Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 47–50

Co-crystallization of isomers of iron(II) complex of a tridentate mixed amine/imine ligand in one unit cell

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Experimental Details

Synthesis of [Fe(*trans*-L)$_2$](PF$_6$)$_2$ 1, mixture of stereoisomers: In a typical experiment, ammonium iron(II) sulfate (392 mg, 1.00 mmol) was dissolved in 5.0 mL of de-ionized water in a 50 mL round bottom flask, after which 15.0 mL of 95% EtOH was added. Pyridine-2-carboxaldehyde (214 mg, 2 mmol) was added in one portion while stirring. Subsequently, racemic *trans*-1,2-diaminocyclohexane (228 mg, 2 mmol) was added dropwise with stirring, immediately giving an indigo solution. The solution was allowed to stir at room temperature for 2 h, after which most of the ethanol and water were removed under reduced pressure. Further purification was achieved by extraction of the hexafluorophosphate salt into CH_2Cl_2 followed by removal of the solvent at ambient temperature and under reduced pressure. Yield after drying (39%). Elemental microanalysis was performed by Micro-Analysis, Inc. laboratory in Wilmington, DE, USA. *It should be noted that upon growing single crystals we observed incorporation of solvents of the process (propionitrile – from synthesis, and diethyl ether – from vapor diffusion method) into the asymmetric unit (ASU) content. This topic analyzed further in S10, S11.*

Elemental analysis for bulk powder: calculated for $C_{24}H_{34}F_{12}FeN_6P_2$: C - 38.31%; H - 4.55%; N - 11.17%; found: C - 38.84%; H - 4.68%; N - 10.91%. Complex decomposes at ~190^{o}C with elimination of PF_5.

Target dry complex represents dichroic solid with crystals being blue-black on reflected light and dark-red on transient light. The complex is soluble in most organic solvents and water, but not in hydrocarbons.

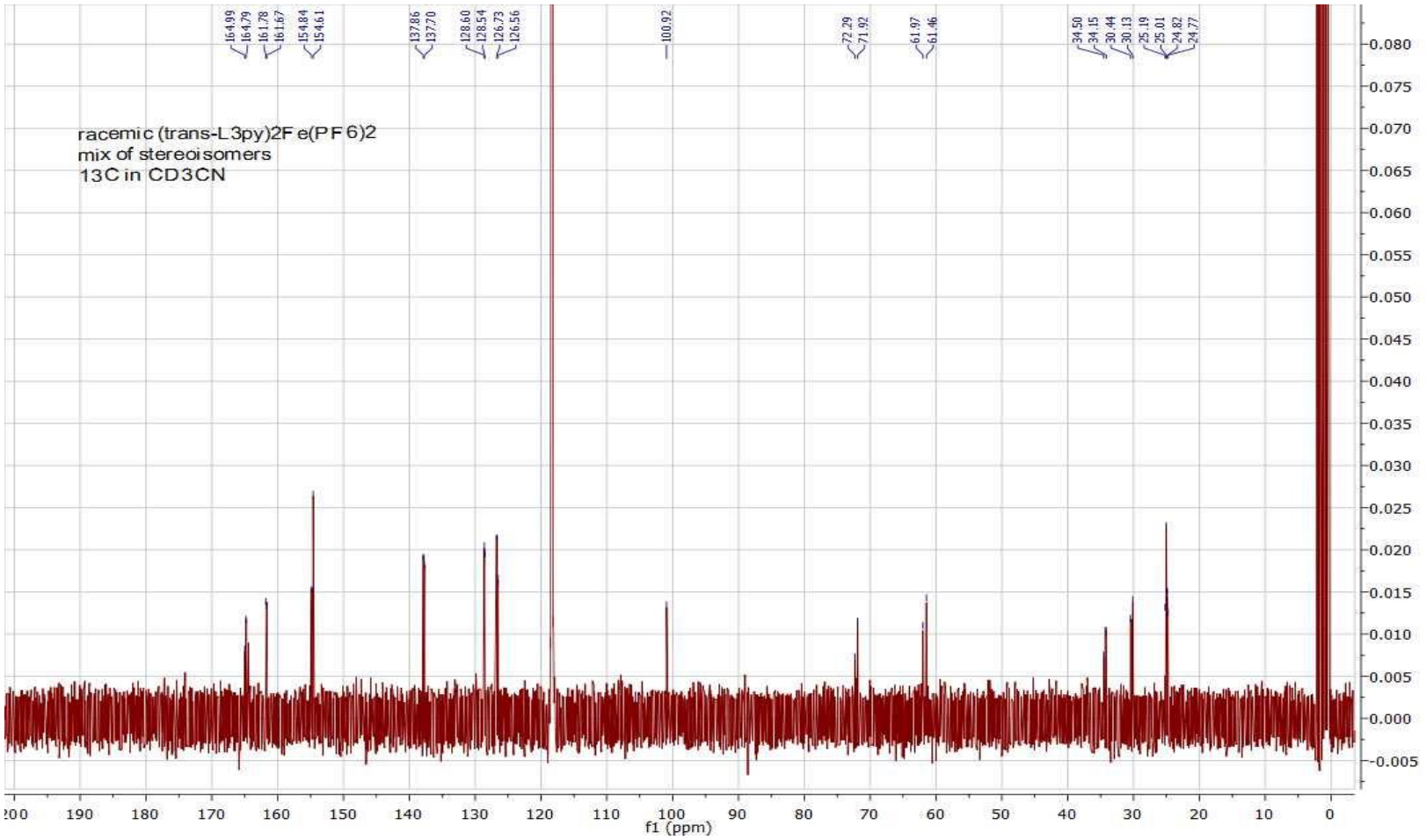
The IR, ^{1}H NMR, ^{13}C{^{1}H} NMR spectra, and electronic spectral data for the target complex [Fe(*trans*-(1R,2R)-**L**)$_2$](PF$_6$)$_2$ were recorded and presented below.

