"Synthesis and Characterization of Two Intensely Colored *tris*(benzoylcyanoxime) iron(II) Anionic Complexes"

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Supporting Information

S1. The electrical conductivity of 1 mM solutions of several ionic reference compounds and $[P(C_6H_5)_4][Fe(BCO)_3]$, **1,** and $Na[Fe(BCO)_3]$, **2**.

Compound	Conductivity (μS)	Electrolyte type
Pure solvent: anhydrous ethanol Pure solvent: anhydrous CH_3CN	0.2 3.7	- -
$N(C_4H_9)_4Br$: ethanol CH_3CN	30.3 138.2	1:1
$P(C_6H_5)_4Br$: ethanol CH_3CN	23 140.1	1:1
1: ethanol CH_3CN	19.4 82.6	1:1
2: ethanol CH_3CN	20.8 88.5	1:1

S2.

checkCIF/PLATON report (full structural check)

No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Datablock: febco3-155k-1

Bond precision: C-C = 0.0028 A Wavelength=0.71073
Cell: a=12.2043(12) b=25.991(3) c=13.8507(13)
alpha=90 beta=92.437(1) gamma=90
Temperature: 155 K

	Calculated	Reported
Volume	4389.5(8)	4389.4(8)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C27 H15 Fe N6 O6, C24 H20 P	C27 H15 Fe N6 O6, C24 H20 P
Sum formula	C51 H35 Fe N6 O6 P	C51 H35 Fe N6 O6 P
Mr	914.67	914.67
Dx,g cm-3	1.384	1.384
Z	4	4
Mu (mm-1)	0.439	0.439
F000	1888.0	1888.0
F000'	1890.52	
h,k,lmax	15,32,17	15,32,17
Nref	8996	9000
Tmin,Tmax	0.877,0.936	0.763,0.937
Tmin'	0.821	

Correction method= AbsCorr=NUMERICAL
Data completeness= Ratio = 1.000 Theta(max)= 26.370
R(reflections)= 0.0329(7255) wR2(reflections)= 0.0837(9000)
S = 1.020 Npar= 586

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.

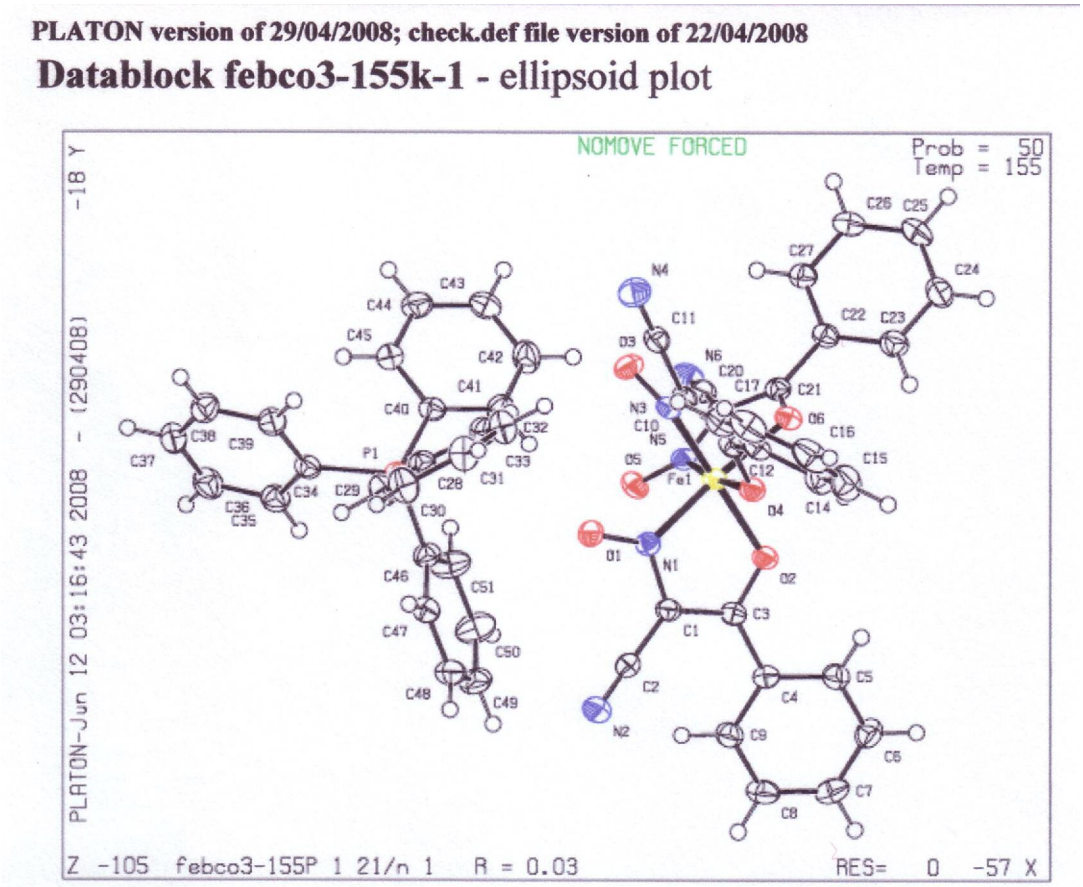
Alert level C

PLAT230_ALERT_2_C	Hirshfeld Test Diff for	C1	--	C2	..	6.09	su
PLAT230_ALERT_2_C	Hirshfeld Test Diff for	C19	--	C20	..	6.10	su
PLAT232_ALERT_2_C	Hirshfeld Test Diff (M-X)	Fe1	--	N3	..	6.79	su
PLAT232_ALERT_2_C	Hirshfeld Test Diff (M-X)	Fe1	--	N5	..	5.92	su
PLAT371_ALERT_2_C	Long C(sp2)-C(sp1) Bond	C1	-	C2	...	1.42	Ang.
PLAT371_ALERT_2_C	Long C(sp2)-C(sp1) Bond	C10	-	C11	...	1.43	Ang.
PLAT371_ALERT_2_C	Long C(sp2)-C(sp1) Bond	C19	-	C20	...	1.42	Ang.

