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The Crystal and Molecular Structures of Hexaquocobalt(II) Diisonicotinate N-Oxide and its Isostructural Nickel(II) Homologue

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In this experiment the crystal and molecular structures of hexaaquocobalt(II)diisonicotinate N-oxide and hexaquonickel(II)diisonicotinate N-oxide were determined from three-dimensional X-ray diffraction data. The crystals belong to the monoclinic space group $P2_1/c$. *The cell parameters are* $a = 7.747(2)$, $b = 9.826(2)$, $c = 11.474(2)$ Å, $\beta = 91.08(2)°$, $V = 873.2(3)$ Å^3 *for the Co-complex, and* $a = 7.765(2)$, $b = 9.725(6)$, $c = 11.363$ Å, $\beta = 91.20(3)°$, $V = 857.9(7)$ Å^3 *for the Ni-complex. Both structures were refined to a final* R*-value of 0.045.*

The X-ray structure analysis showed that there are metal(II)hexaquo cations and isonicotinate N-oxide anions formulated as $Co(H_2O)_6^{2+}\ 2L^-$ *and* $Ni(H_2O)_6^{2+}\ 2L^-$ *in the structures. The strong hydrogen bonds are between aqua ligands and all three oxygens of the isonicotinate N-oxide ions.*

Introduction

In recent years Gelfand *et al.* have intensively studied the metal complexes of the monocarboxylic acid N-oxides [1–6]. On the basis of the spectral and magnetic behaviour of the complexes and on the basis of the structures of pyridine N-oxide [8–13] and pyridine carboxylic acid complexes [14–16] determined earlier, they have proposed the structures of monocarboxylic acid N-oxide complexes. They claim that in $CoL_2 \cdot 6H_2O$ and $NiL_2 \cdot 6H_2O$ the N-inicO ligands form single bridges between the metal ions, coordinating through the N–O and one of the COO oxygens. Of the six water molecules two are coordinated and four are lattice ones [1].

In our laboratory experiments have been carried out by X-ray to determine some metal complexes of monocarboxylic acid N-oxides. A report on the structure of the trinuclear copper complex is in press [17].

In this study the Co(II) and Ni(II) compounds with isonicotinic acid N-oxide proved to be ionic, and no direct coordination between metal ions and N-inicO oxygens existed.

Experimental

Preparation of Compounds

The synthetic procedure employed in preparing metal complexes of monocarboxylic acid N-oxide [1, 7] was slightly modified in order to get suitable crystals for X-ray work. Isonicotinic acid N-oxide and metal acetates were used as received. First, 0.02 mol of the acid was dissolved in hot water by adding $NH_3(aq)$ dropwise. After dissolving the solution was kept hot for about one hour. Secondly, 0.01 mol of $Ni(Ac)_2 \cdot 4H_2O$ and $Co(Ac)_2 \cdot 4H_2O$ were dissolved in 100 ml of hot water. The aqueous solutions of ammonium isonicotinate N-oxide and metal salt were then combined. The final volume was kept at about 200 ml. After filtering the hot solutions crystallization occurred with cooling. The crystals were then filtered off and washed with hot water and ethanol. The crystals of the cobalt compound were light orange pink and those of the nickel were light green.

Physical Methods

Co and Ni were analyzed by EDTA titrations. The chemical analysis for C, N and H was performed by the Central laboratory in Espoo, Finland.

IR spectra were recorded on a Perkin-Elmer 283 Infrared Spectrophotometer. The samples were run as KBr discs in the range 4000–200 cm^{-1}.

Data Collection

The crystal and intensity data were measured on a Syntex $P2_1$ automatic four-circle diffractometer employing graphite monochromatized MoK_α-radiation. The details of the data collection are seen in Table I. The data were corrected for Lorentz and polarisation factors but not for absorption effects.

Structure Determination

Since there are only two molecules of the complex in each unit cell, it was assumed that the molecules were centrosymmetric, with the metal atoms occypying special positions at 0, 0, 0 and 0, ½, ½. Refine-

TABLE I. Experimental Data.