Physical methods and instrumentation used.

The FTIR spectra were obtained on a Thermo Nicolet iS5 spectrophotometer and analyzed with OMNIC software (thermofisher.com). IR spectra were obtained on solid samples *via* ATR using a diamond transmission window. The UV-Visible spectra were obtained using HP 8453 spectrophotometer in dried organic solvents received from commercial vendors and used without further purification.

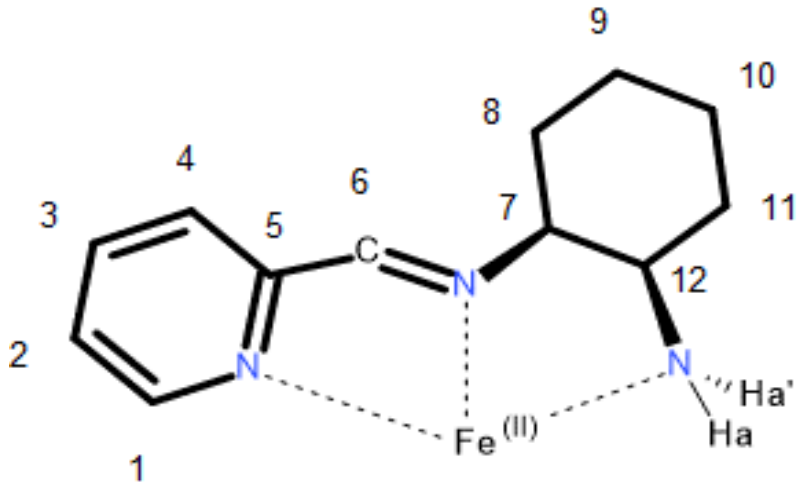
The NMR spectra were recorded in deuterated MeCN on a 300 MHz JEOL ECX-300 FT at 298 K with chemical shifts referenced to signals from the deuterated solvent. Magnetic susceptibility measurements were performed on anhydrous solids of [Fe(*trans*-(1*R*,2*R*)-**L**)$_2$](PF$_6$)$_2$ using a Johnson-Matthey MSB Mk1 magnetic susceptibility balance.

The $^{13}C\{^{1}H\}$ NMR spectrum of stereoisomers of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$ **1** in CD$_3$CN at 290 K showing clearly seen characteristic "doubling" of each resonance due to presence of the mixture.



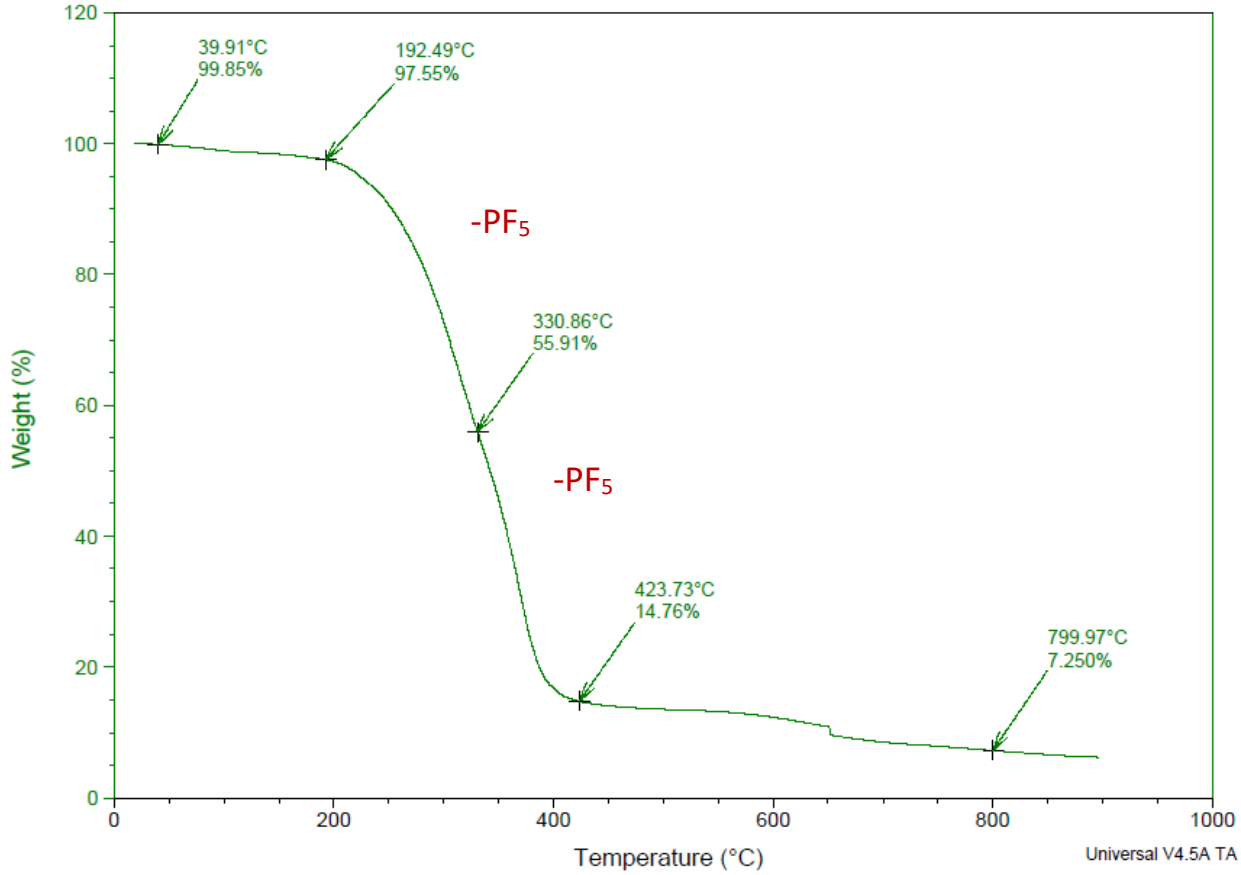
The NMR Characterization of [Fe(*trans*-L)$_2$](PF$_6$)$_2$, mixture of stereoisomers in detail.

