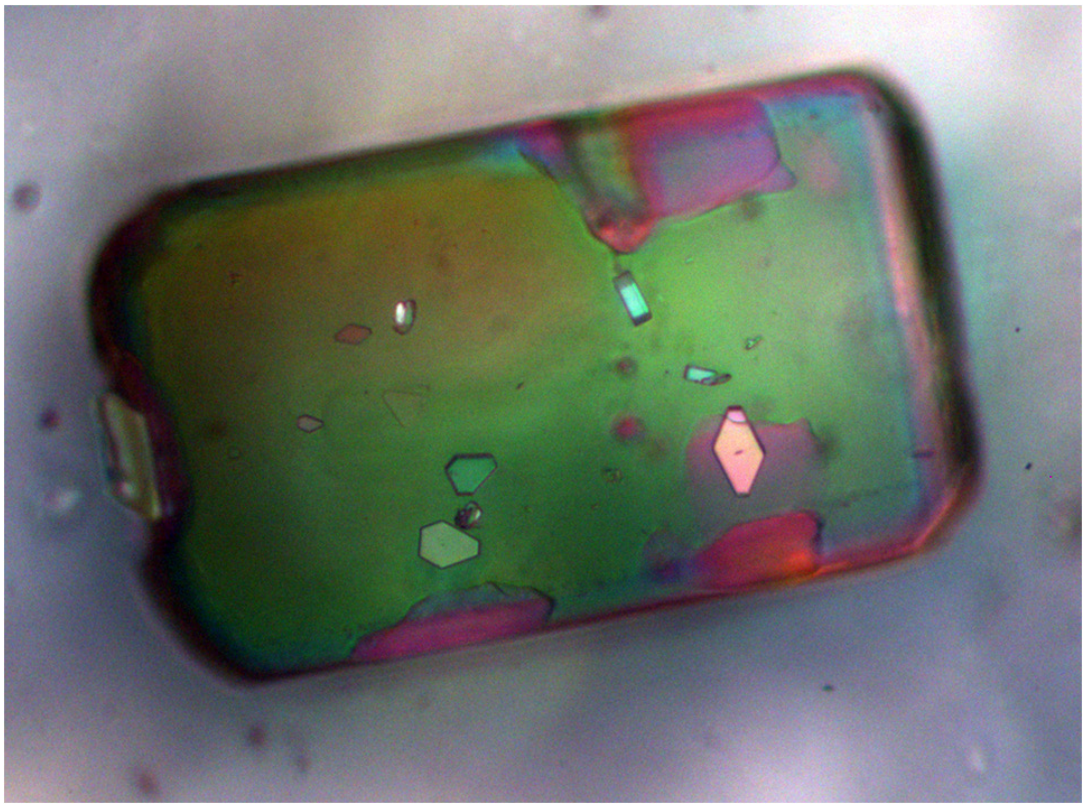
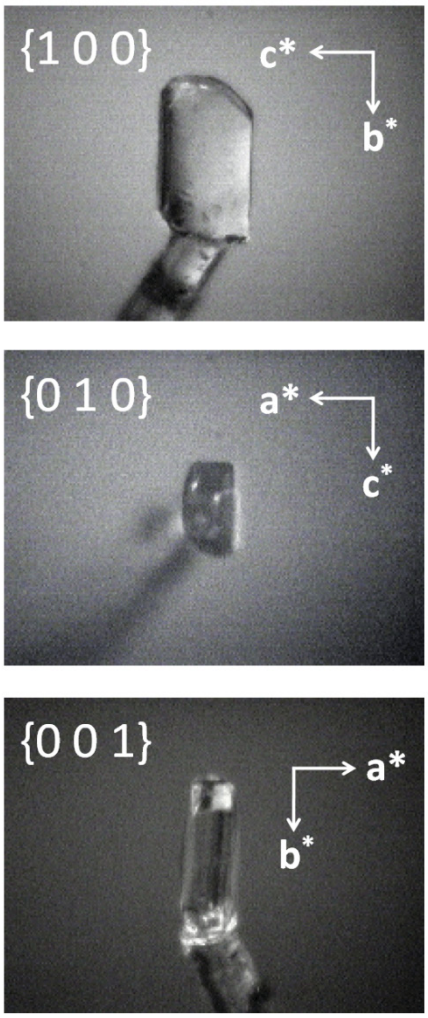
Fig. S-1



