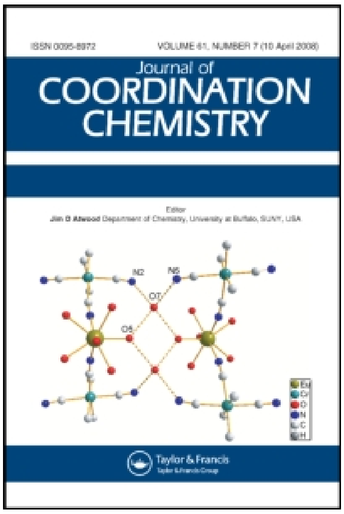

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First heterobimetallic Mn^{II}/M^{II}(M = Cu, Ni) complexes with open-chain aliphatic schiff-base ligands obtained by direct template synthesis

Denys V. Shevchenko[a]; Svitlana R. Petrusenko[a]; Vladimir N. Kokozay[a]; Brian W. Skelton[b]
[a] Department of Inorganic Chemistry, Kyiv National Taras Shevchenko University, Kyiv, 01033 Ukraine [b] Department of Chemistry, University of Western Australia, Crawley, Western Australia 6009, Australia

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FIRST HETEROBIMETALLIC Mn^{II}/M^{II}($M = Cu, Ni$) COMPLEXES WITH OPEN-CHAIN ALIPHATIC SCHIFF-BASE LIGANDS OBTAINED BY DIRECT TEMPLATE SYNTHESIS

DENYS V. SHEVCHENKO[a], SVITLANA R. PETRUSENKO[a,]*,
VLADIMIR N. KOKOZAY[a] and BRIAN W. SKELTON[b]

[a]*Department of Inorganic Chemistry, Kyiv National Taras Shevchenko University, Volodymyrska st. 64, Kyiv, 01033 Ukraine;* [b]*Department of Chemistry, University of Western Australia, Crawley, Western Australia 6009, Australia*

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Four new heterobimetallic complexes $[CuL^1][MnCl_4]$ (**1**), $[CuL^2][MnCl_4]$ (**2**), $[NiL^1][MnCl_4]$ (**3**), $[NiL^2][MnCl_4]$ (**4**) ($L^1 = $4,6,6-trimethyl-1,9-diamino-3,7-di-aza-nona-3-ene; $L^2 = $1,15-dihydroxy-7,9,9-trimethyl-3,6,10,13-tetra-aza-pentadeca-6-ene) have been prepared from elemental metals, ethylenediamine dihydrochloride or its N-(2-hydroxyethyl) derivative and acetone by the template condensation reaction. All complexes have been characterized by elemental analysis, IR and UV-Visible spectroscopy. The structures of **2** and **3** have been determined by X-ray crystallography (**2**: Orthorhombic, $Pna2_1$, a = 20.136(4), b = 11.185(2), c = 10.251(2)Å, Z = 4; **3**: Orthorhombic, $Pca2_1$, a = 14.335(2), b = 11.405(2), c = 11.154(2)Å, Z = 4). Both crystals consist of alternating complex cations $[ML]^{2+}$ and anions $[MnCl_4]^{2-}$ linked together by N–H···Cl–Mn and O–H···Cl–Mn hydrogen bonds forming 2D corrugated sheets in (**2**) and 1D helical chains in (**3**). Complex **2** represents the first single crystal structure elucidation of the complex containing L^2.

Keywords: Heterobimetallic complexes; Direct template synthesis

INTRODUCTION

Heterometallic complexes have received much attention owing to their unique electronic, electrochemical and magnetic properties arising from the metal-metal interaction [1–3]. Macrocyclic and macroacyclic ligands are used for the generation of complexes with peculiar spectroscopic and magnetic properties [4–7]. Template reactions often provide selective routes to these ligands and their metal complexes [8]. Examples of such reactions involving the condensation of amines with acetone and other aliphatic carbonyl compounds have been known since 1960 and are described by Curtis [9]. For the preparation of heterometallic complexes with macrocyclic or macroacyclic ligands usually two or more step syntheses are employed with the initial steps obtaining the homometallic precursor [10–13].

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*Corresponding author. E-mail: spetrusenko@univ.kiev.ua

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In this paper, synthesis of the novel heterometallic complexes [ML][$MnCl_4$] (L^1 = 4,6,6-trimethyl-1,9-diamino-3,7-di-aza-nona-3-ene; L^2 = 1,15-dihydroxy-7,9,9-trimethyl-3,6,10,13-tetra-aza-pentadeca-6-ene; M = Cu, Ni) involving a new "one-pot" synthetic approach termed the "direct template synthesis" is reported. In this method, elemental metals are used as starting materials.

EXPERIMENTAL

Materials and Instruments

Freshly prepared nickel, obtained by treatment of nickel aluminium alloy with excess aqueous alkaline solution, was used. The remaining nickel was washed without filtration three times with water and twice with the solvent to be used in the synthesis and then used immediately in the synthesis. **(Caution: Dry nickel powder obtained in this way is flammable!)** N-(2-hydroxyethyl)-ethylenediamine dihydrochloride was obtained by the evaporation of an aqueous solution of N-(2-hydroxyethyl)-ethylenediamine and hydrochloric acid (1:2), under reduced pressure, and then recrystallized from methanol. Other reagents and solvents were used as received. All experiments were carried out in air. Elemental analyses for the metals were performed by atomic absorption spectroscopy. The chloride anion was determined by standard titrimetric method. Infrared spectra were recorded as KBr discs on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. UV-Vis spectra were recorded on a LOMO SF-46 spectrophotometer in the 250–1100 nm region.