Used numbering scheme for ^{13}C-NMR signals assignments for [Fe(trans-**L**)$_2$](PF$_6$)$_2$**.**



Resonances labeled for "Complex A" are assigned to the set of enantiomers [Fe(*trans*-(1*R*,2*R*)-**L**)$_2$](PF$_6$)$_2$ and [Fe(*trans*-(1*S*,2*S*)-**1**)$_2$](PF$_6$)$_2$ which are indistinguishable by NMR and have identical chemical shifts to the compound made from pure *trans*-(1*R*,2*R*)-diaminocyclohexane: [Fe(*trans*-(1*R*,2*R*)-**L**)$_2$](PF$_6$)$_2$. Resonances labeled for "Complex B", arise from the diastereomer assigned formula [Fe(*trans*-(1*R*,2*R*)-**L**)(*trans*-(1*S*,2*S*)-**L**)](PF$_6$)$_2$. The ^{13}C{^{1}H}-NMR (75.6 MHz, CD$_3$CN, ppm; carbon atom labels are as assigned in **Figure S2**) 165.0, 164.8 (C6A, C6B), 161.8, 161.7 (C5A, C5B), 154.8, 154.6 (C1A, C1B), 137.9, 137.7 (C4A, C4B), 128.6, 128.5 (C3B, C3A), 126.7, 126.6 (C2B, 2A), 72.3, 72.0 (C7B, C7A), 62.0, 61.5 (C12A, C12B), 34.5, 34.2 (C8B, C8A), 30.4, 30.1 (C11B, C11A), 25.2, 25.0 (C9 or C10A, C9 or C10B), 24.82, 24.77 (C9 or C10B and C9 or C10A).

Weight view of the TG/DSC experiment for the [Fe(*trans*-L)$_2$](PF$_6$)$_2$ complex showing two consecutive PF$_5$ weight losses.

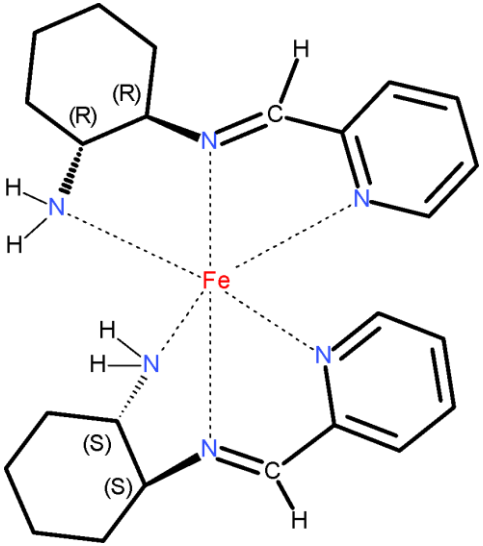


The TG analysis for [Fe(L)$_2$](PF$_6$)$_2$ was performed on a TA Instrument Q-600 (Delaware, USA) in an alumina crucible in the range between 30 – 1000°C under nitrogen flow at 100 ± 1 mL/min and a heating rate of 10 °C/min. The crucible was calcined prior to each experiment using a propane torch. Data of the TG analyses were processed using the TA Universal Analysis software package.

Schematic drawing of stereoisomers of [Fe(*trans*-**L**)$_2$]$^{2+}$ and their manifestation in the NMR spectra.

Diastereomer

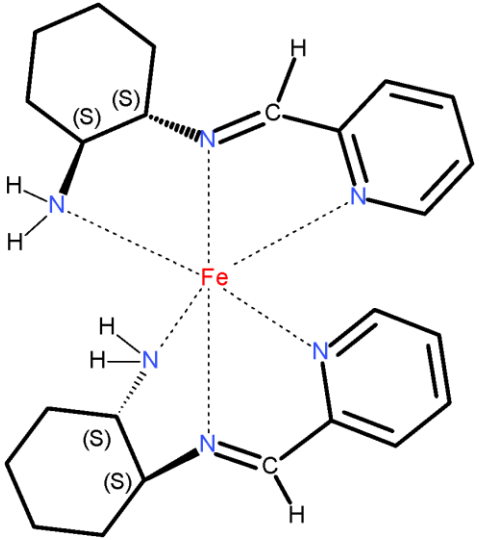
(one set of ^{13}C NMR signals: well observable)



