4)	-405(7)	2472(4)	41(3)
N(29)	9110(5)	2367(7)	4654(4)	49(3)
N(30)	2180(5)	-1865(7)	1641(4)	42(3)
C(1)	8360(6)	2237(9)	5520(6)	60(4)
C(2)	8220(7)	2252(10)	6006(7)	70(5)
C(3)	7738(7)	1775(11)	6037(6)	64(5)
C(4)	7488(6)	1271(10)	5602(6)	56(4)
C(5)	7656(5)	1268(9)	5110(5)	42(3)
C(6)	7078(5)	148(9)	4623(5)	41(3)
C(7)	7182(6)	-412(9)	5079(5)	52(4)
C(8)	6837(6)	-1041(9)	5039(5)	51(4)
C(9)	6378(5)	-1220(9)	4562(5)	43(3)
C(10)	6288(5)	-694(8)	4105(5)	38(3)
C(11)	5584(5)	-1450(8)	3387(5)	35(3)
C(12)	5794(6)	-2222(9)	3524(5)	49(4)

C(13)	5455(6)	-2896(9)	3280(6)	51(4)
C(14)	4939(5)	-2758(9)	2893(5)	45(4)
C(15)	4760(5)	-1996(9)	2723(5)	38(3)
C(16)	3993(5)	-2287(9)	1858(5)	44(4)
C(17)	4303(7)	-2816(11)	1590(6)	69(5)
C(18)	4025(7)	-3218(11)	1112(7)	75(5)
C(19)	3447(7)	-3129(11)	888(6)	68(5)
C(20)	3156(7)	-2606(10)	1149(6)	61(4)
C(21)	9054(6)	392(11)	4738(6)	59(4)
C(22)	9237(6)	-398(12)	4812(7)	72(5)
C(23)	8912(7)	-991(12)	4492(7)	81(6)
C(24)	8369(5)	-757(12)	4094(6)	64(5)
C(25)	8203(6)	61(10)	4038(6)	46(4)
C(26)	7384(5)	-114(9)	3251(5)	46(4)
C(27)	7616(6)	-573(10)	2900(6)	56(4)
C(28)	7259(6)	-950(10)	2436(6)	58(4)
C(29)	6674(6)	-904(10)	2313(5)	56(4)
C(30)	6439(6)	-379(9)	2631(5)	47(4)
C(31)	5466(5)	-290(8)	2020(5)	40(3)
C(32)	5557(5)	-260(10)	1484(5)	58(5)
C(33)	5124(6)	-405(11)	1021(6)	71(5)
C(34)	4555(6)	-463(11)	1073(6)	69(5)
C(35)	4461(5)	-391(8)	1592(5)	40(3)
C(36)	3440(6)	-187(9)	1302(5)	45(4)
C(37)	3402(6)	432(9)	891(6)	55(4)
C(38)	2899(6)	663(10)	543(6)	58(4)
C(39)	2411(7)	357(11)	614(6)	65(5)
C(40)	2458(5)	-250(9)	1001(6)	47(4)
C(41)	8145(7)	3668(11)	4121(6)	68(5)
C(42)	7901(7)	4429(11)	4003(7)	68(5)
C(43)	7301(8)	4453(10)	3884(8)	80(5)
C(44)	7009(7)	3740(10)	3903(6)	60(4)
C(45)	7295(6)	3008(9)	4063(5)	48(4)
C(46)	6503(5)	2227(9)	4192(5)	45(4)
C(47)	6296(6)	2766(10)	4513(6)	59(4)
C(48)	5755(6)	2675(10)	4559(6)	61(4)
C(49)	5415(6)	1997(9)	4307(6)	52(4)
C(50)	5643(5)	1424(8)	4034(5)	32(3)
C(51)	4913(4)	372(7)	3928(5)	31(3)
C(52)	4731(6)	486(9)	4405(5)	46(4)
C(53)	4270(6)	84(10)	4475(5)	57(4)
C(54)	3995(5)	-475(9)	4090(5)	44(4)
C(55)	4157(5)	-607(8)	3592(5)	32(3)
C(56)	3593(5)	-1808(9)	3216(5)	41(3)
C(57)	3750(6)	-2285(10)	3706(6)	57(4)
C(58)	3474(7)	-3001(11)	3725(6)	75(5)
C(59)	3057(7)	-3261(11)	3235(6)	72(5)
C(60)	2944(5)	-2775(9)	2783(6)	46(4)
C(61)	8815(6)	1885(12)	3323(6)	70(5)
C(62)	8877(7)	1830(14)	2801(7)	99(7)
C(63)	8390(7)	1677(13)	2343(7)	90(7)
C(64)	7879(6)	1668(11)	2471(6)	66(5)
C(65)	7833(5)	1769(10)	3005(6)	50(4)
C(66)	6802(5)	1882(9)	2787(5)	40(3)
C(67)	6704(6)	2444(10)	2339(6)	61(4)
C(68)	6146(5)	2597(11)	1992(6)	65(5)
C(69)	5724(6)	2189(9)	2113(6)	54(4)
C(70)	5808(5)	1662(9)	2589(5)	45(4)
C(71)	4823(5)	1437(9)	2622(4)	36(3)
C(72)	4622(5)	2245(9)	2549(5)	50(4)
C(73)	4031(6)	2324(9)	2454(6)	56(4)
C(74)	3677(5)	1693(9)	2433(5)	43(3)
C(75)	3890(5)	938(8)	2521(4)	29(3)
C(76)	3080(5)	218(9)	2678(5)	41(3)
C(77)	2959(5)	739(8)	3094(5)	39(3)
C(78)	2496(7)	659(10)	3253(6)	59(4)
C(79)	2105(6)	5(11)	3014(7)	66(5)
C(80)	2251(5)	-492(10)	2643(6)	55(4)
C(81)	9533(7)	2612(11)	4898(7)	87(6)
C(82)	1758(6)	-2110(9)	1376(6)	58(4)
C(83)	8155(14)	-3039(17)	4605(8)	174(15)
C(84)	5916(9)	-3940(18)	4990(12)	144(10)
C(85)	181	-781	3395	336
C(86)	170	-478	1506	603
C1(1)	7491(4)	-2527(8)	4246(7)	277(7)
C1(2)	8008(5)	-3840(6)	4947(4)	221(5)
C1(3)	8402(5)	-3314(7)	4032(5)	232(5)
C1(4)	5237(4)	-3505(7)	4564(4)	193(4)
C1(5)	5794(5)	-4975(9)	5110(8)	356(10)
C1(6)	6411(4)	-3839(9)	4636(5)	286(7)
C1(7)	64(7)	-1394(12)	3871(7)	367(9)
C1(8)	-341(8)	30(13)	3445(8)	384(9)
C1(9)	651(13)	-226(20)	3428(13)	633(19)
C1(10)	-427	-509	1796	651
C1(11)	796	224	1723	587
C1(12)	368	-1092	1364	648

