The valence tautomeric interconversion in bis-dioxolene cobalt complex with imino-pyridine functionalized by TEMPO moiety. Phase transition coupled with monocrystals destruction

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Supporting Information

Text S 1. Experimental

General considerations.

Initial chemicals and solvents were received from commercial sources (Aldrich, Fluka). Solvents were carefully distilled, dried and stored under vacuum. Most of the synthetic operations have been done in evacuated ampoules in the absence of traces of oxygen and moisture. Tris-o-semiquinonato cobalt complex was synthesized as described in [1]. The magnetic susceptibility of the polycrystalline sample was measured with a Quantum Design MPMSXL SQUID magnetometer in the temperature range 2–300 K with magnetic field of up to 5 kOe. Complex does not exhibit field dependence of molar magnetization at low temperatures. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$. The low-temperature powder X-ray diffraction was carried out on a Shimadzu X-ray diffractometer XRD-6000 (Cu Kα radiation, geometry θ–2θ) in the 2θ range from 5° to 60° with scan increment of 0.02° using Attachment TTK-450 (Anton Paar) in the temperature interval from 200K to 300K.

1. Lange, C. W.; Conklin, B. J.; Pierpont, C. G. Inorg. Chem. 1994, 33, 1276.

Text S2. Synthetic procedures

4-N-TEMPO-iminopyridine

The ligand was synthesized according to literature procedure [2]. Pyridine-2-carbaldehyde (0.252 g, 2.35 mmol) was dissolved in 5 ml of methanol and 4-amino-2,2,6,6,-tetramethylpiperidin-1-oxyl (0.400 g, 2.35 mmol) in 5 ml of methanol was added. The mixture was stirred during 2 hours without heating. Then solvent was evaporated and solid residue was dissolved under refluxing in 20 ml of *n*-hexane. The resulting solution was filtered and kept at -18°C overnight. The pale-orange crystals were isolated by filtration, washed with cold *n*-hexane and dried on air. Yield: 0.569 g (87.4 %). Anal. Calc. for $C_{15}H_{22}N_3O$: C, 69.20, H, 8.52, N, 16.14, O, 6.14. Found: C, 69.75, H, 8.86, N, 16.05. IR (nujol, cm^{-1}): 1647 (s), 1588 (m), 1568 (w), 1458 (s), 1441 (m), 1363 (m), 1338 (m), 1242 (s), 1177 (w), 1048 (w), 992 (w), 858 (w), 787 (m), 700 (w), 622 (w), 576 (w).

(TEMPO-ImPy)Co(3,6-DBSQ)$_2$ (complex **1**)

A warm solution of (TEMPO-ImPy) (0.039 g, 0.14 mmol) in 10 ml of *n*-hexane was added to a warm solution of Co(3,6-DBSQ)$_3$ (0.100 g, 0.14 mmol) in 20 ml of *n*-hexane. The resulting mixture was concentrated threefold by solvent evaporation and allowed standing at room temperature overnight. The dark-green crystals of **1** were isolated by filtration, washed with cold *n*-hexane and dried under vacuum. Yield: 0.082 g (75.5 %). Anal. Calc. for $C_{43}H_{62}CoN_3O_5$ (%): C, 67.96, H, 8.22, Co, 7.76, N, 5.53, O, 10.53. Found: C, 67.85, H, 8.15, N, 5.65. IR (nujol, cm^{-1}): 1645 (w), 1600 (w), 1545 (w), 1465 (s), 1445 (s), 1375 (m), 1355 (m), 1240 (w), 1180 (w), 955 (w), 825 (w), 770 (w), 655 (w).

2. Boymel, P. M.; Eaton, G. R.; Eaton, S. S.; Inorg. Chem. 1980, 19, 121-135.

Text S3. X-ray analysis

Intensity data for complexes **1a** and **1b** were collected on a Bruker D8 Quest Apex II diffractometer (graphite-monochromator, MoK_α-radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by using the SAINT program [3]. SADABS[4] was used to perform area-detector scaling and absorption corrections. The structures were solved by using a direct algorithm and were refined on F^2 using all reflections with the SHELXTL package [5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined in the riding-model ($U_{iso}(H) = 1.5U_{eq}(C)$ in CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ in other ligands). Details of crystallographic, collection and refinement data for **1a** and **1b** are presented in Table 1. CCDC 1572143 for **1a** and 1572142 for **1b** contain the supplementary crystallographic data for this paper.