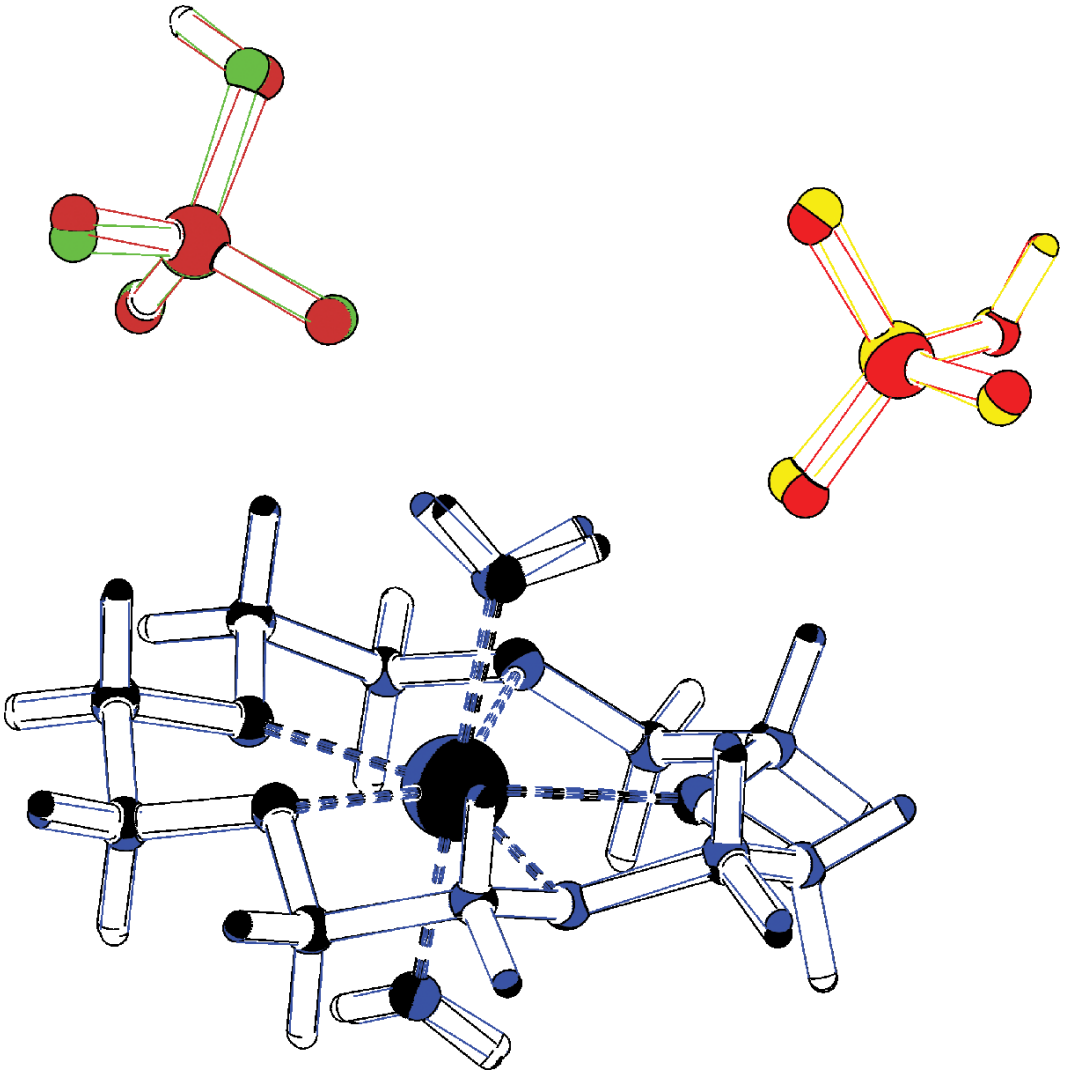
Crystal of $[Ni(H_2O)_2(15C5)](HSO_4)_2$ removed from the mother liquor. Near room temperature, decomposition occurred after an hour, and growth of new green crystallites took place. These crystallites were those of the tetragonal polymorph of $Ni(SO_4)\cdot 6H_2O$.