rangement of nickel(II) configuration.[10,17] The terminal Ni^{II} ions (Ni(1) and Ni(7)) are in a square-pyramidal environment, to give a NiN_4X chromophore. The basal plane consists of four independent $teptra^{3-}$ ligands, and the mean Ni-N distances are about 2.10 Å consistent with a high-spin (S = 1) nickel(II) configuration.[18] These structural analyses of Ni-N bond in heptanickel(II) complexes are similar to those in tri-, pentanickel(II) complexes.[5,10]

The $teptra^{3-}$ ligands act as heptadentate nitrogen chelating ligands. Each ligand is nonplanar, with an average dihedral angle among four pyridine rings of approximately 45° and results in a spiral structure of the two complexes. The molecular structure of the $[Ni_7(teptra)_4]^{2+}$ fragment viewed down the linear metal chain is shown in Fig. 4 and gives a better view of the spiral conformation. If the three negative charges of the $teptra^{3-}$ ligand could be distributed only on the seven nitrogen atoms, there would be 112 resonance structures existing on the $teptra^{3-}$ ligand. According to the statistics of these resonance structures, the probability of negative charge distribution on the seven nitrogen atoms and the π bond order of the ligand are shown in Fig. 5. These charge distributions are qualitatively similar to the calculated net atomic charges obtained from EHMO and Gaussian/DFT calculations.[19] The π bond orders are consistent with the experimental bond lengths in the ligand. These