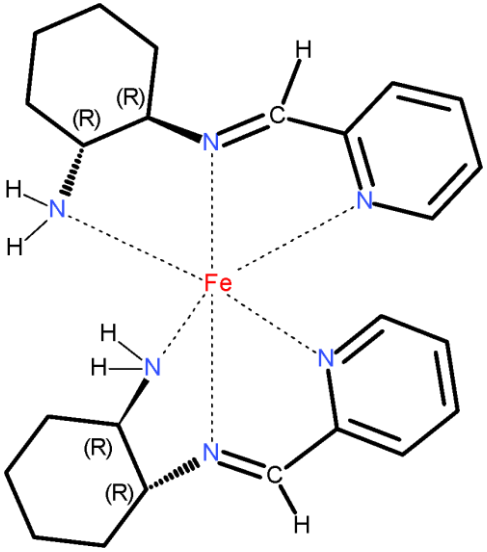
[Fe(*trans*-(1*R*,2*R*)-**L**)(*trans*-(1*S*,2*S*)-**L**)]$^{2+}$

Set of ***Enantiomers***

(second set of ^{13}C NMR signals, unseparable)



[Fe(*trans*-(1*S*,2*S*)-**L**)$_2$]$^{2+}$

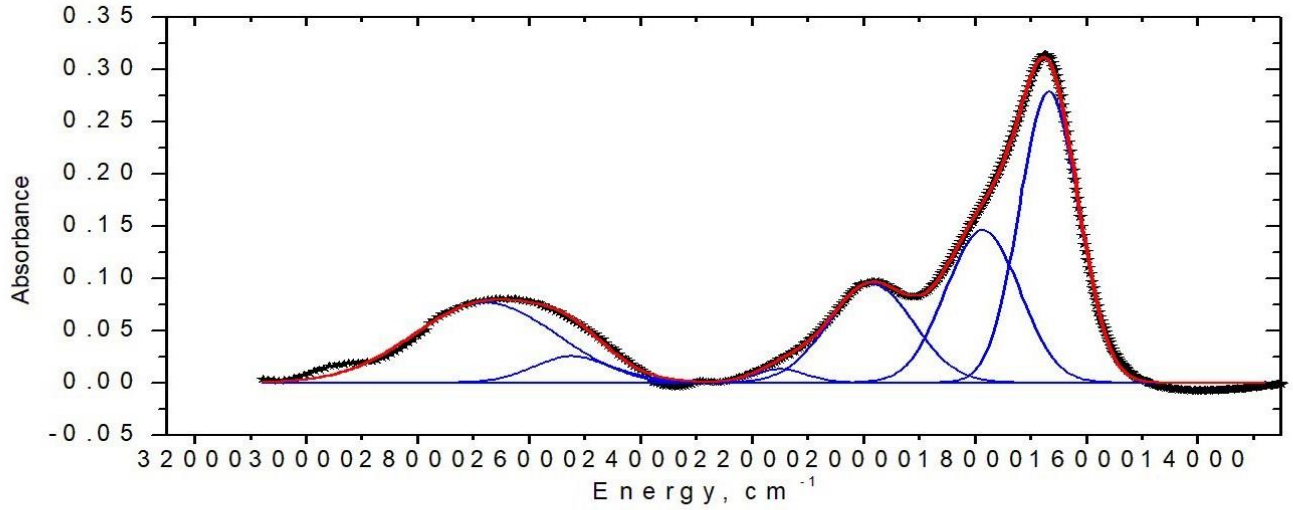


[Fe(*trans*-(1*R*,2*R*)-**L**)$_2$]$^{2+}$

Full line shape analysis of the UV-visible spectrum of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$. Only six Gaussian-type bands are sufficient for analysis.

Line shape analysis for Fe-complex, trans-Schiff base in CH_2Cl_2.

Source File: Data3	Data Set: Data3_I	Date:22
Chi^2=1.334828299E-5	COD=0.9982	# of Data Points=476
SS=0.006113513610	Corr Coef=0.9991	Degree of Freedom=458



Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	371.2	1249.8	0.279	16667.5	33.63
2	Gaussian	243.4	1560.3	0.147	17856.9	22.05
3	Gaussian	182.8	1809.1	0.095	19863.2	16.56
4	Gaussian	15.4	1115.7	0.013	21486.9	1.39
5	Gaussian	44.1	1624.3	0.026	25225.1	3.99
6	Gaussian	246.8	3021.2	0.077	26785.8	22.36
		1103.7				

BLACK: experimental data
RED: sum of theoretical fit
BLUE: individual lines

X-ray Analysis.

A single crystal (dark red plate on transient light, but blue-black on reflected light) containing a mixture of stereoisomers of racemic [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$ was grown using vapor diffusion of diethyl ether anti-solvent into a saturated solution of the complex in propionitrile. *Both those solvents were found to be present in the crystal lattice, and both were observed to be disordered. Thus, propionitrile C_2H_5CN and $(C_2H_5)_2O$ were successfully modelled by two positions with respective site occupancy factors (SOFs) tied to one (see S10, S11 down below).*

Suitable single crystals were inspected, selected, and handled in NVH parathon oil, with subsequent mounting on a thin glass fiber, or placed into a CryoLoop and then attached to a copper pin positioned on the goniometer head of a diffractometer equipped with a CCD area detector. All data sets were measured at low temperatures as specified in the crystal structure and refinement data in the table below. Data were collected in ω scan mode using the Mo tube (Kα radiation; λ = 0.71073 Å) with a highly oriented graphite monochromator. The intensities for the latter radiation were integrated from four series of 364 exposures each, covering 0.5^o in ω, with the total data set being a sphere. The space group determination was done with the aid of XPREP software.[1] The absorption correction was performed using values from face-indexed crystals and numerical values obtained from the set of images recorded with a video-microscope, followed by the SADABS program that was included in the Bruker AXS software package.[2,3]

All structures were solved by direct methods and refined by least squares on weighted F^2 values for all reflections using SHELXS-2013. The structures reported herein are well refined and without apparent errors. All hydrogen atoms in the structures were placed to their hosting atoms (C, N) and refined isotropically. The crystal structures and packing diagrams were drawn using the ORTEP 3v2 [4,5] and Mercury software packages.[6] Thermal ellipsoids appearing in figures are drawn at their 50% probability level.

