

Supplementary materials

Magnetocaloric Effect in 1D-Polymers Bearing 15-Metallacrown-5 {GdCu₅}³⁺ Units and Anionic Oxalate Complexes

Anna V. Pavlishchuk,^{*a, b} Sergey V. Kolotilov,^a Matthias Zeller,^b Vitaly V. Pavlishchuk,^a
Fabrice Pointillart^{*c} and Anthony W. Addison^{*d}

^a L.V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine, Prospect Nauki 31, Kyiv 03028, Ukraine; Email: annpavlis@ukr.net

^b Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IA 47907-2084 U.S.A.; zeller4@purdue.edu

^c Université de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR 6226, F-35000 Rennes, France; fabrice.pointillart@univ-rennes1.fr.

^d Department of Chemistry, Drexel University, Philadelphia, PA 19104-2816, U.S.A.; Email: addisona@drexel.edu

Structure refinement details.

For both compounds and structures, extensive solvent (water) disorder is observed and was modelled. U_{ij} components of ADPs for disordered water atoms closer to each other than 2.0 Å were restrained to be similar. Water H atom positions were refined and O-H and H...H distances were restrained to 0.84(2) and 1.36(2) Å, respectively, while a damping factor was applied. Some water H atom positions were further constrained based on hydrogen bonding considerations. In the final refinement cycles, positions of ill-defined H atoms of minor moiety water molecules were set to ride on their oxygen carrier atoms, and the damping factor was removed.

Complex 1. The water molecule of O36 is disordered around an inversion centre and the position is partially occupied; it was constrained to be close to isotropic. Subject to these

conditions, the occupancy rate refined to 0.396(13) for each of the two symmetry equivalent positions.

The water molecule of O12 was refined as disordered over two positions. The occupancy rate refined to 0.55(3) to 0.45(3).

The main group of waters features two sets of molecules with complementary occupancies (O16, O34, O37, O38, O40, O41 vs. O34B, O37B, O38B, O39B, O40B, O41B). The first group also features three more water molecules with reduced occupancies (O16, O39, O39C, O41C). The second group features two more water molecules with reduced occupancies (O16B, O33). The main occupancy ratio refined to 0.597(6) to 0.403(6). Occupancies of O16, O39, O39C, O41C, O16B and O33 refined to 0.421(11), 0.299(10), 0.182(10), 0.131(9), 0.131(9), 0.322(15), and 0.869(9).

Complex 2. The water molecule of O17 is hydrogen-bonded to its counterpart across an inversion centre and its H atoms were refined as 1:1 disordered. Water molecule O29 is disordered over two positions. This disorder induces disorder for one O and one C atom of the neighboring oxalate, and for the H atoms of the water of O27. The two disordered oxalate moieties were restrained to have similar geometries. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were constrained to be similar. Subject to these conditions, the occupancy ratio refined to 0.494(6) to 0.506(6).

The main group of water molecules features two sets of molecules with complementary occupancies (O16, O31-O34 vs. O16B, O31B, O32B, O34B). The first group also features two more water molecules with reduced occupancies (O36, O36C). Two water molecules are disordered around an inversion centre with half occupancy (O35, O35B). These are compatible with either set of the other water molecules. The main occupancy ratio refined to 0.664(5) to 0.336(5). The occupancy of O36 refined to 0.081(9), that of O36C to 0.154(11).

Table S1. Single crystal data and structure refinement details for complexes **1** and **2**

	Complex 1	Complex 2
Formula	GdCu ₅ CrC ₁₆ H _{56.05} N ₁₀ O _{40.02}	Gd ₂ Cu ₁₃ C ₃₂ H _{87.60} N ₂₀ O _{67.80}
<i>M</i> / g mol ⁻¹	1556.12	2978.24
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	13.547(3)	9.2930(13)
<i>b</i> , Å	25.425(6)	14.602(2)
<i>c</i> , Å	14.885(3)	16.484(2)
α , °	90.00	97.361(2)
β , °	105.569(3)	100.370(2)
γ , °	90.00	99.751(2)
Volume/ Å ³	4939(2)	2139.4(5)
<i>Z</i>	4	1
<i>T</i> / K	100(2)	100(2)
Range of data collection	1.976° < 2 θ < 31.991°	2.068 ° < 2 θ < 31.825 °
ρ_{calc} / g·cm ⁻³	2.093	2.312
Absorption coefficient / mm ⁻¹	3.766	4.813
μ (Mo-K α)	0.71073	0.71073
<i>F</i> (000)	3103	1467
Collected reflections	107685	45021
Reflections unique	16125	13190
<i>R</i> _{int}	0.0399	0.0354
Goodness-of-fit on <i>F</i> ²	1.207	1.047
<i>R</i> ₁ ($[I > 2\sigma(I)]$) ^a	0.0424	0.0306
w <i>R</i> ₂ ($[I > 2\sigma(I)]$) ^b	0.0854	0.0702

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, ^b $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

Table S2. Selected characteristics of crystal structures of **1** and **2**

Complex	1	2
Range of Gd--Cu separations, Å	3.8545(7) – 3.9676(9)	3.9055(6) – 3.9605(6)
Range of Cu--Cu separations, Å	4.529(1) – 4.596(1)	4.5594(7) – 4.6170(7)
Range of Gd–O _{equat} , Å	2.396(3) – 2.561(3)	2.425(2) – 2.4931(19)
Range of Cu–O _{equat} , Å	1.915(3) – 1.962(3)	1.927(2) – 1.954(2)
Range of Cu–N _{equat} , Å	1.894(3) – 2.014(3)	1.905(2) – 2.039(2)
Range of τ^1 values for pentacoordinate Cu(II) ions	0.152 – 0.172	0.001 – 0.142
Coordination number of Gd(III) ions	9	9
Average deviation among non-hydrogen atoms from Cu ₅ plane, Å	0.172	0.167
The largest deviation among non-hydrogen atoms from Cu ₅ plane, Å	0.785	0.395
Deviation of Gd(III) ion from Cu ₅ plane, Å	0.532	0.395
Distance between adjacent Cu ₅ plane in metallacrown dimers, Å	-	6.436
Angle between adjacent Cu ₅ planes, °	75.5	-
Solvent accessible volume, PLATON ² estimation	33.4	22.0

Complex 1**Table S3.** Selected bond lengths (Å) and angles (°) for complex 1

Bond	Å	Bond	Å	Bond	Å
Cu1-O1	1.943(3)	Cu2-O3	1.929(3)	Cu3-O5	1.915(3)
Cu1-O2	1.942(3)	Cu2-O4	1.929(3)	Cu3-O6	1.962(3)
Cu1-N9	1.906(3)	Cu2-N1	1.901(3)	Cu3-N3	1.905(3)
Cu1-N10	2.015(3)	Cu2-N2	2.013(3)	Cu3-N4	2.003(3)
Cu1-O14w	2.434(3)	Cu2-O16w	2.566(8)	Cu3-O12w	2.368(6)
Cu4-O7	1.938(3)	Cu2-O38w	2.514(8)	Cu3-O12Bw	2.51(2)
Cu4-O8	1.942(3)	Cu5-O9	1.932(3)	Cr1-O19	1.984(3)
Cu4-N5	1.894(3)	Cu5-O10	1.953(3)	Cr1-O20	1.993(3)
Cu4-N6	2.014(3)	Cu5-N7	1.900(3)	Cr1-O21	1.953(3)
Cu4-O23	2.587(5)	Cu5-N8	1.996(4)	Cr1-O22	1.977(3)
Gd1-O1	2.458(3)	Cu5-O15w	2.663(5)	Cr1-O25	1.969(3)
Gd1-O3	2.482(3)	Gd1-O9	2.561(3)	Cr1-O26	1.985(3)
Gd1-O5	2.396(3)	Gd1-O11w	2.393(3)	Gd1-O17	2.691(3)
Gd1-O7	2.415(3)	Gd1-O13w	2.402(3)	Gd1-O18	2.535(3)
Angles	deg.	Angles	deg.	Angles	deg.
O1-Cu1-O2	84.49(12)	O3-Cu2-O4	86.02(12)	O5-Cu3-O6	84.48(11)
O1-Cu1-N9	91.02(12)	O3-Cu2-N1	89.91(12)	O5-Cu3-N3	90.44(12)
O2-Cu1-N10	100.10(14)	O4-Cu2-N2	100.49(14)	O6-Cu3-N4	170.17(12)
N9-Cu1-N10	82.93(14)	N1-Cu2-N2	83.52(14)	N3-Cu3-N4	83.58(13)
O7-Cu4-O8	85.19(12)	O9-Cu5-O10	85.18(12)	O1-Gd1-O3	69.63(8)
O7-Cu4-N5	91.07(12)	O9-Cu5-N7	90.40(13)	O5-Gd1-O3	71.56(9)
O8-Cu4-N6	100.09(13)	O10-Cu5-N8	100.92(14)	O5-Gd1-O7	72.22(9)
N5-Cu4-N6	83.35(14)	N7-Cu5-N8	83.03(15)	O7-Gd1-O9	69.50(9)
O19-Cr1-O20	82.46(11)	O22-Cr1-O20	91.07(13)	O1-Gd1-O9	69.72(9)
O19-Cr1-O21	91.91(12)	O25-Cr1-O22	96.26(14)	O11-Gd1-O13	141.07(10)
O19-Cr1-O25	90.86(13)	O26-Cr1-O20	91.42(11)	O11-Gd1-O17	136.12(12)
O19-Cr1-O26	91.42(12)	O25-Cr1-O26	82.28(12)	O11-Gd1-O18	141.39(10)
O21-Cr1-O20	97.19(12)	O22-Cr1-O26	95.18(13)	O13-Gd1-O17	67.27(9)
O21-Cr1-O22	82.49(12)	O21-Cr1-O25	89.42(13)	O13-Gd1-O18	72.85(9)
				O18-Gd1-O17	62.43(8)

Table S4. Continuous shape calculations for Cu^{II} and Cr^{III} ions in the complex **1** obtained using the Shape 2.1 software.³

Polyhedron geometry for pentacoordinate ions in complex 1					
Ion	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
Cu1	25.659	2.232	6.195	1.432	8.953
Cu3A	28.772	2.945	7.092	1.950	10.228
Cu3B	32.309	1.497	6.080	0.876	9.051
Cu4	32.006	2.075	5.908	1.294	9.622
Cu5	29.910	2.980	7.032	1.970	10.284
Polyhedron geometry for hexacoordinate ions in complex 1					
Ion	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Cu2	32.818	24.234	3.308	13.645	26.592
Cr1	32.027	25.422	0.673	12.515	29.052

Pentacoordinate ions:

PP-5 – Pentagon (D_{5h}), VOC-5 – Vacant octahedron (C_{4v}), TBPY-5 – Trigonal bipyramid (D_{3h}), SPY-5 – Spherical square pyramid (C_{4v}), JTBPY-5 – Johnson trigonal bipyramid J12 (D_{3h})

Hexacoordinate ions:

HP-6 – Hexagon (D_{6h}), PPY-6 – Pentagonal pyramid (C_{5v}), OC-6 – Octahedron (O_h), TPR-6 – Trigonal prism (D_{3h}), JPPY-6 – Johnson pentagonal pyramid J2 (C_{5v})

Table S5. Continuous shape calculations for nonacoordinated Gd^{III} ions in the complex **1** obtained using the Shape 2.1 software.³

Polyhedron geometry for nonacoordinate Gd(III) ions in complex 1						
EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9
35.430	21.521	19.818	14.875	11.010	9.731	1.552
MFF-9	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	
0.846	0.469	1.873	1.100	13.336	11.262	

Nonacoordinate ions:

