Supplementary Information for

Revisiting the crystal structure of $[Co(NH_3)_5Cl]Cl_2$ using synchrotron powder diffraction: To what extent single crystal diffraction from 1960's got it right?

Sahnun Mohamud[1] and Silvina Pagola[2*]

[1]*College of William and Mary, Department of Physics, Williamsburg, VA, 23187-8795, U.S.A..*

[2]*College of William and Mary, Department of Applied Science, Williamsburg, VA, 23187-8795, U.S.A..*

E-mail: spagol@wm.edu

I.- Additional Rietveld refinement details

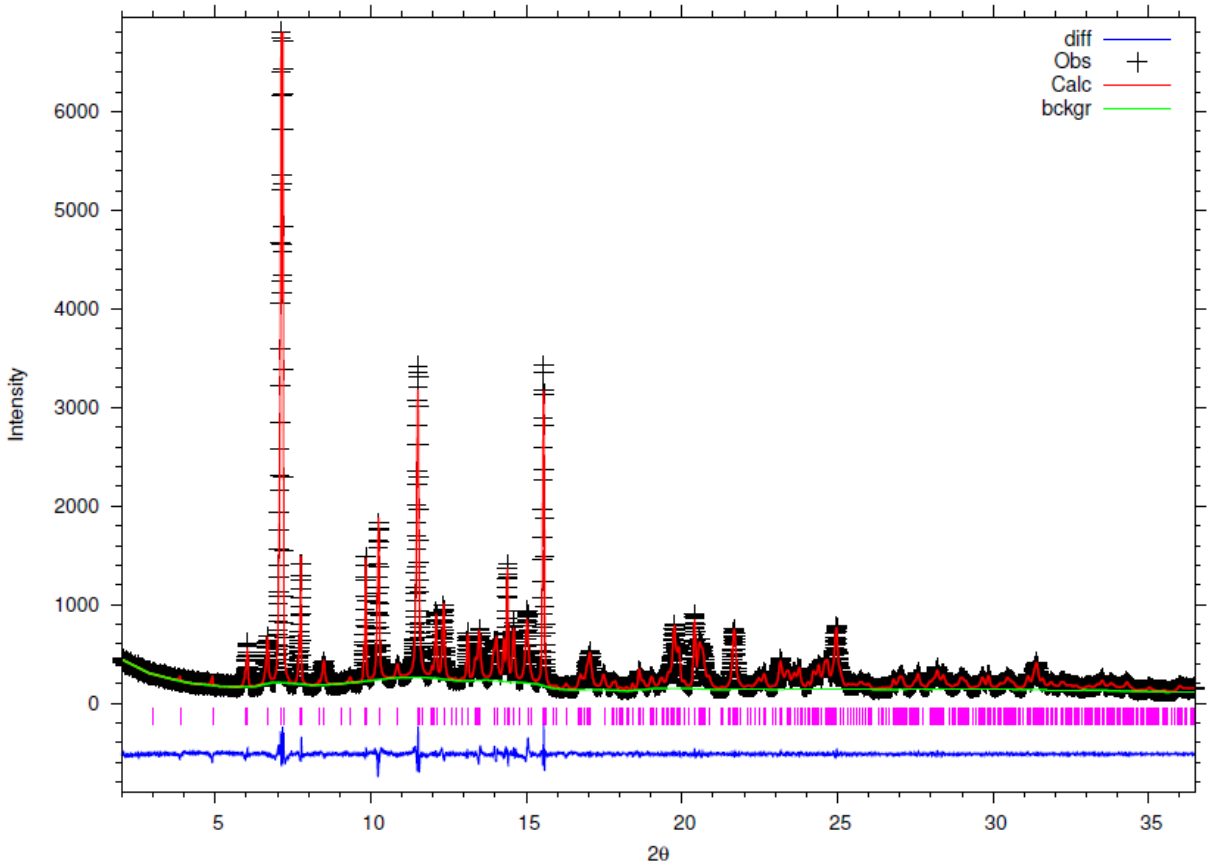

Figure S1. Initial equally-weighted Le Bail fit of $[Co(NH_3)_5Cl]Cl_2$ in *P*222. R_{wp}= 5.07%, χ^2=2.26, R_p=3.98%. The observed diffraction data is represented with black crosses, the calculated profile is shown with a red line, and their difference is shown at the bottom (blue solid line). The background intensity is shown with a green line, and the vertical pink symbols represent allowed peak positions. In this fit, three lattice parameters, zero-point error, 36 background coefficients and six peak profile parameters (profile function No. 3) were varied during the last cycles of refinement.