Fig. S-2



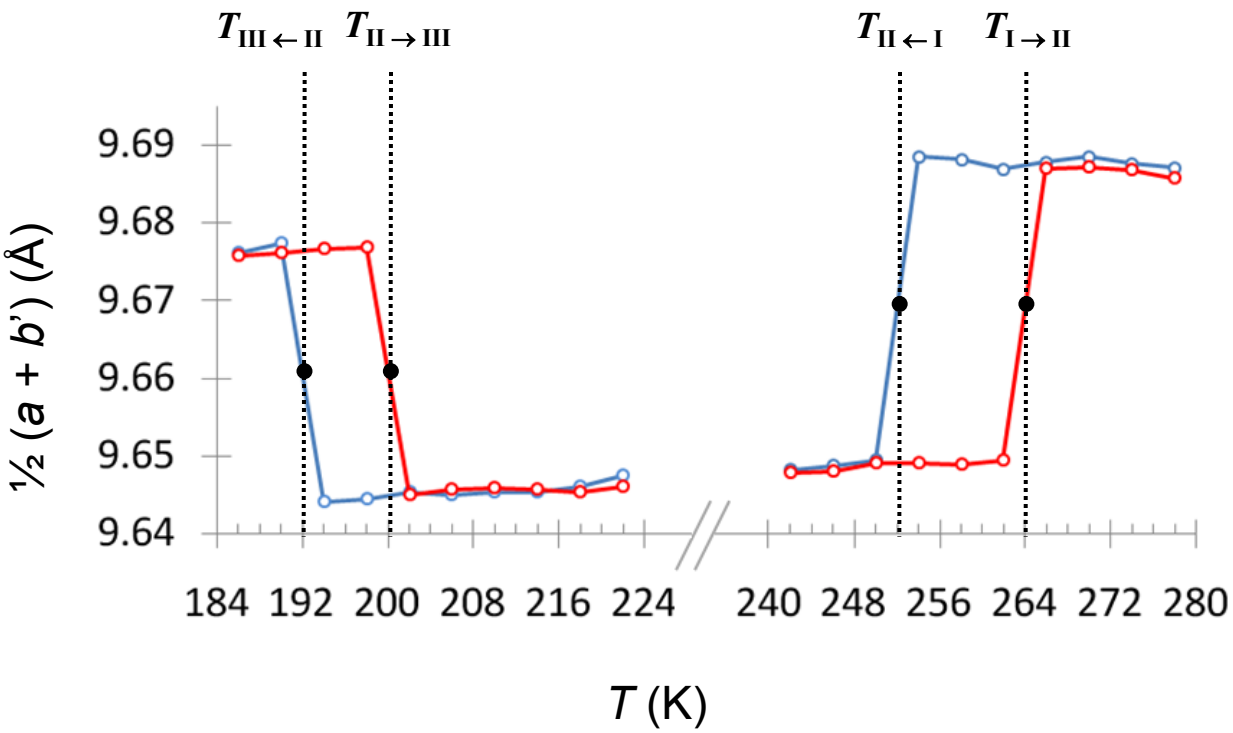

Crystal of $[Ni(H_2O)_2(15C5)](HSO_4)_2$ mounted on the diffractometer. The indices are given in the *Cmc*$2_1$ cell of phase I. The most important crystal faces and directions of the reciprocal crystal axes are shown.

