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Structures of Tetrakis(2-amino-6-methylpyridinium) catena-Bis(acetonitrile)-tetradeca-μ-chloro-pentanickelate(II) and Bis(3-picolinium) catena-Diaquaocta-μ-chloro-trinickelate(II)

By MARCUS R. BOND AND ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, WA 99164, USA

Abstract. $4C_6H_9N_2^+ \cdot [Ni_5Cl_{14}(C_2H_3N)_2]^{4-}$, (I), $M_r = 1308.6$, triclinic, $P\bar{1}$, $a = 8.686$ (1), $b = 12.483$ (2), $c = 12.933$ (2) Å, $\alpha = 73.09$ (1), $\beta = 73.65$ (1), $\gamma = 70.87$ (1)°, $V = 1240.4$ (3) Å^3, $Z = 1$, $D_x = 1.75$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, graphite monochromator, $\mu = 2.670$ mm^{-1}, $F(000) = 658$, $T = 295$ K, 259 parameters refined to $R = 0.0591$ and $wR = 0.0399$ for 1506 unique observed $[F \geq 3\sigma(F)]$ reflections. $2C_6H_8N^+ \cdot [Ni_3Cl_8(H_2O)_2]^{2-}$, (II), $M_r = 684.0$, triclinic, $P\bar{1}$, $a = 7.648$ (1), $b = 8.498$ (1), $c = 9.550$ (1) Å, $\alpha = 85.15$ (1), $\beta = 83.71$ (1), $\gamma = 69.08$ (1)°, $V = 575.6$ (2) Å^3, $Z = 1$, $D_x = 1.97$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, graphite monochromator, $\mu = 3.393$ mm^{-1}, $F(000) = 343$, $T = 295$ K, 132 parameters refined to $R = 0.0246$ and $wR = 0.0339$ for 2177 unique observed $[F \geq 3\sigma(F)]$ reflections. Both structures are built up from $[Ni_nCl_{3n+1}L_2]$ oligomers which contain face-sharing $NiCl_6$ octahedra and are capped on both ends by $NiCl_5L$ octahedra. Di-μ-chloride bridges link these oligomers together into the non-uniform chains characteristic of this new $A_{n-1}[Ni_nCl_{3n-1}L_2]$ family.

Introduction. We are reporting the structures of the first two members of a new family of non-uniform nickel(II) chloride chains. Uniform chains of coordination polyhedra, in which symmetrically equivalent polyhedra are typically linked to their neighbors through one, two or three shared ligands, are a familiar motif of inorganic crystal chemistry. Non-uniform chains, those containing more than one type of coordination polyhedron or more than one type of bridging arrangement, are not uncommon, but are certainly less well known. The greater complexity, both structural and physical, of the non-uniform chain systems discourages the extensive and systematic studies pursued for many uniform chain systems. There is, nevertheless, a sustained interest in non-uniform systems with alternating magnetic properties, such as alternating exchange interactions (Carlin, 1986) or one-dimensional ferrimagnetism (Coronado, Drillon, Nugteren, de Jonghe, Beltran & Georges, 1989).

The title compounds establish a series of nickel halide salts which can be formulated as $A_{n-1}[Ni_n\text{-}Cl_{3n-1}L_2]$ where A is a monopositive organoammonium cation, L is a neutral ligand and n is, to date, an odd integer. The two extreme values of n produce uniform chain structures. Infinite n yields an $A\text{NiCl}_3$-type stoichiometry consisting of tri-μ-chloro-bridged chains of NiCl_6^{4-} octahedra as found in the CsNiCl_3 family (Bond, 1990) and $n = 1$ yields an $[\text{NiCl}_2L_2]$ stoichiometry consisting of di-μ-chloro-bridged chains of $[\text{NiCl}_4L_2]^{2-}$ octahedra as found in $[\text{NiCl}_2(H_2O)_2]$ (Morosin, 1967). Intermediate compounds of the series contain both types of bridging arrangements resulting in oligomeric segments of the tribridged CsNiCl_3-type chain connected by the dichloro bridge of the $[\text{NiCl}_2L_2]$-type chain. In the two systems reported here, A is a substituted pyridinium

cation [(1), $R_1 = NH_2$, $R_2 = CH_3$, $R_3 = H$ for compound (I); $R_1 = R_2 = H$, $R_3 = CH_3$ for compound (II)].