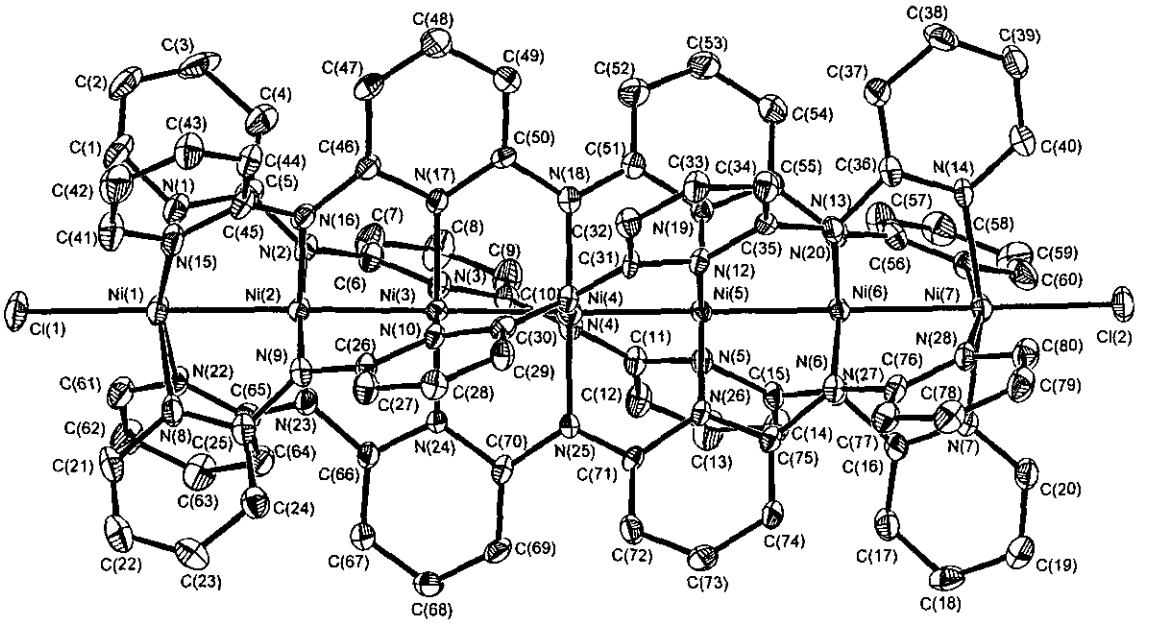


Fig. 1. Crystal structure of $[Ni_7(teptra)_4Cl_2]$ (**1**). Atoms are shown as 20% vibrational thermal ellipsoid.

results indicate that the bonding interaction between the terminal N and Ni atoms should be weaker than the bonding interaction between the central N and Ni atoms. However, this prediction should be reflected directly on the Ni-N distances. From structural analyses, the two terminal Ni-N bond distances (average 2.10 Å) are obviously longer than five central Ni-N bond distances (average 1.91 Å). This result is in good agreement with the prediction according to the charge distribution.

Magnetic Properties of $[Ni_7(teptra)_4Cl_2]$ (1)

The experimental curve of the molar magnetic susceptibility χ_M (O) and effect magnetic moment μ_{eff} (□) with respect to temperature (T) for compound (**1**) are shown in Fig. 6. The experiment curve is almost the same as the one obtained from magnetic simulation[10] (solid line). This result reveals that the electronic configuration of Ni(II) ions derived from structural analyses are in good agreement with the experimental measurement, with five inner Ni(II) ion being in a low-spin (S = 0) states and two terminal Ni(II) ion being in a high-spin (S = 1) states. The coupling constant (J_{17}) obtained form theoretical simulation is -3.8 cm^{-1} indicating a weak anti-ferromagnetic interaction between the two terminal high-spin Ni(II) ions. This interaction is