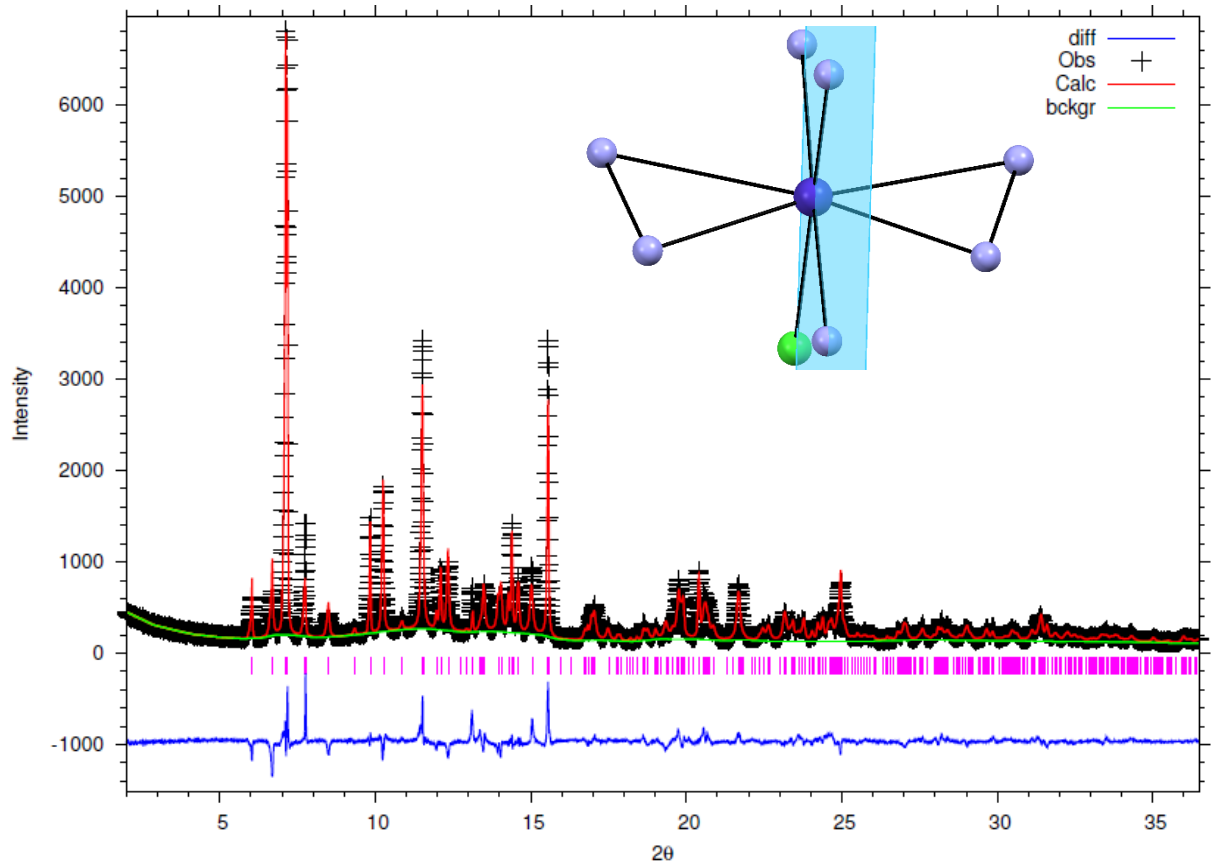

Figure S2. Rietveld fit of $[Co(NH_3)_5Cl]Cl_2$ in *Pnma* (Shigeta *et al.*, 1963). R_{wp}= 10.24%, χ^2=9.22, R_I=5.78%, R_p=7.67%. The observed diffraction data is represented with black crosses, the calculated profile is shown with a red line, and their difference is shown at the bottom (blue solid line). The background intensity is shown with a green line, and the vertical pink symbols represent allowed peak positions. The resulting internal geometry of the coordination complex and a mirror plane (cyan) are shown in the inset. The two N atomic positions from the unrefined model (Shigeta *et al.*, 1963) above and below the mirror plane, split into four after Rietveld refinement (two of them closely separated by ~1.3 Å), rendering the model incorrect. The refinement was carried out without restraints.