	$Co(H_2O)_6^{2+}$ $2(L)^-$	$Ni(H_2O)_6^{2+}$ $2(L)^-$
Space group	$P2_1/c$	$P2_1/c$
	a = 7.747(2)	a = 7.765(2)
	b = 9.826(2)	b = 9.725(6)
	c = 11.474(2)	c = 11.363(6)
	β = 91.08(2)°	β = 91.20(3)°
Diffractometer	Syntex $P2_1$	
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Scan range	$4 < 2\theta < 70°$	$4 < 2\theta < 60°$
Scan rate	1° to 15° min^{-1}	1° to 15° min^{-1}
Radiation	MoK_α	MoK_α
Reflections collected	3389	2814
Criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Observed reflections	1427	1295
d_c	1.68 g cm^{-3}	1.71 g cm^{-3}
d_o	1.60 g cm^{-3}	1.68 g cm^{-3}
Z	2	2
R	0.0446	0.0445
R_w	0.044	0.049
parameters	165	165
$\mu(MoK_\alpha)$	11.0 cm^{-1}	12.0 cm^{-1}

ment was carried out with programs of the X-Ray System [18] on a UNIVAC 1100/60 computer. The scattering factors for Co, Ni, O, N and C were those of Cromer and Mann [19] and for H atoms those of Stewart, Davidson and Simpson [20]. Refinement of all nonhydrogen atoms with isotropic thermal parameters led to an R value of 0.136 and subsequent block-diagonal refinement with isotropic temperature factors led to an R value of 0.056. At this point all hydrogen atoms were located from a difference Fourier map. Three least squares cycles in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters were then computed. After the last cycle the final R value was 0.045 for both structures. The final positional and thermal parameters of the atoms are given in Tables II and III. A table of the calculated and observed structure factors is available from the author.

Results and Discussion

General

Table IV lists the analytical data of the compounds. The cobalt and nickel complexes of isonicotinic acid N-oxide prepared under the conditions

TABLE II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Non-hydrogen Atoms with Their Standard Deviations. The anisotropic thermal parameters are of the form $\exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}))$.

Atom	$Co(H_2O)_6^{2+}2(L)^-$								
	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1.0000	1.0000	1.0000	29.3(2)	23.9(1)	15.6(1)	1.7(3)	–5.2(1)	0.5(3)
O_1	1.4554(2)	0.9895(4)	0.8332(1)	37(9)	241(3)	22.3(7)	6(2)	–11.0(6)	1(2)
O_2	1.1521(3)	1.1062(2)	0.3348(1)	80(1)	41(1)	36(1)	16(1)	–23(1)	–2(1)
O_3	1.1789(3)	0.8822(2)	0.3259(1)	70(1)	33(1)	32(1)	–7(1)	–16(1)	–3(1)
O_4	0.9817(3)	1.1560(1)	0.8791(1)	80(1)	37(1)	30(1)	–7(1)	–22(1)	9(1)
O_5	0.9618(1)	1.1296(2)	1.1375(1)	67(1)	42(1)	31(1)	18(1)	–21(1)	–9(1)
O_6	1.2657(2)	1.0343(2)	1.0180(1)	36(1)	94(2)	35(1)	–0(1)	12(1)	–3(1)
N_1	1.3890(2)	0.9888(4)	0.7261(1)	27(1)	136(2)	23(1)	–2(1)	–8(1)	8(2)
C_1	1.3314(4)	1.1051(4)	0.6810(2)	54(2)	99(3)	36(1)	–5(2)	–6(1)	–28(2)
C_2	1.2651(4)	1.1102(3)	0.5683(2)	48(2)	62(2)	34(1)	3(1)	–6(1)	–9(1)
C_3	1.3181(3)	0.8735(3)	0.5517(2)	45(1)	51(2)	32(1)	–5(1)	–8(1)	14(1)
C_4	1.3801(4)	0.8711(4)	0.6641(2)	45(2)	98(3)	38(1)	5(2)	–10(1)	19(2)
C_5	1.2600(3)	0.9922(3)	0.5014(2)	30(1)	44(1)	24(1)	–9(2)	–8(1)	14(1)
C_6	1.1900(3)	0.9932(3)	0.3781(1)	34(1)	37(1)	25(1)	6(2)	–8(1)	19(1)
	$Ni(H_2O)_6^{2+}2(L)^-$								
Ni	1.0000	1.0000	1.0000	28.8(3)	20.0(2)	15.4(2)	0.9(4)	–4.2(2)	0.0(4)