Table S1. Details of crystallographic, collection and refinement data for complexes **1a** and **1b**.

Complex	**1a**	**1b**
Empirical formula	$C_{43}H_{62}CoN_3O_5$	$C_{43}H_{62}CoN_3O_5$
Formula weight	759.88	759.88
Temperature [K]	296(2)	240(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a[Å]	10.7758(3)	10.7483(2)
b[Å]	15.9404(4)	15.8276(4)
c[Å]	26.6999(8)	26.6639(6)
α[°]	90	90
β[°]	101.6019(13)	101.5058(10)
γ[°]	90	90
Volume [$Å^3$]	4492.6(2)	4444.90(17)
Z	4	4
Calculated density [Mg/m^3]	1.123	1.136
Absorption coefficient [mm^{-1}]	0.424	0.429
Crystal size [mm]	0.50×0.30×0.16	0.50×0.30×0.16
θ [°]	2.222 ÷ 27.997	2.323 ÷ 27.998
Reflections collected / unique	53235 / 10834	52187 / 10731
R_{int}	0.0412	0.0395
Final R indices [I>2sigma(I)]	R_1=0.0536, wR_2=0.1429	R_1=0.0450, wR_2=0.1106
R indices (all data)	R_1=0.0802, wR_2=0.1553	R_1=0.0637, wR_2=0.1186
S	1.048	1.024
Largest diff. peak and hole [$e/Å^3$]	0.352 / -0.545	0.341 / -0.518

3. SAINT. Data Reduction and Correction Program., v. 8.37A, Bruker AXS, Madison, Wisconsin, USA, 2012.

4. Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10. SADABS-2016/2.

5. Sheldrick G. M., Acta Crystallographica Section C Structural Chemistry, 71, 3-8. SHELXTL, v. 2014/7.

Figure S1. XRD powder pattern.

Experimental: The low-temperature X-ray diffraction was carried out on a Shimadzu X-ray diffractometer XRD-6000 (Cu Kα radiation, geometry θ–2θ) in the 2θ range from 5◦ to 60◦ with scan increment of 0.02◦ using Attachment TTK-450 (Anton Paar) in the temperature interval from 200K to 300K.

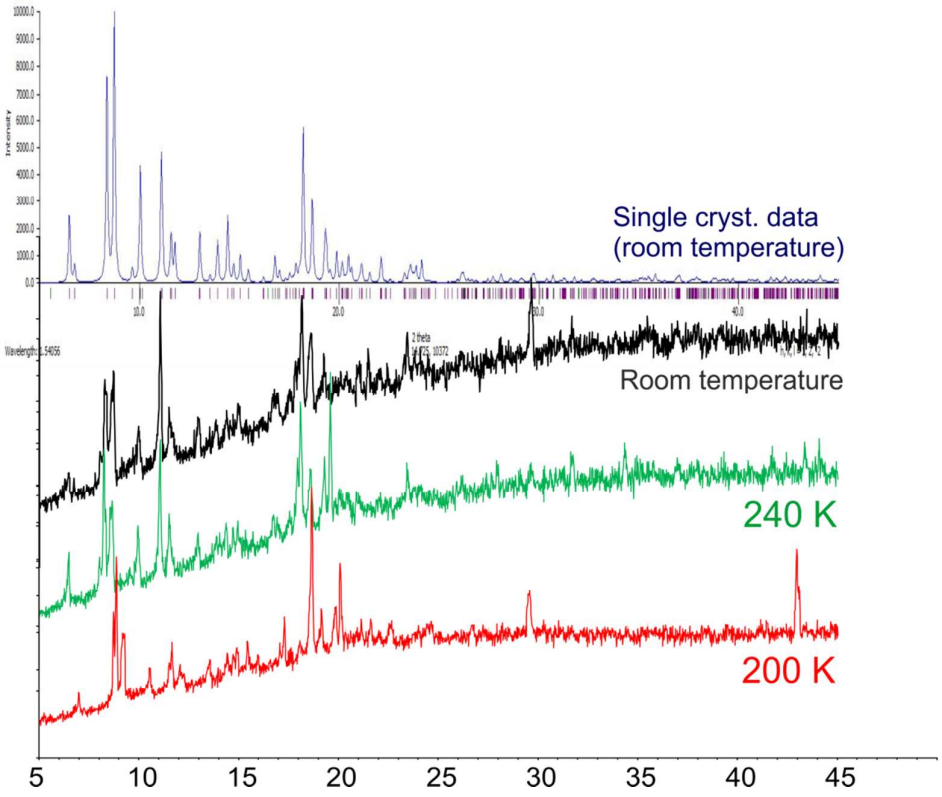


Table S2. Comparison of the main geometric characteristics of complexes **1a** and **1b**.

