Supplementary Material

Bis-citrullinato copper(II) complex: Synthesis, crystal structure, and non-covalent interactions

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Equations: $\boldsymbol{\delta_{FC}} = \frac{\mu_0 \mu_B^2 g_e^2 (S+1)}{9kT} \boldsymbol{\rho_{\alpha\beta}} \cong \boldsymbol{m} \frac{S+1}{T} \boldsymbol{\rho_{\alpha\beta}}$ (S1a)

where: $\boldsymbol{m} = \frac{\mu_0 \mu_B^2 g_e^2 (S+1)}{9kT} = \boldsymbol{2.35 \times 10^7}$ **ppm K au**$^{-1}$

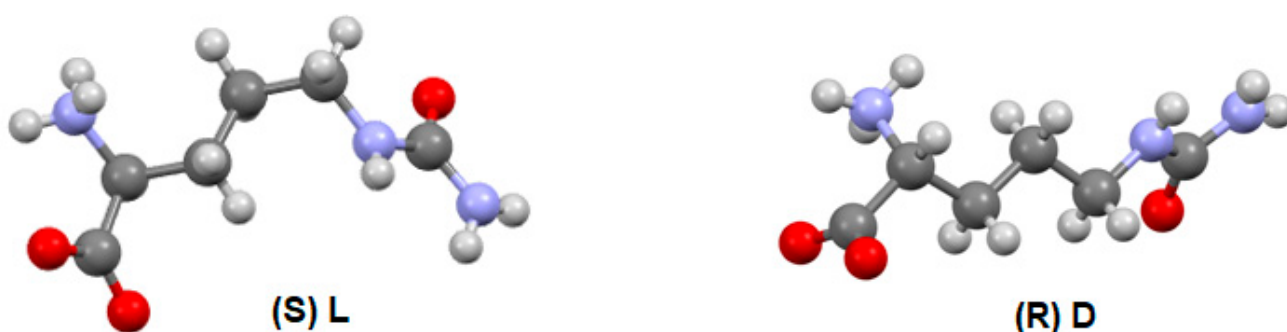$\boldsymbol{\delta_{Total}^{Calc.} = \delta_{FC} + \delta_0}$ (S1b)

Figure S1. Stereoisomers (S) L-Citrulline (FIFGOQ) and (R) D-Citrulline (EYIKUU)
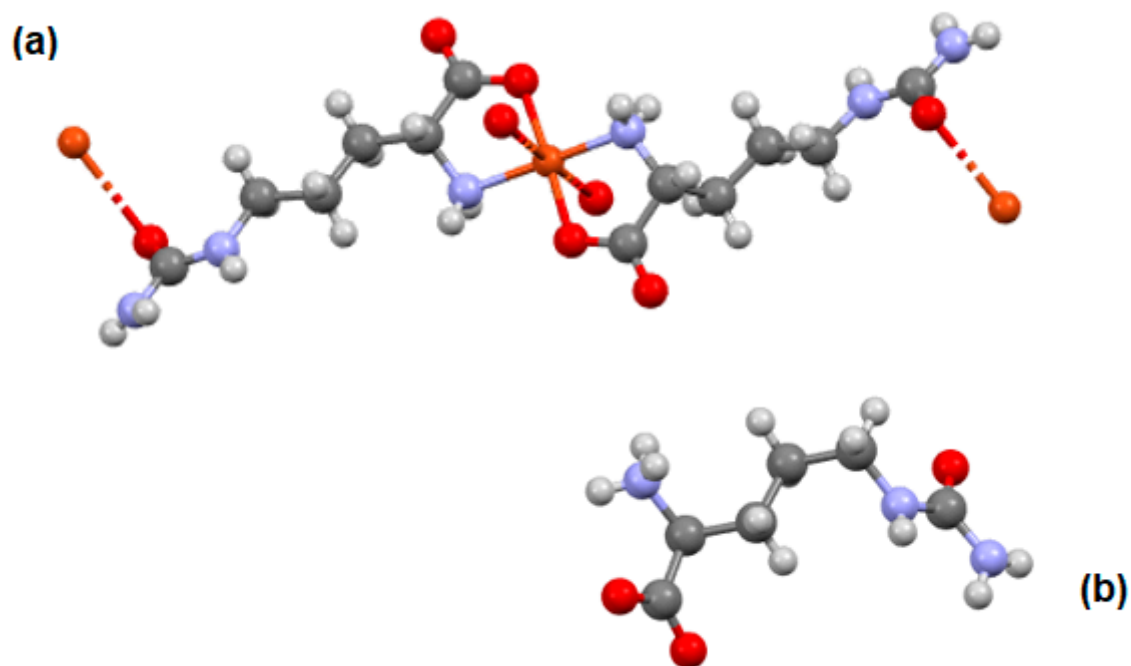
Figure S2. (a) The structure of the complex (R) and (b) the structure of the zwitter ion of L-Citruline from CCDC(FIGOQ)(S).
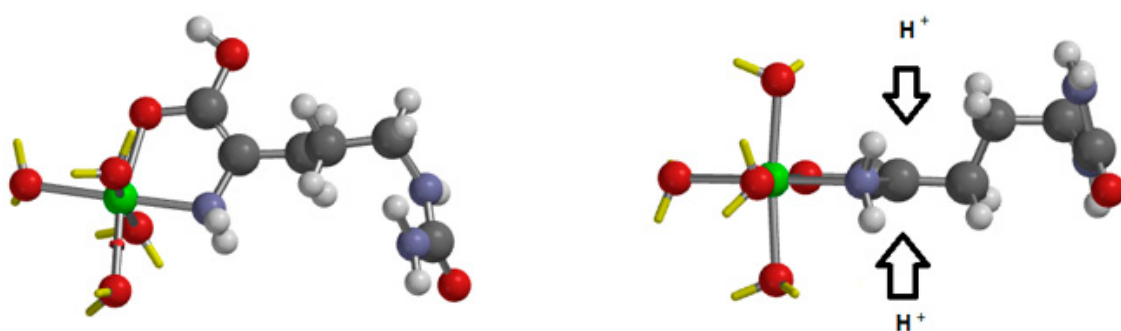