(continued on facing page)

TABLE II. (continued)

Atom	$Ni(H_2O)_6^{2+}2(L)^-$								
	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O_1	1.4563(3)	0.9793(5)	0.8363(2)	41(2)	168(4)	21(1)	14(2)	−11(1)	−2(2)
O_2	1.1489(4)	1.1060(3)	0.3347(2)	72(2)	35(1)	32(1)	11(1)	−18(1)	2(1)
O_3	1.1853(4)	0.8791(2)	0.3227(2)	69(2)	28(1)	29(1)	−4(1)	−14(1)	−1(1)
O_4	0.9638(4)	1.1613(2)	0.8887(2)	59(2)	34(1)	29(1)	−4(1)	−14(1)	6(1)
O_5	0.9490(4)	1.1205(3)	1.1413(2)	55(2)	37(1)	26(1)	15(1)	−13(1)	−8(1)
O_6	1.2583(3)	1.0477(3)	1.0162(2)	35(1)	57(2)	30(1)	−2(1)	−12(1)	−0.6(11)
N_1	1.3904(4)	0.9814(5)	0.7284(2)	35(2)	95(3)	20(1)	−1(2)	−9(1)	−1(2)
C_1	1.3183(6)	1.0993(5)	0.6865(3)	47(2)	67(3)	37(2)	−1(2)	2(2)	−19(2)
C_2	1.2539(5)	1.1037(4)	0.5726(3)	47(2)	45(2)	27(2)	2(2)	−7(2)	−7(2)
C_3	1.3329(5)	0.8688(4)	0.5474(3)	37(2)	44(2)	35(2)	−2(2)	−3(2)	8(2)
C_4	1.3969(5)	0.8682(5)	0.6611(3)	39(2)	77(3)	34(2)	6(2)	−9(2)	19(2)
C_5	1.2610(4)	0.9868(4)	0.5017(2)	30(1)	32(2)	23(1)	−8(2)	−6(1)	2(2)
C_6	1.1920(5)	0.9908(5)	0.3766(2)	38(2)	35(2)	35(2)	23(1)	−10(1)	4(2)

TABLE III. Final Positional Parameters and Isotropic Thermal Parameters ($\times10^2$) for Hydrogen Atoms with Their Standard Deviations.

Atom	$Co(H_2O)_6^{2+}\ 2(L)^-$			
	X	Y	Z	U
H_1	0.663(3)	0.811(3)	0.273(2)	5(1)
H_2	0.219(4)	0.306(3)	0.037(3)	10(1)
H_3	0.315(4)	0.718(3)	0.017(2)	9(1)
H_4	0.557(4)	0.223(4)	0.306(3)	9(1)
H_5	0.274(4)	0.945(3)	0.017(2)	11(1)
H_6	0.334(4)	0.029(4)	0.086(3)	13(1)
H_7	0.074(4)	0.375(3)	0.378(3)	11(1)
H_8	0.070(5)	0.858(4)	0.199(3)	15(1)
H_9	0.054(4)	0.126(3)	0.193(2)	9(1)
H_{10}	0.068(3)	0.713(2)	0.380(2)	3(1)
	$Ni(H_2O)_6^{2+}2(L)^-$			
H_1	0.686(6)	0.824(4)	0.261(3)	6(1)
H_2	0.205(4)	0.310(4)	0.039(4)	7(1)
H_3	0.342(7)	0.722(5)	0.001(4)	8(2)
H_4	0.543(7)	0.202(5)	0.305(4)	8(2)
H_5	0.852(7)	0.985(7)	0.013(4)	12(2)
H_6	0.314(5)	0.028(4)	0.056(3)	6(1)
H_7	0.072(7)	0.351(6)	0.370(4)	12(2)
H_8	0.079(8)	0.854(6)	0.168(5)	13(2)
H_9	0.36(6)	0.109(5)	0.198(4)	9(2)
H_{10}	0.092(7)	0.695(5)	0.366(4)	11(2)

described by Gelfand *et al.* [1] proved to be identical with the cobalt and nickel compounds prepared in this study. Identification was carried out by IR spectra.

