Supporting Information

for

Synthesis, structure and (spectro)electrochemistry of hybrid metal(IV)phthalocyaninato-capped *3d*-metal pyrazoloximates as prospective precursors of ET and/or optically operated stimuli-induced and stimuli-responsive single-molecule magnets, logic gates and qubits

Svetlana A. Belova,[a] Semyon V. Dudkin,[a] Alexander S. Belov,[a] Anastasia A. Danshina,[a,c] Pavel V. Dorovatovskii,[d] Yulia H. Budnikova,[e] Vera V. Khrizanforova,[e] Svetlana Yu. Bratskaya,[f] Denis V. Balatskiy,[f] Yan Z. Voloshin[a,b]

[a]*Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilova str., bld. 1, 119334 Moscow, Russia*

[b]*Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky pr., 119991 Moscow, Russia*

[c]*Moscow Center for Advanced Studies, 20 Kulakova Str., 123592, Moscow, Russia*

[d]*NRC Kurchatov Institute, 1 Kurchatova pl., 123098 Moscow, Russia*

[e]*Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences, 8 Arbuzov st., 420088 Kazan, Russia*

[f]*Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, 159 100-letiya Vladivostoka pr., 690022 Vladivostok, Russia*

*Corresponding author E-mail: voloshin@ineos.ac.ru, voloshin@igic.ras.ru

X-ray data

Table S1. Details of data collection and refinement parameter for the X-rayed crystals of the bi- and pentanuclear hybrid complexes under study

Parameter	$[Fe(PzOx)_3(ZrPc)Cl]\cdot\cdot 4CHCl_3$	$[(Fe(PzOx)_3(ZrPc))_2Fe]\cdot\cdot 8CH_2Cl_2$	$[Co(PzOx)_3(ZrPc)Cl]Cl\cdot\cdot C_6H_6\cdot 2.2H_2O$	$[(Co(PzOx)_3(ZrPc))_2Co]\cdot\cdot 7CHCl_3$
Empirical formula	$C_{51}H_{38}Cl_{13}FeN_{17}O_3Zr$	$C_{102}H_{78}Cl_{16}Fe_3N_{34}O_6Zr_2$	$C_{53}H_{44.4}Cl_2CoN_{17}O_{5.2}Zr$	$C_{101}H_{69}Cl_{21}Co_3N_{34}O_6Zr_2$
Formula weight	1544.90	2793.17	1223.70	2958.58
T, K	100	120	120	100
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*
Z	4	1	2	1
a, Å	12.7743(5)	12.632(2)	11.2098(17)	12.541(3)
b, Å	20.9149(8)	13.972(3)	15.554(2)	13.436(3)
c, Å	24.0058(9)	15.789(3)	15.734(2)	17.462(4)
α, °	105.651(2)	97.067(5)	81.418(9)	84.63(3)
β, °	94.089(2)	101.196(5)	72.559(9)	76.91(3)
γ, °	94.732(2)	92.140(5)	79.554(9)	79.80(3)
V, Å^3	6125.5(4)	2707.4(9)	2560.6(7)	2816.3(11)
D_{calc} (g cm^{-3})	1.675	1.713	1.587	1.744
Linear absorption, μ, cm^{-3}	10.33	10.47	7.01	13.4
F(000)	3096	1406	1248	1479
$2\Theta_{max}$, °	50	50	50.5	53
Reflections measured	55033	22663	16785	20552
Independent reflections	21513	9369	9022	9626
Observed refls ($I > 2\sigma(I)$)	12568	3327	5516	5872
Parameters	1410	713	697	691
R1	0.0796	0.0952	0.0991	0.1531
wR2	0.2444	0.2794	0.3002	0.4304
GOF Goodness-of-fit	1.037	0.968	1.054	1.488
Largest diff. peak/hole, e×Å^{-3} (d_{max}/d_{min})	1.123/-1.283	1.061/-0.770	2.428/-2.156	4.530/-1.522
CCDC number	2347219	2347217	2347218	2347216

Table S2. Symmetry measures[a] of the *3d*-metal-centered MN_6-polyhedra in the molecules of the bi- and pentanuclear hybrid complexes under study

Parameter	[Fe(PzOx)$_3$(ZrPc)Cl]	[(Fe(PzOx)$_3$(ZrPc))$_2$Fe]		[Co(PzOx)$_3$(ZrPc)Cl]Cl	[(Co(PzOx)$_3$(ZrPc))$_2$Co]	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Co^{3+}	Co^{3+}	Co^{2+}
S(HP-6)	33.276	33.665	31.087	31.818	33.566	32.137
S(PPY-6)	23.533	20.557	29.312	25.739	22.653	29.826
S(TAP-6)	1.652	3.354	0.111	0.884	2.017	0.080
S(TRP-6)	9.727	6.092	16.160	12.024	7.852	16.023
S(JPPY-6)	27.165	24.417	32.709	29.507	26.532	33.246

[a]S(HP-6), S(PPY-6), S(TAP-6), S(TRP-6) and S(JPPY-6) are the calculated deviations of a geometry of their FeN_6- and CoN_6-polyhedra from an ideal hexagon (HP-6), pentagonal pyramid (PPY-6), trigonal antiprism (TAP-6), trigonal prism (TPR-6) and Johnson pentagonal pyramid (JPPY-6), respectively

Table S3. Symmetry measures of the capping ZnN_4O_3-polyhedra in the molecules of the bi- and pentanuclear hybrid complexes under study

Parameter	$[Fe(PzOx)_3(ZrPc)Cl]$	$[(Fe(PzOx)_3(ZrPc))_2Fe]$	$[Co(PzOx)_3(ZrPc)Cl]Cl$	$[(Co(PzOx)_3(ZrPc))_2Co]$
S(HP-7)	33.772	35.012	33.488	34.450
S(HPY-7)	19.534	19.658	20.232	19.848
S(PBPY-7)	5.949	5.946	6.731	6.115
S(COC-7)	0.707	0.575	1.674	0.708
S(CTPR-7)	0.966	1.489	0.372	0.884
S(JPBPY-7)	9.666	9.400	10.389	9.695
S(JETPY-7)	20.242	20.244	20.314	19.704

[a]S(HP-7), S(HPY-7), S(PBPY-7), S(COC-7), S(CTRP-7), S(JPBPY-7) and S(JETPY-7) are the calculated deviations of a geometry of the ZrO_3N_4-polyhedron from an ideal heptagon (HP-7), hexagonal pyramid (HPY-7), pentagonal bipyramid (PBPY-7), capped octahedron (COC-7), capped trigonal prism (CTPR-7), Johnson pentagonal bipyramid (JPPY-6) and Elongated triangular pyramid (JETPY-7), respectively.