Selected distances	**1a**, [Å]	**1b**, [Å]	Selected angles	**1a**, [°]	**1b**, [°]
Co-O	2.0150(15) ÷ 2.0747(16)	2.0062(12) ÷ 2.0659(13)	O(3)Co(1)O(1)	169.42(6)	169.94(5)
Co-N	2.1226(18), 2.1586(18)	2.1080(14), 2.1443(15)	O(3)Co(1)O(2)	95.66(6)	95.48(5)
C-O	1.268(3) ÷ 1.274(2)	1.274(2) ÷ 1.279(2)	O(1)Co(1)O(2)	78.89(6)	79.35(5)
O(5)-N(3)	1.266(3)	1.275(2)	O(3)Co(1)O(4)	78.37(6)	78.82(5)
N(1)-C(29)	1.332(3)	1.329(2)	O(1)Co(1)O(4)	92.48(6)	92.46(5)

N(1)-C(33)	1.336(3)	1.343(2)	O(2)Co(1)O(4)	90.11(7)	89.86(6)
N(2)-C(34)	1.267(3)	1.270(2)	O(3)Co(1)N(1)	88.16(6)	88.09(5)
N(2)-C(35)	1.467(3)	1.469(2)	O(1)Co(1)N(1)	101.05(6)	100.64(5)
N(3)-C(37)	1.490(3)	1.489(3)	O(2)Co(1)N(1)	92.38(7)	92.16(6)
N(3)-C(38)	1.486(3)	1.491(4)	O(4)Co(1)N(1)	166.48(7)	166.89(5)
C(1)-C(2)	1.472(3)	1.470(2)	O(3)Co(1)N(2)	93.78(7)	93.66(5)
C(15)-C(16)	1.463(3)	1.464(2)	O(1)Co(1)N(2)	93.43(6)	93.15(5)
O(5)…C(32)	2.915(4)	2.897(3)	O(2)Co(1)N(2)	165.30(7)	165.72(5)
O(5)…H(32)	2.492	2.474	O(4)Co(1)N(2)	102.84(7)	102.69(6)
C(1)…H(31)	2.734	2.693	N(1)Co(1)N(2)	76.67(7)	77.18(6)

Figure S2. Crystallographic data. Chort C…C contacts responsible for 3-D structure.

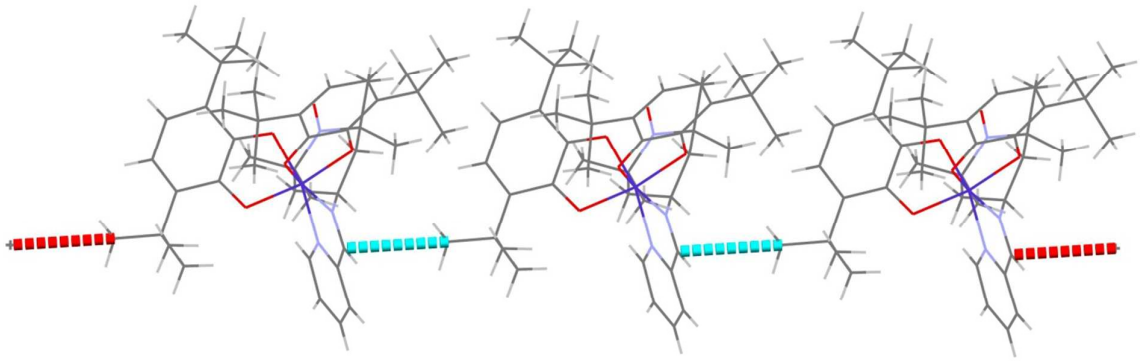


Figure S3. Calculated voids at room temperature (left) and at 240 K (right).