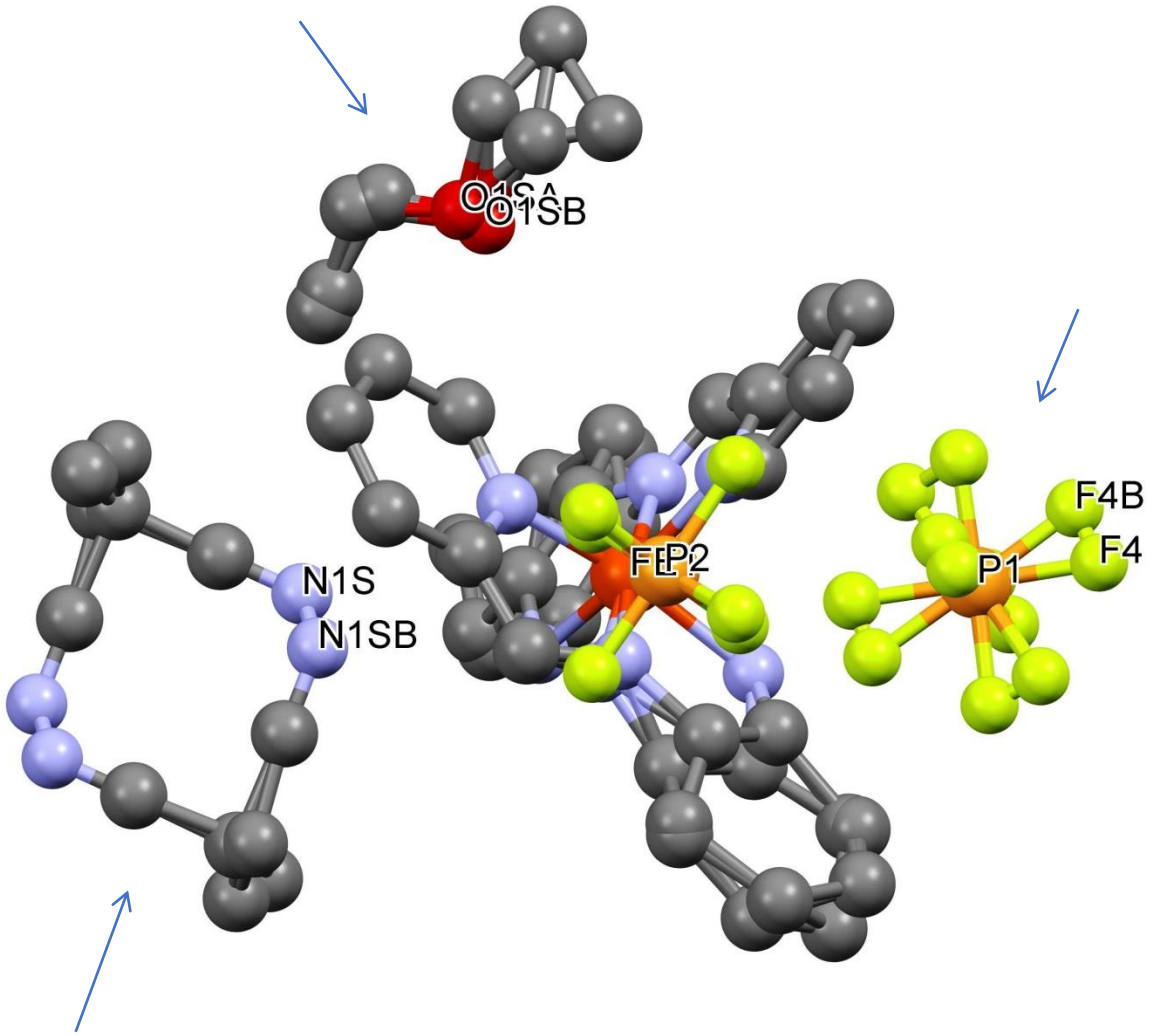
As we stated at the beginning of the Supplementary Materials section the bulk powder of the complex **1** did not contain solvents of inclusion. However, upon crystal growth we detected disordered molecules of two solvents used in the system: propionitrile and diethyl ether. Analytical data for the powdery sample were of satisfactory level, and no attempts to record powder diffraction pattern (PXRD) for bulk sample were made. Having fairly large solvent molecules occluded into the single crystal that had been analyzed using X-ray crystallography certainly changed the atomic content and undoubtedly unit cell dimensions. Therefore, no recording and comparison of PXRD patterns for the bulk powder and single crystal were done.

Table 1. Crystal and refinement data for [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$ **1** (which was a mixture of [Fe(*trans*-(1*R*,2*R*)-**L**)$_2$](PF$_6$)$_2$, [Fe(*trans*-(1*S*,2*S*)-**L**)$_2$](PF$_6$)$_2$, and [Fe(*trans*-(1*R*,2*R*)-**L**)(*trans*-(1*S*,2*S*)-**L**](PF$_6$)$_2$ as ether/propionitrile solvate.