(1)
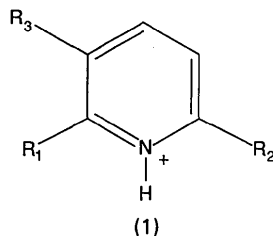
The anionic chains are made up of pentameric segments in compound (I) and trimeric segments in compound (II).

(I)

(II)
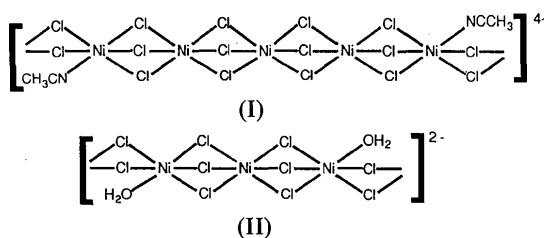
This new class of compounds offers the potential to study systematically a series of spin-one chains with varying degrees of non-uniformity.

Experimental. *Compound* (I). Evaporation of acetonitrile solution containing equimolar amounts of 6-methyl-2-aminopyridinium chloride and nickel(II) chloride yielded small frequently twinned plate-like yellow crystals. Crystal (0.09 × 0.12 × 0.25 mm) sealed in a glass capillary, mounted on a Syntex $P2_1$ diffractometer (upgraded to Nicolet $R3m$ standards). Cell constants from 25 centered reflections ($25 \le 2\theta \le 27°$; Campana, Shepard & Litchman, 1981). Data collected within the range $-9 \le h \le 9$, $-13 \le k \le 13$, $0 \le l \le 13$ {ω scans, 1.0° scan range, scan speed: 3.9–29.3° min^{-1}, $(\sin\theta/\lambda)_{max} = 0.481$ Å^{-1}, 2460 total reflections, 2294 unique reflections, $R_{merge} = 0.0268$, 1506 observed [$F \ge 3\sigma(F)$]}. Check reflections (122, 241) measured every 94 reflections, variations within counting statistics. Lp, empirical absorption corrections (ellipsoidal crystal shape, $T_{max} = 0.959$, $T_{min} = 0.718$), peak profile fitting procedure applied to data. Structure solution and refinement achieved through Nicolet *SHELXTL* crystallographic software (Sheldrick, 1985; atomic form factors from *International Tables for X-ray Crystallography*, 1974, Vol. IV). Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F)]^{-1}$. Intensity statistics suggest $P\bar{1}$ is correct. An Ni ion placed at the origin initially, coordinates of remaining non-H atoms determined from subse-

quent electron-density difference maps. Idealized positions calculated for H atoms (N—H, C—H bond lengths constrained to 0.96 Å) and thermal parameters constrained to 1.2 U_{eq} of the bound C or N atom. Anisotropic thermal parameters refined for all non-H atoms. Final refinement gave $R = 0.0591$, $wR = 0.0399$, $S = 1.349$, $|\Delta/\sigma|_{mean} = 0.002$, $|\Delta/\sigma|_{max} = 0.009$, excursions on final difference map ranging from -0.620 to 0.673 e Å^{-3} [maximum nearest H(2a)].