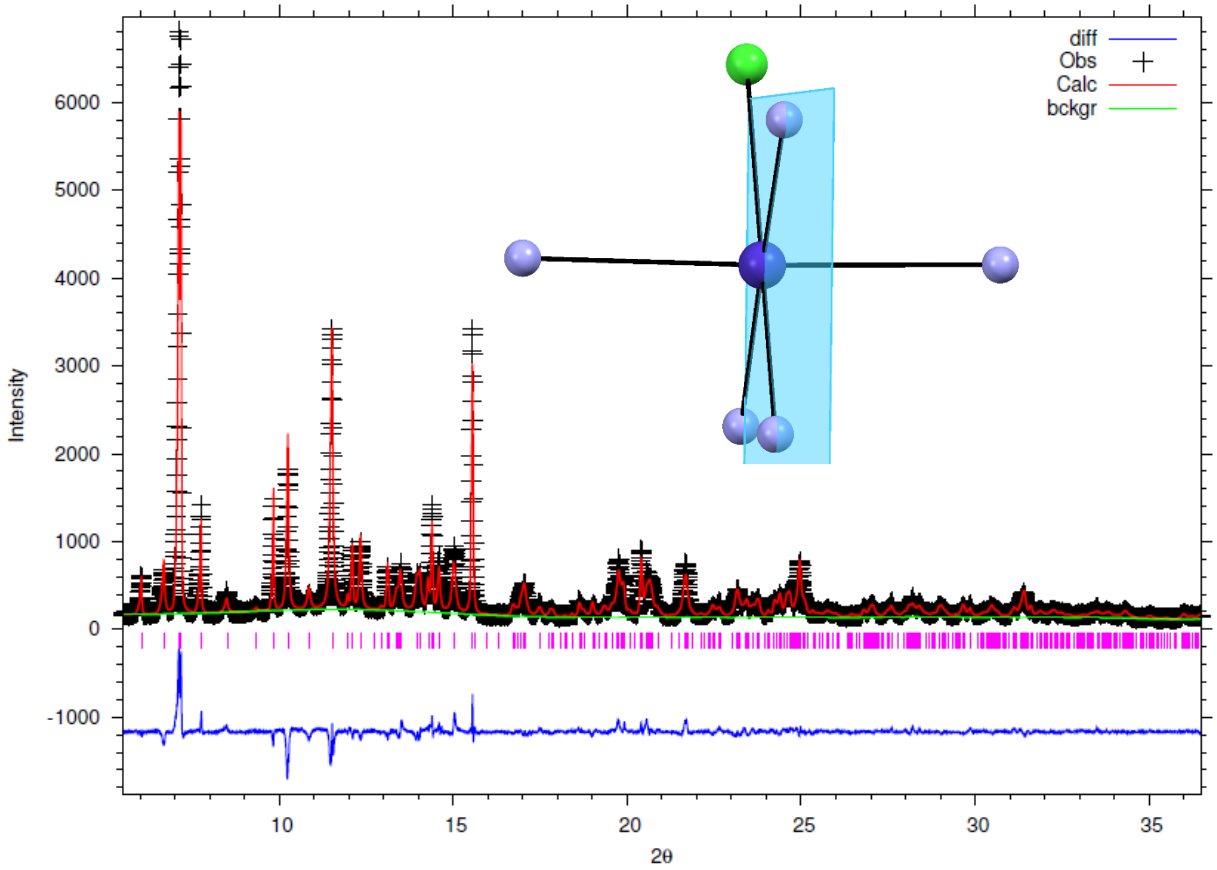

Figure S3. Rietveld fit of $[Co(NH_3)_5Cl]Cl_2$ in *Pnma* (Messmer and Amma, 1968). R_{wp}= 8.48%, χ^2=6.65, R_I=3.50%, R_p=6.94%. The observed diffraction data is represented with black crosses, the calculated profile is shown with a red line, and their difference is shown at the bottom (blue solid line). The background intensity is shown with a green line, and the vertical pink symbols represent allowed peak positions. The resulting internal geometry of the coordination complex and a mirror plane (cyan) are shown in the inset. The refinement was carried out without restraints.