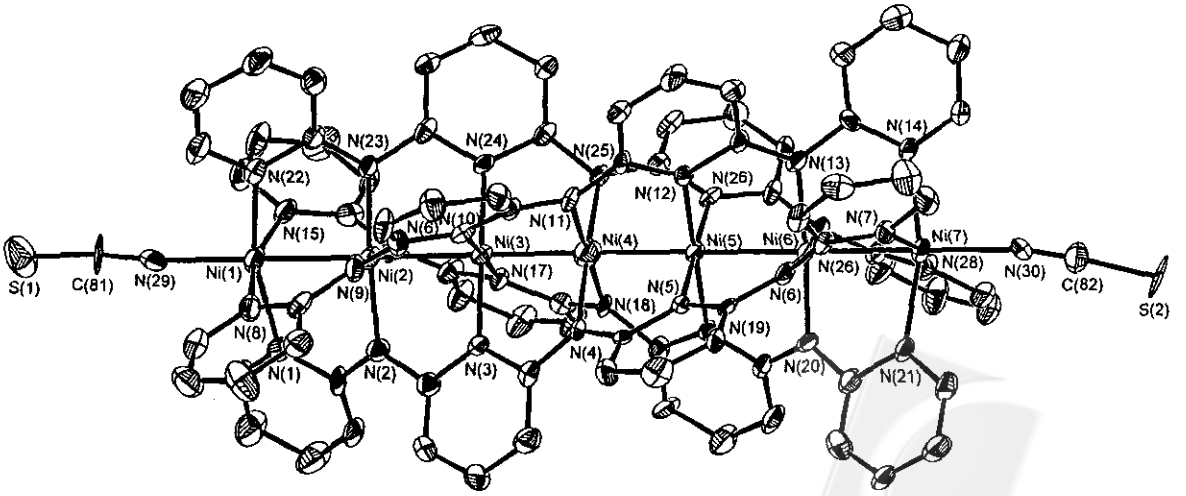


Fig. 2. Crystal structure of $[Ni_7(teptra)_4(NCS)_2]$ (**2**). Atoms are shown as 20% vibrational thermal ellipsoid.

Table 4. Selected Bond Distances and Angles of Compounds (1) and (2)

	(1)	(2)
Ni(1)-Ni(2)	2.383(1)	2.375(2)
Ni(2)-Ni(3)	2.310(1)	2.300(2)
Ni(3)-Ni(4)	2.226(2)	2.194(2)
Ni(4)-Ni(5)	2.214(2)	2.206(2)
Ni(5)-Ni(6)	2.304(1)	2.303(2)
Ni(6)-Ni(7)	2.374(2)	2.354(2)
Ni(1)-$N_{av.}$	2.112(8)	2.10(1)
Ni(2)-$N_{av.}$	1.903(7)	1.89(1)
Ni(3)-$N_{av.}$	1.917(7)	1.93(1)
Ni(4)-$N_{av.}$	1.920(7)	1.93(1)
Ni(5)-$N_{av.}$	1.913(7)	1.93(1)
Ni(6)-$N_{av.}$	1.888(8)	1.90(1)
Ni(7)-$N_{av.}$	2.104(9)	2.11(1)
Ni(1)-Cl(1)	2.369(3)	
Ni(7)-Cl(2)	2.359(3)	
Ni(1)-N(29)		2.06(1)
Ni(2)-N(30)		2.05(1)
Ni(1)-Ni(2)-Ni(3)	179.29(6)	179.40(9)
Ni(2)-Ni(3)-Ni(4)	179.74(7)	179.7(1)
Ni(3)-Ni(4)-Ni(5)	178.87(7)	178.8(1)
Ni(4)-Ni(5)-Ni(6)	179.77(6)	179.9(1)
Ni(5)-Ni(6)-Ni(7)	179.15(6)	179.59(9)
Ni(1)-Ni(2)-Cl(1)	178.9(1)	
Ni(6)-Ni(7)-Cl(2)	179.1(1)	
Ni(1)-Ni(2)-N(29)		179.0(3)
Ni(6)-Ni(7)-N(30)		178.6(3)

smaller than that of J_{15} = -8.3 cm^{-1} in $[Ni_5(tpda)_4Cl_2]$ complex and on order magnitude smaller than that of J_{13} = -99 cm^{-1} in $[Ni_3(dpa)_4Cl_2]$ complex.