As requested by one of the Reviewers of this paper, the detailed comments are given below to explain the Alerts that arise from the not so high quality of X-ray diffraction data collected for each of the four complexes synthesized (Alerts A and B are also explained in the provided cif and checkcif files). In all cases, however, the resulting quality is still high enough to unambiguously support the conclusions drawn from these data in the paper.

Table S5.

Number of components	**R1**	**wR2**	**GOOF**	**ρ_{max}**	**ρ_{min}**	**Occupancies**
1	0.0796	0.2444	1.037	1.123	–1.283	1.0
2	0.0789	0.2415	1.035	1.124	–1.283	0.87302
						0.12698
3	0.0785	0.2391	1.034	1.115	–1.267	0.77671
						0.11247
						0.10943
4	0.0783	0.2390	1.032	1.122	–1.269	0.73364
						0.09902
						0.09785
						0.06833

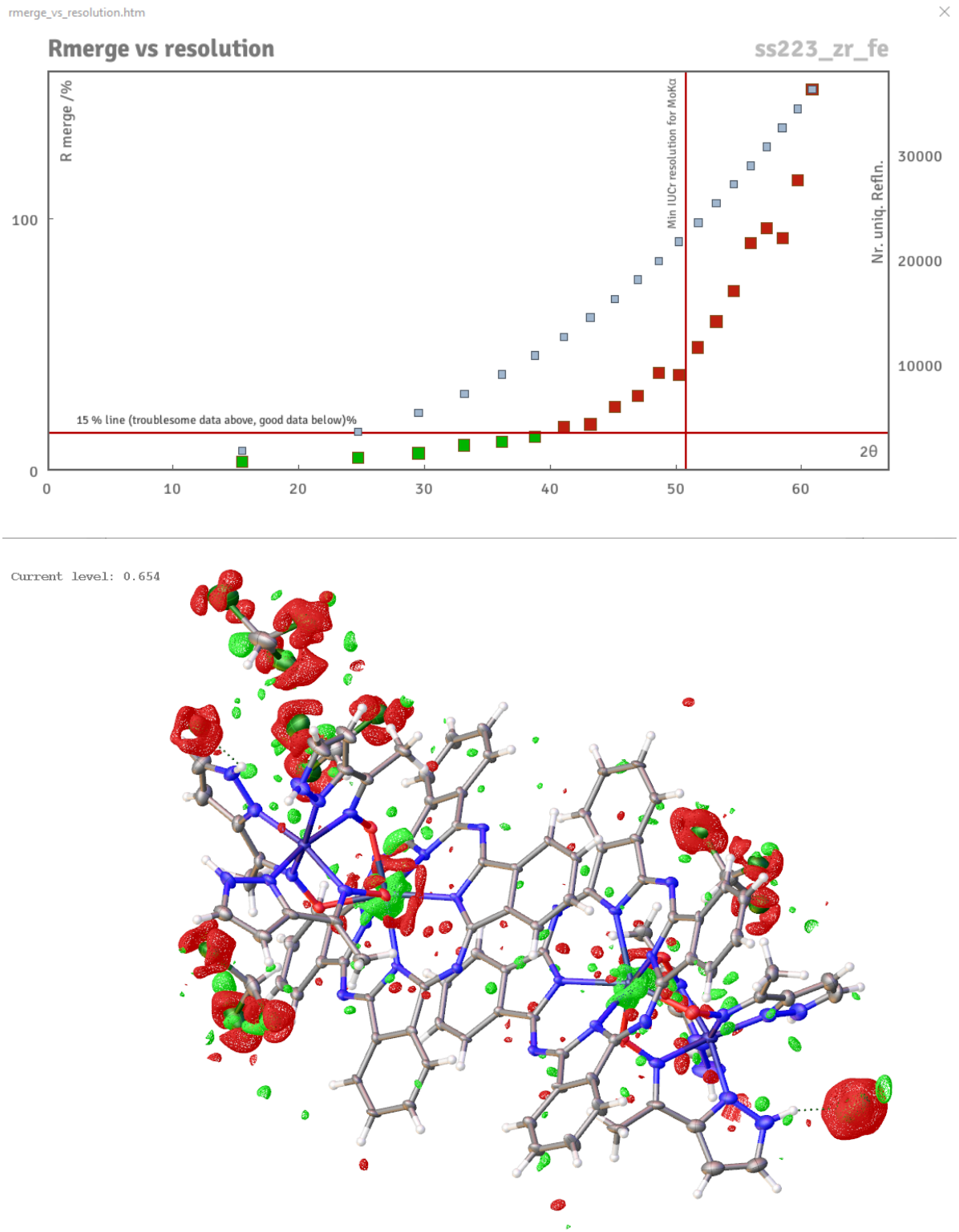


Fig. S9. R_{merge} vs. resolution plot (on top) and the residual electron density distribution (on bottom) for the model with only one position of Cl2 being populated.