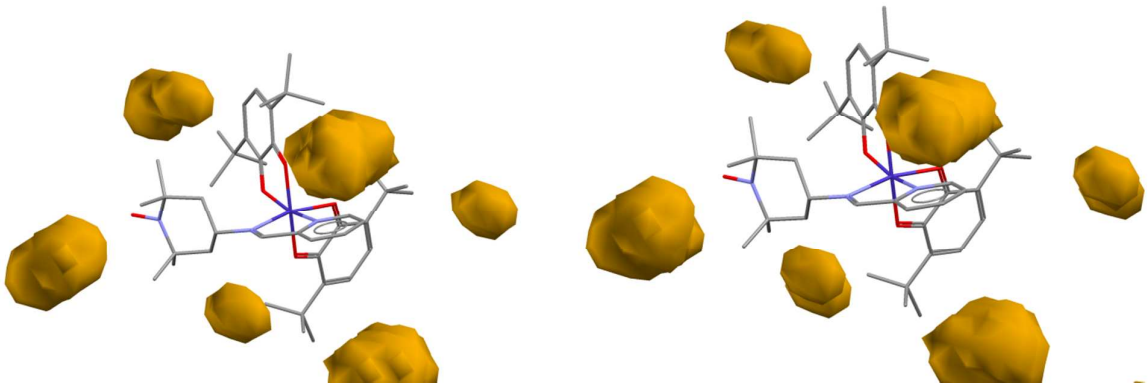


Table S3. Evolution of x-ray experiment

Room temperature experiment was successfully finished. R_1 = 5.36%, accuracy of C-C: 0.0040. Large thermal ellipsoids of *t*-Bu group. It is recommended to define them as disordered.

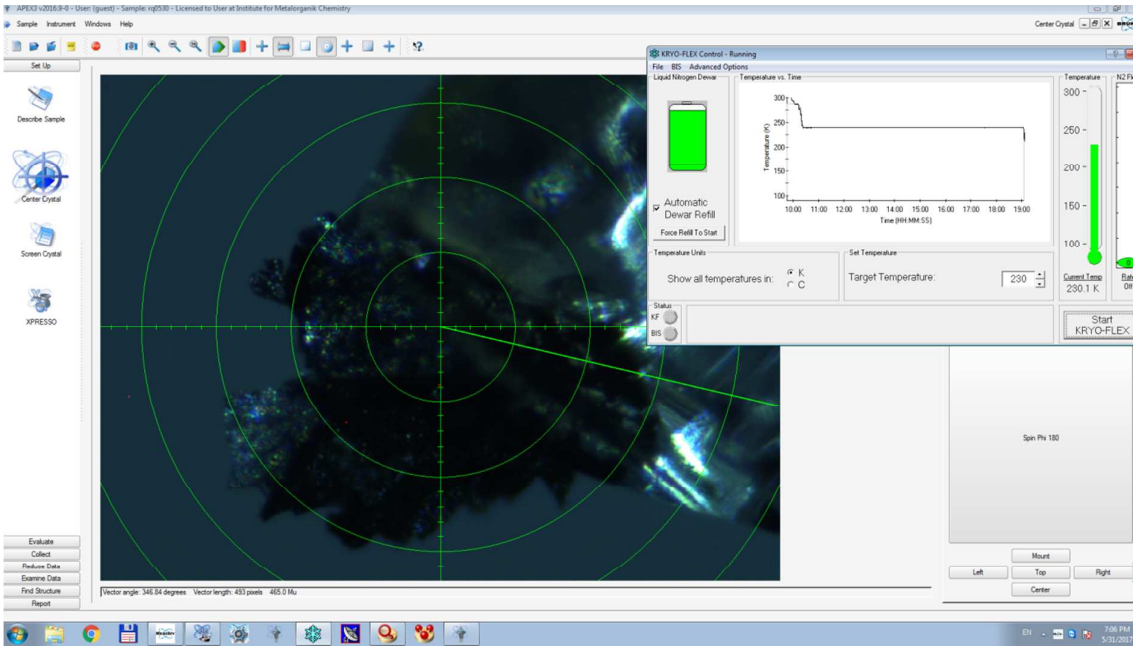
Experiment at 240 K was successfully finished. R_1 = 4.50%, accuracy of C-C: 0.0032.