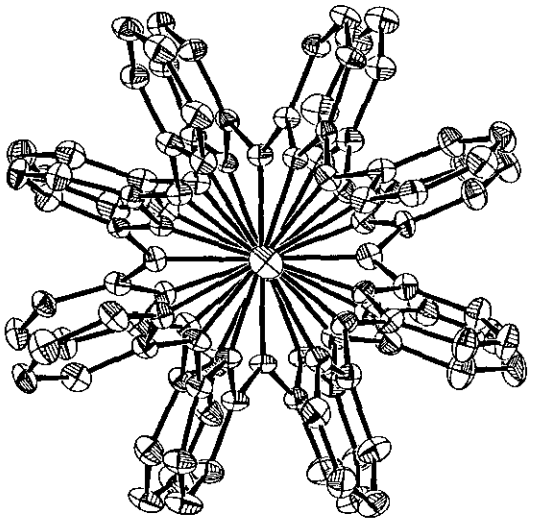


Fig. 3. Helical view of $[Ni_7(teptra)_4Cl_2]$ (1) with the molecule looking down the Ni_7 axis. Atoms are shown as 20% vibrational thermal ellipsoid.

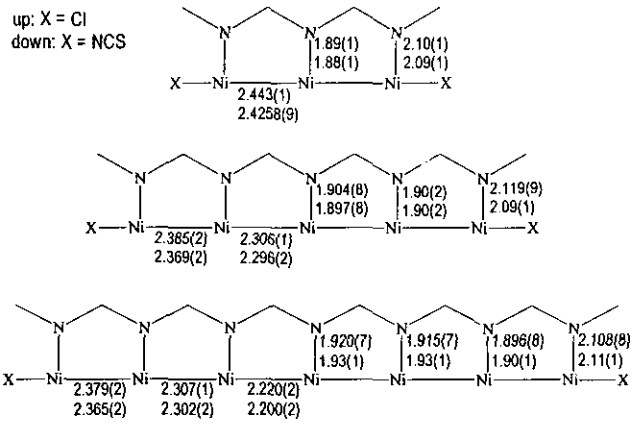


Fig. 4. Comparisons of Ni-Ni, Ni-N distances among tri-, penta- and heptanickel(II) complexes.

CONCLUSION

The linear heptanickel(II) complexes $[Ni_7(teptra)_4X_2]$ ($X = Cl^-, NCS^-$) have been synthesized successfully. The heptanuclear metal chain is helically wrapped by four *syn-syn-syn-syn-syn-syn* type ligands. The structural analyses and electronic configurations are reported and discussed. Three values of Ni-Ni distances are found in these two com-

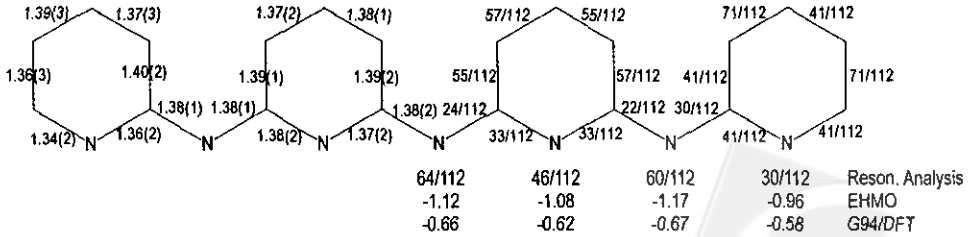


Fig. 5. Left side: Averaged experimental C–C and C–N distances of four $teptra^{3-}$ ligands. Right side: Relative negative charge distributions of N atoms, the C–C and C–N π bond order on the $teptra^{3-}$ ligand according to 112 resonance structures and the net atomic charges of N atoms obtained from EHMO and Gaussian94/DFT calculations.