Infrared Spectra

IR spectra of the cobalt and nickel compounds were almost identical; only minor shifts could be seen in the absorptions of coordinated water and COO group. Table V lists the infrared absorptions due to coordinated H_2O, COO and N–O stretching. Figure 1 illustrates the IR data curves for nickel(II)-hexaquo diisonicotinate N-oxide and isonicotinic acid N-oxide. The carboxylate ion showed anti-symmetric and very strong symmetric stretching bands at 1658 and 1385 cm^{-1} for the Ni compound and at 1668 and 1382 cm^{-1} for the Co compound, respectively. Coordinated water had two strong absorption bands in the regions 3400 and 3100 cm^{-1}. H–O–H bending motion occurred in the range of 1600 cm^{-1}. The band is very strong. The wagging, rocking and metal–oxygen stretching modes of coordinated water were seen in the regions 820–850, 690–750 and 540–600 cm^{-1} in the spectra [21–26]. All these absorption bands were spread and there was fine structure indicating hydrogen bonds in the compounds.

Description and Discussion of the Structure

Interatomic distances and angles with estimated standard deviations in parentheses are given in Table VI. A view and numbering of the compounds is shown in Fig. 2 and the packing of the ions in Fig. 3.

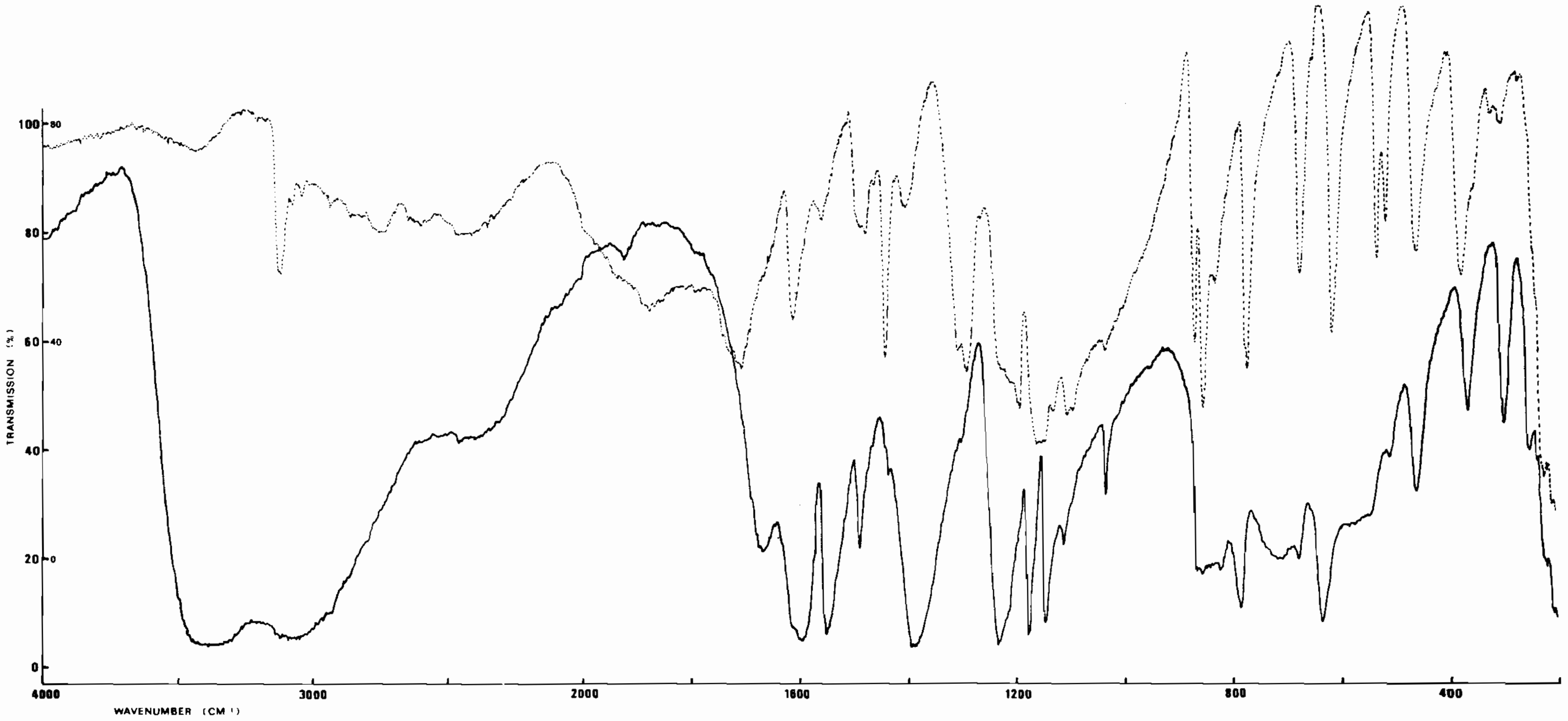

Fig. 1. Infrared spectra of KBr pellets of isonicotinic acid N-oxide (dotted line) and $Ni(H_2O)_6^{2+}$ $2L^-$ (solid line).