Fig. S-3



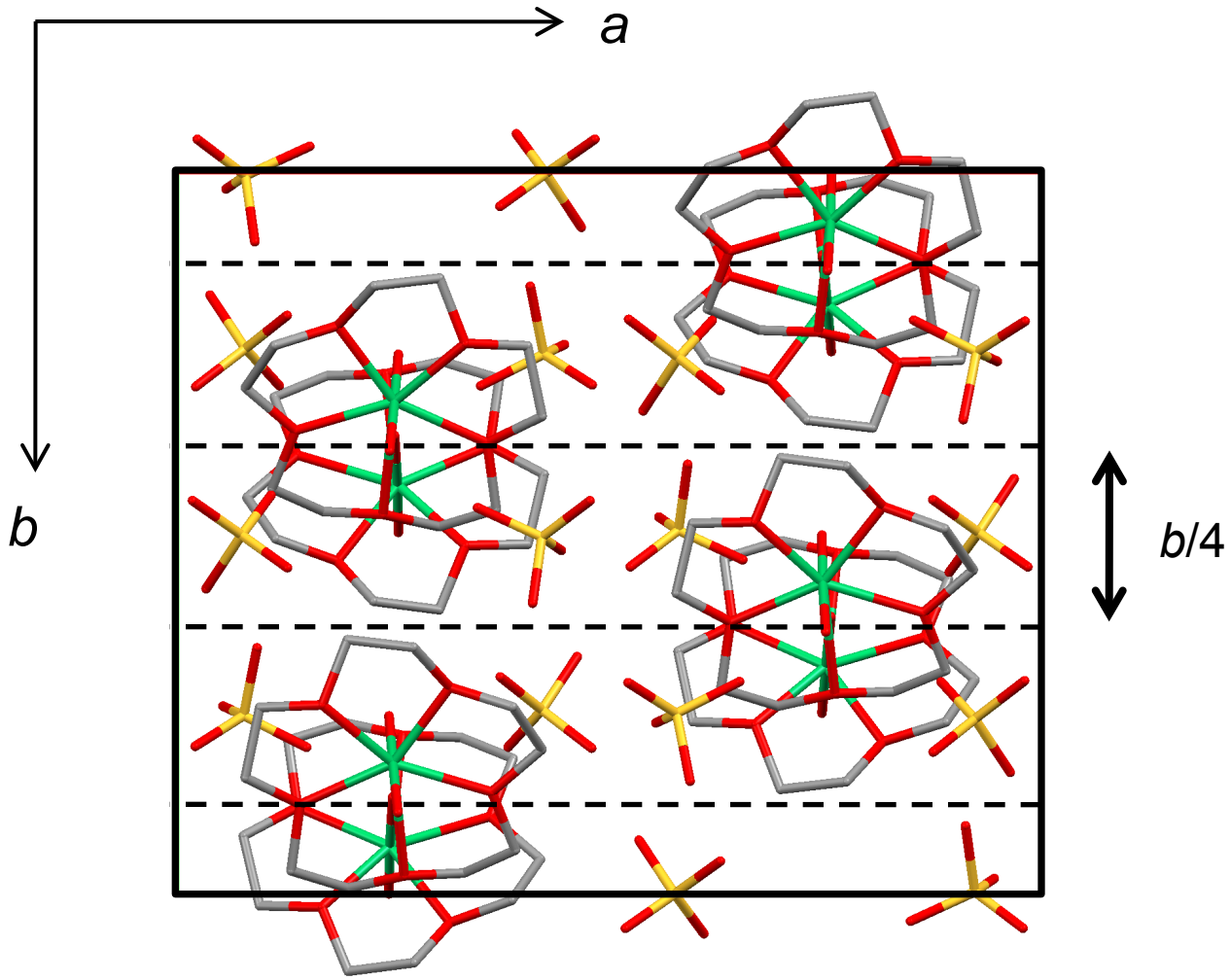
Overlay of the two crystallography independent formula units of $[Ni(H_2O)_2(15C5)](HSO_4)_2$ (phase III, $Z'$ = 2). The two cations nearly superimposed (even the H atoms nearly superimposed except for those of the water ligands), whereas differences in orientations are more noticeable for the counterions.

Fig. S-4




Plots of ½ (*a* + *b*') (Å) versus *T* (K). Values of ½ (*a* + *b*') are measured for the transitions I ↔ II and II ↔ III at ± 4 K for both cooling (blue) and heating (red) regimens. Discontinuities in these values are found for both transitions. The positions of the vertical dotted lines give the estimated transition temperatures.