0 ALERT level A = In general: serious problem
0 ALERT level B = Potentially serious problem
7 ALERT level C = Check and explain
0 ALERT level G = General alerts; check

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

S3. CheckCIF/PLATON report (continued)



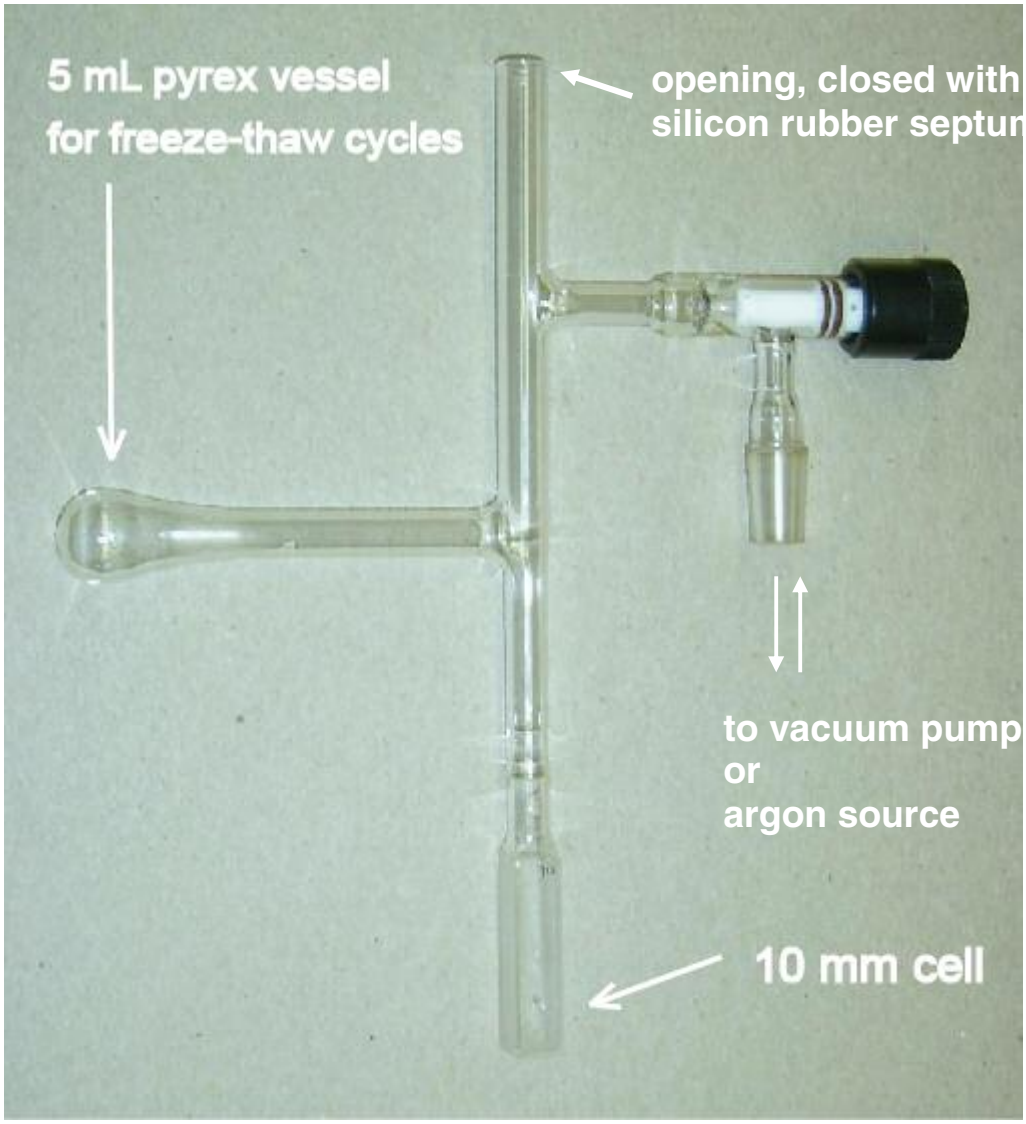
Explanation for PLAT371_ALERT_2_C above:

Bond lengths between central carbon atom and cyano-group in cyanoximes are typically longer than one might expect for a combination of groups with multiple bonds being in close proximity to each other. In other words, in protonated cyanoximes there is no conjugation between the oxime- (double bond) and cyano- (triple bond) groups attached to the cetral carbon atom. Therefore, we have in this particular situation almost pure case of a single bond between CN and C=N-OH groups. We have stressed this point in our previous publications of structures of cyanoximes and their metal complexes (see below) where *sp* carbon atom of the cyano-group was bound to the sp^2 hybridized carbon atom of the amide, heteroaryl, or aryl groups:

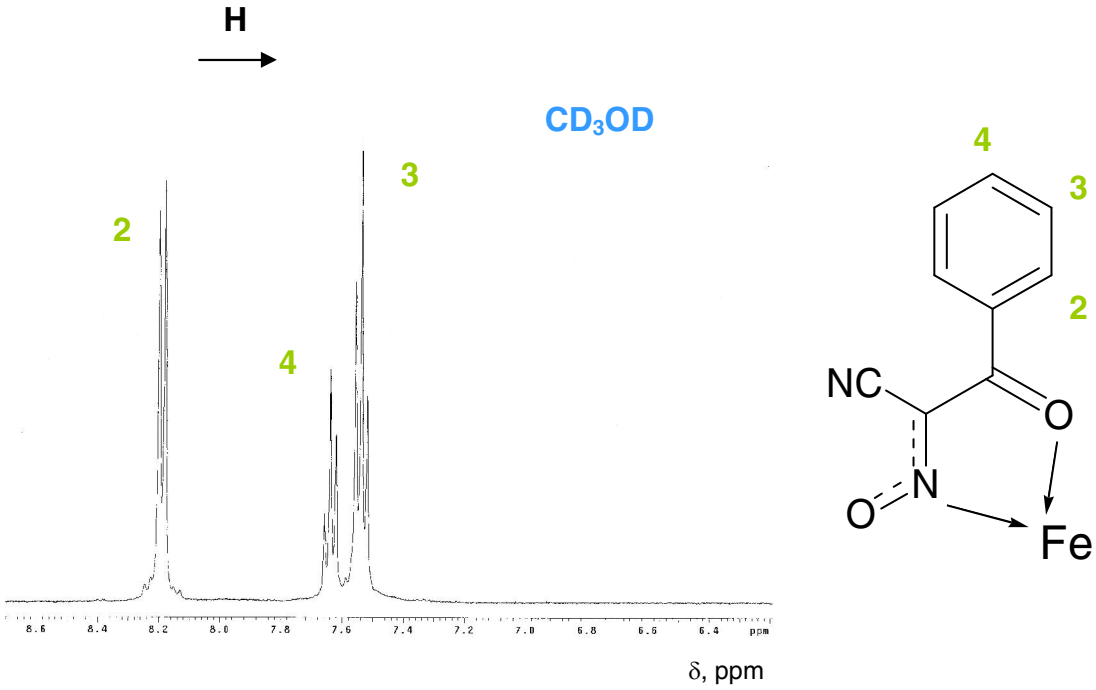
- Gerasimchuk, N.; Goeden, L.; Durham, P.; Barnes, C.; Cannon, J.F. Synthesis and Characterization of Disubstituted Arylcyanoximes and their Several Metal Complexes," **2008**, *Inorganica Chimica Acta, 361,* p.1983-2001.
- Maher, T.; Gerasimchuk, N.; Durham, P.; Domasevitch, K.V.; Wilking, J.; Mokhir, A. "Tin(IV) Cyanoximates: Synthesis, Characterization and in vitro Cytotoxicity." *Inorganic Chemistry*, **2007**, *46,* N°18, p.7268-7284.
- Robertson, D.; Cannon, J.F.; Gerasimchuk, N. "Double-Stranded Metal-Organic Networks for One-Dimensional Mixed Valence Coordination Polymers". *Inorganic Chemistry*. **2005**, *44*, N°23, p.8326-8342.
- Eddings, D., Barnes, C., Durham, P., Gerasimchuk, N.N., Domasevich, K.V. "First bivalent palladuim and platinum cyanoximates: synthesis, characterization and biological activity." *Inorganic Chemistry*, **2004**, *43*, N°13, pp. 3894-3909.

S4. Photograph of the intensely deep blue color of $Na[Fe(BCO)_3]$, **2**.

S5. The specially designed graded-seal quartz cuvette used for the anaerobic UV-visible spectroscopic studies.

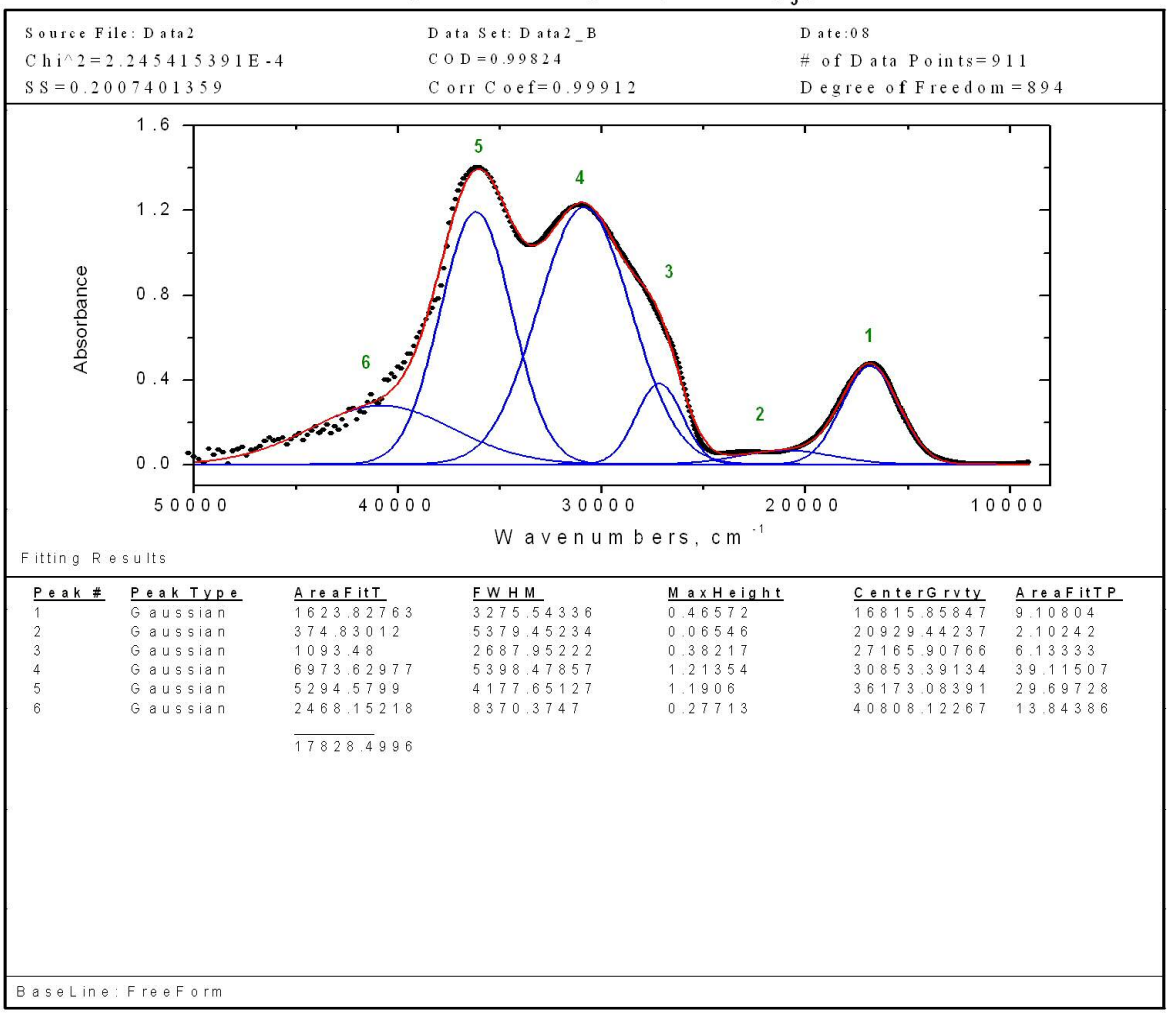


S6. A portion of the ^{1}H NMR spectrum of **2** in CD_3OD showing the three magnetically equivalent benzoylcyanoxime anions in the complex.