EP-9 – Enneagon (D_{9h}), OPY-9 – Octagonal pyramid (C_{8v}), HBPY-9 – Heptagonal bipyramid (D_{7h}), JTC-9 – Johnson triangular cupola J3 (C_{3v}), JCCU-9 – Capped cube J8 (C_{4v}), CCU-9 – Spherical-relaxed capped cube (C_{4v}), JCSAPR-9 – Capped square antiprism J10 (C_{4v}), **CSAPR-9 – Spherical capped square antiprism (C_{4v})**, JTCTPR-9 – Tricapped trigonal prism J51 (D_{3h}), TCTPR-9 – Spherical tricapped trigonal prism (D_{3h}), JTDIC-9 – Tridiminished icosahedron J63 (C_{3v}), HH-9 – Hula-hoop (C_{2v}); MFF-9 – Muffin (C_s)

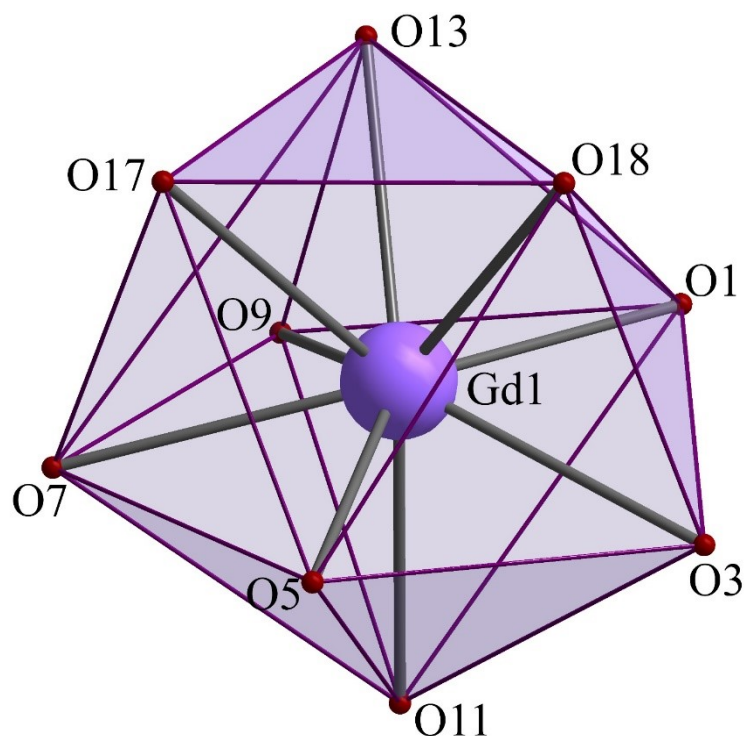


Figure S1. The coordination environment of Gd(III) in **1**.

Complex 2

Table S6. Selected bond lengths (Å) and angles (°) for complex 2

Bond	Å	Bond	Å	Bond	Å
Cu1-O9	1.942(2)	Cu2-O1	1.929(2)	Cu3-O3	1.954(2)
Cu1-O10	1.950(2)	Cu2-O2	1.952(2)	Cu3-O4	1.944(2)
Cu1-N7	1.913(2)	Cu2-N9	1.909(2)	Cu3-N1	1.905(2)
Cu1-N8	2.030(3)	Cu2-N10	2.001(3)	Cu3-N2	2.039(2)
Cu1-O17w	2.416(3)	Cu2-O28w	2.799(4)	Cu3-O27w	2.445(3)
Cu4-O5	1.9377(19)	Cu5-O7	1.927(2)	Cu6-O10	2.341(2)
Cu4-O6	1.953(2)	Cu5-O8	1.947(2)	Cu6-O11	1.968(2)
Cu4-N3	1.907(3)	Cu5-N5	1.907(2)	Cu6-O12	1.998(2)
Cu4-N4	2.018(2)	Cu5-N6	2.006(2)	Cu7-O18	1.969(2)
Cu4-O21	2.512(3)	Cu5-O16w	2.532(4)	Cu7-O19	1.950(2)
Gd1-O1	2.486(2)	Gd1-O13	2.517(5)	Cu7-O22	1.945(2)
Gd1-O3	2.458(2)	Gd1-O13B	2.378(5)	Cu7-O23	1.955(2)
Gd1-O5	2.4931(19)	Gd1-O14	2.458(2)	Cu7-O26w	2.449(2)
Gd1-O7	2.4637(19)	Gd1-O15w	2.375(2)	Cu7-O8	2.731(2)
Gd1-O9	2.425(2)	Gd1-O29w	2.737(4)		
Angles	deg.	Angles	deg.	Angles	deg.
O9-Cu1-O10	84.50(9)	O1-Cu2-O2	85.39(8)	O4-Cu3-O3	85.12(9)
N7-Cu1-O9	91.05(9)	N9-Cu2-O1	91.22(9)	N1-Cu3-O3	90.84(9)
O10-Cu1-N8	101.30(10)	O2-Cu2-N10	99.69(9)	O4-Cu3-N2	100.11(9)
N7-Cu1-N8	82.81(10)	N9-Cu2-N10	83.43(10)	N1-Cu3-N2	82.95(10)
O5-Cu4-O6	85.97(8)	O7-Cu5-O8	85.85(8)	O11-Cu6-O12	85.04(9)
N3-Cu4-O5	88.30(9)	N5-Cu5-O7	91.08(9)	O11-Cu6-O12'	94.96(9)
O6-Cu4-N4	101.14(9)	O8-Cu5-N6	98.94(9)	O11-Cu6-O10	87.96(8)
N3-Cu4-N4	83.80(10)	N5-Cu5-N6	84.05(10)	O12-Cu6-O10	88.99(9)
O19-Cu7-O18	85.49(9)	O7-Gd1-O9	72.15(6)	O13-Gd1-O29	62.99(15)
O22-Cu7-O23	85.21(9)	O9-Gd1-O1	72.50(6)	O14-Gd1-O29	60.92(11)
O1-Gd1-O3	70.52(7)	O13-Gd1-O14	65.89(12)	O15-Gd1-O29	146.27(11)
O3-Gd1-O5	68.44(7)	O13-Gd1-O15	143.38(12)	O13B-Gd1-O14	68.19(13)
O5-Gd1-O7	70.67(6)	O13B-Gd1-O15	149.33(14)	O14-Gd1-O15	138.24(8)

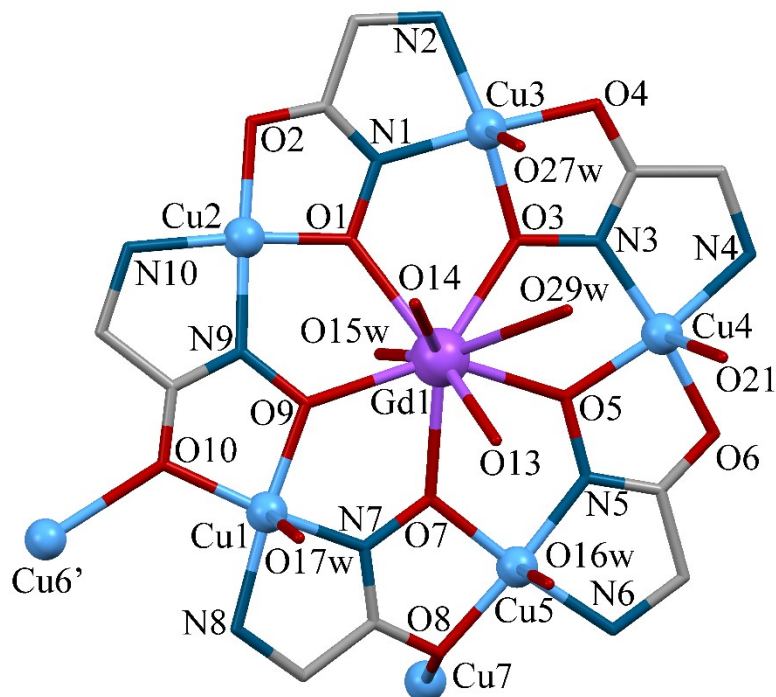


Figure S2. The $[\text{GdCu}_5(\text{GlyHA})_5(\text{H}_2\text{O})_3]^{3+}$ cation in the crystal structure of complex **2**. Hydrogen atoms are omitted for clarity of presentation.

Table S7. Continuous shape calculations for Cu(II) ions in the complex **2** obtained using the Shape 2.1 software.³

Polyhedron geometry for pentacoordinate ions in complex 1					
Ion	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
Cu1	29.481	1.839	4.350	1.253	7.217
Cu2	28.776	3.333	6.178	1.955	10.307
Cu3	32.208	1.805	5.452	1.114	9.040
Cu4	25.810	2.367	6.835	1.605	9.678
Cu5	30.390	1.637	5.860	1.236	8.726
Polyhedron geometry for hexacoordinate ions in complex 1					
Ion	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Cu6	31.324	28.814	0.785	16.483	31.565
Cu7	32.561	27.508	2.334	16.047	29.765

Pentacoordinate ions:

PP-5 – Pentagon (D_{5h}), vOC-5 – Vacant octahedron (C_{4v}), TBPY-5 – Trigonal bipyramid (D_{3h}), SPY-5 – Spherical square pyramid (C_{4v}), JTBPY-5 – Johnson trigonal bipyramid J12 (D_{3h})

Hexacoordinate ions:

HP-6 – Hexagon (D_{6h}), PPY-6 – Pentagonal pyramid (C_{5v}), OC-6 – Octahedron (O_h), TPR-6 – Trigonal prism (D_{3h}), JPPY-6 – Johnson pentagonal pyramid J2 (C_{5v})

Table S8. Continuous shape calculations for nonacoordinated Gd(III) ions in the complex **2** obtained using the Shape 2.1 software.³

Polyhedron geometry for nonacoordinate Gd(III) ions in complex 2						
EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9
35.532	22.582	18.505	15.971	9.987	8.563	1.843
MFF-9	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	
0.832	0.645	2.368	1.468	12.977	11.397	

Nonacoordinate ions:

EP-9 – Enneagon (D_{9h}), OPY-9 – Octagonal pyramid (C_{8v}), HBPY-9 – Heptagonal bipyramid (D_{7h}), JTC-9 – Johnson triangular cupola J3 (C_{3v}), JCCU-9 – Capped cube J8 (C_{4v}), CCU-9 – Spherical-relaxed capped cube (C_{4v}), JCSAPR-9 – Capped square antiprism J10 (C_{4v}), **CSAPR-9 – Spherical capped square antiprism (C_{4v})**, JTCTPR-9 – Tricapped trigonal prism J51 (D_{3h}), TCTPR-9 – Spherical tricapped trigonal prism (D_{3h}), JTDIC-9 – Tridiminished icosahedron J63 (C_{3v}), HH-9 – Hula-hoop (C_{2v})
MFF-9 – Muffin (C_s)

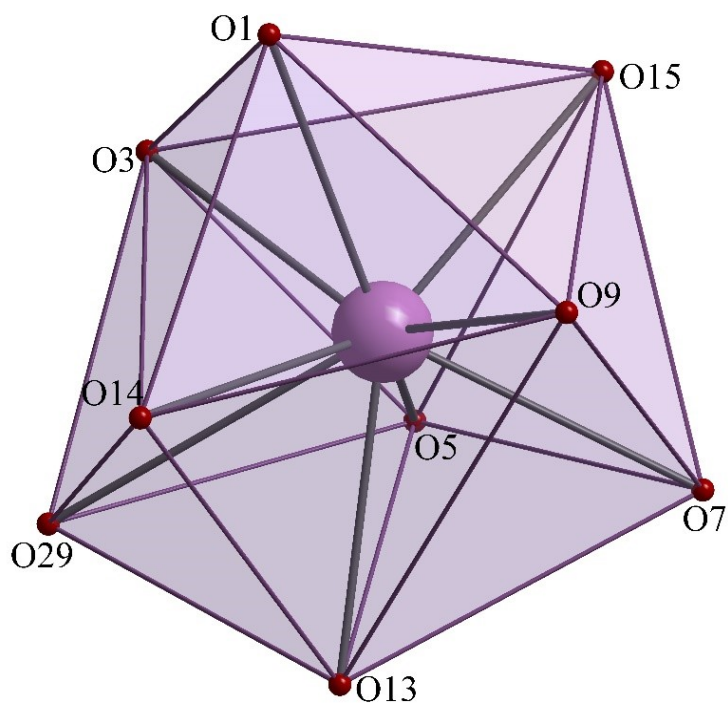


Figure S3. The coordination environment of the Gd^{III} ions in the metallacrown units in **2**.