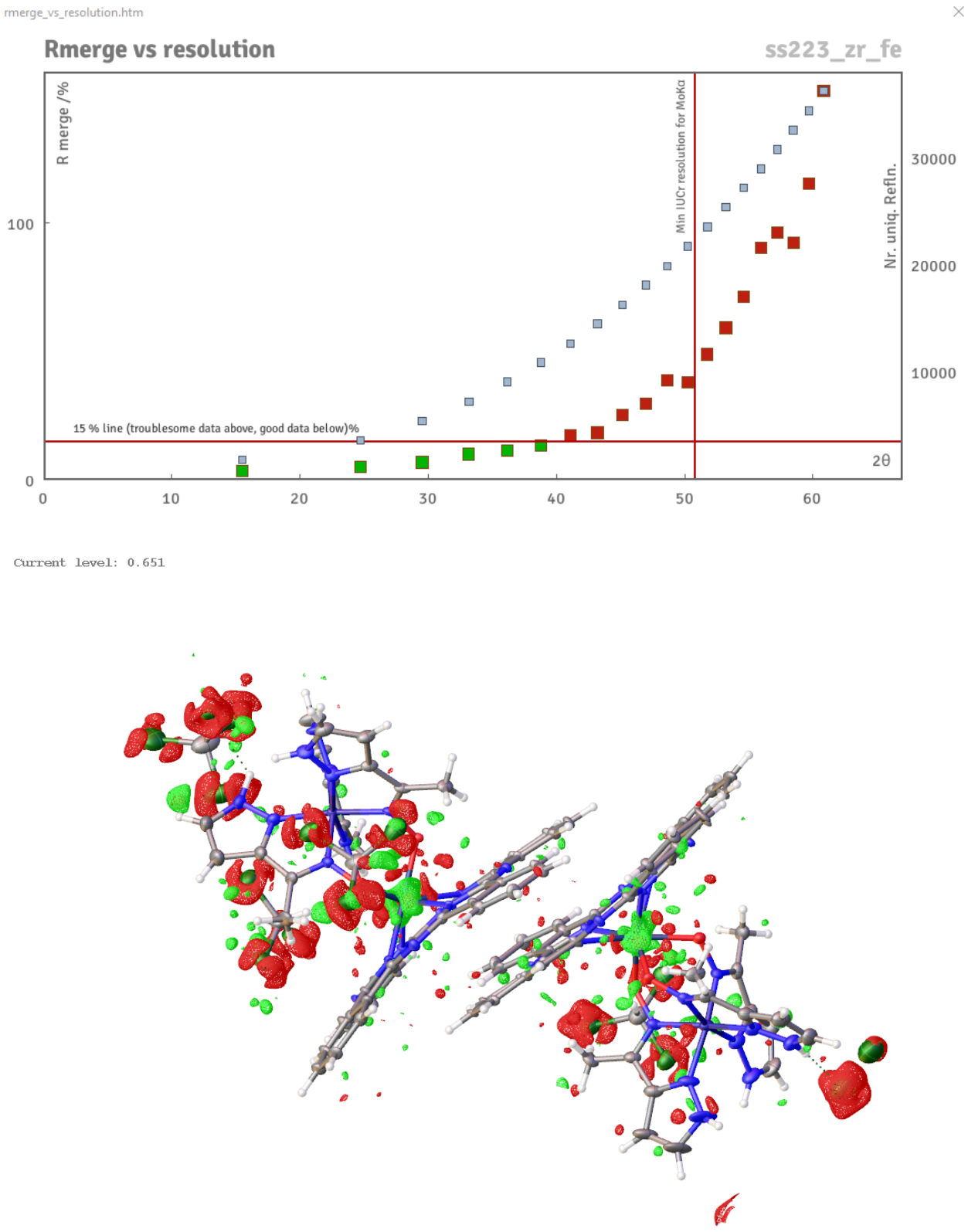
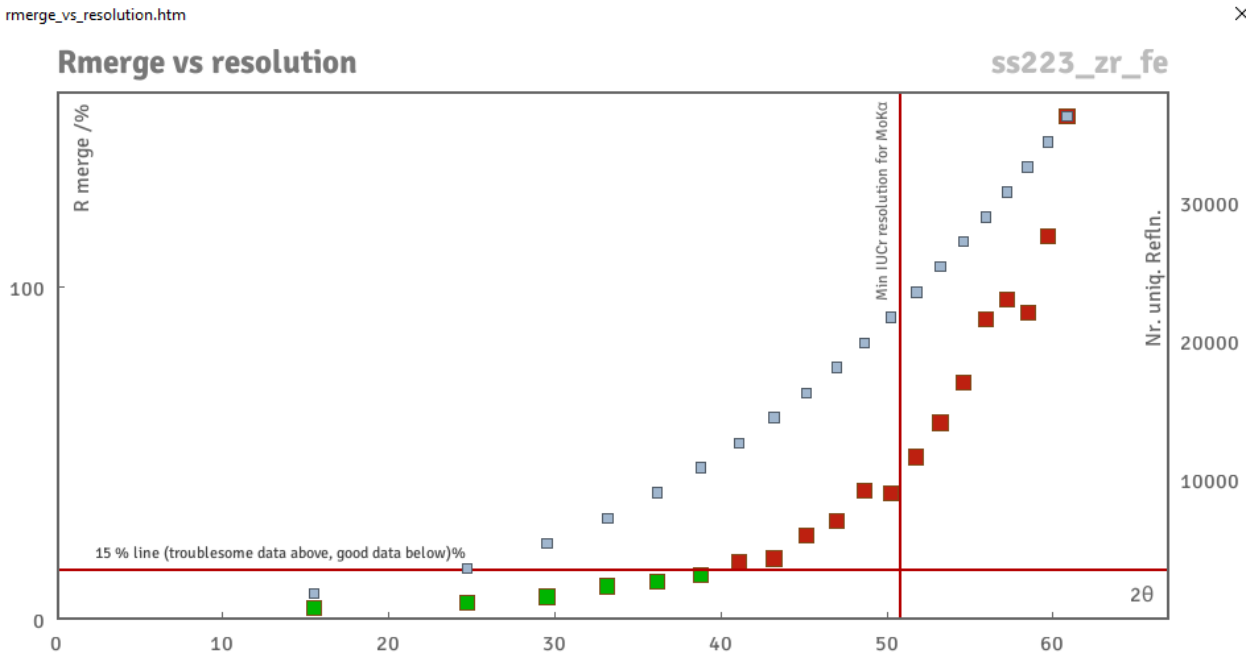


Fig. S10. R_{merge} vs. resolution plot (on top) and the residual electron density distribution (on bottom) for the model with Cl2 being disordered by two positions (for their populations, see Table S1).