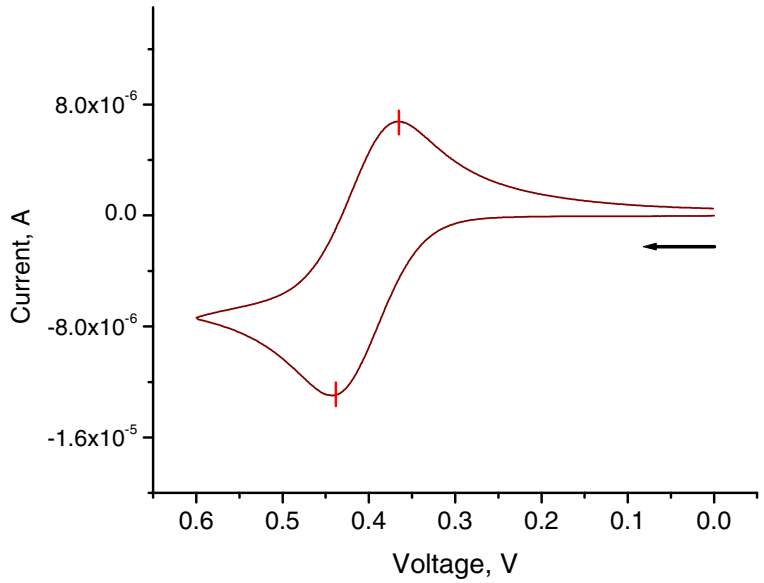
S7. A full line shape analysis of the uv-visible spectrum of **2** obtained in DMF with the minimum six Gaussian peaks required to adequately fit the absorbance.

Peak Analysis: Na[Fe(BCO)$_3$] in DMF

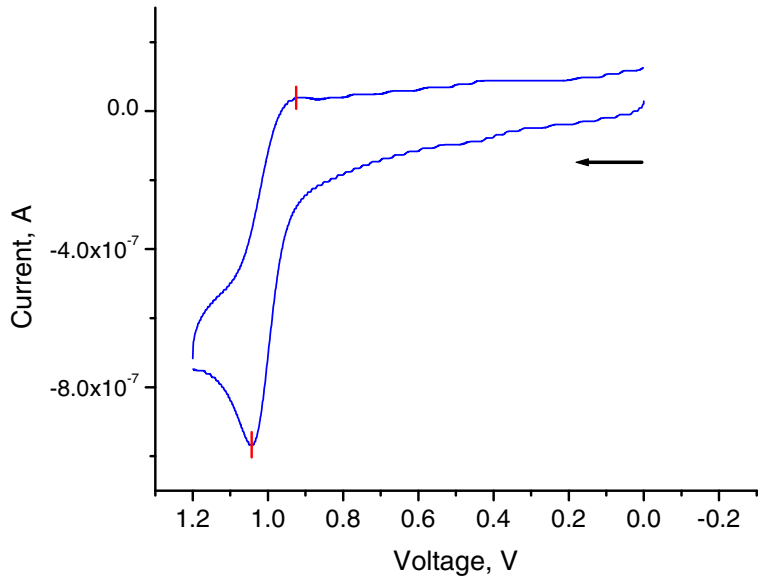


Peak	Peak position: cm^{-1} (nm)	Assignment
1	16816 (595)	L → M charge transfer
2	20929 (477)	n → π* within the cyanoxime anion
3	27165 (368)	π → π* within the cyanoxime anion
4	30853 (324)	π → π* within the cyanoxime anion
5	36173 (276)	π → π* within the cyanoxime anion
6	40808 (245)	π → π* in the DMF solvent

S8. Cyclic voltammetry curves for ferrocene (**A**) and $Na[Fe(BCO)_3]$, **2**, (**B**) obtained in dry acetonitrile at 296 K; the supporting electrolyte is $[N(C_4H_9)_4]PF_6$.