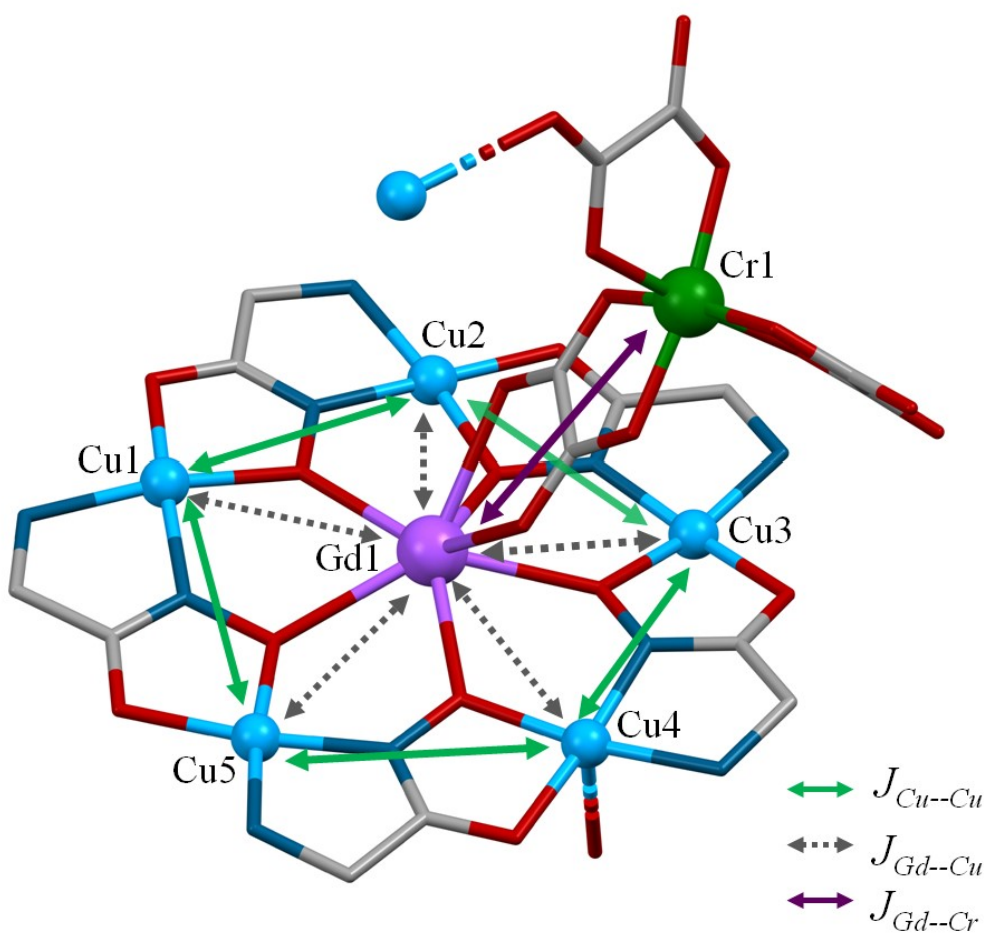


Figure S4. The scheme for exchange interactions amongst paramagnetic centres in complex **1**.

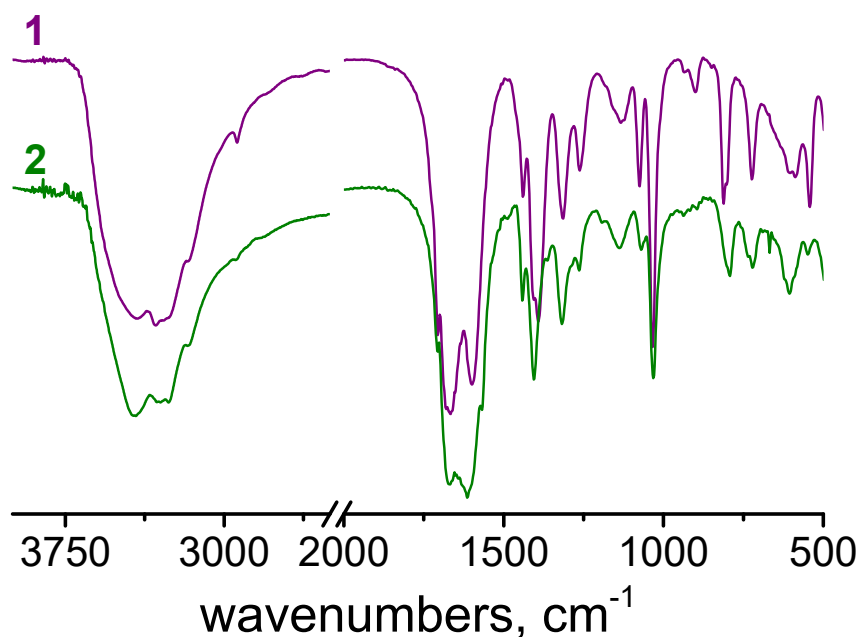


Figure S5. IR spectra of **1** and **2** recorded in KBr pellets.

Powder XRD Measurements

Sample preparation: A sample of complex **1** was dried and hand-ground using an agate mortar and pestle prior to PXRD measurement. For compound **2**, removal from solvent at room temperature leads to rapid (< 20 minutes) loss of water of crystallization and structural transformation (demonstrated by single crystal structure determination on a partially desolvated crystal). For PXRD freshly prepared crystals were thus not ground and the sample was suspended in a small amount of water for P-XRD data collection.

Data collection: Powder diffraction (XRD) data for both complexes were collected under ambient conditions in focusing mode on a Panalytical Empyrean X-ray diffractometer equipped with Bragg-Brentano HD optics, a sealed tube copper X-ray source ($\lambda = 1.54178 \text{ \AA}$), 0.04 rad Soller slits on the incident and 0.02 rad Soller slits at the receiving optics sides, and a PixCel3D Medipix detector. Both samples were packed in silicon single crystal zero background sample holders, 16 mm wide and 0.25 mm deep. A $1/4^\circ$ anti-scatter slit and $1/16^\circ$ divergence slit as well as a 4 mm mask were chosen based on

sample area and starting θ angle. Data were collected between 5 and 60° in 2θ using the Panalytical Data Collector software.⁴

Rietveld refinements were performed against the models of the 100 K single crystal structure data sets using the HighScore⁵ software of Panalytical. Refinement of preferred orientation was included using a spherical harmonics model and split width and shape was modelled. Plots of Rietveld fits for both compounds are given Figures S6 and S7. Complete reports with all Rietveld analysis parameters are given below.

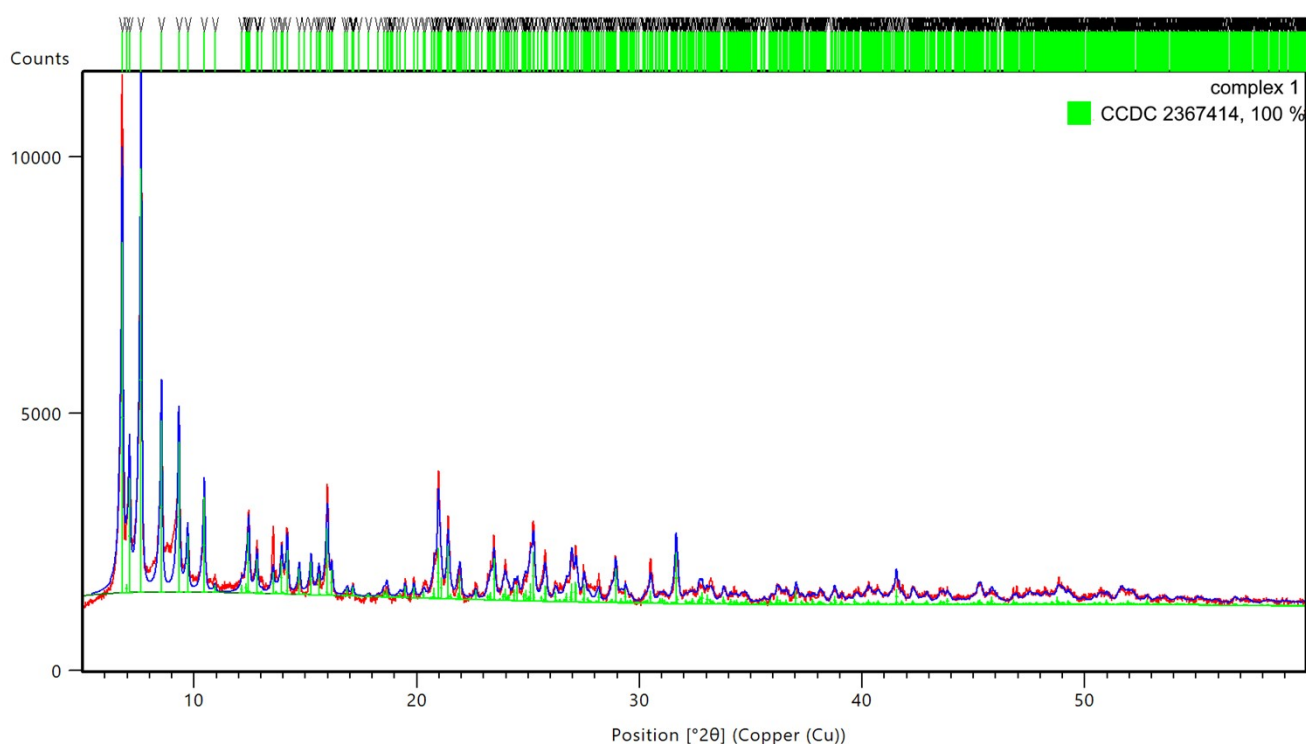


Figure S6. Powder diffraction data (red) and Rietveld refinement (blue) for complex 1. Red: experimental pattern. Blue: Rietveld fit. Green: Miller index tick marks.