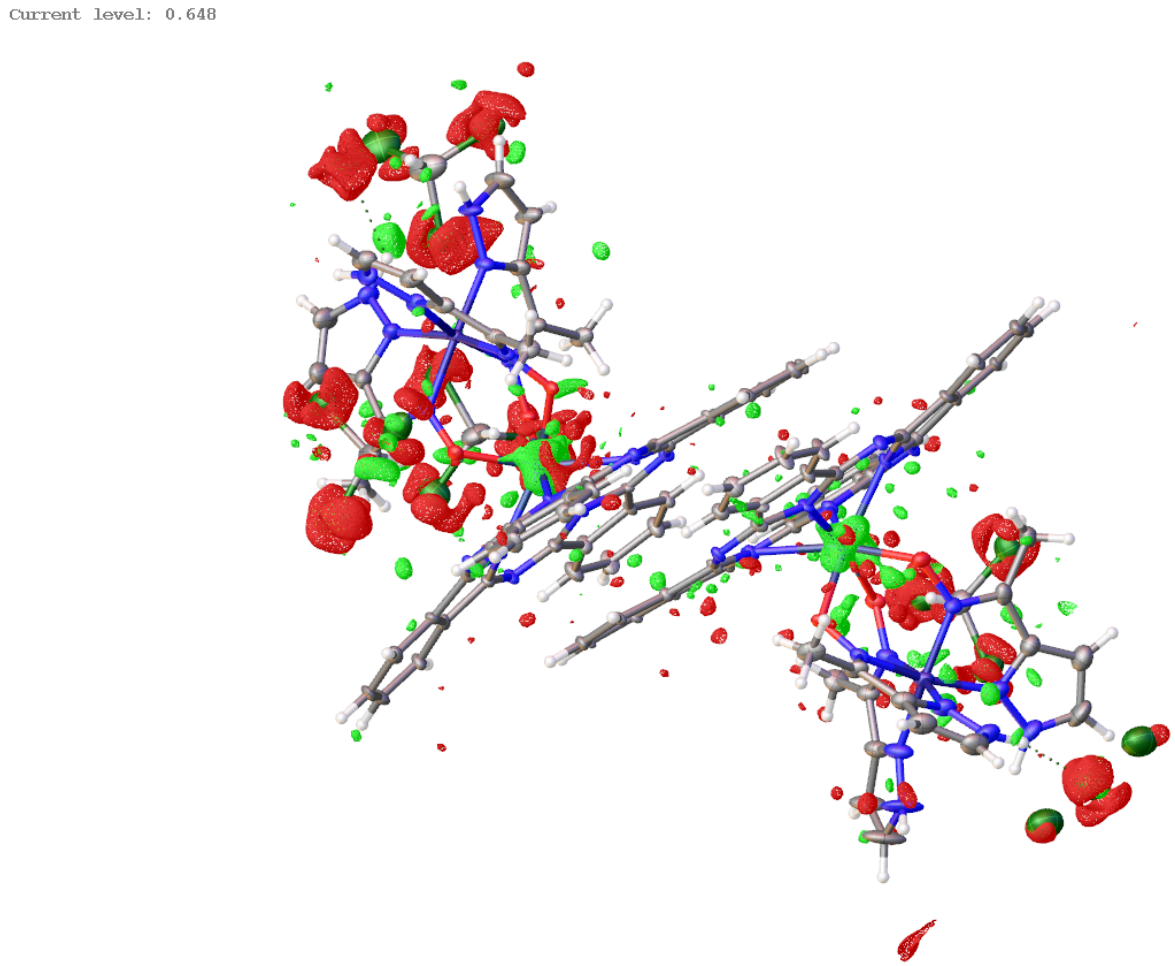


Fig. S11. R_{merge} vs. resolution plot (on top) and the residual electron density distribution (on bottom) for the model with Cl2 being disordered by three positions (for their populations, see Table S1).