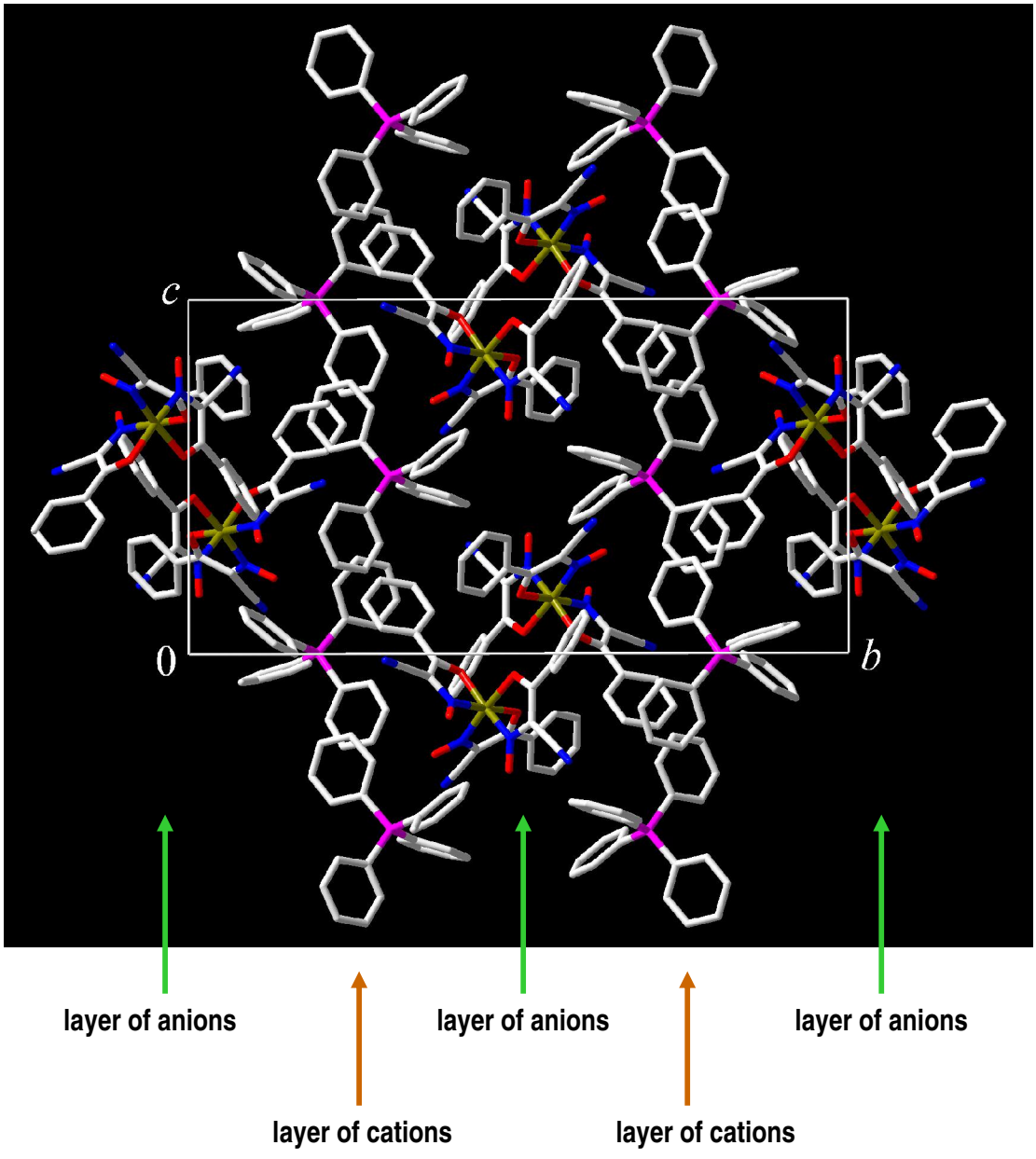


A



B

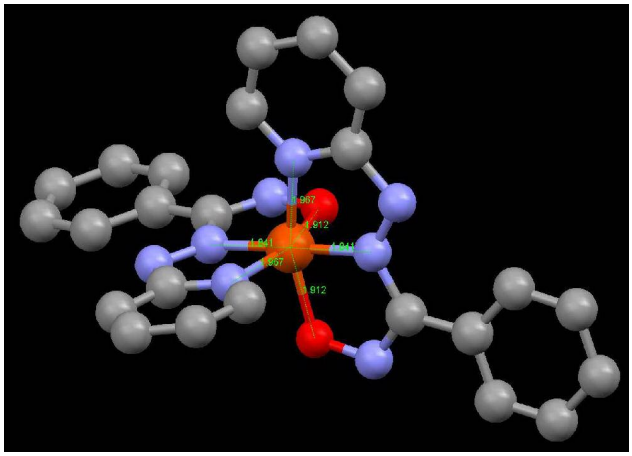
S9. Packing diagram for $PPh_4[Fe(BCO)_3]$, **1**. Shown are the alternating layers of tris(benzoylcyanoximato)iron(II) anions and tetraphenylphosphonium cations. The hydrogen atoms have been omitted for clarity.



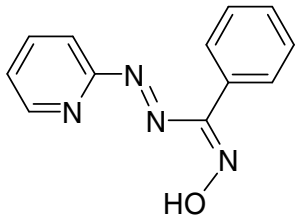
S10.

Results of search in Cambridge Structural Data Base for the Fe(II)-N,O chelates with Fe-N ≤ 1.86 Å, and Fe-O ≤ 1.95 Å bond lengths.

Fragment of crystal structure of cesium *bis*((2-pyridylazo)-benzaldoxime) Fe(II). H-atoms and CH2Cl2 solvate molecule are not shown for clarity.



A coloring scheme on this page:
big red – Fe; grey – C; small red – O;
blue – N; magenta – Cs atoms.



ligand

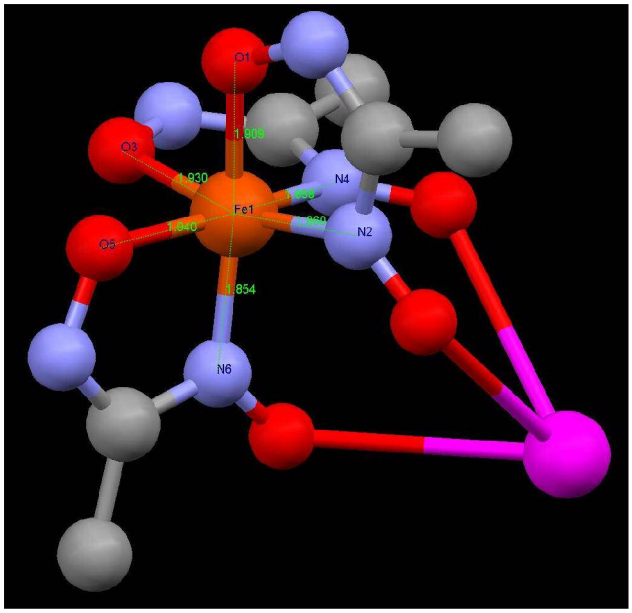
Refcode: LIHBOT

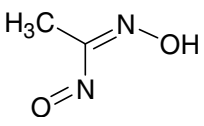
Ganguly, S.; Karmakar, S.; Pal, C.K. et al.
Inorg. Chem. **1999**, *38*, 5984

Average (Fe-N) = 1.841 Å
Average (Fe-O) = 1.912 Å

Sum: 3.753 Å

Fragment of crystal structure of cesium *tris*(ethylnitrosylato)-Fe(II) monohydrate. H-atoms and water molecule are not shown for clarity.





ligand

Refcode: ENTSFE

Gouzerh, P.; Jeannin, Y. et al.
J. Coord. Chem. **1979**, *9*, 221

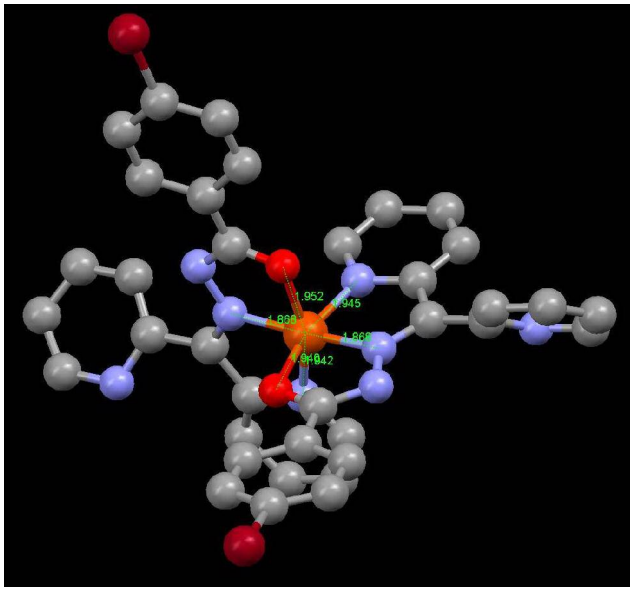
fac-complex;
Average (Fe-N) = 1.857 Å
Average (Fe-O) = 1.926 Å

Sum: 3.783 Å

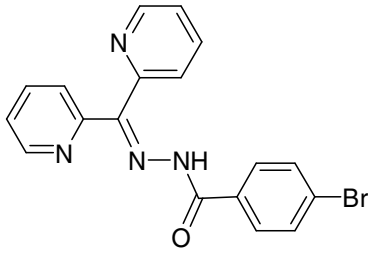
S11.