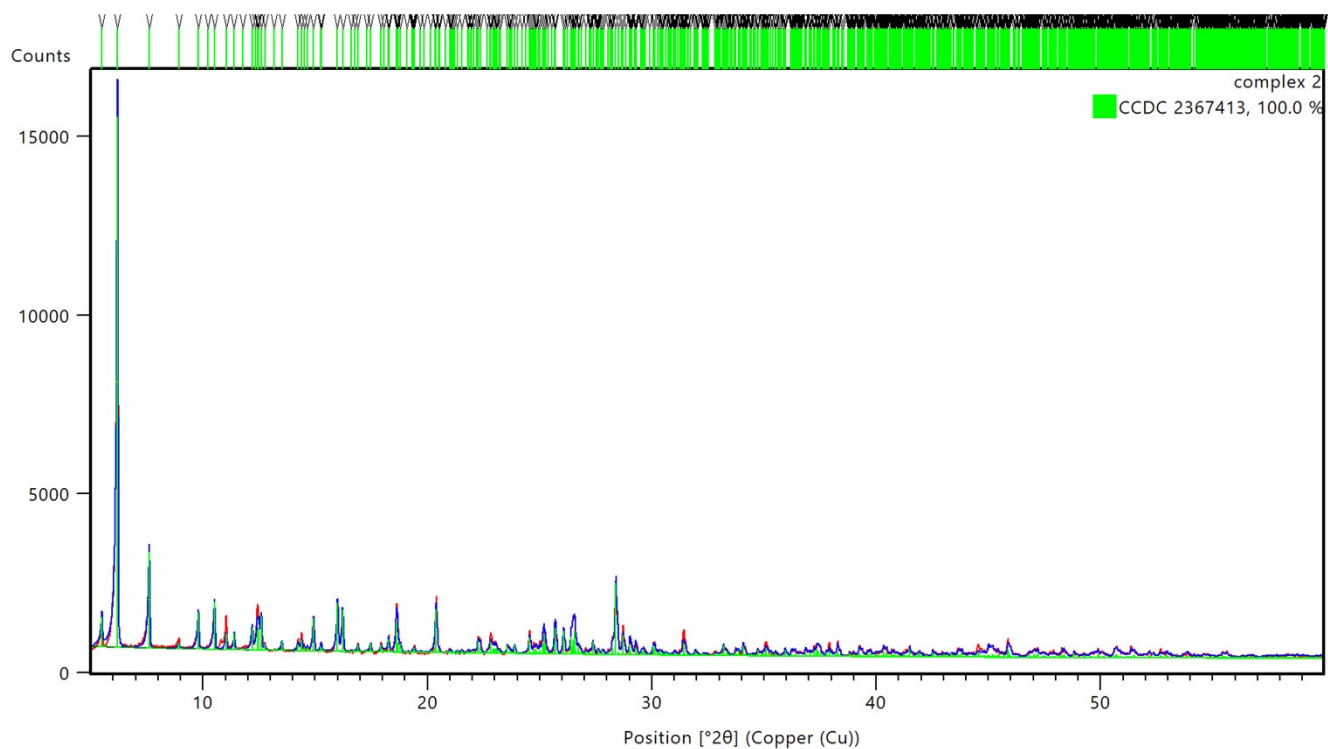


Figure S7. Powder diffraction data (red) and Rietveld refinement (blue) for complex 2. Red: experimental pattern. Blue: Rietveld fit. Green: Miller index tick marks.

Complex 2-RT**Table S9.** Comparison of single crystal data and structure refinement details for complex **2** collected at **100 K** and at **RT** after partial desolvation.

	Complex 2-100K	Complex 2-RT
Formula	Gd ₂ Cu ₁₃ C ₃₂ H _{87.60} N ₂₀ O _{67.80}	Gd ₂ Cu ₁₃ C ₃₂ H ₅₆ N ₂₀ O ₅₂
<i>M</i> / g mol ⁻¹	2978.24	2693.48
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.2930(13)	8.803(2)
<i>b</i> , Å	14.602(2)	13.995(4)
<i>c</i> , Å	16.484(2)	16.256(4)
α , °	97.361(2)	92.029(9)
β , °	100.370(2)	99.867(9)
γ , °	99.751(2)	104.771(9)
Volume/ Å ³	2139.4(5)	1901.3(9)
<i>Z</i>	1	1
<i>T</i> / K	100(2)	298(2)
Range of data collection	2.068 ° < 2 θ < 31.825 °	1.894 ° < 2 θ < 28.628°
ρ_{calc} / g·cm ⁻³	2.312	2.352
Absorption coefficient / mm ⁻¹	4.813	5.387
μ (Mo-K α)	0.71073	0.71073
<i>F</i> (000)	1467	1309
Collected reflections	45021	45083
Reflections unique	13190	9580
<i>R</i> _{int}	0.0354	0.1555
Goodness-of-fit on <i>F</i> ²	1.047	1.029
<i>R</i> ₁ ([<i>I</i> > 2 σ (<i>I</i>)] ^a)	0.0306	0.1273
w <i>R</i> ₂ [I > 2 σ (I)] ^b	0.0702	0.3373

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Structure Refinement Details, complex (2-RT)

The data were obtained from a partially desolvated crystal of complex **2** and were obtained as follows: the crystal was taken fresh from crystallization mother liquor, coated in a small amount of Fomblin oil, mounted on a MiTeGen micromesh mount and rapidly transferred into the coldstream of the diffractometer precooled to 100 K. A full dataset was collected that confirmed the structure previously obtained from a different crystal from an earlier crystallization batch.

After completion of the 100 K data collection, the crystal was warmed up at a rate of 6 °C per minute to room temperature (298 K). The unit cell was re-established and was found to have changed (the volume had become smaller and cell axes and angles had changed). Data quality (achievable resolution) had also changed, as expected for a highly solvated system at warmer temperature, but the crystal had remained largely single crystalline in nature (slight splitting of reflections was observed, but not associated with any perceivable twinning). The unit determination was repeated several times, until no change in unit cell parameters was observed anymore. A full data set was then collected at 298 K.

The structure was solved from the 100 K dataset, and adjustments were made to account for changes of atom arrangements. The arrangement of the metallacrown units and of the bridging bis(oxalato)cuprate anions were largely unchanged. A large fraction of previously present water molecules were not observable anymore (*ca.* 9 water molecules were lost per asymmetric unit, see below), and the remainder of the water molecules were ill-defined. The only loosely bonded bis(oxalato)cuprate anion was found to be highly disordered, with one side (that of O24/O25) swinging by nearly the entire length of the oxalate ligand ($> 2 \text{ \AA}$). The bis(oxalato)cuprate anion was modeled as two-fold disordered. The disorder extends to most of the remaining water molecules, which were also modelled as two-fold disordered. The two disordered bis(oxalato)cuprate moieties were restrained to have similar geometries. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar.

Water H atom positions were initially refined and O-H and H...H distances were restrained to 0.84(2) and 1.36(2) Å, respectively, while a damping factor was applied. Some water H atom positions were further restrained based on hydrogen bonding considerations. In the final refinement cycles the H atoms were constrained to ride on their carrying oxygen atom (AFIX 3) and the damping factor was removed.

The low data quality of the partially desolvated crystal required use of some additional restraints. Atoms N5 and O3 of the main complex were restrained to be close to isotropic. The N-C bond of N10-C10 was restrained to a target value of 1.50(2) Å. Subject to these conditions the occupancy ratio refined to 0.635(11) to 0.365(11).

The structure contains an additional 96 Å³ of solvent accessible pores (4% of the unit cell volume). No substantial electron density peaks were found in the solvent accessible pores (less than 1.6 electron per Å³) and the residual electron density peaks are not arranged in an interpretable pattern. The structure factors were instead augmented *via* reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A.L. Spek (1990). Acta Cryst. A46, 194-201) as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the pore space was used together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 32 electrons within the solvent accessible pores, or *ca* 3 water molecules.

Of the originally *ca.* 23.80 water molecules per unit cell (12.31 bonded to the two metallacrown units and 11.48 interstitial) 12 water molecules were located in difference densities and refined (8 bonded to the two metallacrown units and 4 interstitial). Approximately three more were accounted for by diffuse density, as indicated by the Platon electron count, for a total of 15 of the original *ca.* 24 water molecules, thus indicating a loss of 9 water molecules. This equals 37.5% of water molecules, or *ca.* 5.4% of the original molecular weight. The volume of the unit cell shrank from 2139.3(5) to 1901.3(9), by *ca.* 11% of the original volume (not accounting for contraction upon cooling).

Attempts to cool the partially desolvated crystal (at 6 degrees per minute) resulted in strain buildup and fragmentation of the crystal and attempts to obtain better structural data were not successful.

X-ray structure of complex **2** obtained at room temperature

$\{[(\text{GdCu}_5(\text{GlyHA})_5(\text{H}_2\text{O})_2)\mu_2\text{-}[\text{Cu}(\text{C}_2\text{O}_4)_2]\}_2\mu_4\text{-}[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}\}_n$ complex (**2-RT**).

Overall the structure of the polymeric 1D-chain in complex **2** at room temperature closely resembles the structural particulars of **2** at 100 K. The loss of water molecules in **2** upon warming to room temperature is accompanied with small shifts of the relative positions of 15-metallacrown-5 units and $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ anions in **2-RT** (Figures S8 and S9, Table S10).

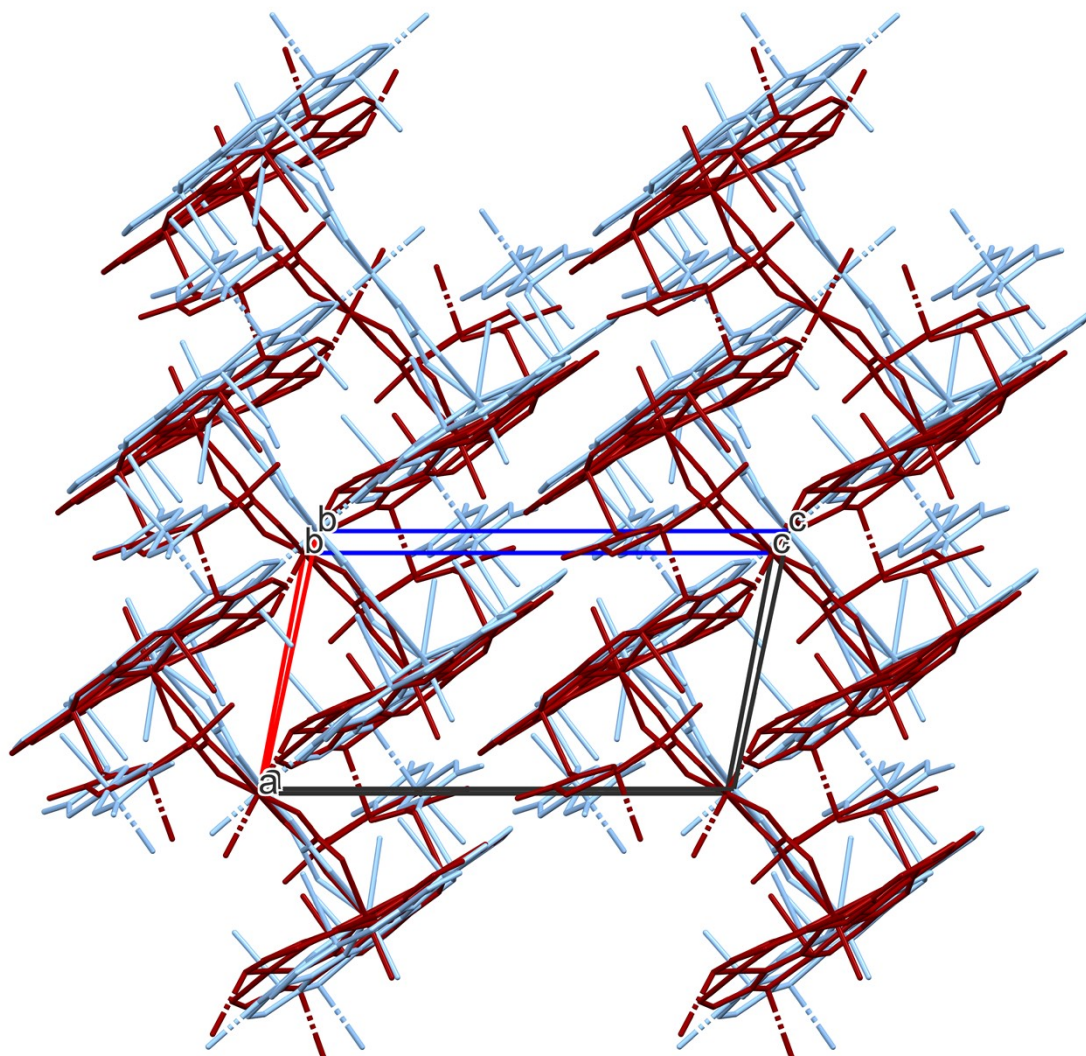


Figure S8. Overlay of the fragments of the crystal structures of complex **2** (view down the *b* axis) obtained at 100 K (light blue) and 298 K (dark red).