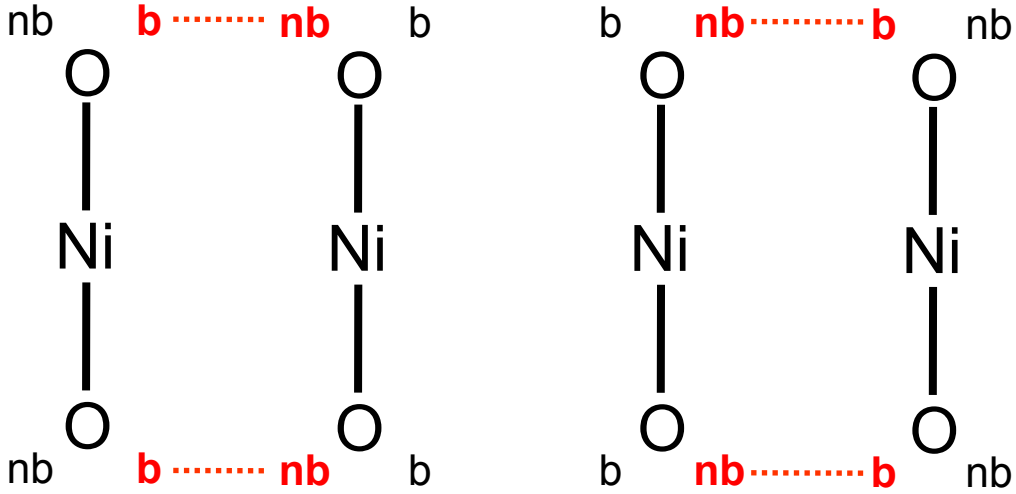
Fig. S-5



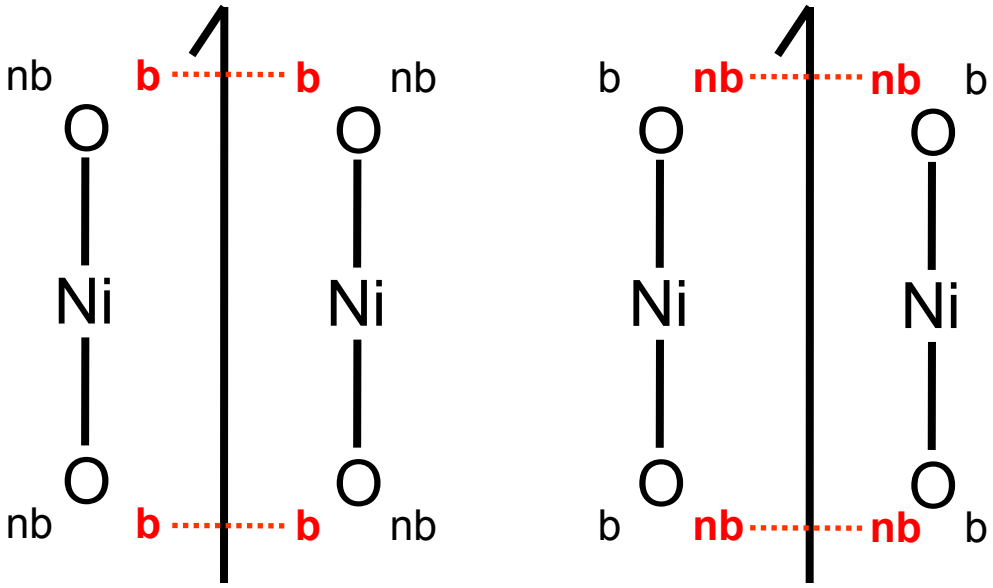

Drawing showing the packing in the unit cell of the *Pbn*$2_1$, *Z'* = 2 structure down the **c** direction. The structure is pseudosymmetric, and there are four non-crystallographic pseudo *c* glide planes (⊥ to *b*) per unit cell separated by *b*/4. The pseudo glide planes are shown as black dashed lines. H atoms are omitted for clarity.

Fig. S-6

(i) non alternations *R R* or *S S*




(ii) alternations *R S* or *S R*




The different geometries of the S−O−H···O−S bridges for non-alternations *R R* (or *S S*) and alternations *R S* (or *S R*) along the **a** ± **b**/2 directions (phase III). For alternations *R S* (or *S R*), the two bridges b···b and nb···nb are related by $2_1$ axes.

Table S-1. Measurement temperature (*T*), number of reflections used for cell refinement, cell constants (*a*, *b*, *c*), and cell volume *V* for the transitions I → II and II → III in the cooling mode (blue), and for the transitions III → II and II → I in the heating mode (red). The cell constants are given in the cells $Cmc2_1$ (I), $Pbc2_1$ (II) and $Pbn2_1$ (III)