TABLE IV. Analytical Data.

Compound	%M		%H		%C		%N	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Co(H_2O)_6^{2+}$ $2L^-$	13.36	13.10	4.57	4.56	32.66	32.46	6.35	6.35
$Ni(H_2O)_6^{2+}$ $2L^-$	13.31	13.09	4.57	4.54	32.68	32.41	6.35	6.40

TABLE V. Infrared Absorption Bands (cm^{-1}).

Compound	ν_{asym} (CO_2)	ν_{sym} (CO_2)	Coordinated water			ν(NO)
			ν(OH)	δ(H–O–H)	wagging, rocking metal–oxygen stretching	
$Co(H_2O)_6^{2+}$ $2L^-$	1658	1385	3395, 3120	1599	822, 727, 542–600	1231
$Ni(H_2O)_6^{2+}$ $2L^-$	1668	1382	3390, 3085	1595	857, 716, 550–600	1230

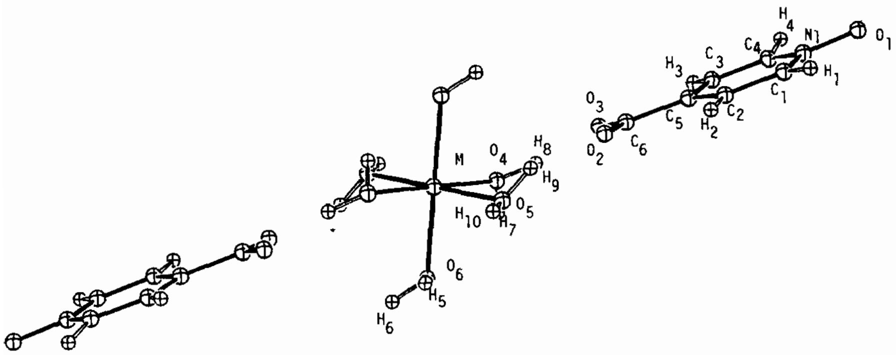

Fig. 2. An ORTEP drawing of an $M(H_2O)_6^{2+}$ $2L^-$ group including atomic labeling scheme.

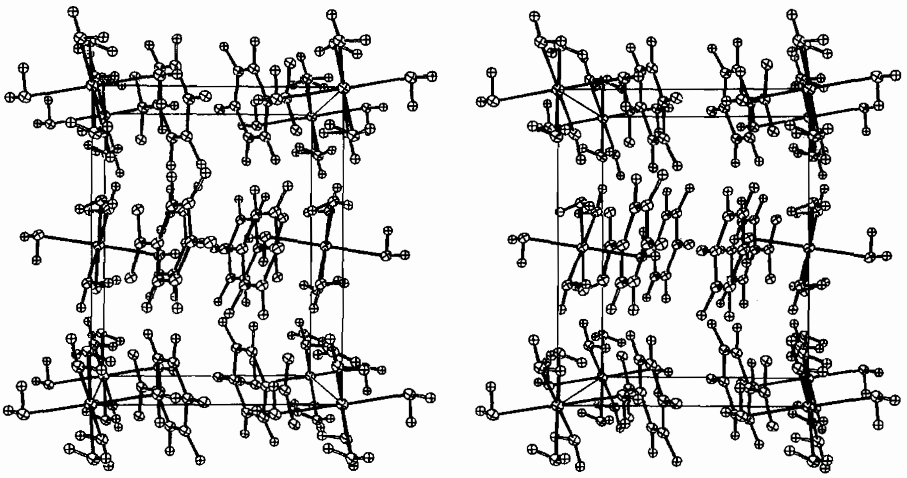

Fig. 3. A stereoview of the packing in the unit cell; projection is on the *ab* plane.