Results of search in Cambridge Structural Data Base (continued)

Fragment of crystal structure of cesium *bis*(di-2-pyridyl ketone 4-bromobenzoyl hydrazone) Fe(II). H-atoms are not shown for clarity.



A coloring scheme on this page:
big red – Fe; grey – C; small red – O;
blue – N; magenta – As atoms.



ligand

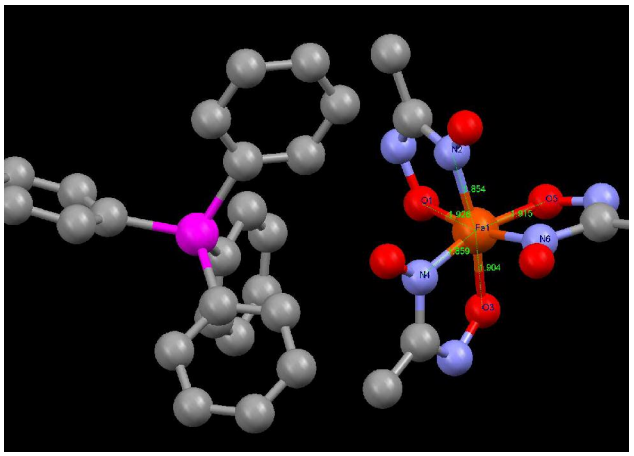
Refcode: DACJUN

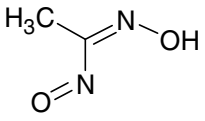
Bernhardt, P.V.; Caldwell, L.M., et al.
J. Biol. Inorg. Chem. **2003**, *8*, 866

Average (Fe-N) = 1.868 Å
Average (Fe-O) = 1.949 Å

Sum: 3.817 Å

Fragment of crystal structure of tetraphenylarsonium *tris*(ethylnitrosylato)-Fe(II). H-atoms are not shown for clarity.





ligand

Refcode: CEYSEE

Gouzerh, P.; Jeannin, Y. et al.
Acta Cryst., Sect. C: Cryst. Struct. Commun.
1984, *40*, 797

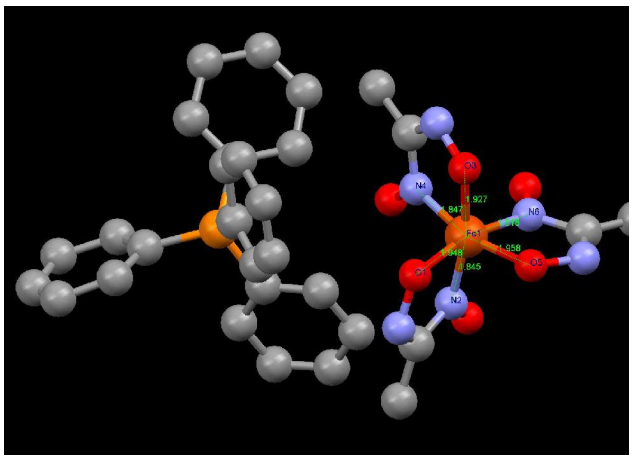
fac-complex;
Average (Fe-N) = 1.871 Å
Average (Fe-O) = 1.915 Å

Sum: 3.786 Å

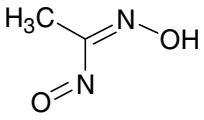
S12.

Results of search in Cambridge Structural Data Base

Fragment of crystal structure of tetraphenylphosphonium *tris*(ethylnitrosylato)-Fe(II).
H-atoms are not shown for clarity.



A coloring scheme on this page:
big red – Fe; grey – C; small red – O;
blue – N; orange – P atoms.



ligand

Refcode: CEYSAA

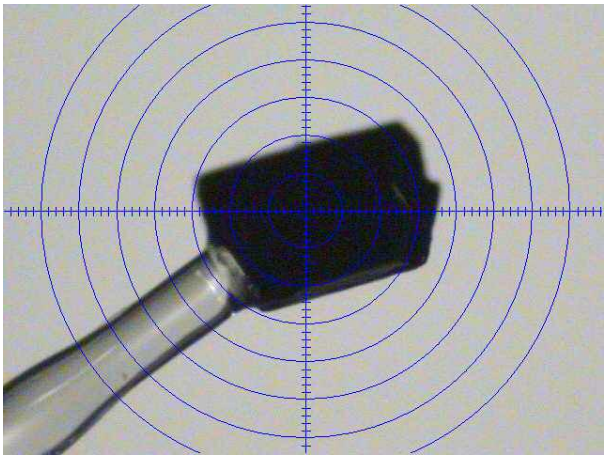
Gouzerh, P.; Jeannin, Y. et al.
Acta Cryst., Sect. C: Cryst. Struct. Commun.
1984, *40*, 797