Preparation of [CuL^1][$MnCl_4$] (1)

Copper powder (0.15 g, 2.5 mmol), manganese powder (0.14 g, 2.5 mmol), ethylenediamine dihydrochloride (0.64 g, 5.0 mmol), 1 mL of acetone and 10 mL of dimethylsulfoxide were heated to 60°C and magnetically stirred until total dissolution of the metals was observed (60 min). The resulting solutions were filtered and slowly layered with 30 mL of a 2-propanol – diethyl ether (1:3 v/v) mixture. The crystalline violet product of **1** formed after 2 days, was filtered off, washed with diethyl ether then dried in air. Yield: 0.75 g (64 %). Anal. Calcd. for $C_{10}H_{24}N_4Cl_4CuMn$ (%): Cl, 30.78; Cu, 13.79; Mn, 11.93. Found: Cl, 30.7; Cu, 13.6; Mn, 11.6; IR (KBr, cm^{-1}): 3320–3150 [$\nu(NH_2)$, $\nu(NH)$]; 1660 [$\nu(C=N)$]; 1590 [$\delta(NH_2)$]; electronic spectrum (nm) (ε, $M^{-1}cm^{-1}$) (dmf): 268(3600), 576(125).

Preparation of [CuL^2][$MnCl_4$] (2)

Copper powder (0.16 g, 2.5 mmol), manganese powder (0.14 g, 2.5 mmol), N-(2-hydroxyethyl)-ethylenediamine dihydrochloride (0.88 g, 5.0 mmol), 1 mL of acetone and 10 mL of acetonitrile were heated to 50 °C and magnetically stirred until total dissolution of the metals was observed (30 min). The resulting dark blue product was filtered off, washed with diethyl ether then dried in air. Crystals of **2** suitable for X-ray diffraction were obtained from dmso solution by layering with 10 mL of diethyl ether within 5 days. Yield: 1.1 g (80%). Anal. Calcd. for $C_{14}H_{32}N_4O_2Cl_4CuMn$ (%): Cl, 25.28; Cu, 11.58; Mn, 10.01. Found: Cl, 25.5; Cu, 11.2; Mn, 9.7. IR (KBr, cm^{-1}): 3385

[ν(OH)]; 3290–3200 [ν(NH)]; 1670 [ν(C=N)]; electronic spectrum (nm) (ε, $M^{-1}cm^{-1}$) (dmf): 269(5460), 560(114).

Preparation of [NiL^1][MnCl$_4$] (3)

Yellow crystals of **3** suitable for X-ray diffraction analysis were obtained by a procedure similar to that for **1**, using freshly prepared nickel powder (0.14 g, 2.5 mmol) instead of copper powder, with most of the metal dissolving within 90 min. Yield: 0.70 g (64%). Anal. Calcd. for $C_{10}H_{24}N_4Cl_4MnNi$ (%): Cl, 31.11; Mn, 12.05; Ni, 12.87. Found: Cl, 30.9; Mn, 12.0; Ni, 12.8. IR (KBr, cm^{-1}): 3270–3220 [ν(NH$_2$)]; 3150 [ν(NH)]; 1670 [ν(C=N)]; 1600 [δ(NH$_2$)]; electronic spectrum (nm) (ε, $M^{-1}cm^{-1}$) (dmf): 270(1450), 440(52).

Preparation of [NiL^2][MnCl$_4$] (4)

The pink crystalline product of **4** was obtained by a procedure similar to **1**, using freshly prepared nickel powder (0.14 g, 2.5 mmol) and N-(2-hydroxyethyl)-ethylenediamine dihydrochloride (0.88 g, 5.0 mmol) instead of copper powder and ethylenediamine dihydrochloride. Dissolution of almost all of the metals was observed in 90 min. Yield: 0.61 g (47 %). Anal. Calcd. for $C_{14}H_{32}N_4O_2Cl_4MnNi$ (%): Cl, 26.07; Mn, 10.10; Ni, 10.79. Found: Cl, 25.9; Mn, 10.0; Ni, 10.5. IR (KBr, cm^{-1}): 3470–3150 [ν(OH), ν(NH)]; 1665 [ν(C=N)]; electronic spectrum (nm) (ε, $M^{-1}cm^{-1}$) (dmf): 265(181), 543(13), 755(6), 1000(3).

X-Ray Structure Determinations

All measurements were performed at 150K on a Bruker SMART CCD diffractometer operating in the ω scan mode equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The data were collected to a maximum 2θ value of 50 (**2**) and 58 (**3**)°. The data were corrected for the effects of absorption using the multi-scan method. The structures were refined by full-matrix least-squares methods on F using XTAL3.7 [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the difference Fourier maps and included in the model at ideal positions. In (**2**), the carbon atoms C2–C6 of one ligand were found to be disordered over two sites, each being assigned occupancy factors of 0.5 after initial trial refinement. Diamond 2.1 [15] program was used to create the molecular graphics and prepare the material for publication. A summary of the crystal data and details of the structure refinement are given in Table I.