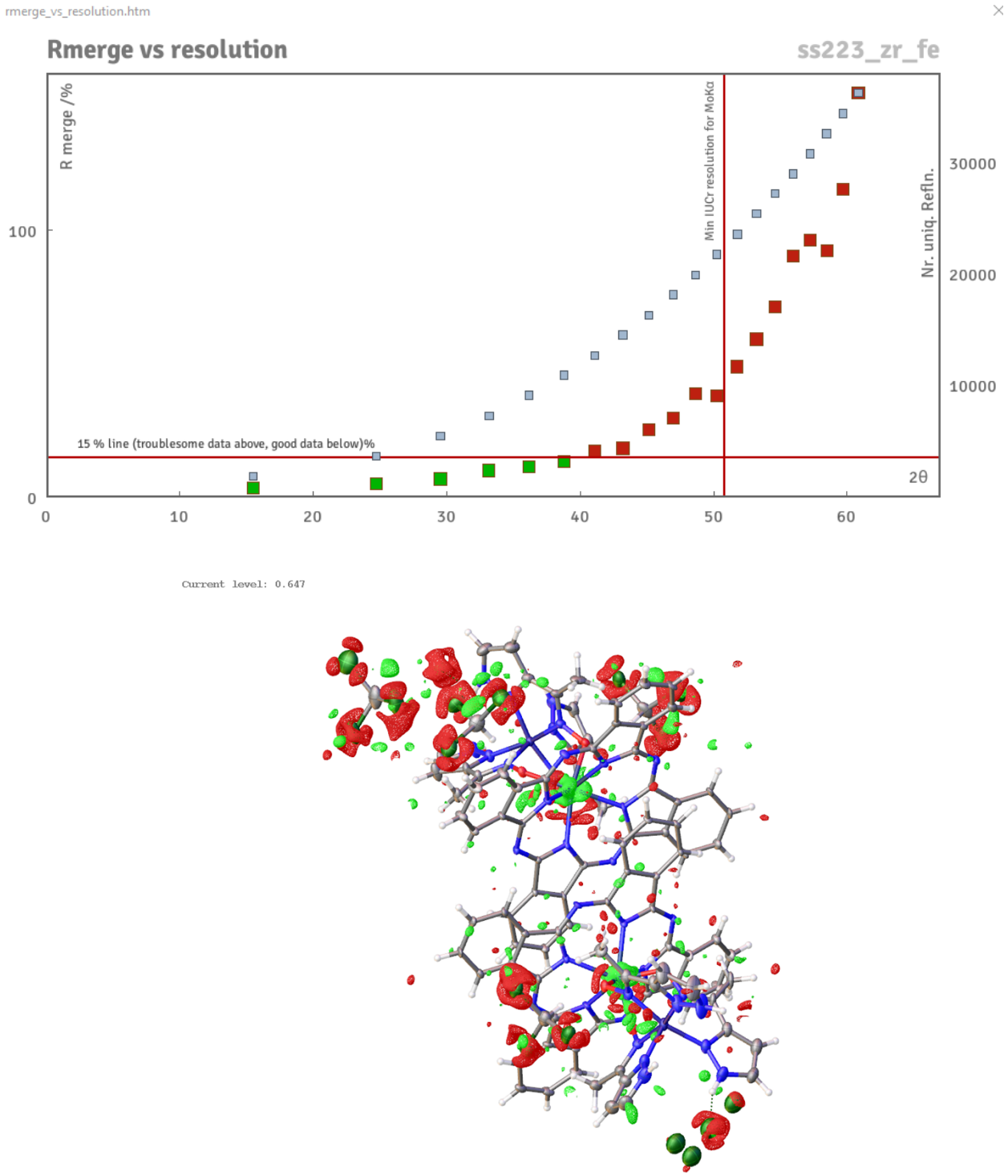
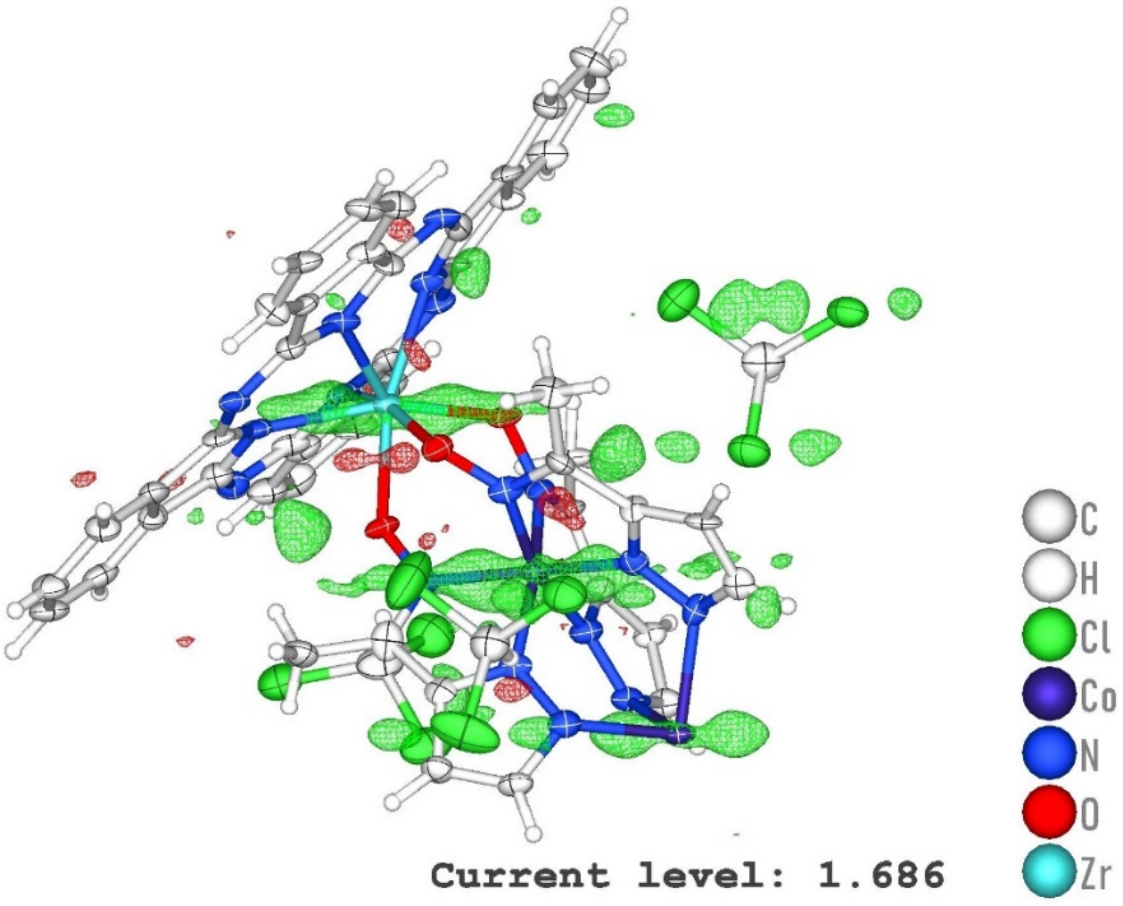


Fig. S12. R_{merge} vs. resolution plot (on top) and the residual electron density distribution (on bottom) for the model with Cl2 being disordered by two positions (for their populations, see Table S1).

CCDC 2347216: C101 H69 Cl21 Co3 N34 O6 Zr2

971_ALERT_2_A Check Calcd Resid. Dens. 0.93Ang From Zr1 5.64 eA-3
971_ALERT_2_A Check Calcd Resid. Dens. 0.87Ang From Zr1 5.04 eA-3
971_ALERT_2_A Check Calcd Resid. Dens. 1.48Ang From N15 5.04 eA-3
971_ALERT_2_A Check Calcd Resid. Dens. 0.87Ang From N5 4.55 eA-3
971_ALERT_2_A Check Calcd Resid. Dens. 0.95Ang From N2 4.36 eA-3
973_ALERT_2_A Check Calcd Positive Resid. Density on Zr1 2.70 eA-3
084_ALERT_3_B High wR2 Value (i.e. > 0.25) ..... 0.43 Report
097_ALERT_2_B Large Reported Max. (Positive) Residual Density 4.53 eA-3
971_ALERT_2_B Check Calcd Resid. Dens. 1.21Ang From N11 3.12 eA-3
971_ALERT_2_B Check Calcd Resid. Dens. 1.00Ang From C2 3.05 eA-3
971_ALERT_2_B Check Calcd Resid. Dens. 1.09Ang From Cl07 3.03 eA-3
971_ALERT_2_B Check Calcd Resid. Dens. 1.04Ang From Co2 3.02 eA-3
The crystal size is reported as 0.07 x 0.07 x 0.01 mm.



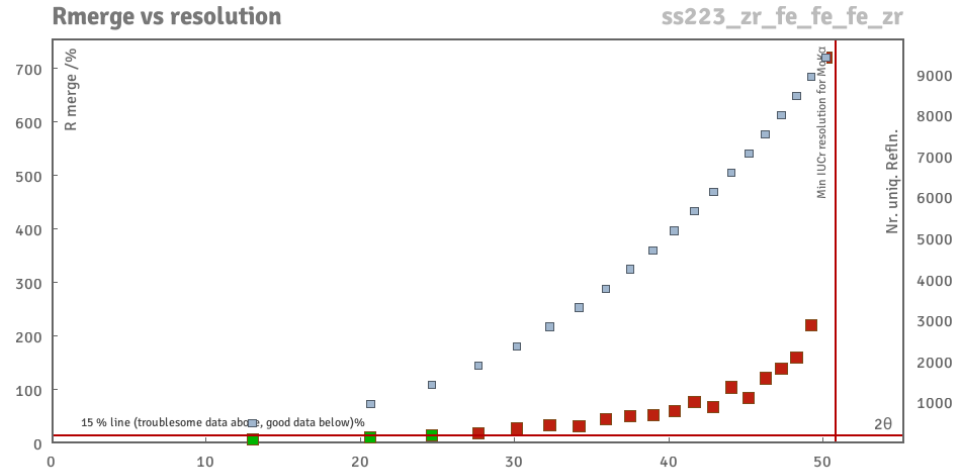
The best available single crystal of this complex (**CCDC 2347216**), selected for the X-ray data collection, was a small and thin plate with low reflective power that suffered from twinning (although a sensible twin law was not found), thereby causing the collected dataset to be of the mediocre quality. The latter, however, is still enough to discuss general structural details, as is done in the paper.