Figure S3. Top and side views of the intermediary of the racemization of Citrulline mediated by copper coordination
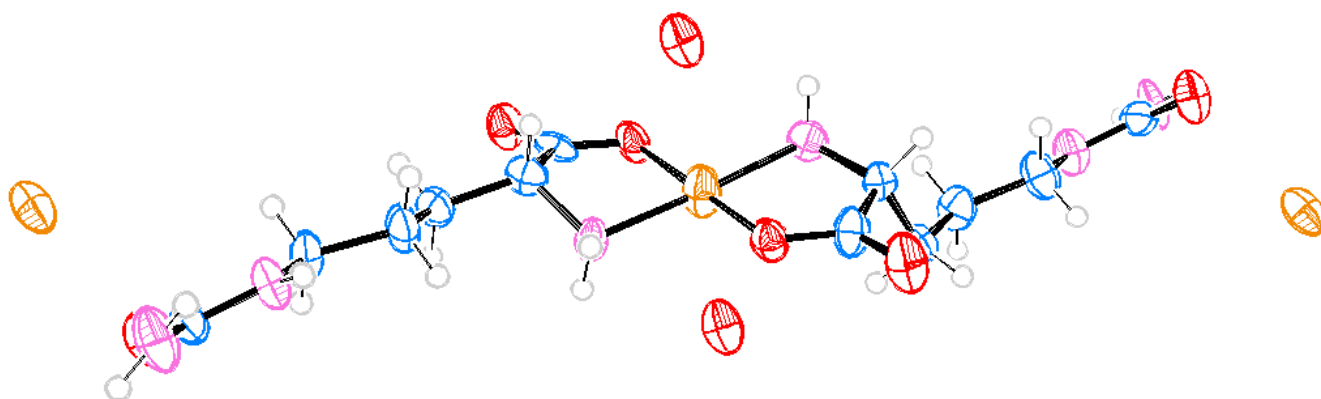
Figure S4. ORTEP representation of a fragment of the bis-citrullinato Cu(II) polymer.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$) for (Cu_citrulline)