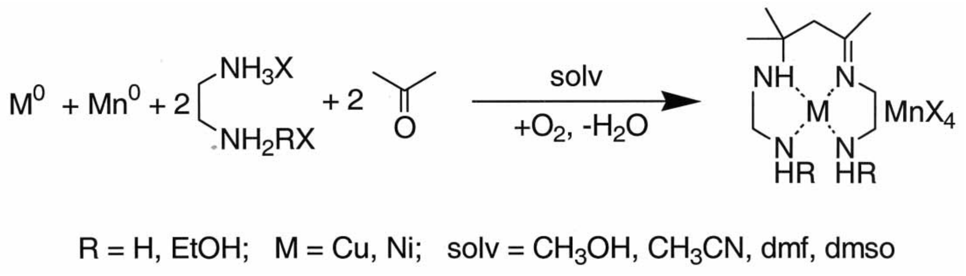
RESULTS AND DISCUSSION

Syntheses and Spectroscopic Characterisation

The reaction of nickel or copper powder, manganese powder, ethylenediamine dihydrochloride or its N-(2-hydroxyethyl) derivative and acetone in a non aqueous solvent, in air, yields the heterobimetallic complexes **1**–**4** with open-chain aliphatic Schiff-base ligands, as shown in Scheme 1. This reaction takes place in a variety of solvents,

TABLE I Crystallographic data

	2	**3**
Empirical formula	$C_{14}H_{32}Cl_4CuMnN_4O_2$	$C_{10}H_{24}Cl_4MnN_4Ni$
M	548.73	455.77
Crystal size (mm)	0.18 × 0.12 × 0.10	0.48 × 0.42 × 0.15
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pna2₁*	*Pca2₁*
a(Å)	20.136(4)	14.335(2)
b(Å)	11.185(2)	11.405(2)
c(Å)	10.251(2)	11.154(2)
$V(\text{Å}^3)$	2308.7(8)	1823.6(5)
Z	4	4
D_{calc} ($g\,cm^{-3}$)	1.579	1.66
μ (mm^{-1})	1.947	2.305
F(000)	1128	932
θ scan range (°)	2.0–25.0	1.8–29.0
Reflections collected	21061	17802
Reflections unique	2145	2480
R_{int}	0.116	0.053
Variables	226	180
Final *R* indices	$R1 = 0.068$	$R1 = 0.042$
$[I > 2\sigma(I)]$	$wR2 = 0.097$	$wR2 = 0.049$
R indices (all data)	$R1 = 0.092$	$R1 = 0.055$
	$wR2 = 0.116$	$wR2 = 0.052$
G.O.F. (*F*)	1.28	1.02
$\Delta(\rho)$ ($e\cdot\text{Å}^{-3}$)	+0.755, −0.596	+0.926, −0.550



SCHEME I

methanol, acetonitrile, dimethylformamide as well as dimethylsulfoxide. Dissolution of copper and manganese in these solvents is complete within 30–60 minutes and the heterobimetallic complexes were isolated in satisfactory yields (> 60%). In the preparation of **1** in methanol, the blue copper homometallic complex $[Cu(en)_2(CH_3OH)_2]Cl_2$ is formed as a by-product. The shortest time observed for complete dissolution of nickel (90 min) was observed when dimethylsulfoxide was used as a solvent and freshly prepared nickel is employed. In others solvents the time required for complete dissolution increases to 4–6 hours. Non-activated nickel can also be used in the syntheses, but longer time (3–4 hours) was needed for complete dissolution in DMSO. In other solvents, 8–10 hours are required probably due to the passivation of the nickel surface by an oxide film. Manganese dissolves within the first 30–60 minutes of the reaction, when copper is involved. Yields of nickel manganese heterobimetallic complexes are about 50–60%. Incomplete isolation of these complexes can be explained by their high solubility in the solvent used.

IR spectra of all complexes show the stretching vibrations of the azomethine group $\nu(C=N)$ at 1660–1670 cm^{-1}. The vibration band of the secondary amine group ν(N-H) at 3150 cm^{-1} appears in the spectra of the complexes synthesized from ethylenediamine (**1** and **3**). The peak at 1600–1590 cm^{-1}, which is attributed to $\delta(NH_2)$ in N-(2-hydroxyethyl)-ethylenediamine, is absent in the spectra of **2** and **4**. The absorbance at 3350–3450 cm^{-1} confirms that the OH groups are not deprotonated in these complexes.

UV-Vis spectra of the copper(II) complexes **1** and **2** in dmf solution display weak broad absorptions with λ_{max} at 576 and 560 nm, respectively, which can be attributed to the *d-d* transitions of Cu(II) in an elongated tetragonal octahedral environment [16, 17]. Comparing these data with the spectra of the complexes $[CuL^1][ZnCl_4]$ and $[CuL^2](NO_3)_2$ in aqueous solutions (λ_{max} at 530 [18] and 565 nm [19], respectively) demonstrates coordinating solvents have more effect on $[CuL^1]^{2+}$ than $[CuL^2]^{2+}$. The band with a λ_{max} at 440 nm in the spectrum of complex **3** in dmf solution is typical for Ni(II) ion in 4N square-planar coordination [9, 17]. The similar complex $[NiL^1][ZnCl_4]$ in water has an absorption band with a very similar value of λ_{max} (434 nm) [18], this demonstrating less tendency of $[NiL^1]^{2+}$ than $[CuL^1]^{2+}$ to structural change in solution. The absorptions of **4** are found with λ_{max} at 543, 755 and 1000 nm indicating octahedral geometry for Ni(II) [17]. In accord with the literature [9], the intense bands around 265-270 nm can be assigned to charge-transfer transitions for the copper(II) complexes and to transitions involving the azomethine chromophore of ligands for the nickel(II) complexes.

Description of the Crystal Structures of 2 and 3

The crystal structure of **2** is shown in Figs. 1 and 2; selected bond distances and angles are listed in Table II.