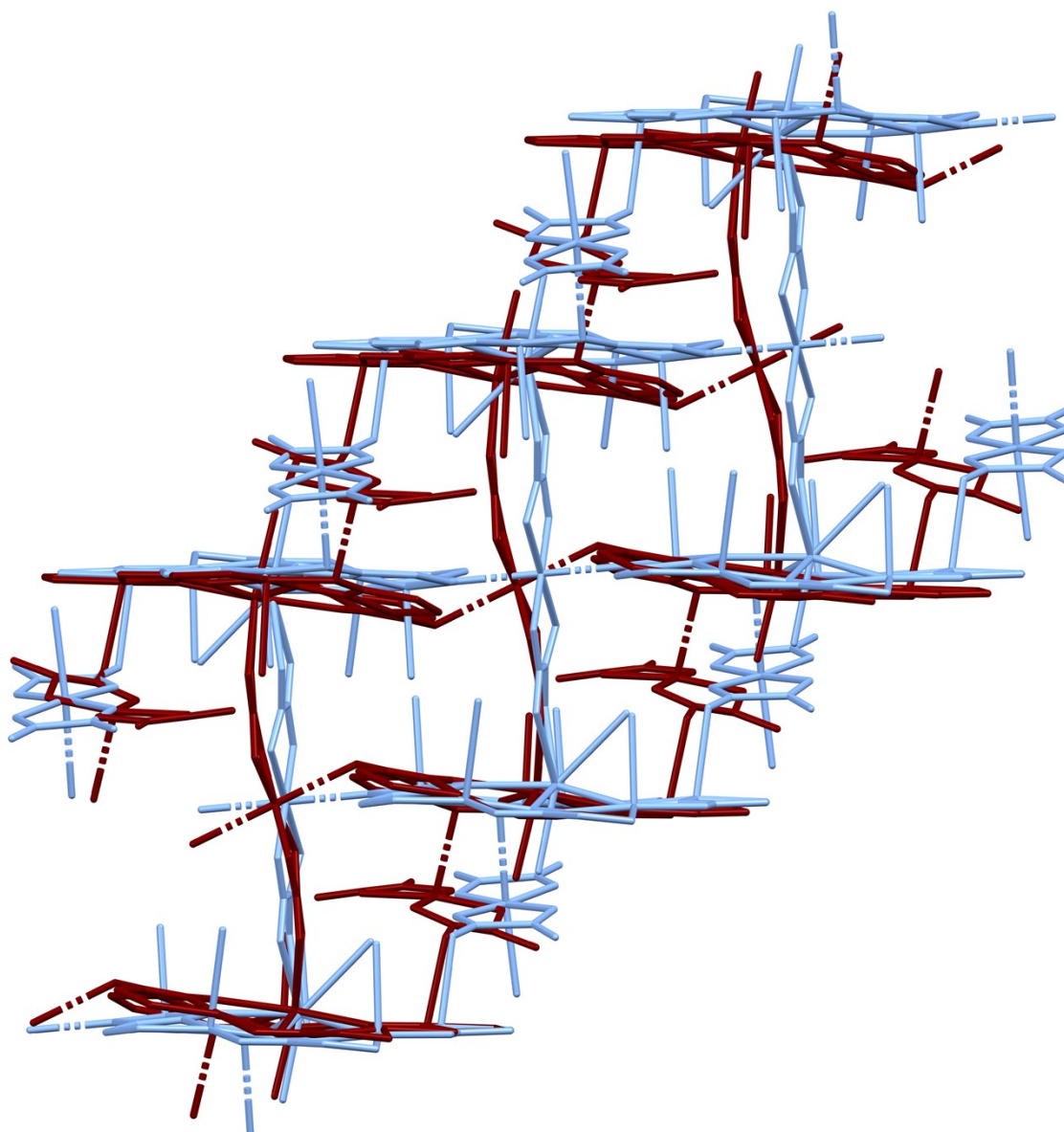


Figure S9. Overlay of the fragments of the crystal structures of complex **2** obtained at 100 K (light blue) and 298 K (dark red).

The equatorial coordination environment of Gd(III) and Cu(II) ions for **2-RT** is similar to the **2-100K**, however the solvent loss at room temperature in **2-RT** leads to changes in the apical coordination environment of the Cu(II) ions compared to **2-100K**. While in the crystal structure of **2-100K** the apical positions of copper ions Cu1 – Cu3 and Cu5 are occupied by coordinated water molecules resulting in square pyramidal coordination environment for these ions, in **2-RT** only the Cu5 ions are pentacoordinate with water molecule coordinated in the apical position.

Table S10. Selected characteristics of crystal structure of **2** collected at 100 and 298 K

Complex	2-100K	2-RT
The angle between Cu ₅ plane in 15-metallacrown-5 unit and CuO ₄ ^a equatorial plane of Cu6 ion from μ_4 -[Cu(C ₂ O ₄) ₂] ²⁻	84.57 °	65.37 °
The angle between Cu ₅ plane in 15-metallacrown-5 unit and CuO ₄ ^b equatorial plane of Cu7 ion from μ_2 -[Cu(C ₂ O ₄) ₂] ²⁻	13.19 °	8.96 °
The distance between Cu ₅ planes in adjacent 15-metallacrown-5 units linked through μ_4 -[Cu(C ₂ O ₄) ₂] ²⁻ anions through O10-Cu6-O10'	0.678 Å	1.720 Å
The Cu6--Cu1 distance, Å	3.7695(5)	3.677(6)
The Cu6-O10-Cu1 angle, °	98.94(8)	112.150(12)

^a mean plane through atoms Cu6O11O12O11'O12' in μ_4 -[Cu(C₂O₄)₂]²⁻

^b mean plane through atoms Cu7O18O19O22O23 in μ_2 -[Cu(C₂O₄)₂]²⁻

The Gd(III) ions in **2-100K** are nine-coordinate with the coordination environment corresponding to a spherically-capped square antiprism (CSAPR-9, C_{4v}, Table S8). In the equatorial plane Gd1 ions are bound by five hydroxamate oxygen atoms. The coordination sphere of Gd1 ions in **2-100K** is completed to nonacoordinated due to the apical coordination of two water molecules (O15 and O29) and bidentate coordination of oxalate anions through oxygen atoms O13 and O14 from μ_4 -[Cu(C₂O₄)₂]²⁻. In the **2-RT** the Gd1 ions are octacoordinate due to the loss of one water molecule (O29) from the coordination sphere during the desolvation process (Figure S10). The coordination environment of the Gd1 ions in the **2-RT** corresponds to a triangular dodecahedron (TDD-8, D_{2d}, Table S11).

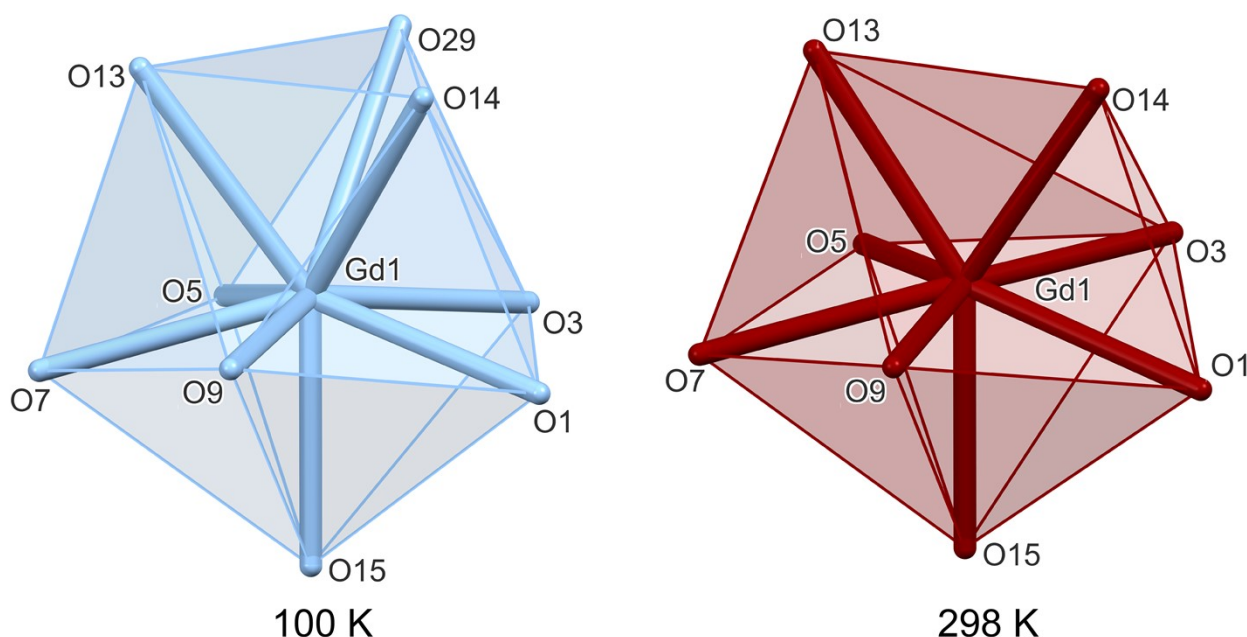


Figure S10. The comparison of the coordination environment of the Gd^{III} ions in the metallacrown units in **2** at 100 K (left) and at 298 K (right).

Table S11. Continuous shape calculations for octacoordinated Gd(III) ions in the complex **2-RT** obtained using the Shape 2.1 software.³

Polyhedron geometry for octacoordinate Gd(III) ions in complex 2-RT						
OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8
32.294	23.909	16.628	11.737	3.092	1.151	13.063
JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8	
27.362	1.927	1.224	3.050	12.395	23.754	

Octacoordinate ions:

OP-8 – Octagon (D_{8h}), HPY-8 – Heptagonal pyramid (C_{7v}), HBPY-8 – Hexagonal bipyramid (D_{6h}), CU-8 – Cube (O_h), SAPR-8 – Square antiprism (D_{4d}), TDD-8 – Triangular dodecahedron (D_{2d}), JGBF-8 – Johnson gyrobifastigium J26 (D_{2d}), JETBPY-8 – Johnson elongated triangular bipyramid J14 (D_{3h}), JBTPR-8 – Biaugmented trigonal prism J50 (C_{2v}), BTPR-8 – Biaugmented trigonal prism (C_{2v}), JSD-8 – Snub diphenoid J84 (D_{2d}), TT-8 – Triakis tetrahedron (T_d), ETBPY-8 – Elongated trigonal bipyramid (D_{3h}).

References:

- 1 Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc. Dalton Trans.* **1984**, 1349-1356. DOI: 10.1039/DT9840001349.
- 2 A. L. Spek, *PLATON – A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, **2006**.
- 3 Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. The Rich Stereochemistry of Eight-Vertex Polyhedra: A Continuous Shape Measures Study. *Chem. Eur. J.* **2005**, *11*, 1479-1494. DOI: 10.1002/chem.200400799.
4. Data Collector, XRD Data Collection software, Version 6.1b, PANalytical B.V., Almelo, The Netherlands, 2019.
5. HighScore, Version 5.2, Malvern PANalytical B.V., Almelo, The Netherlands, 2023.

Complete reports with all Rietveld analysis parameters.