Compound (II). Evaporation of acidic aqueous solution containing equimolar amounts of 3-picolinium chloride and nickel(II) chloride maintained at 333 K gave a few large orange block-shaped crystals buried under a mass of yellow ill-formed crystals. Small crystallite (0.25 × 0.30 × 0.54 mm) cleaved from one large orange crystal, sealed in a glass capillary, mounted on same diffractometer as compound (I). Cell constants from 25 reflections ($39 \le 2\theta \le 41°$; Campana, Shepard & Litchman, 1981). Data collected within the range $0 \le h \le 10$, $-11 \le k \le 11$, $-12 \le l \le 12$ {ω scans, 1.0° scan range, 4.0–29.3° min^{-1} scan speed, $(\sin\theta/\lambda)_{max} = 0.595$ Å^{-1}, 2194 total reflections, 2028 unique reflections, $R_{merge} = 0.0072$, 2177 observed [$F \ge 3\sigma(F)$]}. Check reflections (151, 233, 343) measured every 93 reflections, variations within counting statistics. Lp, empirical absorption corrections (ellipsoidal crystal shape, $T_{max} = 0.232$, $T_{min} = 0.179$) applied to data. Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F) + gF^2]^{-1}$, $g = 0.00021$. Intensity statistics suggest $P\bar{1}$ is correct. An Ni ion placed at the origin initially, coordinates of remaining non-H atoms determined from subsequent electron-density difference maps. Idealized positions calculated for H atoms (N—H, O—H, C—H bond lengths constrained to 0.96 Å). Thermal parameters of water H atoms constrained to 1.2 $U_{eq}(O)$, common isotropic thermal parameters were refined for the groups of aromatic and methyl H atoms. Anisotropic thermal parameters refined for all non-H atoms. Final refinement gave $R = 0.0246$, $wR = 0.0339$, $S = 1.560$, $|\Delta/\sigma|_{mean} = 0.001$, $|\Delta/\sigma|_{max} = 0.003$, excursions on final difference map ranging from -0.364 to 0.343 e Å^{-3} [maximum 1.1 Å from Cl(3)]. Tables of atomic coordinates, bond distances and bond angles presented in Tables 1 and 2* for both structures.