| T (K) | phase | ref # | a (Å) | b (Å) | c (Å) | V(Å3) |
|---|---|---|---|---|---|---|
| 270 | I | 807 | 17.8604(9) | 7.4836(3) | 14.7905(5) | 1976.89(18) |
| 260 | I | 820 | 17.8628(9) | 7.4818(3) | 14.7761(6) | 1974.77(19) |
| 250 | II | 834 | 17.7546(6) | 7.5264(3) | 14.7896(6) | 1976.32(20) |
| 240 | II | 868 | 17.7533(10) | 7.5222(2) | 14.7754(4) | 1973.15(13) |
| 230 | II | 872 | 17.7541(8) | 7.5253(3) | 14.7627(6) | 1972.38(18) |
| 220 | II | 880 | 17.7525(11) | 7.5240(3) | 14.7471(6) | 1969.78(17) |
| 210 | II | 908 | 17.7507(07) | 7.5245(4) | 14.7321(5) | 1967.69(18) |
| 200 | III | 1060 | 17.8507(07) | 14.9346(4) | 14.7071(5) | 3920.81(26) |
| 190 | III | 1177 | 17.8480(6) | 14.9298(7) | 14.6955(5) | 3915.85(37) |
| 180 | III | 1243 | 17.8434(8) | 14.9240(6) | 14.6850(4) | 3910.52(31) |
| 170 | III | 1321 | 17.8424(7) | 14.9226(7) | 14.6749(5) | 3907.29(39) |
| 160 | III | 1339 | 17.8416(4) | 14.9203(4) | 14.6648(4) | 3903.81(26) |
| 150 | III | 1388 | 17.8410(6) | 14.9171(5) | 14.6533(4) | 3899.75(33) |
| 140 | III | 1416 | 17.8386(6) | 14.9170(6) | 14.6421(5) | 3896.23(26) |
| 130 | III | 1461 | 17.8396(8) | 14.9132(6) | 14.6331(6) | 3893.06(32) |
| 120 | III | 1485 | 17.8392(8) | 14.9111(7) | 14.6228(6) | 3889.69(36) |
| 110 | III | 1479 | 17.8377(9) | 14.9086(8) | 14.6118(7) | 3885.78(39) |
| 110 | III | 1519 | 17.8395(8) | 14.9060(6) | 14.6111(7) | 3885.34(42) |
| 120 | III | 1495 | 17.8406(10) | 14.9100(8) | 14.6227(6) | 3889.70(50) |
| 130 | III | 1451 | 17.8396(10) | 14.9124(7) | 14.6338(5) | 3893.02(39) |
| 140 | III | 1419 | 17.8404(8) | 14.9152(6) | 14.6428(6) | 3896.34(39) |
| 150 | III | 1398 | 17.8410(7) | 14.9188(6) | 14.6536(6) | 3900.30(31) |
| 160 | III | 1347 | 17.8416(8) | 14.9213(6) | 14.6642(6) | 3903.89(27) |
| 170 | III | 1311 | 17.8437(10) | 14.9237(6) | 14.6754(5) | 3907.99(33) |
| 180 | III | 1268 | 17.8474(8) | 14.9272(5) | 14.6852(4) | 3912.29(29) |
| 190 | III | 1207 | 17.8444(7) | 14.9288(6) | 14.6985(4) | 3915.62(32) |
| 200 | III | 1131 | 17.8500(6) | 14.9305(6) | 14.7088(4) | 3920.03(34) |
| 210 | II | 902 | 17.7525(12) | 7.5236(4) | 14.7342(6) | 1967.95(21) |
| 220 | II | 912 | 17.7534(8) | 7.5241(3) | 14.7479(5) | 1970.00(18) |
| 230 | II | 884 | 17.7528(8) | 7.5253(3) | 14.7633(5) | 1972.30(15) |
| 240 | II | 872 | 17.7546(11) | 7.5261(4) | 14.7761(6) | 1974.44(20) |
| 250 | II | 861 | 17.7556(9) | 7.5255(3) | 14.7893(6) | 1976.13(19) |
| 260 | II | 850 | 17.7549(9) | 7.5274(4) | 14.8023(6) | 1978.31(18) |
| 270 | I | 807 | 17.8605(10) | 7.4850(4) | 14.792(10) | 1977.49(18) |