Rietveld Refinement Parameters and results for Complex 1

Number of used phases	1
Number of variables	37
Number of constraints	0
Zero shift/ °2Theta	0.000000
Specimen displacement/ mm	-0.045(2)
Specimen Packing Factor	0.000000
Profile function	Pseudo Voigt
Background	Polynomial
Amorphous fraction/ %	-6037(107)
R (expected)/ %	2.43176
R (profile)/ %	4.09031
R (weighted profile)/ %	5.81345
GOF	2.39063
d-statistics	0.20281
Weighted d-statistics	0.21631
Mixture MAC/ cm ² /g	68.42
U standard	0.000000
V standard	0.000000
W standard	0.010000
TCH U Left	0.000000
TCH V Left	0.000000
TCH W Left	0.010000
TCH Z Left	0.000000

TCH X Left	0.000000
TCH Y Left	0.000000
TCH U Right	0.000000
TCH V Right	0.000000
TCH W Right	0.010000
TCH Z Right	0.000000
TCH X Right	0.000000
TCH Y Right	0.000000
Asymmetry Type	No Asymmetry Function
Asymmetry 1	0.025000
Asymmetry 2	0.025000
Use shape function	No
Shape 1 Left	0.600000
Shape 2 Left	0.000000
Shape 3 Left	0.000000
Shape 1 Right	0.600000
Shape 2 Right	0.000000
Shape 3 Right	0.000000
Wavelength [Å]	1.540598
K- α 2 / K- α 1 Intensity Ratio	0.44(2)
K- β 1 / K- α 1 Intensity Ratio	0.000000
K- β 2 / K- α 1 Intensity Ratio	0.000000
K- β 3 / K- α 1 Intensity Ratio	0.000000
Tungsten L- α Intensity Ratio	0.000000
Crystal Shape Factor K	1.0000
Absorption Edge Position [Å]	1.378680
White Radiation Area [% peak area]	0.000000
White Radiation Width [eV]	385.000000
Absorption Edge Extra Intensity	0.000000
Absorption Edge Sharpness [Scan axis]	0.090000
White Radiation Position [Å]	1.378680
Instrumental FWHM Curve Type	Caglioti function
Instr. Gauss Curve Coefficient A	0.0045(5)
Instr. Gauss Curve Coefficient B	-0.0032(9)
Instr. Gauss Curve Coefficient C	0.0046(3)
Instr. Lorentz Curve Coefficient A	0.0062(7)
Instr. Lorentz Curve Coefficient B	-0.004(1)
Instr. Lorentz Curve Coefficient C	0.0064(5)
Active Solver ID	Sol:LM:bccg.1.7
Sol:LM:bccg.1.7 criterion	Rwp
Sol:LM:bccg.1.7 delta	0.03125
Sol:LM:bccg.1.7 iter_limit	100
Sol:LM:bccg.1.7 iter_to_go	3
Sol:LM:bccg.1.7 lambda0	2.1
Sol:LM:bccg.1.7 max_exponent	11
Sol:LM:bccg.1.7 nu	2
Sol:LM:bccg.1.7 reduction	2.1
Sol:LM:bccg.1.7 small_count	6
Sol:LM:bccg.1.7 small_factor	200
Sol:LM:bccg.1.7 tolerance	0.001

Relevant parameters of 2367414

Bibliographic data

Audit creation method SHELXL-2018/3

Chemical name systematic ?

Comment

Crystal color: blue

Crystal description: plate

Formula sum	$C_{16}H_{56.05}CrCu_5GdN_{10}O_{40.02}$
Structure and profile data	
Formula sum	$C_{64.00}H_{224.18}Cr_{4.00}Cu_{20.00}Gd_{4.00}N_{40.00}O_{160.09}$
Formula mass/ g/mol	6224.2070
Density (calculated)/ g/cm ³	2.0828
F(000)	3100.9200
Mass Absorption Coefficient/ cm ² /g	68.4241
Volume fraction/ %	100.0000
Weight fraction/ %	100.000000
K-Factor Corrected Weight/ %	6137(107)
Space group (No.)	P 1 21/c 1 (14)
Lattice parameters	
a/ Å	13.6221(7)
b/ Å	25.439(1)
c/ Å	14.9092(8)
alpha/ °	90
beta/ °	106.186(1)
gamma/ °	90
V/ 10 ⁶ pm ³	4961.70000
V ESD/ 10 ⁶ pm ³	0.4387652
Overall displacement parameter	0.2(1)
Extinction	0.000000
Phase Layer Displacement [mm]	0.000000
Flat Plate Absorption Correction	0.000000
Porosity	0.000000
Roughness	0.000000
Fitting mode	Rietveld Fit
U Left	-0.01(2)
V Left	-0.006(7)
W Left	0.0190(6)
U Right	0.07(1)
V Right	-0.007(5)
W Right	0.0060(3)
Spherical Harmonics Order	6
Texture Index	1.03228
AVP603-cif Coefficient Y20	-0.190(8)
AVP603-cif Coefficient Y22p	0.250(7)
AVP603-cif Coefficient Y22m	-0.14(1)
AVP603-cif Coefficient Y40	-0.02(1)
AVP603-cif Coefficient Y42p	-0.006(5)
AVP603-cif Coefficient Y42m	0.00(1)

AVP603-cif Coefficient Y44p -0.05(1)
 AVP603-cif Coefficient Y44m 0.12(1)
 AVP603-cif Coefficient Y60 -0.104(8)
 AVP603-cif Coefficient Y62p 0.021(6)
 AVP603-cif Coefficient Y62m 0.145(9)
 AVP603-cif Coefficient Y64p 0.018(7)
 AVP603-cif Coefficient Y64m -0.156(9)
 AVP603-cif Coefficient Y66p 0.08(1)
 AVP603-cif Coefficient Y66m -0.14(1)
 Asymmetry parameter 1 0.025000
 Asymmetry parameter 2 0.025000
 Peak shape
 parameter 1 Left 1.33(1)
 parameter 2 Left 0.000000
 parameter 3 Left 0.000000
 R (Bragg)/ % 1.90510

Atom	Wyck	s.o.f.	x	y	z	B/ 10 ⁴ pm ²
C1	4e	1.000000	0.187500	0.126450	0.033800	1.618615
C2	4e	1.000000	0.296800	0.144680	0.047900	2.037086
H2A	4e	1.000000	0.342660	0.113770	0.054720	2.447662
H2B	4e	1.000000	0.318270	0.165760	0.105800	2.447662
C3	4e	1.000000	0.126500	0.272960	0.206800	2.226583
C4	4e	1.000000	0.128100	0.237700	0.125800	3.031942
H4A	4e	1.000000	0.177290	0.251770	0.093130	3.632014
H4B	4e	1.000000	0.151240	0.202110	0.149040	3.632014
C5	4e	1.000000	0.724400	0.286870	0.029000	1.310683
C6	4e	1.000000	0.614800	0.218180	0.470300	1.587032
H6A	4e	1.000000	0.612360	0.214970	0.403500	1.894964
H6B	4e	1.000000	0.587640	0.253200	0.480360	1.894964
C7	4e	1.000000	0.564700	0.434410	0.206800	1.973921
C8	4e	1.000000	0.499800	0.473200	0.243300	3.347770
H8A	4e	1.000000	0.509880	0.005740	0.294730	4.026799
H8B	4e	1.000000	0.431480	0.457850	0.238770	4.026799
C9	4e	1.000000	0.155800	0.517590	0.472600	1.665989
C10	4e	1.000000	0.095600	0.502980	0.374800	1.879173
H10A	4e	1.000000	0.093990	0.464230	0.367960	2.289748
H10B	4e	1.000000	0.129660	0.517830	0.329350	2.289748
C11	4e	1.000000	0.259900	0.739380	0.214700	1.421223
C12	4e	1.000000	0.147400	0.723330	0.173900	1.373849
C13	4e	1.000000	0.264200	0.582530	0.052200	3.087212
C14	4e	1.000000	0.191400	0.548170	0.093100	3.339874
C15	4e	1.000000	0.594700	0.094500	0.130800	2.029191
C16	4e	1.000000	0.685300	0.113660	0.093600	1.768633
Cr1	4e	1.000000	0.256990	0.630710	0.215800	1.669937
Cu1	4e	1.000000	0.019770	0.078160	0.049650	1.512813
Cu2	4e	1.000000	0.173230	0.323330	0.365940	1.811270
Cu3	4e	1.000000	0.074110	0.781770	0.400910	1.336739
Cu4	4e	1.000000	0.632060	0.363770	0.108430	1.437014

Cu5	4e	1.000000	0.300110	0.533440	0.628820	1.635196
Gd1	4e	1.000000	0.123460	0.854390	0.187430	1.094342
N1	4e	1.000000	0.124400	0.361410	0.455200	1.594928
N2	4e	1.000000	0.306000	0.323020	0.467200	2.179209
H2C	4e	1.000000	0.322650	0.289390	0.486330	2.605576
H2D	4e	1.000000	0.356960	0.336120	0.444500	2.605576
N3	4e	1.000000	0.039700	0.295190	0.203700	1.381745
N4	4e	1.000000	0.024900	0.234450	0.059700	1.887068
H4C	4e	1.000000	0.001950	0.200690	0.056990	2.289748
H4D	4e	1.000000	0.028540	0.243810	0.001680	2.289748
N5	4e	1.000000	0.736900	0.315890	0.101700	1.468597
N6	4e	1.000000	0.550400	0.176270	0.496200	1.744946
H6C	4e	1.000000	0.494660	0.308920	0.009220	2.052878
H6D	4e	1.000000	0.528000	0.153780	0.447450	2.052878
N7	4e	1.000000	0.655200	0.426280	0.260100	1.610719
N8	4e	1.000000	0.551900	0.485970	0.342300	3.047734
H8C	4e	1.000000	0.521610	0.467960	0.380610	3.632014
H8D	4e	1.000000	0.454190	0.020960	0.147510	3.632014
N9	4e	1.000000	0.109400	0.549530	0.516100	1.484389
N10	4e	1.000000	0.010600	0.023460	0.145100	1.855486
H10C	4e	1.000000	0.029170	0.037920	0.203100	2.210791
H10D	4e	1.000000	0.054500	0.503420	0.643510	2.210791
O1	4e	1.000000	0.023700	0.378790	0.442800	1.571241
O2	4e	1.000000	0.161300	0.100180	0.098670	1.918651
O3	4e	1.000000	0.039210	0.327680	0.278950	1.286996
O4	4e	1.000000	0.209400	0.279240	0.274200	3.513579
O5	4e	1.000000	0.162800	0.819060	0.342200	1.618615
O6	4e	1.000000	0.798300	0.261980	0.006870	1.476493
O7	4e	1.000000	0.715500	0.391780	0.225270	1.515971
O8	4e	1.000000	0.528200	0.412440	0.125600	2.273957
O9	4e	1.000000	0.163800	0.562260	0.607360	1.484389
O10	4e	1.000000	0.246900	0.000710	0.008000	1.997608
O11	4e	1.000000	0.076300	0.573150	0.769800	2.755594
H11A	4e	1.000000	0.123000	0.555000	0.804000	4.105755
H11B	4e	1.000000	0.030000	0.923000	0.297000	4.105755
O12	4e	0.550000	0.051600	0.858500	0.483400	2.368705
H12A	4e	0.550000	0.008000	0.882000	0.458000	3.474101
H12B	4e	0.550000	0.057000	0.641000	0.041300	3.474101
O12B	4e	0.450000	0.001400	0.347900	0.011100	4.421583
H12C	4e	0.450000	0.054000	0.152000	0.490000	6.711331
H12D	4e	0.450000	0.049000	0.661000	0.033000	6.711331
O13	4e	1.000000	0.173000	0.834850	0.047760	1.531763
H13A	4e	1.000000	0.188000	0.804100	0.036000	2.289748
H13B	4e	1.000000	0.216000	0.644700	0.534000	2.289748
O14	4e	1.000000	0.028300	0.641610	0.347100	2.092356
H14A	4e	1.000000	0.005000	0.136000	0.207600	3.158273
H14B	4e	1.000000	0.090700	0.640000	0.351000	3.158273
O15	4e	1.000000	0.297100	0.049450	0.237400	3.395144
H15A	4e	1.000000	0.257000	0.063000	0.187000	5.053237
H15B	4e	1.000000	0.295000	0.074900	0.277000	5.053237
O16	4e	0.421000	0.124000	0.231100	0.409100	2.289748
H16A	4e	0.421000	0.157680	0.231680	0.368660	3.474101