Comparison of bonds lengths:

Bond	RT, Å	240 K, Å
Co(1)-O(3)	2.0150(15)	2.0062(12)
Co(1)-O(1)	2.0366(15)	2.0271(12)
Co(1)-O(2)	2.0433(16)	2.0329(13)
Co(1)-O(4)	2.0747(16)	2.0659(13)
Co(1)-N(1)	2.1226(18)	2.1080(14)
Co(1)-N(2)	2.1586(18)	2.1443(15)
O(1)-C(1)	1.274(2)	1.279(2)
O(2)-C(2)	1.271(3)	1.275(2)
O(3)-C(15)	1.268(3)	1.274(2)
O(4)-C(16)	1.273(3)	1.276(2)
O(5)-N(3)	1.266(3)	1.275(2)
N(1)-C(29)	1.332(3)	1.329(2)
N(1)-C(33)	1.336(3)	1.343(2)
N(2)-C(34)	1.267(3)	1.270(2)
N(2)-C(35)	1.467(3)	1.469(2)
N(3)-C(37)	1.490(3)	1.489(3)
N(3)-C(38)	1.486(3)	1.491(4)
C(1)-C(2)	1.472(3)	1.470(2)
C(15)-C(16)	1.463(3)	1.464(2)

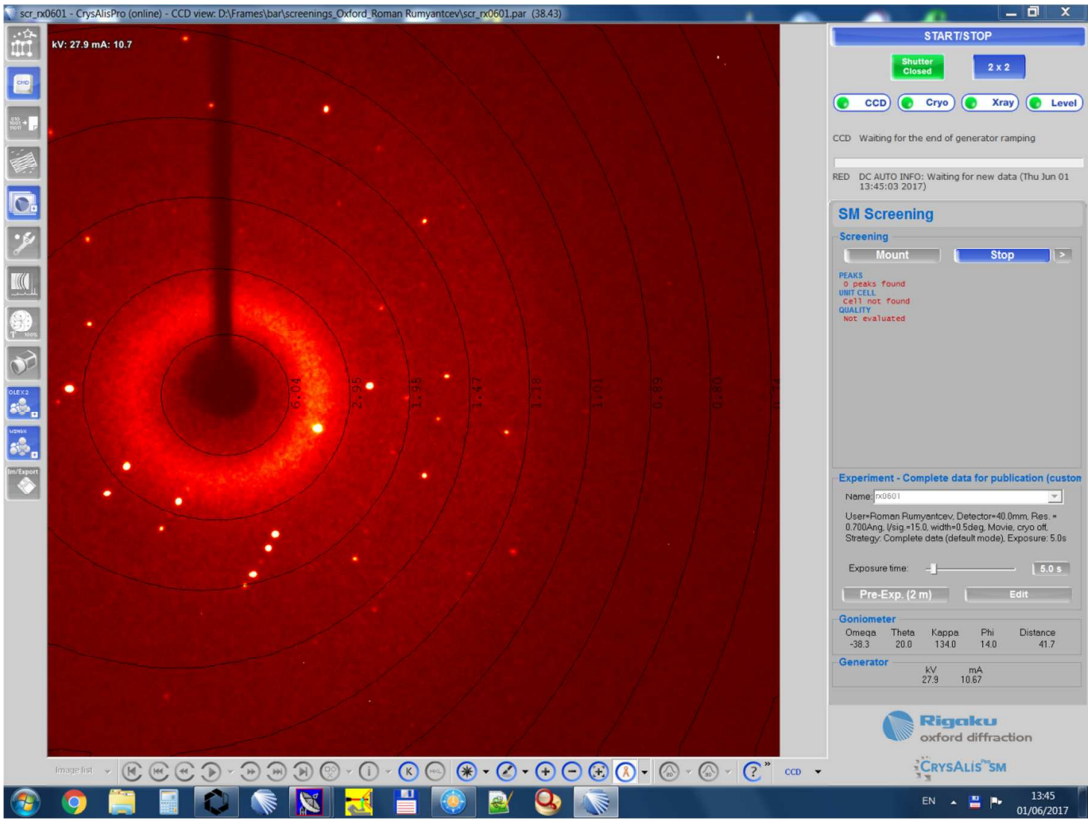
Further cooling with ordinary rate 120 K/hour down to ~228 K.