Table S-2. Measurement temperature (*T*), number of reflections used for cell refinement, cell constants (*a*, *b*, *c*), and cell volume *V* for the transitions I → II (cooling, blue) and II → I (heating, red). The cell constants are given in the cells $Cmc2_1$ (I) and $Pbc2_1$ (II)

| T (K) | phase | refl. # | a (Å) | b (Å) | c (Å) | V(Å$^3$) |
|---|---|---|---|---|---|---|
| 278 | I | 833 | 17.8575(8) | 7.4881(3) | 14.8071(5) | 1979.99(17) |
| 274 | I | 723 | 17.8589(7) | 7.4876(3) | 14.8025(5) | 1979.40(16) |
| 270 | I | 852 | 17.8610(8) | 7.4875(3) | 14.7970(5) | 1978.86(18) |
| 266 | I | 834 | 17.8600(8) | 7.4859(3) | 14.7911(6) | 1977.53(19) |
| 262 | I | 857 | 17.8581(9) | 7.4858(4) | 14.7853(6) | 1976.53(20) |
| 258 | I | 847 | 17.8619(8) | 7.4838(3) | 14.7792(5) | 1975.60(18) |
| 254 | I | 860 | 17.8627(9) | 7.4833(3) | 14.7748(7) | 1974.98(20) |
| 250 | II | 888 | 17.7593(7) | 7.5275(3) | 14.7928(6) | 1977.56(20) |
| 246 | II | 894 | 17.7576(10) | 7.5286(3) | 14.7869(6) | 1976.86(18) |
| 242 | II | 899 | 17.7567(5) | 7.5276(3) | 14.7815(5) | 1975.77(15) |
| 242 | II | 899 | 17.7564(8) | 7.5267(3) | 14.7828(4) | 1975.68(15) |
| 246 | II | 913 | 17.7568(8) | 7.5270(3) | 14.7875(6) | 1976.43(18) |
| 250 | II | 896 | 17.7582(9) | 7.5288(4) | 14.7926(5) | 1977.75(19) |
| 254 | II | 878 | 17.7586(7) | 7.5279(3) | 14.7978(5) | 1978.24(14) |
| 258 | II | 883 | 17.7584(10) | 7.5277(4) | 14.8032(7) | 1978.90(21) |
| 262 | II | 878 | 17.7593(7) | 7.5279(3) | 14.8090(5) | 1979.82(16) |
| 266 | I | 840 | 17.8586(7) | 7.4858(2) | 14.7914(5) | 1977.41(15) |
| 270 | I | 843 | 17.8585(7) | 7.4869(3) | 14.7955(4) | 1978.23(18) |
| 274 | I | 840 | 17.8574(9) | 7.4876(3) | 14.8017(6) | 1979.11(21) |
| 278 | I | 828 | 17.8546(6) | 7.4886(3) | 14.8081(4) | 1979.94(14) |

Table S-3. Measurement temperature (*T*), number of reflections used for cell refinement, cell constants (*a*, *b*, *c*), and cell volume *V* for the transitions II → III (cooling, blue) and III → II (heating, red). The cell constants are given in the cells $Pbc2_1$ (II) and $Pbn2_1$ (III)

| T (K) | phase | refl. # | a (Å) | b (Å) | c (Å) | V(Å$^3$) |
|---|---|---|---|---|---|---|
| 222 | II | 900 | 17.7557(10) | 7.5269(2) | 14.7553(5) | 1971.98(17) |
| 218 | II | 904 | 17.7525(10) | 7.5266(3) | 14.7487(5) | 1970.66(16) |
| 214 | II | 909 | 17.7514(11) | 7.5260(3) | 14.7429(7) | 1969.60(23) |
| 210 | II | 906 | 17.7516(10) | 7.5258(3) | 14.7385(6) | 1968.98(18) |
| 206 | II | 923 | 17.7506(9) | 7.5259(3) | 14.7334(5) | 1968.21(17) |
| 202 | II | 915 | 17.7518(10) | 7.5252(3) | 14.7273(8) | 1967.37(20) |
| 198 | II | 923 | 17.7504(10) | 7.5236(3) | 14.7225(6) | 1966.12(23) |
| 194 | II | 918 | 17.7494(10) | 7.5242(3) | 14.7182(6) | 1965.60(19) |
| 190 | III | 1165 | 17.8453(9) | 14.9355(7) | 14.6997(6) | 3917.88(40) |
| 186 | III | 1156 | 17.8427(7) | 14.9349(6) | 14.6965(6) | 3916.32(44) |
| 186 | III | 1186 | 17.8417(8) | 14.9352(7) | 14.6951(5) | 3915.80(38) |
| 190 | III | 1147 | 17.8425(6) | 14.9353(6) | 14.7012(5) | 3917.64(33) |
| 194 | III | 1124 | 17.8434(8) | 14.9375(8) | 14.7050(6) | 3919.43(42) |
| 198 | III | 1105 | 17.8430(8) | 14.9409(5) | 14.7083(6) | 3921.08(33) |
| 202 | II | 921 | 17.7514(10) | 7.5240(3) | 14.7264(6) | 1966.88(17) |
| 206 | II | 926 | 17.7520(7) | 7.5260(3) | 14.7323(5) | 1968.26(16) |
| 210 | II | 908 | 17.7527(10) | 7.5256(3) | 14.7371(6) | 1968.87(16) |
| 214 | II | 925 | 17.7523(11) | 7.5255(4) | 14.7434(7) | 1969.65(25) |
| 218 | II | 909 | 17.7515(10) | 7.5257(4) | 14.7487(6) | 1970.31(23) |
| 222 | II | 901 | 17.7531(9) | 7.5258(2) | 14.7431(5) | 1971.11(16) |