Discussion. Fig. 1 depicts the actual geometry of a pentameric segment of the inorganic chain in compound (I). Here, as in the trimeric segment in com-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for compounds (I) and (II)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Compound (I)				
Ni(1)	0	0	0	29 (1)
Ni(2)	399 (2)	-2031 (2)	1941 (2)	27 (1)
Ni(3)	885 (2)	-4155 (1)	3840 (1)	27 (1)
Cl(1)	-513 (4)	28 (3)	1942 (3)	30 (2)
Cl(2)	-1419 (4)	-1511 (3)	639 (3)	30 (2)
Cl(3)	2486 (4)	-1521 (3)	333 (3)	30 (2)
Cl(4)	-1667 (4)	-2623 (3)	3518 (3)	33 (2)
Cl(5)	307 (4)	-4246 (3)	5766 (3)	37 (2)
Cl(6)	1408 (4)	-4043 (3)	1871 (3)	29 (2)
Cl(7)	2131 (4)	-2499 (3)	3267 (3)	33 (2)
N	3158 (15)	-5293 (10)	4000 (10)	42 (7)
C(1)	4307 (18)	-5955 (13)	4217 (12)	42 (8)
C(2)	5847 (15)	-6784 (11)	4482 (13)	83 (10)
N(11)	1466 (11)	5062 (9)	8274 (8)	32 (5)
N(12)	3728 (13)	3563 (9)	7711 (9)	57 (7)
C(11)	3085 (15)	4517 (12)	8154 (11)	40 (7)
C(12)	4109 (15)	4947 (12)	8531 (10)	53 (8)
C(13)	3410 (17)	5925 (12)	8898 (11)	53 (9)
C(14)	1707 (17)	6511 (11)	8986 (10)	38 (8)
C(15)	718 (16)	6051 (11)	8690 (10)	33 (7)
C(16)	-1112 (15)	6510 (10)	8737 (11)	53 (8)
N(21)	-7632 (11)	417 (8)	2769 (8)	36 (6)
N(22)	-5521 (13)	-490 (9)	1468 (9)	52 (7)
C(21)	-6004 (14)	60 (10)	2298 (10)	32 (7)
C(22)	-4855 (18)	280 (12)	2721 (13)	71 (10)
C(23)	-5407 (18)	809 (13)	3595 (13)	74 (10)
C(24)	-7141 (18)	1158 (13)	4054 (12)	67 (10)
C(25)	-8234 (15)	968 (10)	3641 (11)	46 (7)
C(26)	-10083 (15)	1322 (11)	3972 (11)	60 (8)
Compound (II)				
Ni(1)	3800 (1)	-2851 (1)	-22 (1)	21 (1)
Ni(2)	0	0	0	22 (1)
Cl(1)	5071 (1)	-4958 (1)	-1741 (1)	29 (1)
Cl(2)	2371 (1)	-680 (1)	1640 (1)	28 (1)
Cl(3)	2645 (1)	-595 (1)	-1762 (1)	30 (1)
Cl(4)	666 (1)	-3071 (1)	118 (1)	25 (1)
O	6350 (3)	-2500 (3)	-168 (2)	38 (1)
N	449 (5)	2910 (4)	3099 (3)	53 (1)
C(1)	2102 (5)	2687 (4)	3568 (3)	47 (1)
C(2)	2276 (4)	2602 (4)	4990 (3)	38 (1)
C(3)	683 (5)	2740 (4)	5881 (3)	43 (1)
C(4)	1007 (5)	2987 (4)	4634 (4)	54 (1)
C(5)	-1112 (5)	3066 (4)	3945 (4)	53 (1)
C(6)	4132 (6)	2362 (5)	5526 (5)	69 (2)