Parameter	**Data for complex**
Empirical formula	$C_{31}H_{49}F_{12}FeN_7OP_2$
Formula weight, g/M	881.09
Temperature, K	120(2)
Crystal system	monoclinic
Color /habitus	dark-red plate
Crystal size (mm)	0.047 × 0.226 × 0.311
Space group	$P2_1/c$, #14
Cell constants, Å/°	
a	9.3699(7)
b	20.0609(15)
c	21.0430(16)
α	90
β	100.187(1)
γ	90
Volume (Å^3)	1102.5(6)
Z	4
ρ_{calc} (g/cm^3)	1.503
μ (mm^{-1})	0.564
F(000)	1822
2θ range for data (°)	3.92 to 50.484
Index ranges:	-13 < h < 13
	-28 < k < 28
	-29 < l < 29
Reflections collected	61453
Independent	4553 [R_{int}=0.0288; R_σ= 0.0226]
Data/Restraints/Parameters	11407 / 948 / 753
Goodness-of-fit on F^2	1.034
Final R indices:	9383 [I>2σ(I)]; R1 = 0.0398, wR2 = 0.0526
All data:	R1 = 0.0917; wR2 = 0.0975
Peak/hole difference, e(A^{-3})	+0.845 / -0.642
Volume taken, A^3 (%)	2740.1 (70.4)

The asymmetric unit (ASU) in the crystal structure of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$ **1** co-crystallized isomers.

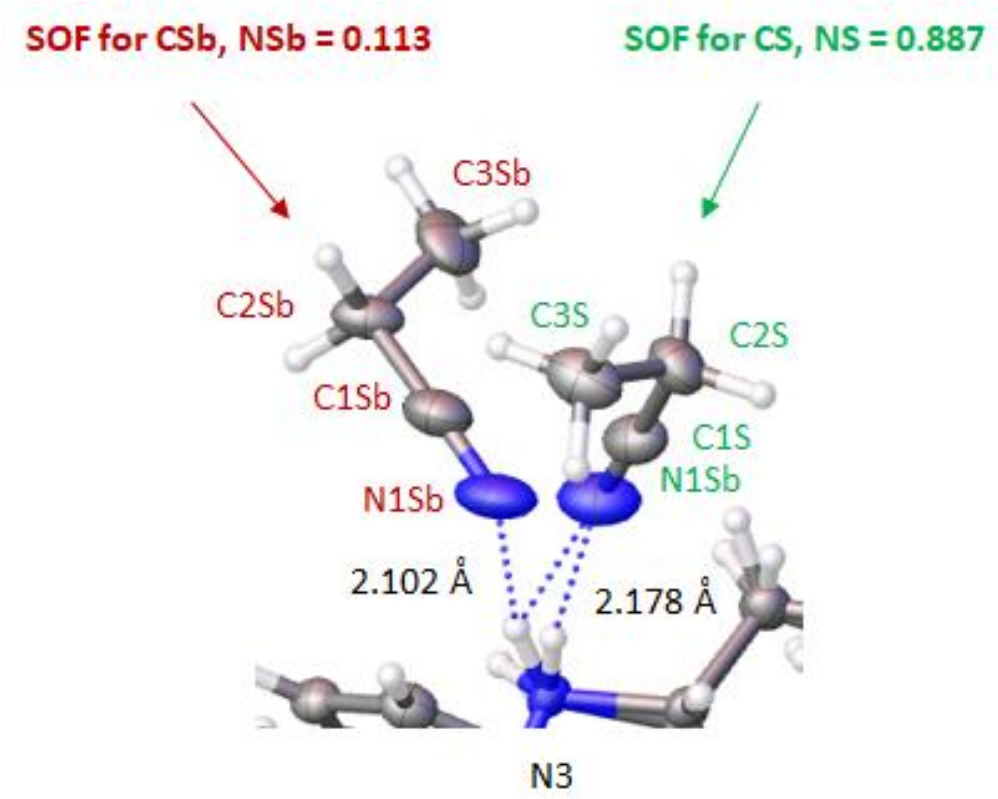
Disordered PF_6^- anion (at P1) and two stoichiometric molecules of solvents of crystallization C_2H_5CN and diethyl ether are shown with arrows. Hydrogen-atoms are omitted for clarity.



Details of the disorder:

Explanation and presentation of disordered fragments in the structure of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$: disordered by two positions molecules of the solvent of reaction - propionitrile. The geometry of long electrostatic C-H---N contacts is shown.