	x	y	z	$U_{iso}*/U_{eq}$
Cu1	0.2150 (4)	0.5043 (3)	0.25290 (10)	0.0487 (6)
O1	0.0266 (17)	0.6868 (9)	0.2266 (4)	0.039 (2)
N1	0.459 (2)	0.5751 (11)	0.1755 (5)	0.033 (2)
H1A	0.585048	0.629340	0.198898	0.039*
H1B	0.531339	0.500935	0.151659	0.039*
C1	0.1040 (19)	0.7497 (15)	0.1663 (7)	0.035 (3)
O2	0.0257 (19)	0.8704 (10)	0.1443 (5)	0.045 (2)
N2	0.914 (2)	0.6746 (12)	−0.0937 (5)	0.041 (2)
H2	0.907157	0.581383	−0.092429	0.049*
C2	0.291 (2)	0.6637 (14)	0.1181 (6)	0.036 (3)
H2A	0.184777	0.595489	0.085433	0.043*
O3	1.107 (2)	0.8719 (9)	−0.1413 (5)	0.045 (2)
N3	1.205 (2)	0.6487 (13)	−0.1865 (6)	0.053 (3)
H3A	1.357824	0.684189	−0.196377	0.064*
H3B	1.122875	0.565968	−0.191756	0.064*
C3	0.446 (2)	0.7555 (14)	0.0631 (6)	0.039 (3)
H3C	0.325507	0.814750	0.030548	0.047*
H3D	0.560981	0.820326	0.094008	0.047*
O4	0.4012 (16)	0.3233 (9)	0.2733 (4)	0.0355 (18)
N4	−0.0321 (19)	0.4282 (12)	0.3250 (5)	0.038 (2)
H4A	−0.074792	0.497998	0.357736	0.045*
H4B	−0.177338	0.399005	0.298006	0.045*
C4	0.606 (2)	0.6651 (15)	0.0113 (6)	0.042 (3)
H4C	0.493993	0.596373	−0.017838	0.050*
H4D	0.735731	0.610634	0.043253	0.050*
O5	0.423 (2)	0.1341 (10)	0.3523 (6)	0.053 (3)
N5	−0.332 (2)	0.3433 (12)	0.6015 (5)	0.042 (3)

H5	−0.329297	0.436036	0.607388	0.051*
C5	0.743 (2)	0.7614 (13)	−0.0457 (6)	0.036 (3)
H5A	0.613438	0.811466	−0.079768	0.043*
H5B	0.846993	0.834041	−0.016644	0.043*
O6	−0.516 (2)	0.1314 (10)	0.6374 (5)	0.051 (3)
N6	−0.629 (2)	0.3429 (11)	0.6917 (6)	0.046 (3)
H6A	−0.616713	0.435858	0.695359	0.055*
H6B	−0.733709	0.296467	0.719910	0.055*
C6	1.079 (2)	0.7398 (13)	−0.1389 (6)	0.034 (3)
C7	0.321 (3)	0.2475 (14)	0.3300 (6)	0.037 (3)
C8	0.084 (2)	0.3063 (14)	0.3696 (6)	0.034 (3)
H8	−0.045775	0.229003	0.373275	0.041*
C9	0.182 (2)	0.3560 (15)	0.4525 (6)	0.039 (3)
H9A	0.279879	0.276577	0.477763	0.047*
H9B	0.303604	0.435713	0.447359	0.047*
C10	−0.024 (3)	0.4044 (14)	0.5064 (6)	0.044 (3)
H10A	0.058403	0.467785	0.546110	0.052*
H10B	−0.153540	0.461607	0.475956	0.052*
C11	−0.161 (3)	0.2876 (15)	0.5462 (7)	0.045 (3)
H11A	−0.261681	0.230233	0.507291	0.054*
H11B	−0.032892	0.224261	0.572985	0.054*
C12	−0.491 (2)	0.2736 (15)	0.6444 (6)	0.038 (3)