Result:



Xcalibur:

Crystal 1. RT.

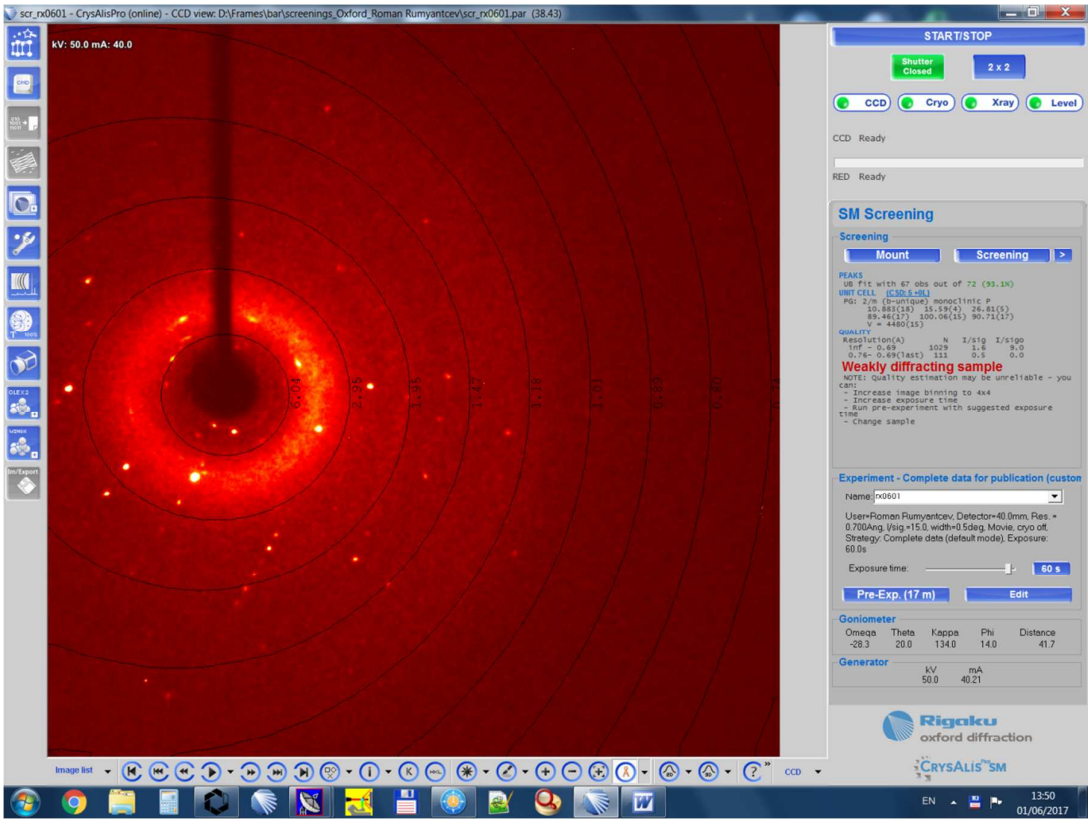


Sequence of cooling:

1. Down to 240 K cooling rate 120 K/hour
2. Down to 235 K cooling rate 60 K/hour
3. Down to 230 K cooling rate 30 K/hour
4. Down to ~218.00 K cooling rate 15 K/hour

Cooling ~218.75 ÷ ~218.55 video file 1cryst. Destroyed at ~218.6 K.

Nevertheless it seems that the major part of crystal remained in initial state. At 218.00 K cooling was stopped and the screening was started. The unit cell parameters were the same as before cooling (93% reflections). Picture reflects appearing of admixtures in the background.