fac-complex;
Average (Fe-N) = 1.87 Å
Average (Fe-O) = 1.944 Å

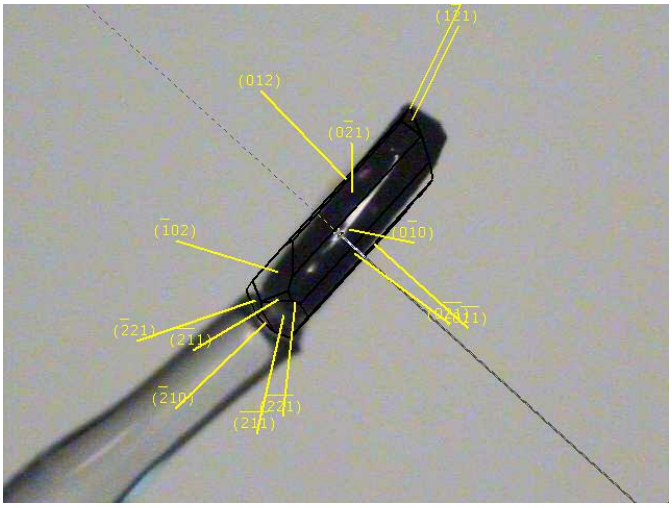
Sum: 3.814 Å

S13

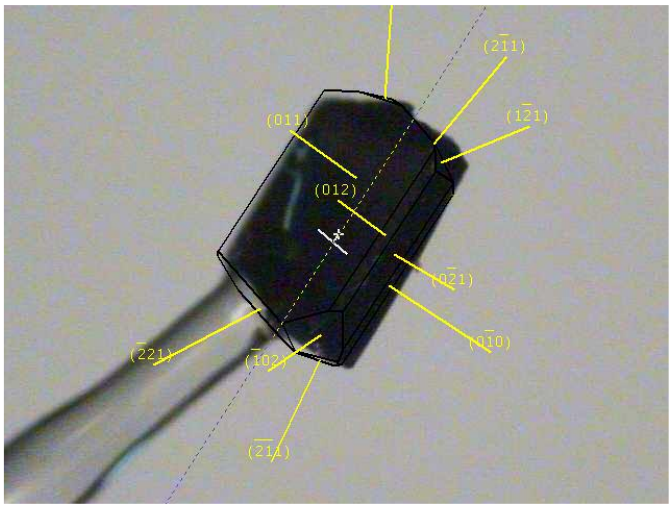
A photograph of a crystal of 1 used for structure determination (A) and crystal faces (B) indexed for numerical absorption correction procedure using SADABS.



A

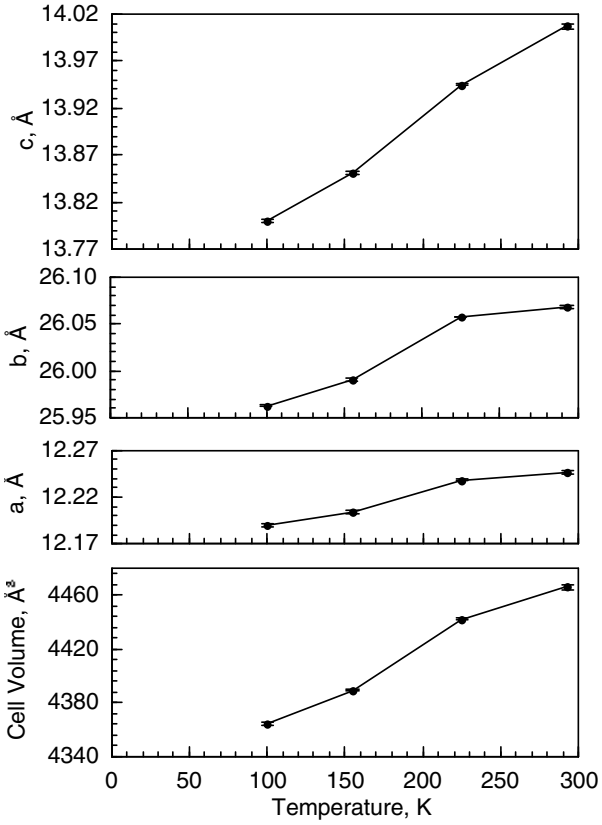


B

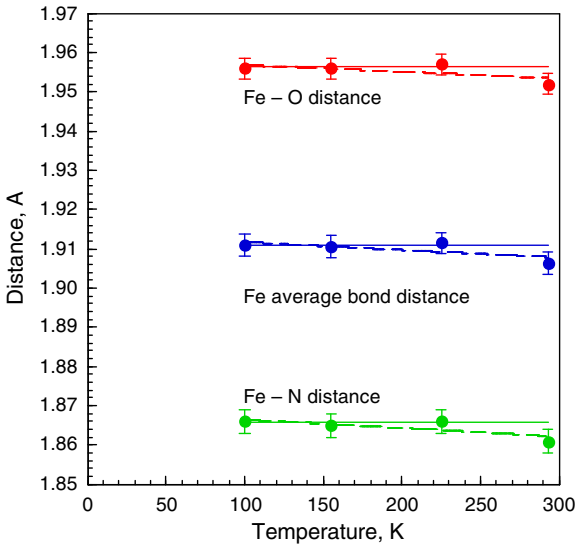


S14

Effect of temperature on cell constants (A) and Fe-ligand bond lengths (B) in the structure of complex 1.



A



B

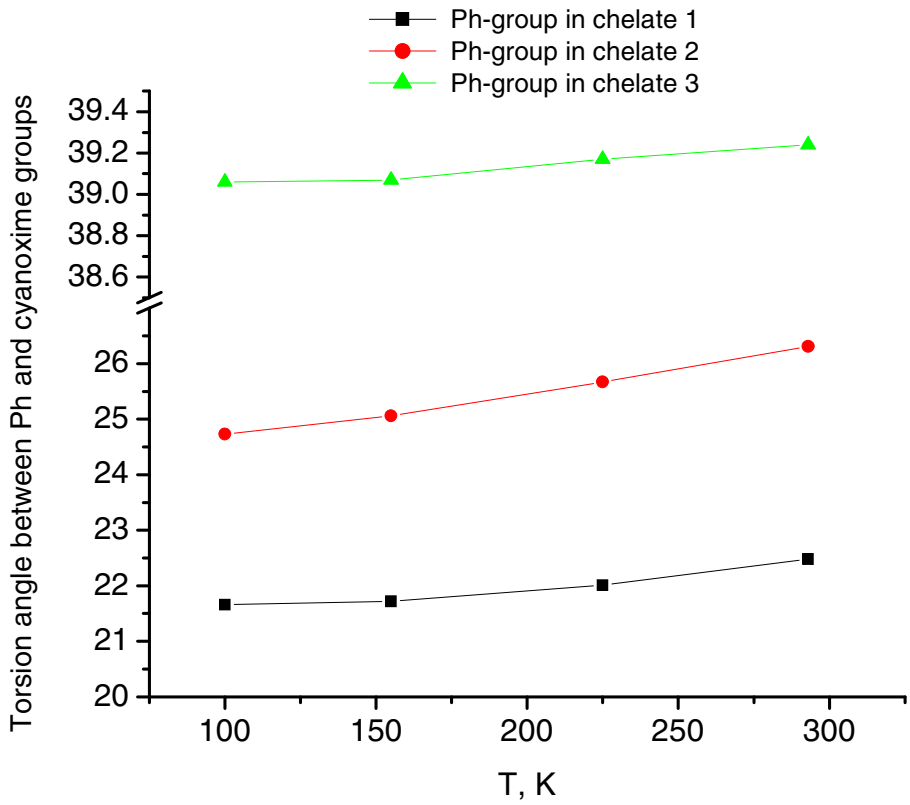
Error bars are ca. 2 x sigma of an individual bond length.