The main structural blocks in the crystal of **2** are $[CuL^2]^{2+}$ cations and $[MnCl_4]^{2-}$ anions (Figs. 1 and 2). The coordination environment of Cu(II) atom is formed by six (4N + 2O) donor atoms of L^2. The geometry of the CuN_4O_2 chromophore is best described as an elongated tetragonal octahedron (ETO) with four nitrogen atoms (from three amine and one imine groups) in the equatorial plane and two oxygen atoms (from hydroxo groups) in axial positions. The Cu–N and Cu–O bond distances [1.98(2)–2.05(2) and 2.46(1), 2,51(2) Å, respectively] are consistent with the corresponding in-plane Cu–N (1.99–2.14 Å) and out-of-plane Cu–O (2.22–2.89 Å) bond-length data for copper(II) complexes with ETO stereochemistry [20]. The difference in the values of the bond lengths $Cu–N_{amine}$ [mean 2.03(2) Å] and $Cu–N_{imine}$ [1.98(2) Å] of *ca.* 0.05 Å is normal for transition metal complexes with amine imine ligands [9, 21]. The angular deviations from ideal *Oh* geometry are also significant. Thus, the *trans* angles around Cu are 153.2(5) for O1–Cu–O17, 164.5(5) for N4–Cu–N11 and 169.5(7)° for N7–Cu–N14 (Table II). The four nitrogen atoms exhibit a slight tetrahedral distortion, the deviations from the plane being: N4-0.23(2), N7-0.24(2), N11-0.15(2), N14-0.28(2)Å, with the copper atom deviation is 0.075(2) towards O17. L^2 is hexadentate and forms four five- and one six-membered chelate rings with copper(II). All the five-membered chelate rings adopt *gauche* conformations, and the six-membered chelate ring has a half-chair conformation (displacements of atoms from relevant CuON or CuN_2 planes: C2,2′ −0.21(5), 0.46(6), C3,3′ 0.41(6), −0.34(5), C5,5′ −0.57(5), 0.03(4), C6,6′ −0.12(5), −0.57(6), C8 −0.12(4), C9 0.23(3), C10 −0.47(3), C12 −0.20(3), C13 0.51(3), C15 −0.10(3), C16 0.62(3) Å). The presence

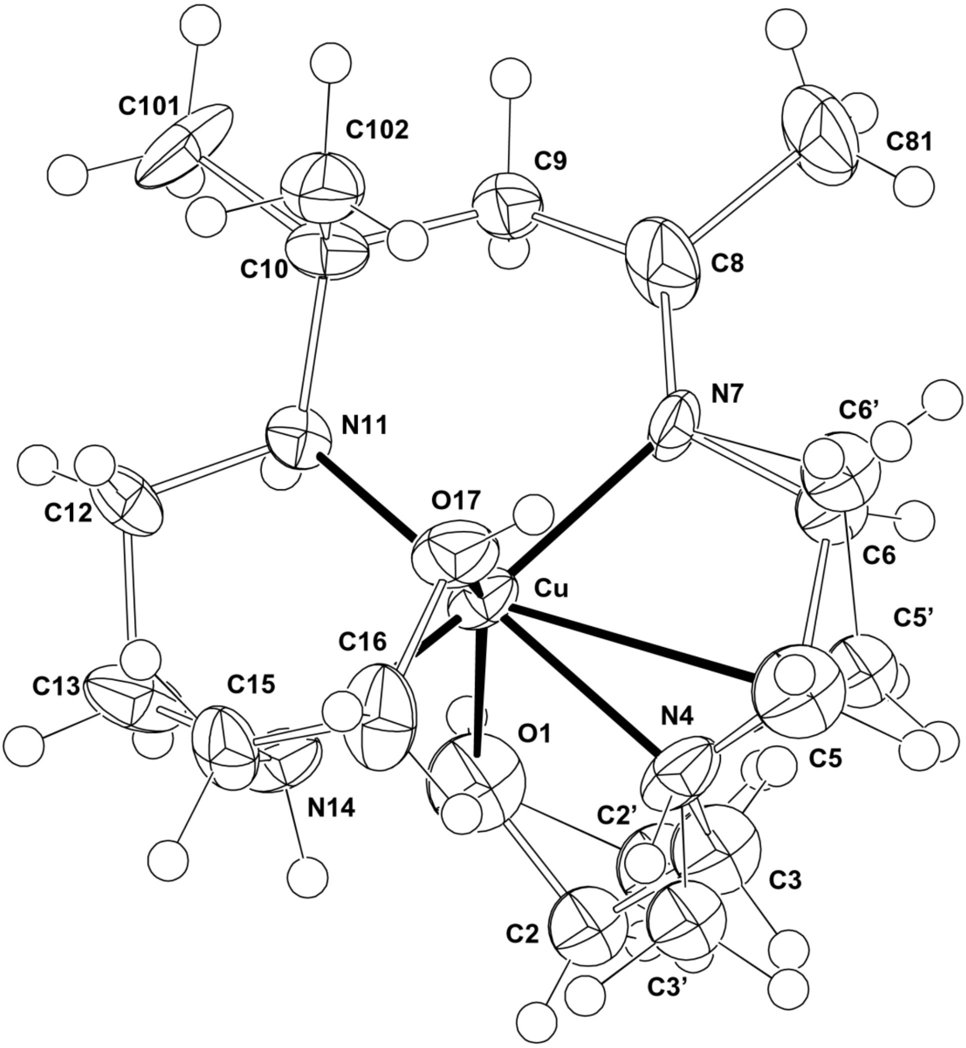


FIGURE 1 A drawing of the cation of **2** with the numbering scheme. The non-hydrogen atoms are shown as 50% thermal ellipsoids; hydrogen atoms have arbitrary radius of 0.1 Å.

of the imine groups N(7) = C(8) in L^2 is confirmed by the distances of 1.29(3) Å, and the trigonal bond angles about these atoms (Cu–N7–C6′ 114(2), Cu–N7–C8 128(2), C6′–N7–C8 115(2); the sum 357°; N7–C8–C81 124(2), N7–C8–C9 119(2), C81–C8–C9 115(2); the sum 358°).