Table 2. Bond lengths (Å) and angles (°) for compounds (I) and (II)

Compound (I)

Ni(1)—Cl(1)	2.432 (3)	Ni(1)—Cl(2)	2.410 (4)
Ni(1)—Cl(3)	2.411 (3)	Ni(2)—Cl(1)	2.429 (4)
Ni(2)—Cl(2)	2.438 (4)	Ni(2)—Cl(3)	2.425 (3)
Ni(2)—Cl(4)	2.421 (3)	Ni(2)—Cl(6)	2.394 (4)
Ni(2)—Cl(7)	2.416 (4)	Ni(3)—Cl(4)	2.454 (3)
Ni(3)—Cl(5)	2.374 (4)	Ni(3)—Cl(6)	2.428 (4)
Ni(3)—Cl(7)	2.473 (4)	Ni(3)—N	2.044 (11)
Ni(3)—Cl(5')	2.405 (5)	N—C(1)	1.114 (18)
C(1)—C(2)	1.456 (18)		
N(11)—C(11)	1.333 (14)	N(11)—C(15)	1.378 (17)
N(12)—C(11)	1.356 (20)	C(11)—C(12)	1.423 (25)
C(12)—C(13)	1.331 (21)	C(13)—C(14)	1.407 (19)
C(14)—C(15)	1.360 (24)	C(15)—C(16)	1.493 (18)
N(21)—C(21)	1.352 (14)	N(21)—C(25)	1.379 (17)
N(22)—C(21)	1.336 (18)	C(21)—C(22)	1.394 (25)
C(22)—C(23)	1.366 (25)	C(23)—C(24)	1.424 (19)
C(24)—C(25)	1.323 (25)	C(25)—C(26)	1.489 (17)
Cl(1)—Ni(1)—Cl(2)	85.4 (1)	Cl(1)—Ni(1)—Cl(3)	85.7 (1)
Cl(2)—Ni(1)—Cl(3)	86.4 (1)	Cl(1)—Ni(2)—Cl(2)	84.8 (1)
Cl(1)—Ni(2)—Cl(3)	85.4 (1)	Cl(2)—Ni(2)—Cl(3)	85.7 (1)
Cl(1)—Ni(2)—Cl(4)	97.1 (1)	Cl(2)—Ni(2)—Cl(4)	93.8 (1)
Cl(3)—Ni(2)—Cl(4)	177.3 (2)	Cl(1)—Ni(2)—Cl(6)	177.3 (1)
Cl(2)—Ni(2)—Cl(6)	95.3 (1)	Cl(3)—Ni(2)—Cl(6)	91.9 (1)
Cl(4)—Ni(2)—Cl(6)	85.6 (1)	Cl(1)—Ni(2)—Cl(7)	93.7 (1)
Cl(2)—Ni(2)—Cl(7)	178.0 (1)	Cl(3)—Ni(2)—Cl(7)	95.7 (1)
Cl(4)—Ni(2)—Cl(7)	85.2 (1)	Cl(6)—Ni(2)—Cl(7)	86.3 (1)
Cl(4)—Ni(3)—Cl(5)	94.6 (1)	Cl(4)—Ni(3)—Cl(6)	84.2 (1)
Cl(5)—Ni(3)—Cl(6)	178.7 (1)	Cl(4)—Ni(3)—Cl(7)	83.3 (1)
Cl(5)—Ni(3)—Cl(7)	96.0 (1)	Cl(6)—Ni(3)—Cl(7)	84.3 (1)
Cl(4)—Ni(3)—N	173.3 (4)	Cl(5)—Ni(3)—N	88.1 (4)
Cl(6)—Ni(3)—N	93.2 (4)	Cl(7)—Ni(3)—N	90.4 (4)
Cl(4)—Ni(3)—Cl(5')	95.9 (1)	Cl(5)—Ni(3)—Cl(5')	88.8 (2)
Cl(6)—Ni(3)—Cl(5')	90.8 (1)	Cl(7)—Ni(3)—Cl(5')	175.1 (1)
N—Ni(3)—Cl(5')	90.3 (4)	Ni(1)—Cl(1)—Ni(2)	76.5 (1)
Ni(1)—Cl(2)—Ni(2)	76.8 (1)	Ni(1)—Cl(3)—Ni(2)	77.0 (1)
Ni(2)—Cl(4)—Ni(3)	77.5 (1)	Ni(2)—Cl(6)—Ni(3)	78.5 (1)
Ni(2)—Cl(7)—Ni(3)	77.2 (1)	Ni(3)—Cl(5)—Ni(3')	91.2 (1)
Ni(3)—N—C(1)	171.5 (11)	N—C(1)—C(2)	177.6 (18)
C(11)—N(11)—C(15)	124.6 (14)	N(11)—C(11)—N(12)	120.8 (15)
N(11)—C(11)—C(12)	118.1 (13)	N(12)—C(11)—C(12)	121.1 (11)
N(11)—C(15)—C(16)	114.9 (14)	N(11)—C(15)—C(14)	117.6 (11)
C(14)—C(15)—C(16)	127.4 (12)	C(13)—C(14)—C(15)	118.4 (13)
C(12)—C(13)—C(14)	123.4 (16)	C(11)—C(12)—C(13)	117.6 (12)
C(21)—N(21)—C(25)	124.9 (13)	N(21)—C(21)—N(22)	121.1 (13)
N(21)—C(21)—C(22)	117.3 (13)	N(22)—C(21)—C(22)	121.6 (11)
C(21)—C(22)—C(23)	119.3 (13)	C(22)—C(23)—C(24)	120.4 (17)
N(21)—C(25)—C(26)	114.4 (14)	N(21)—C(25)—C(24)	117.8 (11)
C(24)—C(25)—C(26)	127.8 (13)	C(23)—C(24)—C(25)	120.2 (15)

Compound (II)