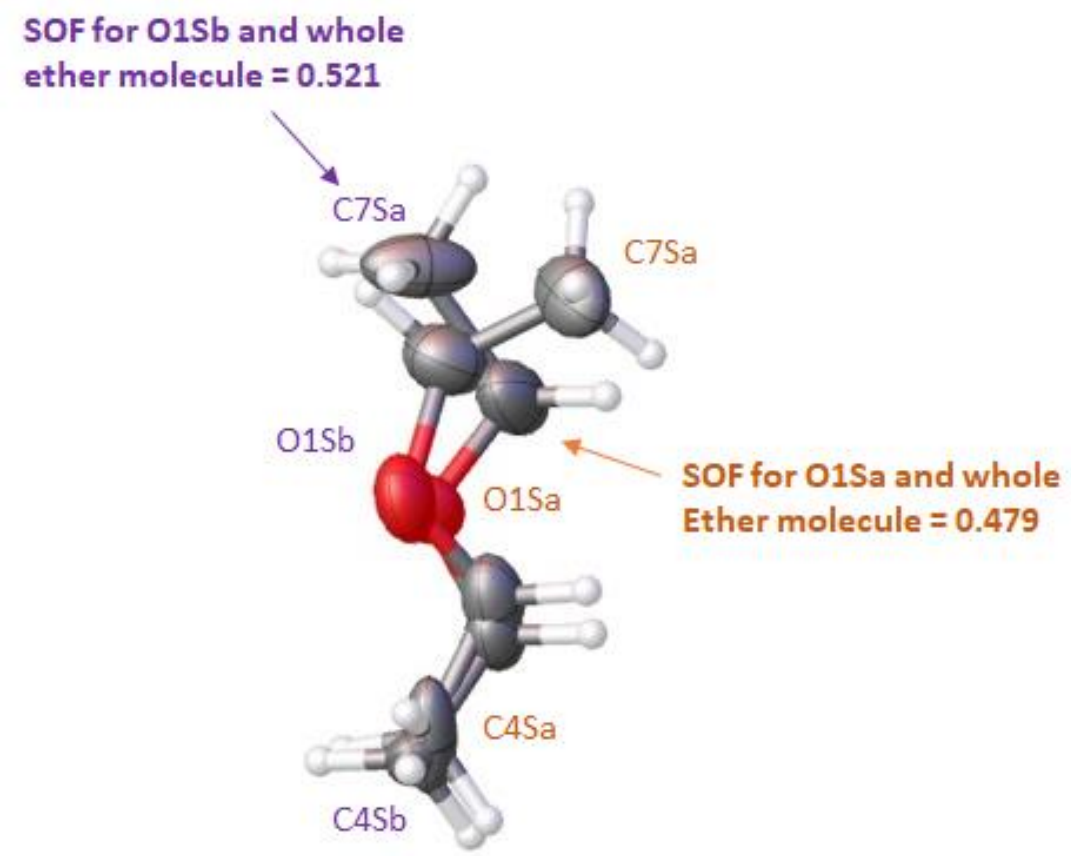
SOF = site occupancy factor with the sum being equal to 1 for modeled two-positional disorder.



Details of the disorder:

Explanation and presentation of disordered fragments in the structure of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$: disordered by two positions molecules of the "pushing" solvent of crystallization – diethyl ether.

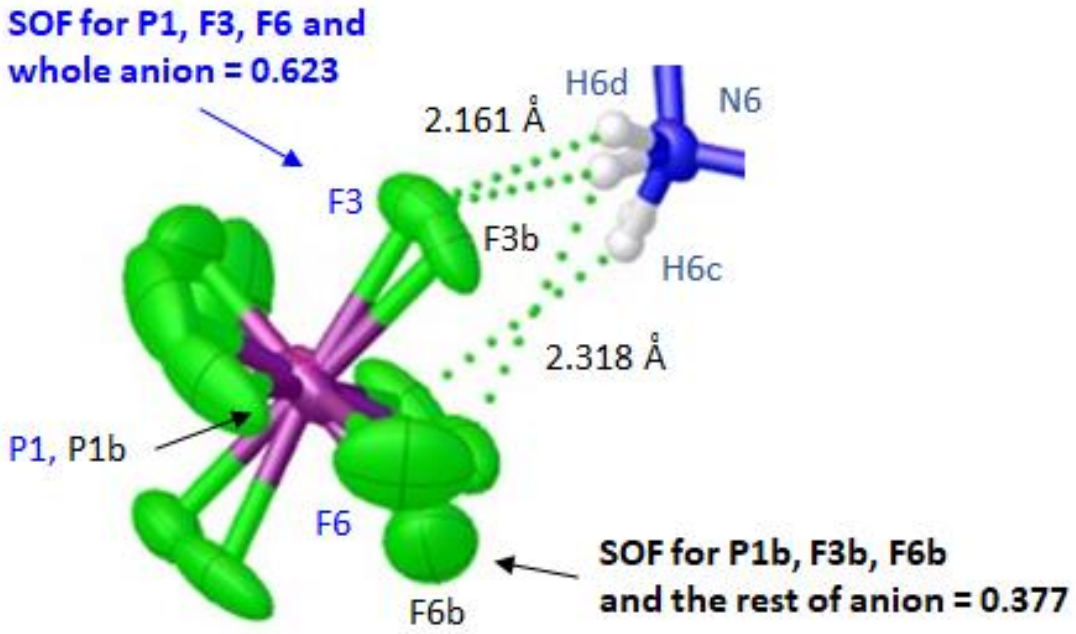
SOF = site occupancy factor with the sum being equal to 1 for modeled two-positional disorder.



Details of the disorder:

Explanation and presentation of disordered fragments in the structure of [Fe(*trans*-**L**)$_2$](PF$_6$)$_2$: disordered by two positions one of the counter ions – PF$_6$. The geometry of long electrostatic N-H---F contacts is also shown.