The solid lines are the average of the 100, 155, and 225 K values.

The dashed lines is the linear best fit of 100-293 K.

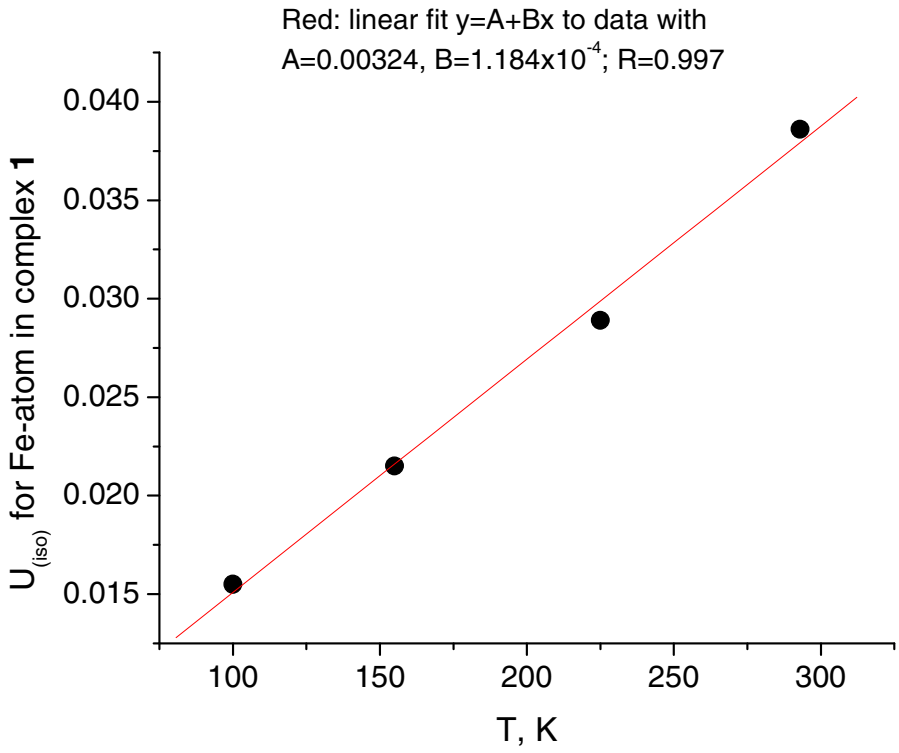
S15

Effect of temperature on torsion angles between phenyl group and conjugated cyanoxime-ketone core in three chelate rings of acidoligands in the structure of complex anion 1.



S16

Effect of temperature on U(iso) parameter for iron(II) atom in complex anion 1.



S 17 **Crystal data for the structure of tetraphenylphosphonium fac-{*tris*(benzoylcyanoximato)iron(II)}, $PPh_4[Fe(BCO)_3]$, 1 at different temperatures. Details in common: blue-purple plate, $C_{51}H_{35}FeN_6O_6P$, 914.67 g/mol, monoclinic P2(1)/n, Z=4, and indices range was -15 < h < 15, -32 < k < 32, - 17 < l < 17**

Parameter	**Temperature points**			
Temperature, K:	100(2)	155(2)	225(2)	293(2)
Unit cell, Å, ^{o}				
	a = 12.1899(11)	12.2043(12)	12.2384(7)	12.247(2)
	b = 25.963(2)	25.991(3)	26.0580(15)	26.068(5)
	c = 13.8001(12)	13.8507(13)	13.9447(8)	14.007(3)
	α = 90.00	α = 90.00	α = 90.00	α = 90.00
	β = 92.3020(10)	β = 92.4370(10)	β = 92.634(4)	β = 92.835(2)
	γ = 90.00	γ = 90.00	γ = 90.00	γ = 90.00
Volume, $Å^3$:	4364.1(7)	4389.4(7)	4442.4(4)	4466.1(14)
Density, Mg/m^3:	1.392	1.384	1.368	1.360
θ range,^{o}:	1.57 – 26.37	1.57 – 26.37	0.99 – 25.00	1.56 – 26.02
Reflections total/unique:	44748 / 8925	45003 / 9000	47628 / 8737	43945 / 8796
GOF on F^2:	1.026	1.020	1.018	1.015
Largest peak/deepest hole:	0.390 / -0.41	0.370 / -0.385	0.270 / -0.321	0.361 / -0.305

S 18 (continued) **Crystal data for the structure of tetraphenylphosphonium fac-{*tris*(benzoylcyanoximato)iron(II)}, $PPh_4[Fe(BCO)_3]$, 1 at different temperatures. Details in common: blue-purple plate, $C_{51}H_{35}FeN_6O_6P$, 914.67 g/mol, monoclinic P2(1)/n, Z=4, and indices range was -15 < h < 15, -32 < k < 32, - 17 < l < 17**

Parameter	**Temperature points**			
Final R:	0.0312 for 7471 Fo > 4σ(Fo)	0.0329 for 7255 Fo > 4σ(Fo)	0.034 for 6759 Fo > 4σ(Fo)	0.0389 for 6312 Fo > 4σ(Fo)
R (all data):	0.0412 for all 8925 data	0.0466 for all 9000 data	0.0511 for all 8737 data	0.0637 for all 8796 data
	Averaged bond lengths Fe – N:			
	1.866 Å	1.866 Å	1.866 Å	1.861 Å
	Averaged bond lengths Fe – O:			
	1.956 Å	1.956 Å	1.957 Å	1.952 Å
	Sum of Fe-N and Fe-O bonds:			
	3.822 Å	3.822 Å	3.823 Å	3.813 Å