Table S2. Atomic displacement parameters ($Å^2$) for (Cu_citrulline)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0510 (10)	0.0474 (9)	0.0501 (8)	0.0140 (11)	0.0206 (9)	0.0099 (8)
O1	0.027 (4)	0.042 (5)	0.048 (4)	0.005 (4)	0.016 (4)	0.013 (4)
N1	0.038 (5)	0.028 (5)	0.033 (4)	0.009 (4)	0.009 (4)	0.007 (3)
C1	0.012 (5)	0.041 (8)	0.051 (6)	0.002 (5)	0.008 (5)	−0.006 (5)
O2	0.044 (5)	0.039 (5)	0.055 (5)	0.008 (5)	0.016 (4)	0.011 (4)
N2	0.045 (6)	0.036 (6)	0.044 (5)	−0.007 (5)	0.018 (5)	0.003 (4)
C2	0.033 (6)	0.039 (7)	0.038 (5)	0.003 (5)	0.008 (5)	−0.005 (5)
O3	0.048 (6)	0.033 (5)	0.055 (4)	−0.004 (5)	0.022 (4)	0.000 (4)
N3	0.061 (8)	0.041 (7)	0.062 (7)	0.004 (6)	0.037 (6)	0.001 (5)
C3	0.031 (6)	0.048 (7)	0.040 (5)	0.003 (6)	0.009 (5)	0.006 (5)
O4	0.031 (4)	0.036 (4)	0.041 (3)	0.004 (4)	0.012 (3)	0.005 (3)
N4	0.030 (5)	0.045 (6)	0.040 (4)	0.008 (5)	0.011 (4)	0.002 (4)
C4	0.043 (6)	0.046 (7)	0.038 (5)	0.002 (6)	0.016 (5)	0.011 (5)
O5	0.059 (6)	0.038 (5)	0.065 (5)	0.013 (5)	0.031 (5)	0.009 (4)
N5	0.052 (7)	0.031 (5)	0.046 (5)	0.002 (5)	0.015 (5)	−0.001 (4)
C5	0.043 (7)	0.031 (6)	0.035 (5)	0.005 (5)	0.015 (5)	0.008 (5)
O6	0.065 (7)	0.038 (5)	0.052 (5)	0.000 (5)	0.026 (5)	0.004 (4)
N6	0.060 (7)	0.025 (5)	0.057 (6)	−0.013 (5)	0.027 (6)	0.004 (4)
C6	0.035 (7)	0.034 (7)	0.033 (5)	−0.009 (6)	0.007 (5)	−0.001 (4)
C7	0.053 (8)	0.023 (6)	0.037 (6)	0.006 (5)	0.009 (5)	0.003 (4)
C8	0.034 (6)	0.038 (6)	0.031 (5)	−0.005 (5)	0.003 (4)	0.006 (5)
C9	0.034 (6)	0.044 (7)	0.040 (5)	−0.002 (6)	0.007 (5)	0.005 (5)
C10	0.048 (7)	0.051 (7)	0.033 (5)	0.005 (6)	0.013 (5)	0.000 (5)
C11	0.051 (8)	0.038 (7)	0.047 (6)	−0.003 (6)	0.020 (6)	−0.003 (5)
C12	0.032 (6)	0.048 (8)	0.033 (5)	−0.002 (6)	0.002 (5)	0.001 (5)

Table S3. Geometric parameters (Å, º) for (Cu_citrulline)