The geometry of $[MnCl_4]^{2-}$ is near regular tetrahedral, the average Cl–Mn–Cl bond angle being 109.5°. The mean value of the Mn–Cl bond lengths [2.358(7) Å] is in accordance with those found in the complexes containing discrete tetrahedra $[MnCl_4]^{2-}$, *e.g*. 2.365(7) Å in $(Me_3PhP)_2MnCl_4$ [22], 2.361(2) Å in $(Me_4N)_2MnCl_4$ [22], 2.3712(2) Å in $(Py_4H)_2MnCl_4$ [23], 2.35(4) Å in $[HL]_2MnCl_4 \cdot H_2O$ [24].

Hydrogen bonding plays a very important role in the formation of the crystal lattice of **2** (Fig. 2, Table III), which is not surprising taking into account the potential

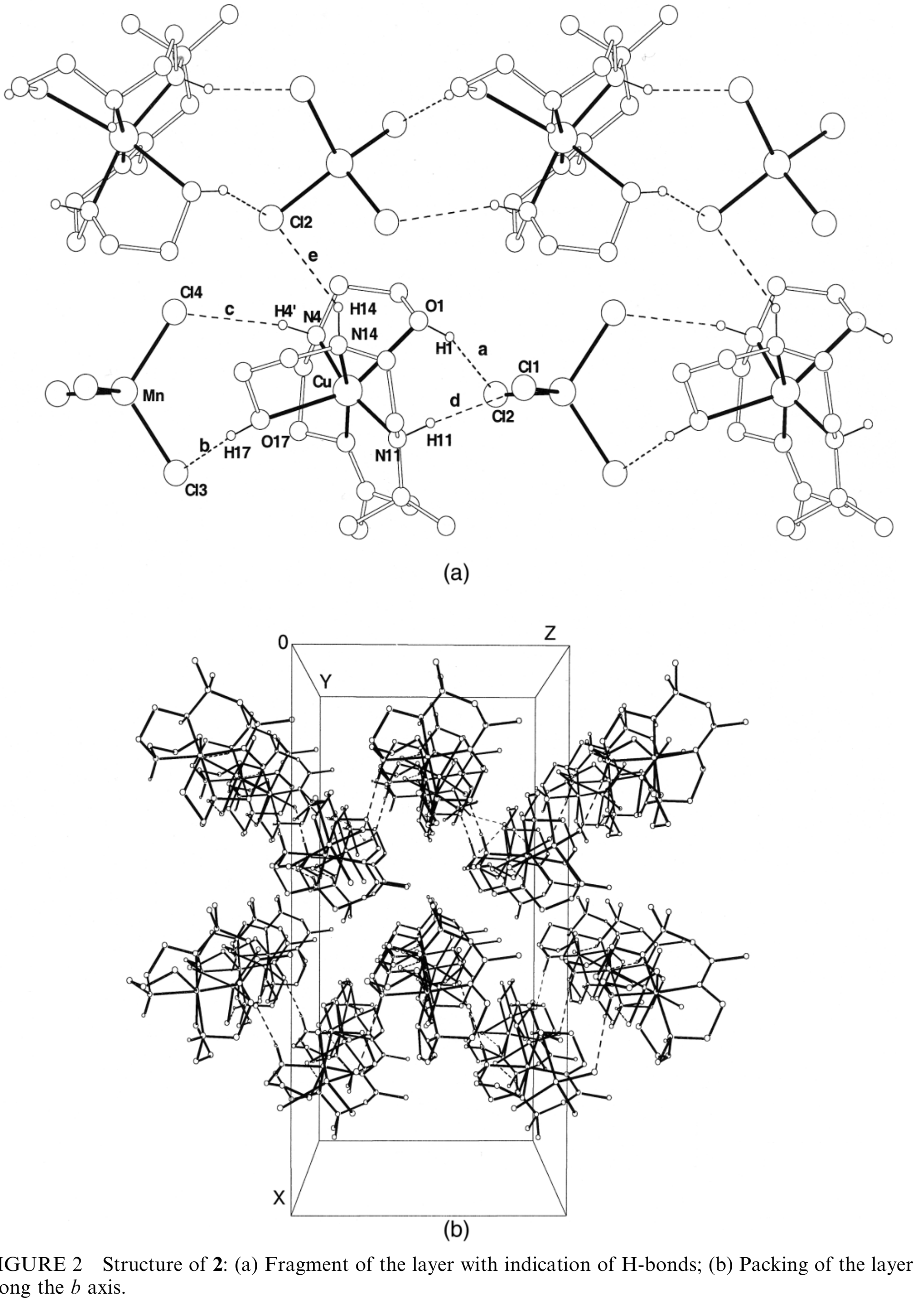


FIGURE 2 Structure of **2**: (a) Fragment of the layer with indication of H-bonds; (b) Packing of the layers along the *b* axis.

capacity of $[CuL^2]^{2+}$ to act as a hydrogen donor and the $[MnCl_4]^{2-}$ anion to act as a hydrogen acceptor. Indeed all of the five hydrogens (at the NH and OH groups of the ligand) and all the chlorine atoms from the anion are involved in the N–H···Cl (*ca.* 3.52–3.64 Å) and O–H···Cl (*ca.* 3.13–3.19 Å) bonds. The bonds **a** plus **c** and **b**