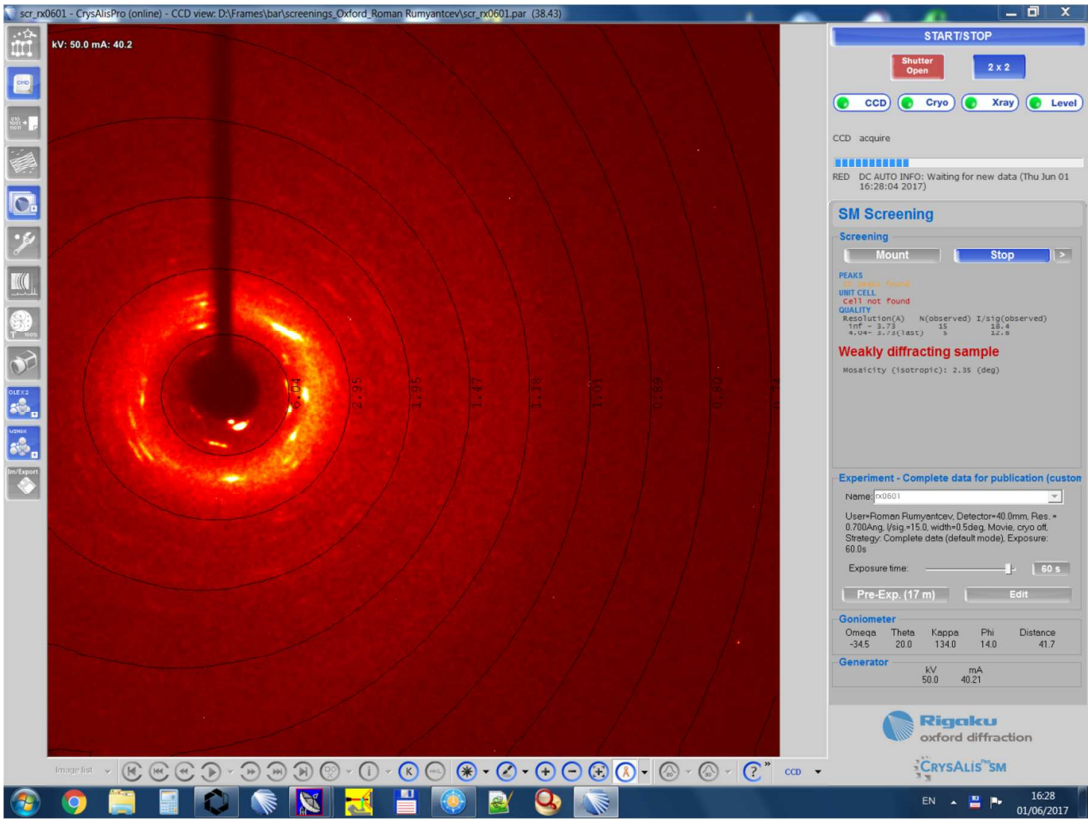
Crystal 2. (encapsulated in epoxy glue)

Sequence of cooling:

1. Down to 240 K cooling rate 120 K/hour
2. Down to 235 K cooling rate 60 K/hour
3. Down to 230 K cooling rate 30 K/hour
4. Down to 220 K cooling rate 15 K/hour
5. Down to ~218.00 K cooling rate 5 K/hour

Cooling ~218.93 ÷ ~218.89 K video file 2cryst. It was destroyed at ~218.91 K. One can see how the crystal has broken the glue matrix.

Video file 2cryst100K describes the following cooling of the crystal 2 down to 100 K with ordinary rate 120 K/hour. It is seen breaking off the pieces of crystal. Crystal becomes smaller. No monocrystal at the end of cooling.


scr_rx0601 - CrysAlisPro (online) - CCD view: D:\Frames\bar\screenings_Oxford_Roman Rumyantcev\scr_rx0601.par (38.43)
kV: 50.0 mA: 40.2
START/STOP
Shutter Open
2 x 2
CCD
Cryo
Xray
Level
CCD acquire
RED DC AUTO INFO: Waiting for new data (Thu Jun 01 16:28:04 2017)
SM Screening
Screening
Mount
Stop
PEAKS
UNIT CELL
Cell not found
QUALITY
Resolution(A) N(observed) I/sig(observed)
Weakly diffracting sample
Mosaicity (isotropic): 2.35 (deg)
Experiment - Complete data for publication (custom
Name: rx0601
User=Roman Rumyantcev, Detector=40.0mm, Res.= 0.700Ang, I/sig.=15.0, width=0.5deg. Movie, cryo off. Strategy: Complete data (default mode). Exposure: 60.0s
Exposure time:
60 s
Pre-Exp. (17 m)
Edit
Goniometer
Omega Theta Kappa Phi Distance
-34.5 20.0 134.0 14.0 41.7
Generator
kV mA
50.0 40.21
Rigaku
oxford diffraction
CrysAlis SM
EN
16:28
01/06/2017