Cu1—O1	1.974 (9)	N4—C8	1.461 (16)
Cu1—N1	1.993 (9)	C4—H4C	0.9700
Cu1—O4	1.940 (8)	C4—H4D	0.9700
Cu1—N4	1.958 (9)	C4—C5	1.525 (15)
O1—C1	1.270 (14)	O5—C7	1.218 (16)
N1—H1A	0.8900	N5—H5	0.8600
N1—H1B	0.8900	N5—C11	1.429 (15)
N1—C2	1.502 (15)	N5—C12	1.303 (16)
C1—O2	1.231 (16)	C5—H5A	0.9700
C1—C2	1.529 (15)	C5—H5B	0.9700
N2—H2	0.8600	O6—C12	1.320 (17)
N2—C5	1.477 (14)	N6—H6A	0.8600
N2—C6	1.327 (14)	N6—H6B	0.8600
C2—H2A	0.9800	N6—C12	1.282 (16)
C2—C3	1.529 (15)	C7—C8	1.531 (16)
O3—C6	1.226 (15)	C8—H8	0.9800
N3—H3A	0.8740	C8—C9	1.542 (15)
N3—H3B	0.8730	C9—H9A	0.9700
N3—C6	1.364 (16)	C9—H9B	0.9700
C3—H3C	0.9700	C9—C10	1.518 (17)
C3—H3D	0.9700	C10—H10A	0.9700
C3—C4	1.502 (16)	C10—H10B	0.9700
O4—C7	1.285 (14)	C10—C11	1.476 (18)
N4—H4A	0.8900	C11—H11A	0.9700
N4—H4B	0.8900	C11—H11B	0.9700
O1—Cu1—N1	83.7 (4)	C5—C4—H4D	109.6
O4—Cu1—O1	177.2 (3)	C11—N5—H5	115.4
O4—Cu1—N1	94.4 (4)	C12—N5—H5	115.4
O4—Cu1—N4	84.9 (4)	C12—N5—C11	129.3 (12)
N4—Cu1—O1	96.9 (4)	N2—C5—C4	111.0(10)
N4—Cu1—N1	177.2 (5)	N2—C5—H5A	109.4
C1—O1—Cu1	113.4 (7)	N2—C5—H5B	109.4
Cu1—N1—H1A	110.8	C4—C5—H5A	109.4
Cu1—N1—H1B	110.8	C4—C5—H5B	109.4
H1A—N1—H1B	108.9	H5A—C5—H5B	108.0
C2—N1—Cu1	104.8 (7)	H6A—N6—H6B	120.0
C2—N1—H1A	110.8	C12—N6—H6A	120.0
C2—N1—H1B	110.8	C12—N6—H6B	120.0
O1—C1—C2	116.4 (11)	N2—C6—N3	114.7(11)
O2—C1—O1	123.1 (11)	O3—C6—N2	123.2 (12)
O2—C1—C2	120.4 (11)	O3—C6—N3	122.0 (11)
C5—N2—H2	119.8	O4—C7—C8	116.5(11)
C6—N2—H2	119.8	O5—C7—O4	123.4 (11)
C6—N2—C5	120.4 (11)	O5—C7—C8	120.1 (11)
N1—C2—C1	106.3 (9)	N4—C8—C7	110.4 (8)
N1—C2—H2A	107.2	N4—C8—H8	109.7

N1—C2—C3	113.9 (9)	N4—C8—C9	110.4 (10)
C1—C2—H2A	107.2	C7—C8—H8	109.7
C1—C2—C3	114.7 (11)	C7—C8—C9	107.1 (10)
C3—C2—H2A	107.2	C9—C8—H8	109.7
H3A—N3—H3B	137.8	C8—C9—H9A	108.1
C6—N3—H3A	110.6	C8—C9—H9B	108.1
C6—N3—H3B	110.6	H9A—C9—H9B	107.3
C2—C3—H3C	109.0	C10—C9—C8	116.7(11)
C2—C3—H3D	109.0	C10—C9—H9A	108.1
H3C—C3—H3D	107.8	C10—C9—H9B	108.1
C4—C3—C2	112.7 (11)	C9—C10—H10A	108.3
C4—C3—H3C	109.0	C9—C10—H10B	108.3
C4—C3—H3D	109.0	H10A—C10—H10B	107.4
C7—O4—Cu1	115.1 (7)	C11—C10—C9	116.1(11)
Cu1—N4—H4A	109.6	C11—C10—H10A	108.3

Cu1—N4—H4B	109.6	C11—C10—H10B	108.3
H4A—N4—H4B	108.1	N5—C11—C10	112.2 (12)
C8—N4—Cu1	110.2 (7)	N5—C11—H11A	109.2
C8—N4—H4A	109.6	N5—C11—H11B	109.2
C8—N4—H4B	109.6	C10—C11—H11A	109.2
C3—C4—H4C	109.6	C10—C11—H11B	109.2
C3—C4—H4D	109.6	H11A—C11—H11B	107.9
C3—C4—C5	110.5 (11)	N5—C12—O6	119.8 (11)
H4C—C4—H4D	108.1	N6—C12—N5	120.3 (13)
C5—C4—H4C	109.6	N6—C12—O6	119.8 (11)