TABLE II Selected bond lengths (Å) and angles (°) for **2** and **3**

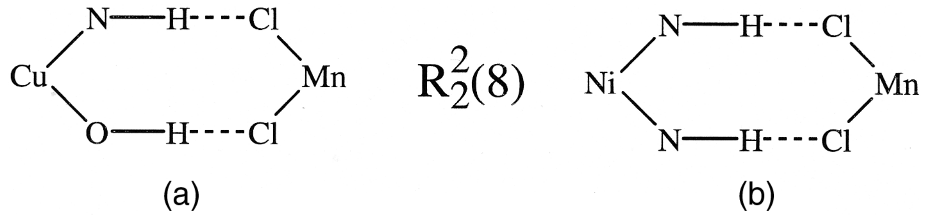
Compound **2**					
Cu–O1	2.506(16)	O1–C2′	1.56(5)	C2′–C3′	1.55(6)
Cu–O17	2.464(12)	O17—C16	1.44(2)	C5′–C6′	1.58(6)
Cu–N4	2.028(13)	N4–C3′	1.36(4)	C8–C81	1.55(3)
Cu–N7	1.977(15)	N4–C5′	1.58(4)	C8–C9	1.49(3)
Cu–N11	2.013(13)	N7–C6′	1.56(5)	C9–C10	1.54(3)
Cu–N14	2.055(18)	N7–C8	1.29(3)	C10–C101	1.56(3)
Mn–Cl1	2.338(6)	N11—C10	1.45(2)	C10–C102	1.56(3)
Mn–Cl2	2.376(6)	N11–C12	1.45(2)	C12–C13	1.52(3)
Mn–Cl3	2.374(7)	N14–C13	1.50(2)	C15–C16	1.50(3)
Mn–Cl4	2.344(7)	N14–C15	1.49(2)		
O1–Cu–N4	74.9(5)	N4–Cu–N14	98.0(6)	N14–Cu–O17	76.3(5)
O1–Cu–N7	108.5(6)	N4–Cu–O17	92.5(5)	Cl1–Mn–Cl2	109.7(2)
O1–Cu–N11	91.0 (5)	N7–Cu–N11	94.2(6)	Cl1–Mn–Cl3	107.4(2)
O1–Cu–N14	82.0(6)	N7–Cu–N14	169.5(6)	Cl1–Mn–Cl4	110.8(2)
O1–Cu–O17	153.2(5)	N7–Cu–O17	93.4(5)	Cl2–Mn–Cl3	111.0(2)
N4–Cu–N7	84.4(7)	N11–Cu–N14	86.2(6)	Cl2–Mn–Cl4	106.6(2)
N4–Cu–N11	164.5(5)	N11–Cu–O17	103.0(4)	Cl3–Mn–Cl4	111.4(2)
Compound **3**					
Ni–N1	1.928(6)	Mn–Cl4	2.351(3)	C2–C3	1.465(10)
Ni–N4	1.888(5)	N1–C2	1.499(9)	C5–C51	1.512(9)
Ni–N8	1.894(6)	N4–C3	1.482(8)	C5–C6	1.475(10)
Ni–N11	1.899(5)	N4–C5	1.289(8)	C6–C7	1.532(10)
Mn–Cl1	2.384(2)	N8–C7	1.491(9)	C7–C71	1.525(11)
Mn–Cl2	2.374(2)	N8–C9	1.472(9)	C7–C72	1.532(10)
Mn–Cl3	2.336(2)	N11–C10	1.443(9)	C9–C10	1.488(11)
N1–Ni–N4	85.3(2)	N4–Ni–N11	175.8(2)	Cl1–Mn–Cl4	106.18(8)
N1–Ni–N8	176.7(2)	N8–Ni–N11	86.9(2)	Cl2–Mn–Cl3	114.86(7)
N1–Ni–N11	91.6(2)	Cl1–Mn–Cl2	102.88(6)	Cl2–Mn–Cl4	104.66(7)
N4–Ni–N8	96.1(2)	Cl1–Mn–Cl3	111.75(7)	Cl3–Mn–Cl4	115.36(9)

TABLE III Hydrogen-bond parameters (Å, °) for **2** and **3**

			D–H	*H···A*	*D–A*	*D–H···A*
2	a	O(1)–H(1)···$Cl(2)^{i}$	0.902	2.422	3.192(17)	143.4
	b	O(17)–H(17)···Cl(3)	0.932	2.225	3.134(14)	164.8
	c	N(4)–H(4’)···Cl(4)	0.939	2.795	3.639(16)	150.1
	d	N(11)–H(11)···$Cl(1)^{i}$	0.928	2.629	3.515(12)	160.0
	e	N(14)–H(14)···$Cl(2)^{ii}$	0.941	2.785	3.581(17)	142.9
3	a	N(1)–H(1a)···$Cl(2)^{iii}$	0.932	2.511	3.348(6)	149.6
	b	N(1)–H(1b)···Cl(4)	0.915	2.486	3.352(6)	158.1
	c	N(11)–H(11a)···Cl(1)	0.933	2.819	3.452(6)	126.0
	d	N(11)–H(11a)···Cl(2)	0.933	2.626	3.436(6)	145.5
	e	N(11)–H(11b)···$Cl(1)^{iii}$	0.925	2.383	3.297(7)	169.1
	f	N(8)–H(8)···$Cl(3)^{iii}$	0.924	2.578	3.386(7)	146.4

Symmetry codes: (i) x, 1 + y, z; (ii) 1.5 − x, 0.5 + y, −0.5 + z; (iii) 1 − x, 1 − y, 0.5 + z.

plus **d** may be considered as the hydrogen-bonded motifs, graph set $R_2^2(8)$ [25], (Scheme IIa) of which the alternating ions form the chains along the *b* axis (Fig. 2a). These chains are further linked by the N–H···Cl interactions (**e**) (Table III) into the two-dimensional network. The corrugated layers are packed along the *b* axis in the unit cell as shown in Fig. 2b.