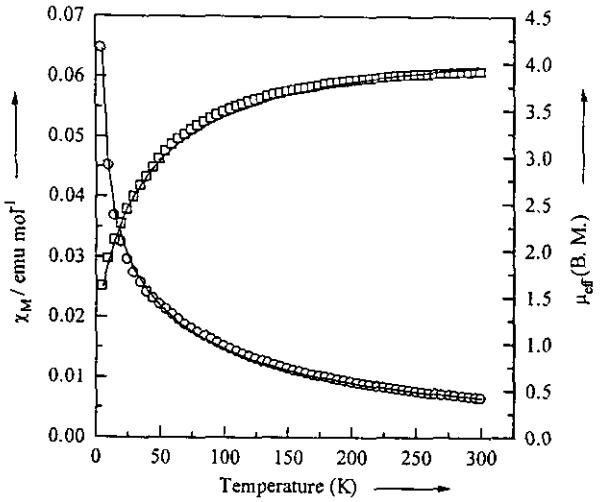


Fig. 6. Magnetic data for $[Ni_7(teptra)_4Cl_2]$ (**1**). The solid line represents the results of theoretical simulation. (O) indicates the observed magnetic susceptibility (χ_M) and (□), the observed effect magnetic moment (μ_{eff}).

pounds and the Ni-Ni distances among tri-, penta-, heptanickel(II) complexes are compared. A weak antiferromagnetic interaction with the negative J_{17} value (-3.8 cm^{-1}) between two terminal high-spin Ni(II) ions is found and the other five center Ni(II) ions are in a low-spin configurations.

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Key Words

Ni–Ni string complexes; Metal-Metal bond; Molecular metalwires; Oligo-α-pyridylamido complexes.

REFERENCES

1. Yang, M. H.; Lin, T. W.; Chou, C. C.; Lee, H. C.; Chang, H. C.; Lee, G. H.; Leung, M. K.; Peng, S. M. *Chem. Commun.* **1997**, 2279.
2. (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *J. Am. Chem. Soc.* **1997**, *119*, 10223. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Chem. Commun.* **1998**, 39.
3. Yang, E. C.; Cheng, M. C.; Tsai, M. S.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2377.
4. (a) Cotton, F. A.; Daniels, L. M.; Jordan, G. T. IV *Chem. Commun.* **1997**, 421. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T. IV; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377.
5. (a) Wu, L. P.; Field, P.; Morrisey, T.; Murphy, C.; Nagle, P.; Hathaway, B.; Simmons, C.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3835. (b) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84.
6. Aduldecha, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1991**, 993.
7. Sheu, J. T.; Liu, C. C.; Chao, I.; Wang, C. C.; Peng, S. M. *Chem. Commun.* **1996**, 315.
8. Chang, H. C.; Lin, T. W.; Li, J. T.; Lee, H. C.; Wang, C. C.; Lee, G. H.; Peng, S. M. *European Journal of Inorganic Chemistry*, **1999**.
9. Shieh, S. J.; Chou, C. C.; Lee, G. H.; Wang, C. C.; Peng, S. M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 56.
10. Wang, C. C.; Lo, W. C.; Chou, C. C.; Lee, G. H.; Chen, J. M.; Peng, S. M. *Inorg. Chem.* **1998**, *37*, 4059.
11. Lai, S. Y.; Lin, T. W.; Chen, Y. H.; Wang, C. C.; Lee, G. H.; Yang, M.-H.; Leung, M. K.; Peng, S. M. *J. Am. Chem. Soc.* **1999**, *121*, 250.
12. Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240.
13. *SMART V 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
14. *SAINT V 4.035 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
15. Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.
16. Chen, Y. H.; Chou, C. C., Wang, C. C.; Peng, S. M., unpublished work.
17. Sacconi, L.; Mani, F.; Bencini, A. in *Comprehensive Coodination Chemistry*, eds. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Pergamon, Oxford, 1987, Vol. 5, section 50.
18. Long, G. J.; Schlemper, E. O. *Inorg. Chem.* **1974**, *13*, 279.
19. The net atomic net charges of the N atoms on $teptra^{3-}$ ligand are [-0.93, -1.17, -1.04, -1.12, -1.11, -1.17, -0.99] and [-0.56, -0.67, -0.62, -0.66, -0.61, -0.66, -0.59] for EHMO and G94/DFT calculations, respectively.