Cu1—O1—C1—O2	−173.9 (10)	C3—C4—C5—N2	176.5 (10)
Cu1—O1—C1—C2	9.7 (13)	O4—C7—C8—N4	9.5 (15)
Cu1—N1—C2—C1	40.4 (11)	O4—C7—C8—C9	−110.6 (12)
Cu1—N1—C2—C3	167.7 (8)	N4—C8—C9—C10	65.9 (14)
Cu1—O4—C7—O5	−177.0 (11)	O5—C7—C8—N4	−170.2 (12)
Cu1—O4—C7—C8	3.3 (13)	O5—C7—C8—C9	69.7 (15)
Cu1—N4—C8—C7	−17.1 (11)	C5—N2—C6—O3	2.8 (19)
Cu1—N4—C8—C9	101.1 (9)	C5—N2—C6—N3	−173.2 (10)
O1—C1—C2—N1	−34.7 (14)	C6—N2—C5—C4	−170.3 (11)
O1—C1—C2—C3	−161.5 (10)	C7—C8—C9—C10	−173.9 (11)
N1—C2—C3—C4	63.0 (13)	C8—C9—C10—C11	81.1 (16)
C1—C2—C3—C4	−174.3 (10)	C9—C10—C11—N5	174.0 (11)
O2—C1—C2—N1	148.8 (11)	C11—N5—C12—O6	−2 (2)
O2—C1—C2—C3	22.0 (16)	C11—N5—C12—N6	179.4 (13)
C2—C3—C4—C5	176.5 (10)	C12—N5—C11—C10	176.6 (13)

Dear Depositor,

Thank you for depositing your crystal structure(s) via the joint CCDC/FIZ Karlsruhe deposition service.

The data have been assigned the following deposition numbers which can either be quoted as CCDC Numbers or CSD Numbers. A CCDC Number is usually quoted for an organic or metal-organic structure, whereas a CSD Number is usually quoted for an inorganic structure.

CCDC XXXXXXX-YYYYYYY (generally used for organic and metal-organic structures)

CSD XXXXXXX-YYYYYYY (generally used for inorganic structures)

Deposition Number 2172421

Summary of Data - Deposition Number 2172421

Compound Name:
Data Block Name: data_cu_citrulina
Unit Cell Parameters: a 5.1270(2) b 9.2086(4) c 17.1099(7) P21
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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) Cu_citrulina

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PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED
CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: Cu_citrulina

```
Bond precision:    C-C = 0.0166 A              Wavelength=1.54178

Cell:              a=5.1270(2)      b=9.2086(4)          c=17.1099(7)
                   alpha=90         beta=93.972(2)       gamma=90
Temperature:       298 K

                   Calculated                  Reported
Volume             805.86(6)                   805.86(6)
Space group        P 21                        P2(1)
Hall group         P 2yb                       P 2yb
Moiety formula     C12 H24 Cu N6 O6            C12 H24 Cu N6 O6
Sum formula        C12 H24 Cu N6 O6            C12 H24 Cu N6 O6
Mr                 411.92                      411.91
Dx,g cm-3          1.698                       1.698
Z                  2                           2
Mu (mm-1)          2.339                       2.339
F000               430.0                       430.0
F000'              427.35
h,k,lmax           6,10,20                     6,10,20
Nref               2844[ 1520]                 1461
Tmin,Tmax          0.755,0.791                 0.062,0.164
Tmin'              0.755

Correction method= # Reported T Limits: Tmin=0.062 Tmax=0.164
AbsCorr = MULTI-SCAN

Data completeness= 0.96/0.51        Theta(max)= 66.613
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R(reflections)= 0.0497(1438)

wR2(reflections)=
0.1520(1461)

S = 1.147   Npar= 228

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 B
PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ....   0.01663 Ang.

🟡 Alert level C
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full   ! Check
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ....   6.39 Note
PLAT193_ALERT_1_C Cell and Diffraction Temperatures Differ by ....   3 Degree
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=   0.595   64 Report
PLAT914_ALERT_3_C No Bijvoet Pairs in FCF for Non-centro Structure   Please Check

⚪ Alert level G
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension   2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ....   10 Report
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..   ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .   Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still   99% Note
PLAT931_ALERT_5_G CIFcalcFCF Twin Law (4 0-1)   Est.d BASF   0.37 Check
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File   1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ....   1.0 Low

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

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

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT341_Cu_citrulina
;
PROBLEM: Low Bond Precision on  C-C Bonds ...............    0.01663 Ang.
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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