Table S-4. Geometrical parameters for OH•••O hydrogen bonds found in phases I, II and III of $[Ni(H_2O)_2(15C5)](HSO_4)_2$

| | O–H···O (Å) | H···O (Å) | O···O (Å) | O–H–O (°) |
|---|---|---|---|---|
| **Phase I** | | | | |
| O6–H···O8 | 0.767(19) | 1.91(2) | 2.667(3) | 168(4) |
| O6–H···O8' | 0.767(19) | 2.02(2) | 2.743(4) | 157(4) |
| O7–H···O9 | 0.797(17) | 1.889(18) | 2.650(3) | 159(3) |
| O7–H···O8' | 0.797(17) | 2.06(2) | 2.767(5) | 149(3) |
| O11–H···O10 | 0.82 | 1.82 | 2.581(8) | 153 |
| O11–H···O10' | 0.82 | 1.82 | 2.619(14) | 164 |
| **Phase II** | | | | |
| O6–H···O8 | 0.79(2) | 1.88(2) | 2.663(4) | 168(4) |
| | 0.81(2) | 1.87(2) | 2.676(3) | 174(3) |
| O6–H···O8' | 0.79(2) | 2.00(3) | 2.728(5) | 154(4) |
| | 0.81(2) | 2.01(3) | 2.757(16) | 153(4) |
| O7–H···O9 | 0.79(2) | 1.89(2) | 2.645(4) | 161(4) |
| | 0.81(2) | 1.87(2) | 2.672(3) | 170(4) |
| O7–H···O8' | 0.79(2) | 2.02(3) | 2.724(5) | 148(3) |
| | 0.81(2) | 2.15(4) | 2.799(18) | 137(3) |
| O11–H···O10 | 0.83 | 2.03 | 2.596(5) | 125 |
| | 0.83 | 2.12 | 2.69(2) | 126 |
| O11–H···O10' | 0.83 | 1.67 | 2.44(3) | 153 |
| | 0.83 | 1.70 | 2.50(2) | 160 |
| **Phase III** | | | | |
| O6–H···O8 | 0.85(2) | 1.88(2) | 2.712(3) | 168(3) |
| | 0.87(2) | 1.91(2) | 2.730(3) | 158(3) |
| | 0.78(2) | 1.97(2) | 2.738(3) | 165(3) |
| | 0.83(2) | 1.89(2) | 2.697(3) | 162(3) |
| O7–H···O8 | 0.77(2) | 1.99(2) | 2.748(3) | 164(3) |
| | 0.86(2) | 1.88(2) | 2.729(3) | 173(3) |
| O7–H···O9 | 0.84(2) | 1.85(2) | 2.686(3) | 176(3) |
| | 0.82(2) | 1.87(2) | 2.671(3) | 167(3) |
| O11–H···O10 | 0.84(2) | 1.76(2) | 2.583(3) | 166(3) |
| | 0.87(2) | 1.75(2) | 2.579(3) | 158(3) |
| | 0.82(2) | 1.77(2) | 2.565(3) | 163(3) |
| | 0.85(2) | 1.76(2) | 2.583(3) | 161(3) |