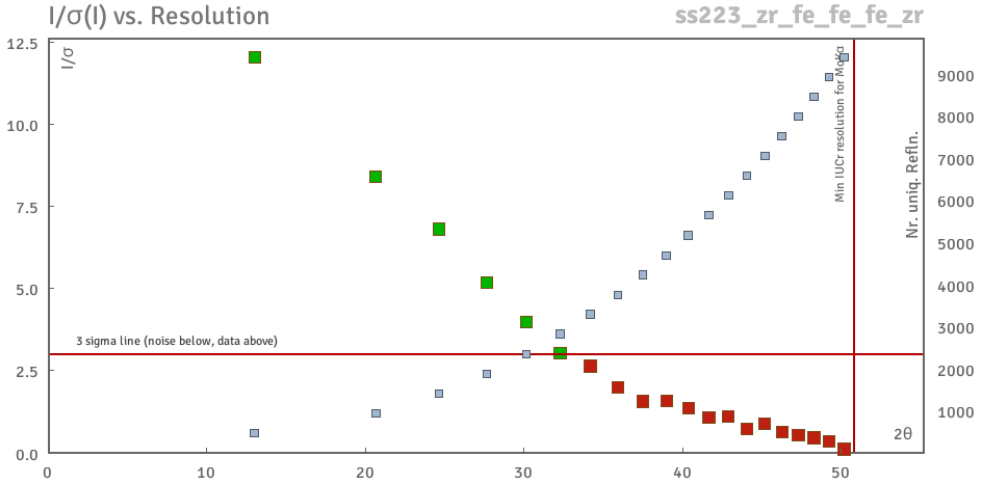
Although there is a chance that after many new attempts at recrystallization a crystal with a superior quality could be obtained, slightly lower R-factors and other quality indicators and smaller e.s.d's on the reported geometric parameters with conceptually the same conclusions drawn from them do not warrant such addition efforts, which still can fail, as did all the previous attempts at recrystallization.

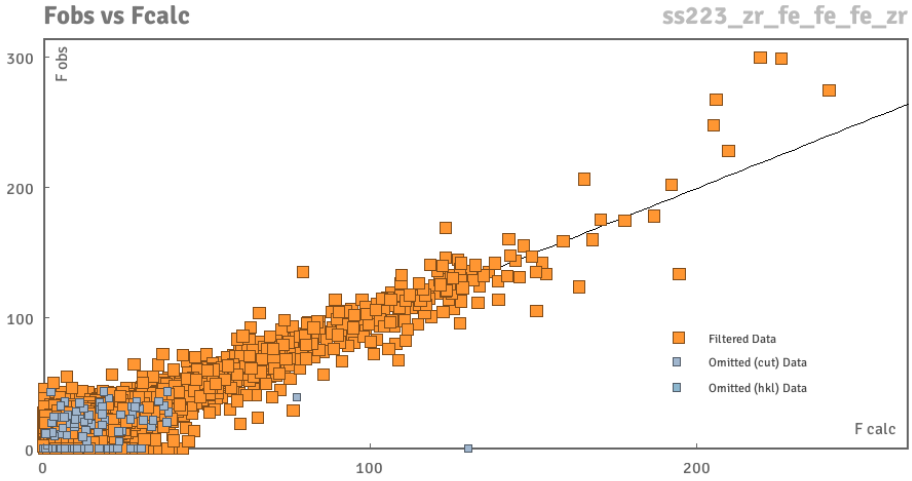
CCDC 2347217: C102 H78 Cl16 Fe3 N34 O6 Zr2