Ni(1)—Cl(2)	2.407 (1)	Ni(2)—Cl(3)	2.418 (1)
Ni(1)—Cl(4)	2.459 (1)	N—C(1)	1.332 (5)
Ni(1)—Cl(1")	2.398 (1)	C(1)—C(2)	1.371 (4)
Ni(2)—Cl(2)	2.407 (1)	C(2)—C(6)	1.501 (6)
Ni(2)—Cl(4)	2.469 (1)	C(4)—C(5)	1.362 (5)
Ni(1)—Cl(3)	2.407 (1)	N—C(5)	1.338 (5)
Ni(1)—C(1)	2.384 (1)	C(2)—C(3)	1.382 (5)
Ni(1)—O	2.064 (2)	C(3)—C(4)	1.373 (5)
Cl(2)—Ni(1)—Cl(3)	84.3 (1)	Cl(1")—Ni(1)—Cl(1")	87.6 (1)
Cl(3)—Ni(1)—Cl(4)	85.9 (1)	Cl(3)—Ni(1)—O	91.0 (1)
Cl(3)—Ni(1)—Cl(1)	178.8 (1)	Cl(1)—Ni(1)—O	84.7 (1)
Cl(2)—Ni(1)—Cl(1")	176.9 (1)	Cl(2)—Ni(2)—Cl(3)	84.0 (1)
Cl(4)—Ni(1)—Cl(1")	92.9 (1)	Cl(3)—Ni(2)—Cl(4)	85.4 (1)
Cl(2)—Ni(1)—O	93.0 (1)	Ni(1)—Cl(2)—Ni(2)	78.5 (1)
Cl(4)—Ni(1)—O	176.3 (1)	Ni(1)—Cl(4)—Ni(2)	76.4 (1)
Cl(1")—Ni(1)—O	89.3 (1)	C(1)—N—C(5)	123.6 (3)
Cl(2)—Ni(2)—Cl(4)	94.5 (1)	C(1)—C(2)—C(3)	117.0 (3)
Ni(1)—Cl(1)—Ni(1")	92.4 (1)	C(3)—C(2)—C(6)	122.5 (3)
Ni(1)—Cl(3)—Ni(2)	78.3 (1)	C(3)—C(4)—C(5)	119.4 (3)
Cl(2)—Ni(1)—Cl(4)	84.7 (1)	N—C(1)—C(2)	120.2 (3)
Cl(2)—Ni(1)—Cl(1)	94.5 (1)	C(1)—C(2)—C(6)	120.5 (3)
Cl(4)—Ni(1)—Cl(1)	94.3 (1)	C(2)—C(3)—C(4)	121.5 (3)
Cl(3)—Ni(1)—Cl(1")	93.6 (1)	N—C(5)—C(4)	118.3 (4)

Symmetry code: (i) $-x$, $-1-y$, $-z$; (ii) $1-x$, $-1-y$, $-z$.

pound (II), the octahedral coordination of the nickel(II) cations is regular with bonding parameters conforming to those expected for six-coordinate Ni^{II}: Ni—Cl bond lengths in the range 2.38–2.47 Å, Ni^{II}—O or Ni^{II}—N bond lengths of 2.0 Å, and Cl—Ni—Cl or —L bond angles within a few degrees of 90 or 180°. Elongation of the polyhedra, along the trigonal axis (when tri-bridged to a neighbor) or along the dihedral axis (when bi-bridged to a neighbor), is evident from the acute interior Cl—Ni—Cl angles and results from electrostatic repulsion between neighboring Ni^{II} cations. The low symmetry of the Ni^{II} sites ($\bar{1}$ for the central cation and 1 for the remaining cations of the oligomer) allows for further distortion of the polyhedra. One might expect the least regular complex, the terminal $NiCl_5L$ complex, to exhibit the largest distortion with the central Ni^{II} complex showing the least distortion. This appears to be the case for the pentamer, where the range of Ni—Cl bond lengths increases as one moves from the center to the ends: 2.410–2.432 Å for Ni(1), 2.394–2.438 Å for Ni(2), 2.374–2.473 Å for Ni(3), but not for the trimer, where the range of Ni—Cl

bond lengths is comparable for the central (2.407–2.469 Å) and terminal (2.407–2.459 Å) nickel ions. A reliable description of bonding trends within this family, however, can only be made from the study of a larger collection of structures than we have presented here.