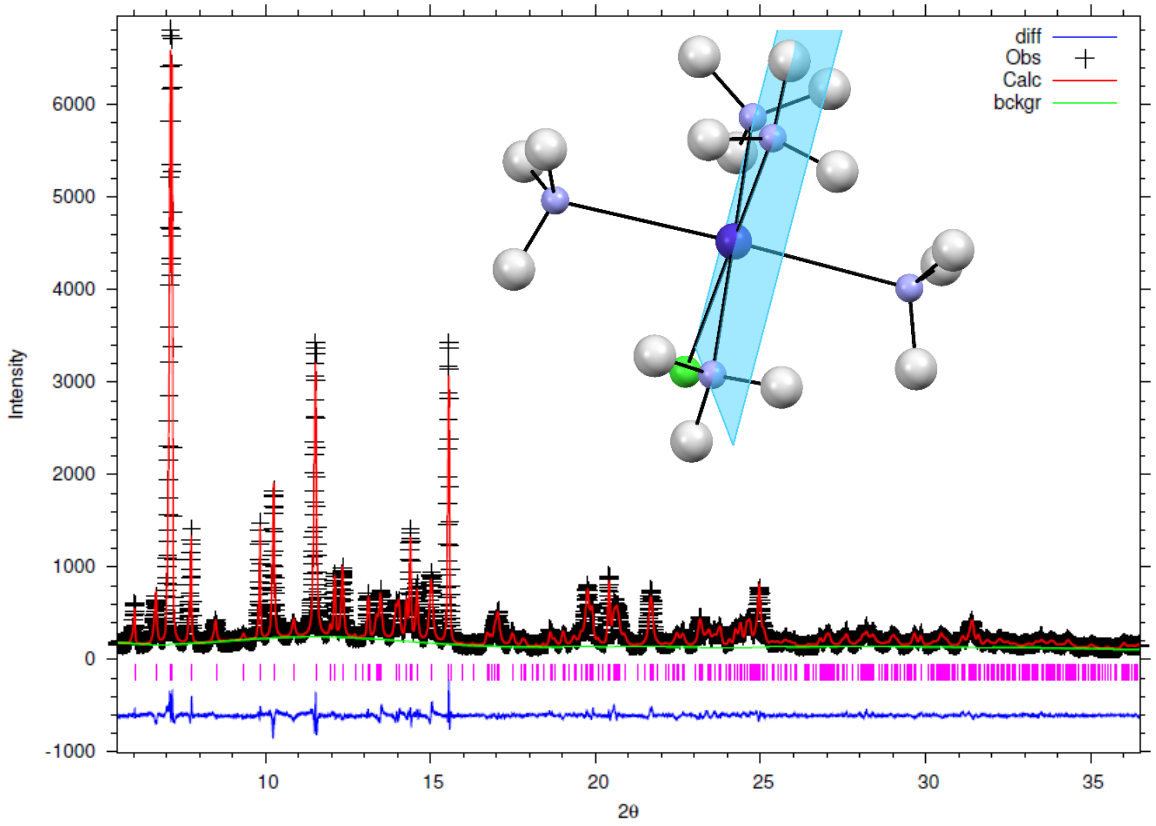

Figure S4. Rietveld fit of $[Co(NH_3)_5Cl]Cl_2$ in *Pnma* (Messmer and Amma, 1968) after adding hydrogen atoms (not reported in 1968) to the Rietveld-refined coordinates corresponding to the fit shown in Figure S3. R_{wp}= 6.67%, χ^2=4.14, R_I=3.15%, R_p=5.35%. The observed diffraction data is represented with black crosses, the calculated profile is shown with a red line, and their difference is shown at the bottom (blue solid line). The background intensity is shown with a green line, and the vertical pink symbols represent allowed peak positions. The resulting internal geometry of the coordination complex and a mirror plane (cyan) are shown in the inset. The refinement of the hydrogen positions was carried out with 12 distance and 24 angle restraints. The isotropic atomic displacement parameters were refined subjected to a group constraint, so that the value for hydrogen atoms is 1.2 times the refined value for non-Hydrogen atoms.

Table S.I. – Atomic coordinates in Shigeta *et al.* (1963). Space group *Pnma* (No. 62).

Atom	x	y	z	Wyckoff site
Co	0.395	0.25	0.176	4 *c*
Cl(1)	0.528	0.25	-0.033	4 *c*
N1	0.283	0.25	0.353	4 *c*
N2	0.303	0.25	-0.055	4 *c*
N3	0.487	0.25	0.407	4 *c*
N4	0.395	0.059	0.176	8 *d*
N5	0.395	0.441	0.176	8 *d*
Cl(2)	0.148	0.000	0.158	8 *d*

Table S.II. – Atomic coordinates in Messmer and Amma (1968). Space group *Pnma* (No. 62).

Atom	x	y	z	Wyckoff site
Co	0.1046(7)	0.25	0.1797(12)	4 *c*
Cl(1)	-0.0257(13)	0.25	-0.0393(26)	4 *c*
Cl(2)	0.3524(10)	0.0011(12)	0.1587(17)	8 *d*
N(1)	0.2161(50)	0.25	0.3691(91)	4 *c*