SCHEME II Hydrogen-bonded motifs generating the chains of alternating cations and anions for the structures of **2** (a) and **3** (b).

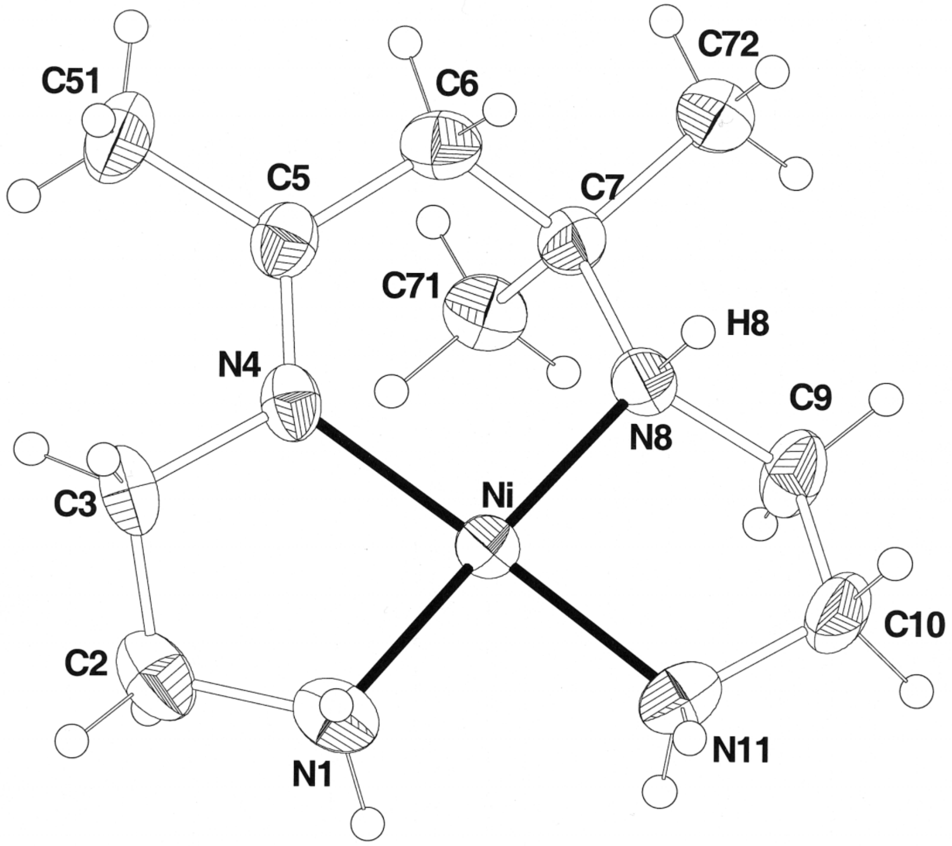


FIGURE 3 A drawing of the cation of **3** with the numbering scheme. The non-hydrogen atoms are shown as 50 % thermal ellipsoids; hydrogen atoms have arbitrary radius of 0.1 Å.

The crystal structure of **3** is shown in Figs. 3 and 4; selected bond distances and angles are listed in Table II. Parameters of the hydrogen bonds are given in Table III. The crystal structure of compound **3** has some similarity to the structure of compound **2**. The crystal structure of **3** also consists of the two-charged complex ions, $[NiL^1]^{2+}$ and $[MnCl_4]^{2-}$, connected by a dense hydrogen bonding network. However, the L^1 ligand is tetradentante and the coordination environment of the nickel atom, NiN_4,