The oligomers are linked together through di-μ-chloro bridges, as shown in Fig. 2, to form chains parallel to [1$\bar{1}$0] in the trimer system and to [0$\bar{1}$1] in the pentamer system. The inversion centers between neighboring oligomers in the chain force the Ni_2Cl_2 bridging unit to be planar. In contrast, this bridging unit is distinctly non-planar in many $[NiX_2(H_2O)_2]$ systems {e.g. $[NiCl_2(H_2O)_2]$ (Morosin, 1967) or $[(CH_3)_3NH][NiCl_3(H_2O)_2]$ (Hoogerbeets, Wiegers, van Duyneveldt, Willett & Geiser, 1984)} where canting of the H_2O—Ni—OH_2 axis produces a dihedral angle between adjacent NiX_4 planes, although this canting is absent in other $[M_2X_2L_2]$ systems where L is a non-hydrogen-bonding ligand {e.g. $[CoCl_2$-(pyridine)$_2]$ (Clark & Milledge, 1975)}. Within the trimer system the chains are arranged into layers parallel to the xy plane and interleaved with layers of organic cations (Fig. 3). Hydrogen bonding between a coordinated H_2O molecule on one chain to a chloride ion on an adjacent chain facilitates and strengthens the layer structure. A layer structure is also found in the pentameric system, but parallel to the (0$\bar{1}$1) plane instead. Distances between chain axes of nearest neighbors within the layer, 7.564 (1) Å (2×) for (I) and 6.612 (1) Å (2×) for (II), are significantly shorter than those between neighbouring
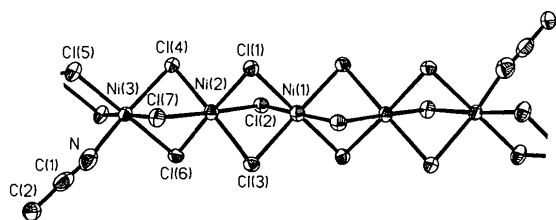
layers, 10.203 (2) Å (2×) for (I) and 9.481 (1) Å (2×) for (II). Fig. 3. shows a stereoscopic view of compound (II).

Our knowledge of magneto-structural correlations in Ni^{II} chloride compounds permits us to make some simple predictions concerning the intrachain magnetic exchange (Bond, 1990). The di-μ-chloro bridge in both structures is planar with an Ni—Cl—Ni bridging angle close to 90° [91.2 (1) and 92.4 (1)° for (I) and (II), respectively] and we would expect the interoligomer coupling to be strongly ferromagnetic as a result. The Ni—Cl bond distances of the bridge, however, are remarkably short [average: 2.39 (2) and 2.39 (1) Å, respectively], contributing to increased overlap between magnetic orbitals and a possible reduction of the magnitude of the ferromagnetic exchange. Ni—Cl—Ni angles within the oligomers are relatively large; all lie within the range 76.4 (1) to 78.5 (1)° and are bounded by values for the antiferromagnetic NH_4NiCl_3 [75.7 (1)°] and the ferromagnetic $(C_6H_5NH)NiCl_3$ [average: 77.6 (6)°] (Bond, 1990). These intermediate values of the bridging angle lead us to predict weak exchange coupling within the oligomer. Single ion properties of the metal centers are also of interest, particularly those of the unusual $NiCl_5L$ complex, but cannot yet be predicted with any confidence.

Note added in proof: A closely related family of non-uniform chains with the formula $A_{n-1}Cu_nCl_{3n-1}$ has been identified in copper(II) halide crystal chemistry. Specifically, an $n = 5$ chain is found with $A = Et_3MeN^+$ (Bond & Willett, 1991) while an $n = 4$ chain is obtained with $A = Et_2Me_2N^+$ (Fujii & Willett, 1993, in preparation). These contain units of $(n - 1)$ tri-bridged halide linkages separated by single bi-bridged units and may be considered to be derived from the $A_{n-1}Ni_nCl_{3n-1}L_2$ structures described in this paper by removal of the two L ligands. Thus two

Fig. 1. View of an oligomeric segment of the chain in the $(C_6H_9N_2)_4[Ni_5Cl_{14}(CH_3CN)_2]$ structure illustrating the manner of bridging within the segment.

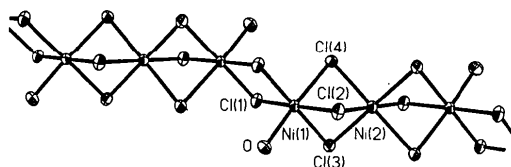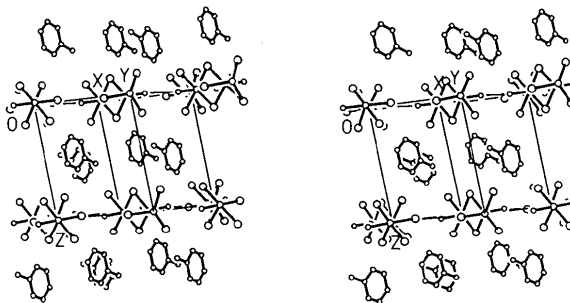

Fig. 2. View of two linked oligomeric segments of the chain in the $(C_6H_8N)_2[Ni_3Cl_8(H_2O)_2]$ structure illustrating the manner of bridging between the segments.