020_ALERT_3_B The Value of Rint is Greater Than 0.12 ..... 0.227 Report

026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 36%



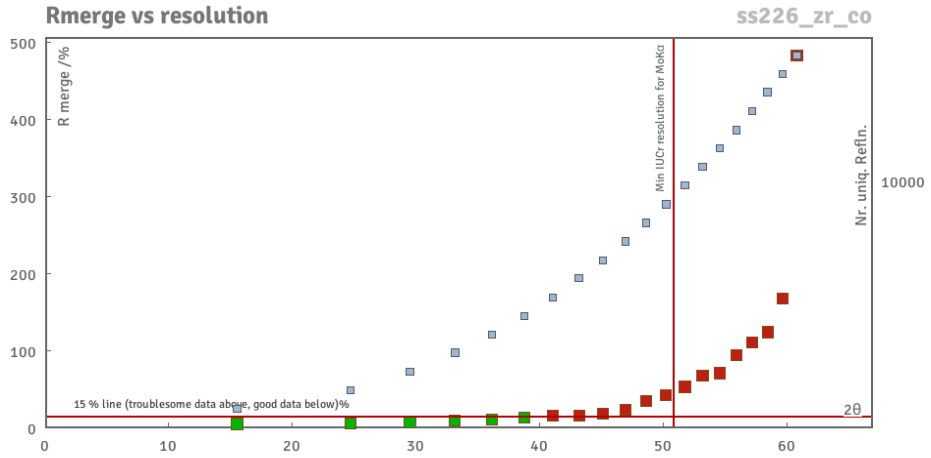


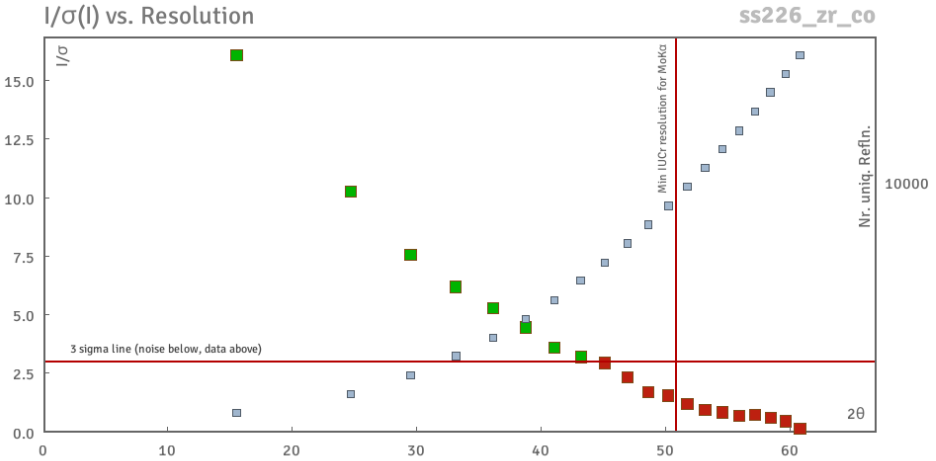


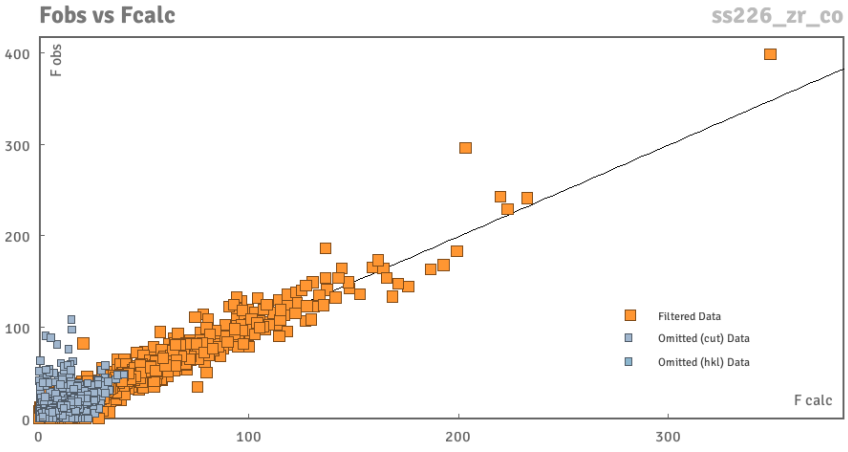
The best available single crystal of this complex (**CCDC 2347217**) selected for the X-ray data collection was a small and thin plate with low reflective power, thereby causing the collected dataset to be of the mediocre quality. The latter, however, is still enough to discuss general structural details, as is done in the paper.

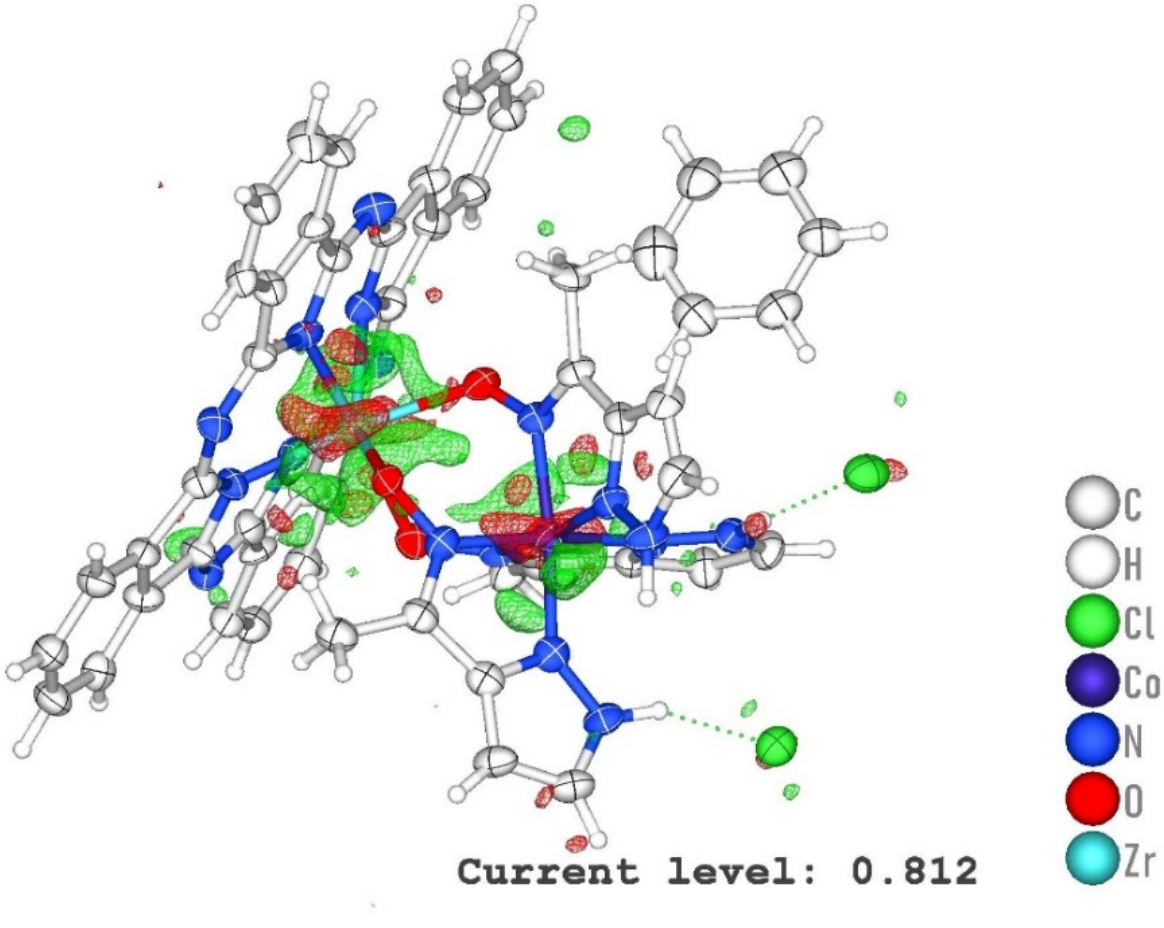
Although there is a chance that after many new attempts at recrystallization a crystal with a superior quality could be obtained, slightly lower R-factors and other quality indicators and smaller e.s.d's on the reported geometric parameters with conceptually the same conclusions drawn from them do not warrant such addition efforts, which still can fail, as did all the previous attempts at recrystallization.