H16B	4e	0.421000	0.061420	0.230520	0.380150	3.474101
O16B	4e	0.322000	0.103100	0.182100	0.372000	10.000000
H16C	4e	0.322000	0.098240	0.148620	0.358840	10.000000
H16D	4e	0.322000	0.040900	0.190650	0.368710	10.000000
O17	4e	1.000000	0.718900	0.286410	0.283200	1.808112
O18	4e	1.000000	0.081800	0.758390	0.149480	1.413327
O19	4e	1.000000	0.677800	0.200980	0.258800	1.752842
O20	4e	1.000000	0.130800	0.673750	0.168380	1.587032
O21	4e	1.000000	0.293700	0.624780	0.097900	2.076565
O22	4e	1.000000	0.180400	0.565420	0.171000	2.321331
O23	4e	1.000000	0.711300	0.431300	0.017900	4.768993
O24	4e	1.000000	0.151700	0.508670	0.052800	6.166529
O25	4e	1.000000	0.613100	0.096160	0.220200	2.281853
O26	4e	1.000000	0.235200	0.627770	0.342300	1.887068
O27	4e	1.000000	0.515000	0.079640	0.076200	2.605576
O28	4e	1.000000	0.676000	0.114490	0.009400	2.147626
O29	4e	1.000000	0.344100	0.454500	0.386200	5.763849
H29A	4e	1.000000	0.390000	0.431000	0.401000	8.685252
H29B	4e	1.000000	0.321000	0.461000	0.432000	8.685252
O30	4e	1.000000	0.473300	0.366700	0.391400	4.958489
H30A	4e	1.000000	0.493000	0.351000	0.350000	7.421943
H30B	4e	1.000000	0.524000	0.380000	0.430000	7.421943
O31	4e	1.000000	0.507200	0.304100	0.252100	6.553417
H31A	4e	1.000000	0.570000	0.301000	0.256000	9.790648
H31B	4e	1.000000	0.489000	0.278000	0.278000	9.790648
O32	4e	1.000000	0.369500	0.281400	0.057500	4.934802
H32A	4e	1.000000	0.342000	0.313800	0.055000	7.421943
H32B	4e	1.000000	0.396000	0.276400	0.115100	7.421943
O33	4e	0.869000	0.037200	0.076700	0.331100	4.153130
H33A	4e	0.869000	0.023900	0.572000	0.166000	6.237590
H33B	4e	0.869000	0.070000	0.052000	0.365000	6.237590
O35	4e	1.000000	0.065600	0.429350	0.133600	3.474101
H35A	4e	1.000000	0.070000	0.457300	0.103000	5.211151
H35B	4e	1.000000	0.122000	0.425000	0.178000	5.211151
O34	4e	0.597000	0.451700	0.128200	0.304700	2.724011
H34A	4e	0.597000	0.492000	0.120000	0.273000	4.105755
H34B	4e	0.597000	0.398000	0.110000	0.283000	4.105755
O37	4e	0.597000	0.387200	0.228600	0.256500	5.369065
H37A	4e	0.597000	0.332000	0.240000	0.267000	8.053597
H37B	4e	0.597000	0.407000	0.203200	0.293000	8.053597
O41C	4e	0.131000	0.143000	0.135000	0.321000	10.000000
H41E	4e	0.131000	0.110130	0.112360	0.341750	10.000000
H41F	4e	0.131000	0.150950	0.161580	0.355820	10.000000
O34B	4e	0.403000	0.465100	0.102700	0.329200	4.895324
H34C	4e	0.403000	0.426000	0.078000	0.303000	7.342986
H34D	4e	0.403000	0.500000	0.112000	0.293000	7.342986
O37B	4e	0.403000	0.384100	0.220800	0.302600	5.132194
H37C	4e	0.403000	0.342000	0.246000	0.288000	7.737770
H37D	4e	0.403000	0.350000	0.193000	0.299000	7.737770
O38B	4e	0.403000	0.255900	0.393500	0.216200	3.063525
H38C	4e	0.403000	0.289000	0.409000	0.265000	4.579496
H38D	4e	0.403000	0.257000	0.361000	0.229000	4.579496

O39B	4e	0.403000	0.324300	0.393300	0.058300	4.105755
H39C	4e	0.403000	0.388000	0.392000	0.086000	6.237590
H39D	4e	0.403000	0.293000	0.399600	0.099000	6.237590
O40B	4e	0.403000	0.237500	0.035800	0.404500	5.369065
H40C	4e	0.403000	0.244270	0.004280	0.428710	8.132554
H40D	4e	0.403000	0.270870	0.055660	0.450850	8.132554
O41B	4e	0.403000	0.252000	0.149400	0.379800	10.000000
H41C	4e	0.403000	0.190560	0.156530	0.353570	10.000000
H41D	4e	0.403000	0.256900	0.142860	0.436350	10.000000
O36	4e	0.396000	0.486000	0.013000	0.468800	7.342986
H36A	4e	0.396000	0.426830	0.025710	0.461180	10.000000
H36B	4e	0.396000	0.520420	0.481840	0.050580	10.000000
O38	4e	0.597000	0.230600	0.391400	0.268300	3.481996
H38A	4e	0.597000	0.257000	0.408000	0.316000	5.211151
H38B	4e	0.597000	0.231000	0.359000	0.280000	5.211151
O39	4e	0.299000	0.340900	0.355700	0.149100	3.474101
H39A	4e	0.299000	0.320000	0.376000	0.184000	5.211151
H39B	4e	0.299000	0.402000	0.348000	0.175000	5.211151
O39C	4e	0.182000	0.219600	0.348000	0.093200	2.842446
H39E	4e	0.182000	0.250000	0.363000	0.056000	4.263669
H39F	4e	0.182000	0.220000	0.369000	0.137000	4.263669
O40	4e	0.597000	0.314500	0.424300	0.017600	7.027158
H40A	4e	0.597000	0.269240	0.447800	0.030080	10.000000
H40B	4e	0.597000	0.363980	0.425990	0.066420	10.000000
O41	4e	0.597000	0.196400	0.002400	0.353400	2.534514
H41A	4e	0.597000	0.236000	0.015000	0.322000	3.789928
H41B	4e	0.597000	0.768000	0.485000	0.103000	3.789928

Rietveld Refinement Parameters and results for Complex 2

Number of used phases	1
Number of variables	47
Number of constraints	0
Zero shift/ °2Theta	0.000000
Specimen displacement/ mm	0.047(1)
Specimen Packing Factor	0.000000
Profile function	Pseudo Voigt
Background	Polynomial
Amorphous fraction/ %	-2504(361)
R (expected)/ %	3.81895
R (profile)/ %	4.98942
R (weighted profile)/ %	6.74441
GOF	1.76604
d-statistics	0.46431
Weighted d-statistics	0.38894
Mixture MAC/ cm ² /g	65.31
U standard	0.000000
V standard	0.000000
W standard	0.010000
TCH U Left	0.000000
TCH V Left	0.000000

TCH W Left	0.010000
TCH Z Left	0.000000
TCH X Left	0.000000
TCH Y Left	0.000000
TCH U Right	0.000000
TCH V Right	0.000000
TCH W Right	0.010000
TCH Z Right	0.000000
TCH X Right	0.000000
TCH Y Right	0.000000
Asymmetry Type	No Asymmetry Function
Asymmetry 1	0.025000
Asymmetry 2	0.025000
Use shape function	No
Shape 1 Left	0.600000
Shape 2 Left	0.000000
Shape 3 Left	0.000000
Shape 1 Right	0.600000
Shape 2 Right	0.000000
Shape 3 Right	0.000000
Wavelength [Å]	1.540598
K- α 2 / K- α 1 Intensity Ratio	0.500000
K- β 1 / K- α 1 Intensity Ratio	0.000000
K- β 2 / K- α 1 Intensity Ratio	0.000000
K- β 3 / K- α 1 Intensity Ratio	0.000000
Tungsten L- α Intensity Ratio	0.000000
Crystal Shape Factor K	1.0000
Absorption Edge Position [Å]	1.378680
White Radiation Area [% peak area]	0.000000
White Radiation Width [eV]	385.000000
Absorption Edge Extra Intensity	0.000000
Absorption Edge Sharpness [Scan axis]	0.090000
White Radiation Position [Å]	1.378680
Instrumental FWHM Curve Type	Caglioti function
Instr. Gauss Curve Coefficient A	0.0045(5)
Instr. Gauss Curve Coefficient B	-0.0032(9)
Instr. Gauss Curve Coefficient C	0.0046(3)
Instr. Lorentz Curve Coefficient A	0.0062(7)
Instr. Lorentz Curve Coefficient B	-0.004(1)
Instr. Lorentz Curve Coefficient C	0.0064(5)
Active Solver ID	Sol:LM:bccg.1.7
Sol:LM:bccg.1.7 criterion	Rwp
Sol:LM:bccg.1.7 delta	0.03125
Sol:LM:bccg.1.7 iter_limit	100
Sol:LM:bccg.1.7 iter_to_go	3
Sol:LM:bccg.1.7 lambda0	2.1
Sol:LM:bccg.1.7 max_exponent	11
Sol:LM:bccg.1.7 nu	2
Sol:LM:bccg.1.7 reduction	2.1
Sol:LM:bccg.1.7 small_count	6
Sol:LM:bccg.1.7 small_factor	200
Sol:LM:bccg.1.7 tolerance	0.001

Relevant parameters of CCDC 2367413,

Bibliographic data

Audit creation method SHELXL-2018/3
 Chemical name systematic ?

Comment

Crystal color: blue

Crystal description: plate

Formula sum $C_{32}H_{87.60}Cu_{13}Gd_2N_{20}O_{67.80}$
 Structure and profile data
 Formula sum $Gd_{2.00}Cu_{13.00}O_{67.80}C_{32.00}N_{20.00}H_{87.60}$
 Formula mass/ g/mol 2978.0990
 Density (calculated)/ g/cm³ 2.2982
 F(000) 1466.9800
 Mass Absorption Coefficient/ cm²/g 65.3106
 Volume fraction/ % 100.0000
 Weight fraction/ % 100.000000
 K-Factor Corrected Weight/ % 2604(361)
 Space group (No.) P -1 (2)
 Lattice parameters
 a/ Å 9.3393(3)
 b/ Å 14.6149(3)
 c/ Å 16.4722(6)
 alpha/ ° 97.1844(5)
 beta/ ° 100.3308(4)
 gamma/ ° 99.7801(5)
 V/ 10⁶ pm³ 2151.52400
 V ESD/ 10⁶ pm³ 0.1147867
 Overall displacement parameter 0.000000
 Extinction 0.000000
 Phase Layer Displacement [mm] 0.000000
 Flat Plate Absorption Correction 0.000000
 Porosity 0.000000
 Roughness 0.000000
 Fitting mode Rietveld Fit
 U Left 0.106(5)
 V Left -0.068(2)
 W Left 0.0141(4)
 U Right 0.091(6)
 V Right -0.016(2)
 W Right 0.0032(1)
 Spherical Harmonics Order 6
 Texture Index 1.34265
 CCDC 2367413, Coefficient Y20 -0.5(2)
 CCDC 2367413, Coefficient Y21p 0.0(1)
 CCDC 2367413, Coefficient Y21m 0.2(4)
 CCDC 2367413, Coefficient Y22p -0.89(6)

CCDC 2367413, Coefficient Y22m	-0.2(1)
CCDC 2367413, Coefficient Y40	0.1(2)
CCDC 2367413, Coefficient Y41p	-0.19(4)
CCDC 2367413, Coefficient Y41m	-0.51(9)
CCDC 2367413, Coefficient Y42p	0.2(3)
CCDC 2367413, Coefficient Y42m	0.4(2)
CCDC 2367413, Coefficient Y43p	-0.1(1)
CCDC 2367413, Coefficient Y43m	0.2(1)
CCDC 2367413, Coefficient Y44p	0.39(6)
CCDC 2367413, Coefficient Y44m	0.07(7)
CCDC 2367413, Coefficient Y60	-0.32(6)
CCDC 2367413, Coefficient Y61p	0.24(5)
CCDC 2367413, Coefficient Y61m	0.50(4)
CCDC 2367413, Coefficient Y62p	-0.24(4)
CCDC 2367413, Coefficient Y62m	-0.21(5)
CCDC 2367413, Coefficient Y63p	0.23(6)
CCDC 2367413, Coefficient Y63m	-0.05(7)
CCDC 2367413, Coefficient Y64p	-0.01(5)
CCDC 2367413, Coefficient Y64m	-0.14(7)
CCDC 2367413, Coefficient Y65p	0.04(4)
CCDC 2367413, Coefficient Y65m	-0.01(3)
CCDC 2367413, Coefficient Y66p	0.02(2)
CCDC 2367413, Coefficient Y66m	-0.14(3)
Asymmetry parameter 1	0.025000
Asymmetry parameter 2	0.025000
Peak shape	
parameter 1 Left	1.24(1)
parameter 2 Left	0.000000
parameter 3 Left	0.000000
R (Bragg)/ %	2.79292