Fig. 3. Stereoscopic view of the environment about one unit cell of the $(C_6H_8N)_2[Ni_3Cl_8(H_2O)_2]$ structure. The [1$\bar{1}$0] (chain) axis is out of the page and the crystallographic c axis is almost vertical. The figure shows the layers of chains (parallel to the xy plane) interleaved with layers of 3-picolinium cations.

of the Cu^{II} ions attain a five-coordinate geometry while the remaining $(n - 2)$ Cu^{II} ions retain a distorted octahedral geometry.

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Structure of an Erbium Coordination Compound with L-Proline, {[Er(Pro)₂(H₂O)₅]Cl₃}ₙ

BY MA AI-ZENG, LI LAI-MING, LIN YONG-HUA AND XI SHI-QUAN*

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, People's Republic of China

Abstract. catena-Poly[{pentaaqua(L-proline-O)-erbium-μ-(L-proline-O:O')} trichloride], {[Er(C₅H₉-NO₂)₂(H₂O)₅]Cl₃}ₙ, $M_r = 594.0$, monoclinic, $P2_1$, $a = 8.294$ (1), $b = 10.981$ (3), $c = 11.934$ (3) Å, $\beta = 107.04$ (2)°, $V = 1039.2$ (4) Å³, $Z = 2$, $D_x = 1.90$ g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 45.2$ cm⁻¹, $F(000) = 586$, $T = 298$ K, $R = 0.0244$ for 1711 unique reflections $[I > 3\sigma(I_o)]$. The crystal consists of one-dimensional chains of infinite length in which one L-proline ligand bridges two neighboring Er ions, the other L-proline ligand being monodentate.

Introduction. Rare-earth elements are now used extensively in agriculture, medicine and biochemical research. It is therefore important to understand their biological effects. The structures and properties of some rare-earth amino acid coordination compounds have been investigated (Gao, Tang, Song, Fu & Liu, 1990; Jin, Yang, Yang, Wu & Xu, 1989; Legendiewicz, Huskowska, Argay & Waskowska, 1984; Li & Pan, 1985; Mathur & Srivastava, 1970). In this paper, the crystal structure of an erbium trichloride L-proline coordination compound is reported.

Experimental. The title compound was prepared by the reaction of equimolar amounts of erbium tri-

chloride with L-proline in an aqueous solution at pH≈4 for 8 h. The resulting solution was concentrated in a thermostat bath at 323 K until most of the water had evaporated. The concentrated solution was dried in a vacuum desiccator over phosphorus pentoxide for several weeks and colorless crystals were obtained. A prism-shaped crystal of dimensions $0.38 \times 0.44 \times 0.12$ mm was selected for crystal-structure determination. Intensity data were collected at room temperature using a Nicolet $R3/m$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters were obtained by a least-squares method using 25 reflections with $5.14 < 2\theta < 21.76°$. Data were collected with $3.00 < 2\theta < 48.00°$ using the ω–2θ scan method, and were corrected for Lorentz, polarization and absorption effects (transmission coefficients: min. 0.481, max. 0.933). The range for h was 0 to 10, for k 0 to 14 and for l −15 to 15. The intensity variation of one standard reflection (42$\bar{3}$) was ±2% about the mean value. The main computer program used was SHELXTL (Sheldrick, 1983). Of the 1907 reflections measured, 1845 were independent, of which 1711 were observed $[I > 3\sigma(I_o)]$ and were used in the refinements. The structure was solved by Patterson techniques. Full-matrix least-squares refinement on F of positional and anisotropic thermal parameters. H atoms were placed in calculated positions and assigned isotropic thermal parameters $(U = 0.08$ Å²) and 225 least-

* Author to whom correspondence should be addressed.