N(2)	0.1993(49)	0.25	-0.0442(85)	4 *c*
N(3)	0.1023(32)	0.0603(36)	0.1773(60)	8 *d*
N(4)	0.0084(51)	0.25	0.4052(95)	4 *c*

II.- Analysis of the *"longest distance"* effect (Messmer and Amma, 1968) from powder diffraction coordinates

The two longest distances are compared, 2.07(8) Å and 1.95(3) Å.

For 1σ (68% confidence interval):

(2.07 + 0.08) Å = 2.15 Å

(2.07 - 0.08) Å = 1.99 Å (shortest value for the longest distance)

(1.95 + 0.03) Å = 1.98 Å (longest value for the shortest distance)

(1.95 - 0.03) Å = 1.92 Å

1.99 Å > 1.98 Å; thus 2.07(8) Å is the longest distance between the two compared, within 68% confidence level, assuming uncorrelated errors.

For 2σ (95% confidence interval):

(2.07 + 0.08×2) Å = 2.23 Å

(2.07 - 0.08×2) Å = 1.91 Å (shortest value of the above longest distance)

(1.95 + 0.03×2) Å = 2.01 Å (longest value of the above shortest distance)

(1.95 - 0.03×2) Å = 1.91 Å

2.01 Å > 1.91 Å; thus 2.07(8) Å is the not the longest distance between the two compared, within 95% confidence level, assuming uncorrelated errors.

III.- Analysis of the *trans* effect (Shigeta *et al.*, 1963) from powder diffraction coordinates

The two shortest distances are compared, 1.84(3) Å and 1.88(8) Å.

For 1σ (68% confidence interval):

(1.84 + 0.03) Å = 1.87 Å (longest value of the shortest distance)

(1.84 - 0.03) Å = 1.81 Å

(1.88 + 0.08) Å = 1.96 Å

(1.88 - 0.08) Å = 1.80 Å (shortest value of the longest distance)

1.87 Å > 1.80 Å; thus 1.84(3) Å is not the shortest distance between the two compared, within 68% confidence level, assuming uncorrelated errors.