Atom	Wyck.	s.o.f.	x	y	z	B/ 10 ⁴ pm ²
Gd1	2i	1.000000	0.007070	0.909020	0.219200	1.267257
Cu1	2i	1.000000	0.260910	0.119800	0.623990	1.317790
Cu2	2i	1.000000	0.890730	0.151040	0.271620	1.490705
Cu3	2i	1.000000	0.164890	0.079980	0.077490	1.649408
Cu4	2i	1.000000	0.183370	0.764310	0.056040	1.128293
Cu5	2i	1.000000	0.119510	0.360940	0.777920	1.125135
Cu6	1f	1.000000	0.500000	0.000000	0.500000	1.185932
Cu7	2i	1.000000	0.498800	0.516010	0.173620	1.475703
O1	2i	1.000000	0.961000	0.066950	0.194440	1.255414
O2	2i	1.000000	0.954100	0.247610	0.206700	1.697572
O3	2i	1.000000	0.109700	0.951350	0.098620	2.329227
O4	2i	1.000000	0.278300	0.026180	0.002000	1.350162
O5	2i	1.000000	0.041300	0.767240	0.128670	1.302788
O6	2i	1.000000	0.146700	0.628330	0.054520	1.318579
O7	2i	1.000000	0.143100	0.232950	0.749320	1.255414
O8	2i	1.000000	0.259300	0.392680	0.706210	1.579137
O9	2i	1.000000	0.141300	0.040420	0.683070	1.452806
O10	2i	1.000000	0.327500	0.004720	0.587140	1.942338

O11	2i	1.000000	0.381100	0.068550	0.427050	1.421223
O12	2i	1.000000	0.633100	0.115780	0.569670	1.721259
C12	2i	0.494000	0.739300	0.092600	0.613100	1.144874
O13	2i	0.494000	0.148000	0.852400	0.341900	1.247518
C12B	2i	0.506000	0.724200	0.095500	0.633500	1.373849
O13B	2i	0.506000	0.180200	0.847700	0.311400	1.602824
O14	2i	1.000000	0.183300	0.034750	0.320180	2.044982
O18	2i	1.000000	0.603200	0.588530	0.101290	1.602824
O19	2i	1.000000	0.419100	0.628730	0.200990	1.879173
O20	2i	1.000000	0.588700	0.719520	0.046290	2.005504
O21	2i	1.000000	0.418600	0.770180	0.160830	2.416079
O22	2i	1.000000	0.594400	0.408850	0.154180	1.665989
O23	2i	1.000000	0.406900	0.446130	0.250920	2.005504
O24	2i	1.000000	0.599200	0.268500	0.194710	3.047734
O25	2i	1.000000	0.401800	0.307300	0.295800	4.421583
N1	2i	1.000000	0.036300	0.122120	0.145820	1.136978
N2	2i	1.000000	0.173900	0.210500	0.044770	1.381745
H2C	2i	1.000000	0.120210	0.205630	0.991220	1.658094
H2D	2i	1.000000	0.271310	0.237740	0.046220	1.658094
N3	2i	1.000000	0.188100	0.895150	0.054410	1.721259
N4	2i	1.000000	0.688700	0.223320	0.030310	1.444910
H4C	2i	1.000000	0.737930	0.261120	0.079960	1.737050
H4D	2i	1.000000	0.601030	0.242930	0.012660	1.737050
N5	2i	1.000000	0.003000	0.675360	0.145890	1.334371
N6	2i	1.000000	0.086700	0.490550	0.815630	1.500180
H6C	2i	1.000000	0.824200	0.471590	0.156310	1.816007
H6D	2i	1.000000	0.051600	0.516400	0.769780	1.816007
N7	2i	1.000000	0.227200	0.230920	0.686740	1.239622
N8	2i	1.000000	0.383200	0.214800	0.570760	1.958130
H8C	2i	1.000000	0.481110	0.207820	0.581000	2.368705
H8D	2i	1.000000	0.348320	0.203220	0.513800	2.368705
N9	2i	1.000000	0.826900	0.050540	0.328560	1.444910
N10	2i	1.000000	0.786500	0.223480	0.345990	1.792320
H10C	2i	1.000000	0.727390	0.256390	0.314940	2.131835
H10D	2i	1.000000	0.143920	0.733820	0.613960	2.131835
C1	2i	1.000000	0.027900	0.209900	0.155840	1.168561
C2	2i	1.000000	0.111200	0.270500	0.104150	1.279101
H2A	2i	1.000000	0.193080	0.317780	0.141600	1.500180
H2B	2i	1.000000	0.042390	0.304470	0.072580	1.500180
C3	2i	1.000000	0.265300	0.936900	0.007220	1.255414
C4	2i	1.000000	0.654800	0.123500	0.043440	1.381745
H4A	2i	1.000000	0.545860	0.099160	0.026770	1.658094
H4B	2i	1.000000	0.686330	0.120280	0.103490	1.658094
C5	2i	1.000000	0.060000	0.612200	0.107640	1.247518
C6	2i	1.000000	0.022600	0.513640	0.128600	1.389640
H6A	2i	1.000000	0.114880	0.495760	0.156540	1.658094
H6B	2i	1.000000	0.019620	0.531910	0.923600	1.658094
C7	2i	1.000000	0.280100	0.312500	0.669690	1.302788
C8	2i	1.000000	0.374800	0.312200	0.603900	1.831799
H8A	2i	1.000000	0.331030	0.342680	0.557720	2.210791
H8B	2i	1.000000	0.476550	0.348780	0.628710	2.210791
C9	2i	1.000000	0.732000	0.061700	0.376500	1.650198

C10	2i	1.000000	0.692900	0.158700	0.387600	2.487140
H10A	2i	1.000000	0.710080	0.184080	0.447940	3.000360
H10B	2i	1.000000	0.586060	0.153990	0.363010	3.000360
C11	2i	1.000000	0.277800	0.012300	0.374100	1.602824
C13	2i	1.000000	0.558100	0.666000	0.095810	1.484389
C14	2i	1.000000	0.456700	0.692600	0.158260	1.665989
C15	2i	1.000000	0.557100	0.344600	0.196800	1.894964
C16	2i	1.000000	0.447000	0.366300	0.254400	2.321331
O15	2i	1.000000	0.230700	0.111770	0.870360	1.894964
H15A	2i	1.000000	0.245000	0.076000	0.904000	2.842446
H15B	2i	1.000000	0.291000	0.162000	0.885000	2.842446
O16	2i	0.664000	0.090700	0.661900	0.347800	3.071421
H16A	2i	0.664000	0.132000	0.716300	0.348000	4.579496
H16B	2i	0.664000	0.154000	0.627000	0.347000	4.579496
O32	2i	0.664000	0.270600	0.527500	0.369700	3.268813
H32A	2i	0.664000	0.292000	0.528000	0.423700	4.895324
H32B	2i	0.664000	0.334000	0.511000	0.343000	4.895324
O33	2i	0.664000	0.001000	0.410000	0.322400	2.613471
H33A	2i	0.664000	0.003000	0.362000	0.289000	3.947842
H33B	2i	0.664000	0.081000	0.446000	0.350000	3.947842
O31	2i	0.664000	0.253300	0.551800	0.626900	3.797824
H31A	2i	0.664000	0.165000	0.561000	0.623000	5.684892
H31B	2i	0.664000	0.252000	0.498000	0.641000	5.684892
O34	2i	0.664000	0.010900	0.720000	0.493100	7.342986
H34A	2i	0.664000	0.038000	0.679000	0.461000	10.000000
H34B	2i	0.664000	0.066000	0.301000	0.492000	10.000000
O35	2i	0.500000	0.543700	0.454600	0.473700	6.948201
H35A	2i	0.500000	0.368220	0.534040	0.535770	10.000000
H35B	2i	0.500000	0.497230	0.413100	0.424600	10.000000
O35B	2i	0.500000	0.594900	0.385100	0.486400	10.000000
H35C	2i	0.500000	0.662400	0.376360	0.460150	10.000000
H35D	2i	0.500000	0.406530	0.556990	0.506970	10.000000
O16B	2i	0.336000	0.238200	0.664700	0.328100	4.895324
H16C	2i	0.336000	0.212820	0.716520	0.320390	7.342986
H16D	2i	0.336000	0.294200	0.656210	0.289470	7.342986
O32B	2i	0.336000	0.124100	0.427400	0.306400	3.237230
H32C	2i	0.336000	0.208000	0.451000	0.296000	4.895324
H32D	2i	0.336000	0.090000	0.377000	0.271000	4.895324
O31B	2i	0.336000	0.178000	0.513500	0.590800	10.000000
H31C	2i	0.336000	0.084830	0.492790	0.573500	10.000000
H31D	2i	0.336000	0.207070	0.481080	0.627100	10.000000
O34B	2i	0.336000	0.018400	0.354900	0.497900	5.369065
H34C	2i	0.336000	0.030000	0.602000	0.518000	8.053597
H34D	2i	0.336000	0.067000	0.343000	0.461000	8.053597
O17	2i	1.000000	0.057700	0.098300	0.504700	5.203255
H17A	2i	1.000000	0.003000	0.869000	0.483000	7.816727
H17B	2i	0.500000	0.014000	0.040600	0.496000	7.816727
H17C	2i	0.500000	0.067000	0.105200	0.455000	7.816727
O26	2i	1.000000	0.294400	0.464390	0.051110	1.760737
H26A	2i	1.000000	0.265000	0.515000	0.044000	2.605576
H26B	2i	1.000000	0.331000	0.451000	0.009500	2.605576
O27	2i	1.000000	0.379700	0.109600	0.194090	2.376601

H27A	2i	0.494000	0.424000	0.164000	0.223000	3.553058
H27B	2i	0.494000	0.296000	0.099000	0.208000	3.553058
H27C	2i	0.506000	0.455000	0.153000	0.199000	3.553058
H27D	2i	0.506000	0.406000	0.059000	0.183000	3.553058
O28	2i	1.000000	0.169300	0.225600	0.376700	5.337482
H28A	2i	1.000000	0.239000	0.260000	0.364000	7.974640
H28B	2i	1.000000	0.181000	0.170000	0.370000	7.974640
O29	2i	0.494000	0.306900	0.920100	0.229300	1.413327
H29A	2i	0.494000	0.645000	0.028000	0.776000	2.131835
H29B	2i	0.494000	0.345000	0.874000	0.215000	2.131835
O29B	2i	0.506000	0.479200	0.040400	0.790400	5.921763
H29C	2i	0.506000	0.529000	0.094000	0.788000	8.922122
H29D	2i	0.506000	0.390000	0.040000	0.793000	8.922122
O36	2i	0.081000	0.234000	0.428100	0.468800	2.289748
H36A	2i	0.081000	0.228790	0.440580	0.519280	3.395144
H36B	2i	0.081000	0.330070	0.436250	0.469360	3.395144
O36C	2i	0.154000	0.064000	0.436300	0.457800	4.342626
H36C	2i	0.154000	0.116970	0.468920	0.505650	6.553417
H36D	2i	0.154000	0.040980	0.488180	0.447960	6.553417