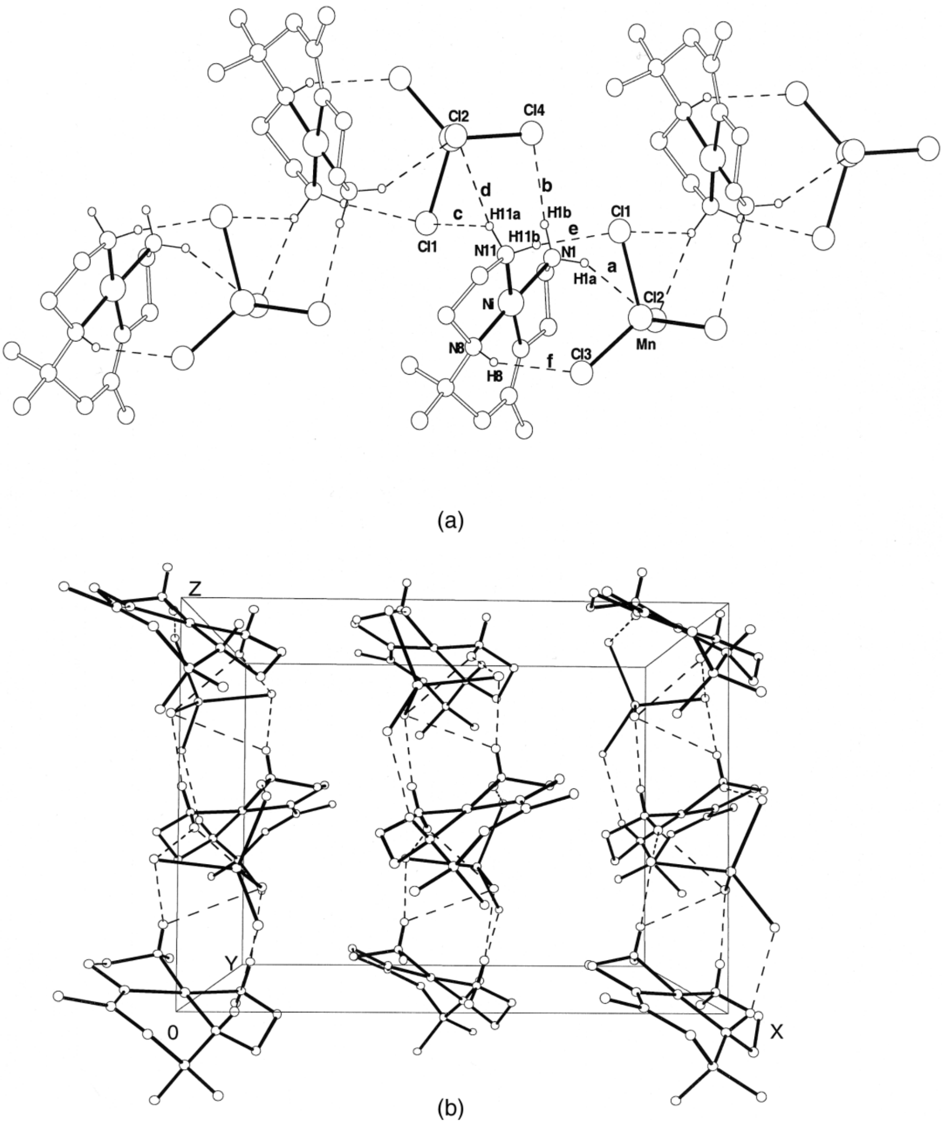


FIGURE 4 Structure of **3**: (a) Fragment of the helical chain with indication of H-bonds; (b) Packing of the chains along the *c* axis.

closely approximates a square-planar stereochemistry (deviations of N atoms from the N4 plane being less than 0.001 Å with the Ni atom deviation being −0.048(1) Å). The mean Ni–N distance of 1.902(6) Å is in accordance with the values observed for NiN_4 square planar complexes with open chain multidentate ligands, e.g. 1.909(3) Å in $[Ni(C_{15}H_{32}N_4)][ZnCl_4]$ [26] and 1.90(3) Å in $[Ni(C_9H_{22}N_6)]$ $(ClO_4)_2$ [27]. Herewith, the Ni–N1 bond distance of 1.928(6) Å which are *ca* 0.04 Å longer than the Ni–N11 bond distance contradicts a common situation that bonds to imine N atoms are usually shorter than those to amine N atoms [9]. The five-membered chelate ring Ni, N1, C2, C3, N4 possesses a *gauche* conformation, with C2 and C3 displaced from the NiN_2 plane by −0.70(1) and 0.14(1) Å, respectively. The other five-membered chelate ring has an envelope conformation with atoms Ni, N8, C10, N11 essentially coplanar ($\chi 2$ 14, maximum deviation; C10 0.03(1) Å, with C9 displaced from this plane by −0.57(1) Å. The six-membered chelate ring Ni, N4, C5, C6, C7, N8 adopts a half-chair conformation with displacements from the NiN_2 plane of 0.12(1) for C5, 0.22(1) C6 and −0.59(2) Å C7. The value of the N4=C5 distance of 1.289(8) Å and the trigonal bond angles about these atoms (C3–N4–C5 118.6(5), Ni–N4–C3 113.4(4) and Ni–N4–C5 127.9(4); the sum 359.9; N4–C5–C51 121.7(5), N4–C5–C6 121.2(6), C51–C5–C6 117.0(5); the sum 360.0°) are typical for an imine group.

The tetrahedral symmetry of $[MnCl_4]^{2-}$ in **3** is more distorted than in **2** as seen in the Cl–Mn–Cl angles which range from 102.88(6) to 115.36(9)°. The mean length of the Mn–Cl bonds is equal to 2.361(3) Å and the maximal difference in the Mn–Cl bond distances is *ca*. 0.05 Å. There is some correlation between the Mn–Cl bond lengths and the participation of chlorine atoms in hydrogen bonding. For instance, in the case of the Cl(1) and Cl(2) atoms, which act as bifurcated acceptors, the Mn–Cl bond distances are equal *ca*. 2.38 Å, while in the case of the Cl(3) and Cl(4) atoms which form segregate H-bonds, the Mn-Cl distances are noticeably shorter, *ca*. 2.34 Å (Tables II and III).

All amine and imine hydrogen atoms from L^1 and the chlorine atoms from $[MnCl_4]^{2-}$ take part in the formation of the complex system of N–H···Cl hydrogen bonds (*ca* 3.30–3.45 Å) (Fig. 4a, Table III). It should be noted that in both complexes hydrogen bonds including H_{imine} atoms are minimum 0.05 Å shorter than those with H_{amine} atoms: 3.52(1) Å (**2**) and 3.297(7) Å (**3**). Because of the existence of a bifurcated hydrogen bond for H(11a) (the sum of the angles N11–H11a–Cl1, N11–H11a–Cl2 and Cl1–H11a–Cl2 is equal to *ca*. 358°) [**A**], we can distinguish five hydrogen-bonded motifs $R_2^2(8)$ (Scheme IIb), which link the ions $[NiL^1]^{2+}$ and $[MnCl_4]^{2-}$ in a helical chain array (Fig. 4a). The packing of the chains in the unit cell is shown in Fig. 4b.

SUPPLEMENTARY MATERIAL

CCDC reference numbers are 231137 for **2** and 231136 for **3**. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) or at http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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