CCDC 2347218: C53 H40 Cl2 Co N17 O3 Zr





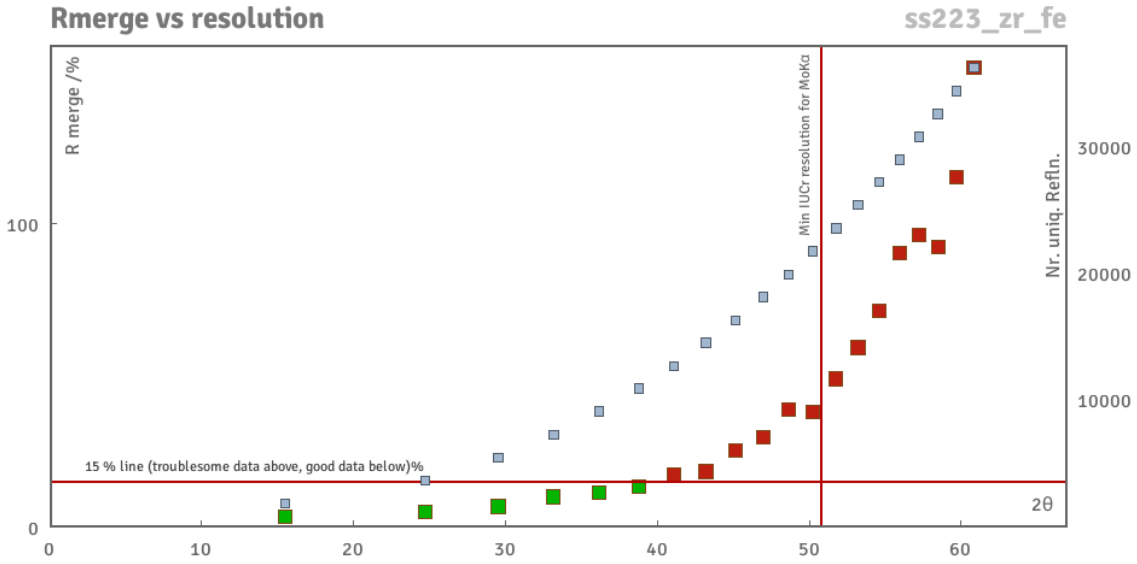


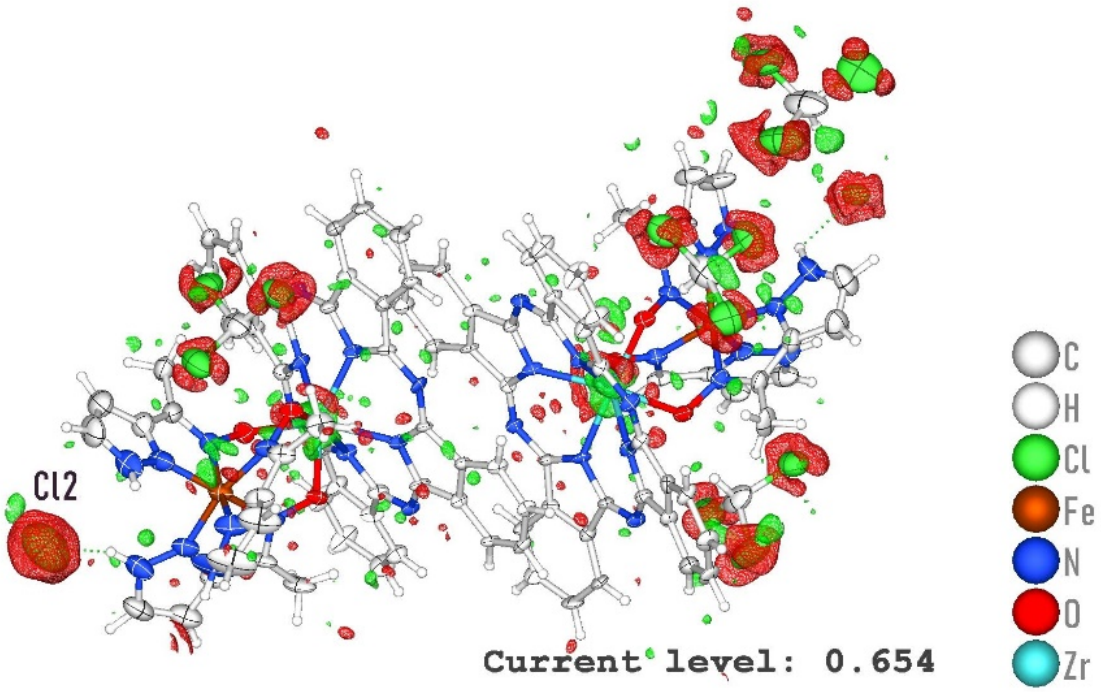


Like other members from this hard-to-crystallize family of polynuclear intracomplexes, the best available single crystal for this complex (**CCDC 2347218**) was a small and thin plate. The quality of the collected dataset is again on the lower side, it, however, even does not produce alerts A or B.

Although there is also a chance that after many new attempts at recrystallization a crystal with a superior quality could be obtained, slightly lower R-factors and other quality indicators and smaller e.s.d's on the reported geometric parameters with conceptually the same conclusions drawn from them do not warrant such addition efforts, which still can fail, as did all the previous attempts at recrystallization.

CCDC 2347219: C49 H36 Cl7 Fe N17 O3 Zr





Like other members from this hard-to-crystallize family of polynuclear intracomplexes, the best available single crystal for this complex (**CCDC 2347219**) was a small and thin plate. The quality of the collected dataset is again on the lower side, it, however, even does not produce alerts A or B.

Although there is a chance that after many new attempts at recrystallization a crystal with a superior quality could be obtained, slightly lower R-factors and other quality indicators and smaller e.s.d's on the reported geometric parameters with

conceptually the same conclusions drawn from them do not warrant such addition efforts, which still can fail, as did all the previous attempts at recrystallization.

Also note the thermal ellipsoid of the atom Cl2 that is larger than for other chloride anions, which, however, does not produce alerts A or B. As this cannot arise from a superposition with a neutral molecule (otherwise, the crystal won't be charge neutral, thus containing the intracomplex species), the most probable reason is the disorder of Cl2. Our attempts to model it with two, three and four positions with freely refined populations, however, resulted only in minor changes in R-factors and other quality indicators, thereby making its modelling superfluous.