TABLE VI. Interatomic Distances (Å) and Angles (°) with Their Standard Deviations.

	M = Co	M = Ni
$M-O_4$	2.070(2)	2.031(2)
$M-O_5$	2.052(2)	2.033(2)
$M-O_6$	2.092(2)	2.063(3)
O_1-N_1	1.324(2)	1.319(3)
N_1-C_1	1.328(5)	1.358(6)
N_1-C_4	1.358(5)	1.342(6)
C_1-C_2	1.383(4)	1.378(5)
C_2-C_5	1.390(4)	1.395(5)
C_5-C_3	1.373(4)	1.374(6)
C_3-C_4	1.368(4)	1.375(5)
C_5-C_6	1.505(3)	1.509(4)
C_6-O_2	1.249(4)	1.260(5)
C_6-O_3	1.246(3)	1.248(5)
O_4-M-O_5	92.68(7)	91.13(9)
O_4-M-O_6	90.11(8)	90.20(10)
O_5-M-O_6	88.85(7)	89.70(10)
$O_1-N_1-C_1$	118.6(3)	119.2(4)
$O_1-N_1-C_4$	120.4(3)	119.9(4)
$C_5-C_6-O_2$	117.2(3)	117.7(3)
$C_5-C_6-O_3$	117.8(3)	116.8(4)
$O_2-C_6-O_3$	125.0(2)	125.5(3)

The structures of hexaquocobalt(II) and hexaquonickel(II) diisonicotinate N-oxide are isomorfic. The same is true of Co(II) and Ni(II) complexes of picolinic acid N-oxides [27, 7]. The metal ions are situated at the special points of the space group $P2_1/c$ and octahedrally coordinated by six water molecules. The $M(H_2O)_6^{2+}$ cation is also found in solid 2,2′-dithiobisbenzoic acid Co(II) and Ni(II) compounds [28] and in fluosilicates of the same metals [29].

The octahedral coordination around Co and Ni ions is almost undisturbed. The $M-O_w$ distances are 2.052–2.092 Å for Co(II) and 2.031–2.063 Å for Ni(II) compounds, respectively. $Ni-O_w$ distances are somewhat shorter than $Co-O_w$ distances. These values compare well with the $M-O_w$ distance values in the water octahedron reported in the literature [28, 29].

Isonicotinic acid N-oxide is an anion in the structure. In the carboxylate group the carbon–oxygen distances C_6-O_2 and C_6-O_3 are 1.249 and 1.246 Å for the Co(II) compound, and 1.260 and 1.248 Å for the Ni(II) compound. There is no direct coordination between metals and isonicotinate N-oxide ions. All distances between metal ions and three oxygens (O_1, O_2, O_3) of isonicotinate N-oxide ions are longer than the contact distance 3.8 Å.

The structure determination verified that these Co and Ni compounds are ionic including metal hexaquo cations and isonicotinate N-oxide anions lattice. The structures are held together by strong hydrogen bonds which are situated between the coordinated water molecules and the oxygens of the two anions. The hydrogen bonds are listed in Table VII, and they are about 2.7 Å. The anions form double bridges between coordinated water molecules. The bridge chains go diagonally through the cell.

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TABLE VII. The Hydrogen Bonds.

A–H···B	A–H	H···B	A–B	<AHB°	sym. opr. code
$Co(H_2O)_6^{2+}\ 2L^-$					
$O_6-H_6\cdots O_1$	0.94(3)	1.87(3)	2.639(2)	153(3)	*
$O_5-H_9\cdots O_2$	0.95(3)	1.80(3)	2.687(2)	156(3)	**
$O_4-H_8\cdots O_3$	0.99(3)	1.68(4)	2.667(2)	174(3)	***
$Ni(H_2O)_6^{2+}\ 2L^-$					
$O_6-H_6\cdots O_1$	0.65(3)	2.14(4)	2.667(4)	160(4)	*
$O_5-H_9\cdots O_2$	0.93(5)	1.77(5)	2.668(4)	162(4)	**
$O_4-H_8\cdots O_3$	0.73(5)	1.94(6)	2.673(3)	175(6)	***

*   x, y, z

**   x, y, ½ + z

***   1 – x, 1 – y, ½ – z

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