SOF = site occupancy factor with the sum being equal to 1 for modeled two-positional disorder.



checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) steroisomers_mixture-Fe-2

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: steroisomers_mixture-Fe-2

Bond precision: C-C = 0.0024 A Wavelength=0.71073

Cell: a=9.3699(7) b=20.0609(15) c=21.0430(16)
alpha=90 beta=100.187(1) gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	3893.1(5)	3893.1(5)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C24 H34 Fe N6, 2(F6 P), C4 H10 O, C3 H5 N	C24 H34 Fe N6, 2(F6 P), C4 H10 O, C3 H5 N
Sum formula	C31 H49 F12 Fe N7 O P2	C31 H49 F12 Fe N7 O P2
Mr	881.56	881.09
Dx,g cm-3	1.504	1.503
Z	4	4
Mu (mm-1)	0.564	0.564
F000	1824.0	1822.0
F000'	1827.31	
h,k,lmax	13,28,29	13,28,29
Nref	11448	11407
Tmin,Tmax	0.857,0.974	0.669,0.745
Tmin'	0.839	

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Tmax=0.745 AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 30.083

R(reflections)= 0.0398(9383) wR2(reflections)= 0.0975(11407)

S = 1.034 Npar= 753

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.9 Note
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4 Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 2 Report

Alert level G

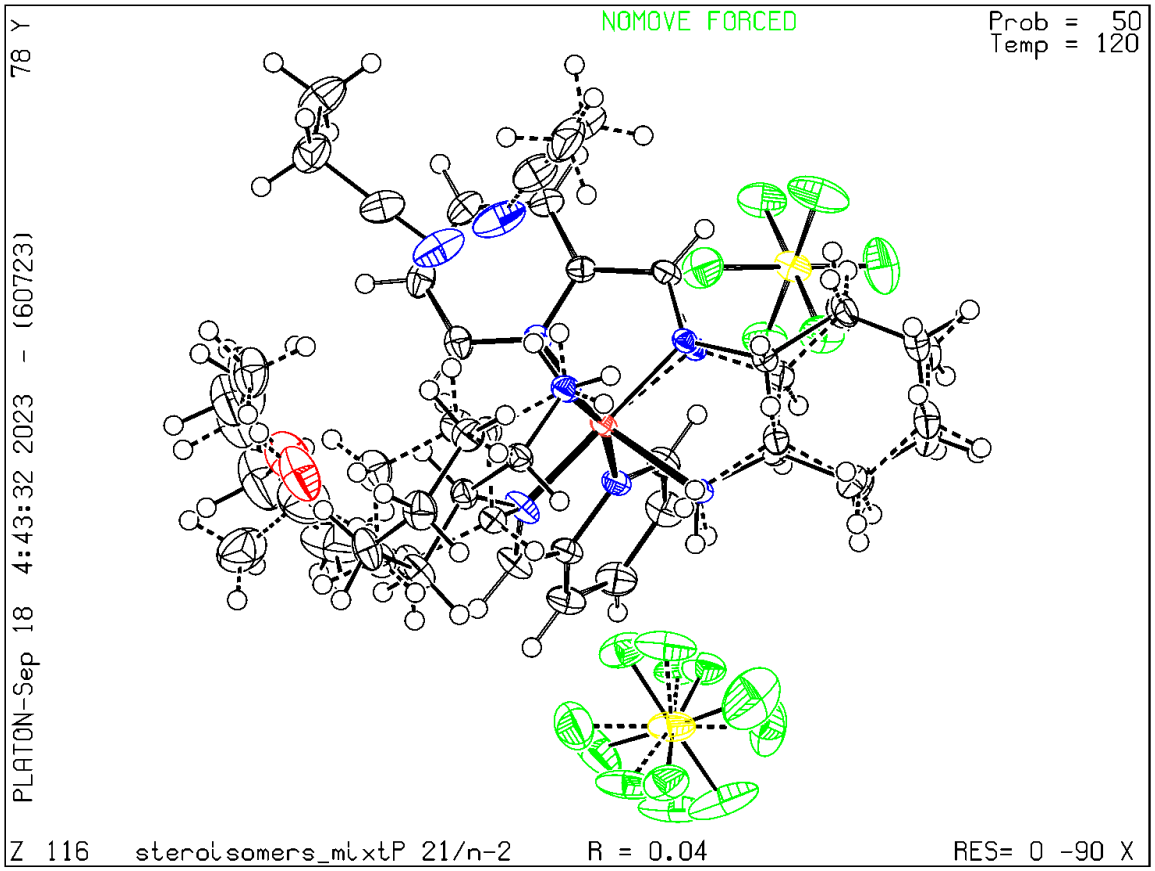
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 59 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 58 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 8 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 6 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 3 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 5 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used 0.0100 Report
And 4 other PLAT188 Alerts
More ...
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) P1 --F1 . 6.0 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) P1 --F6 . 8.5 s.u.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of P2 Check
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 42% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 100% Note
And 5 other PLAT302 Alerts
More ...
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 2) 4.36 Check
And 5 other PLAT304 Alerts
More ...
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O1SA . 107.8 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O1SB . 108.0 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 48 Note
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C4SB --C5SB 1.75 Ang.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 948 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT899_ALERT_4_G SHELXL2018 is Deprecated and Succeeded by SHELXL 2019/3 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 39 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 7 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
40 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
9 ALERT type 3 Indicator that the structure quality may be low
23 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock steroisomers_mixture-Fe-2 - ellipsoid plot



Necessary references for Supplemental Materials section:

1. G. S. Girolami, A Guide to Using the SHELXTL Crystallographic Software Package. Department of Chemistry, University of Illinois at Urbana-Champaign; 2004.

2. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33.

3. G. M. Sheldrick, Bruker APEX2 and APEX3 Software Suits; Bruker AXS, Madison, WI, USA.

4. L. J. Farrugia, *J. Appl. Cryst*., 1997, **30**, 565.

5. M. N. Burnett, C. K. Johnson, ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations., Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1996.

6. Mercury Software, CCDC (Cambridge Crystal Data Centre), Cambridge, England, 4.2 edn., 2016.