TECHNICAL ARTICLE

Revisiting the crystal structure of [Co(NH$_3$)$_5$Cl]Cl$_2$ using synchrotron powder diffraction: to what extent single-crystal diffraction from 1960s got it right?

S. Mohamud[1] and S. Pagola[2,a)]
[1]*Department of Physics, College of William and Mary, Williamsburg, Virginia 23185*
[2]*Department of Applied Science, College of William and Mary, Williamsburg, Virginia 23185*

The crystal structure of the purpureo salt, [Co(NH$_3$)$_5$Cl]Cl$_2$, first reported in 1963 and later revised in 1968 (in both cases from single-crystal diffraction) in the space group *Pnma* (No. 62), has been recently re-examined from synchrotron X-ray powder diffraction using direct methods and the software EXPO2013. The comparison of the Rietveld analysis results using the two published models and the atomic coordinates obtained from powders leads to an improved crystal structure description in the lower symmetry space group *Pn*2$_1$*a* (No. 33). As a result, the overall atom connectivity and crystal packing remain similar; however, the symmetry and internal geometry of the coordination complex are changed. The distortions from an idealized geometry in *Pnma* (No. 62) are likely because of energetically favorable hydrogen-bonding motifs in the crystal. The three models are compared, and their validity and limitations are discussed. © 2017 International Centre for Diffraction Data.
[doi:10.1017/S0885715617000677]

I. INTRODUCTION

The topic of crystal structure solution from powders is still young (Le Bail *et al.*, 2009). The direct-space methods for crystal structure determination from powder diffraction have been validated by academic and industrial laboratories around the world, bringing a new capability to the powder diffraction technique. However, generally, crystal structures from powders are less accurate and often less "credible" than the outcome of single-crystal diffraction analysis. Several contributing factors can be mentioned: the projection of the three-dimensional reciprocal lattice into one dimension in the powder diffraction pattern, and the consequent loss of independently measurable diffraction intensities; the possible error correlation in Rietveld parameters obscuring model deficiencies; the limited experience of the scientific community, the lack of automation, and considerable need of human intervention in powder data analysis; the lack of an absolute scale to distinguish between good and poor Rietveld agreement factors (R_{wp}, χ^2, R_I, R_p); and consequently, the partially subjective assessment of the model validity (Toby, 2006).

Although in the general case, crystal structure determinations by single-crystal diffraction render coordinates closer to the true values than those obtained from powders, advances in instrumentation, algorithms, and software make nowadays possible to tackle structural problems from powders, which have been simply not solvable during most of the 20th century, opening up new possibilities for the revision and improvement of early structural models. This article describes such case revealed through the redetermination of the crystal structure of [Co(NH$_3$)$_5$Cl]Cl$_2$, the "purpureo salt," previously reported from X-ray single-crystal diffraction in the space group *Pnma* (No. 62) (Shigeta *et al.*, 1963; Messmer and Amma, 1968). The analysis of its modern synchrotron X-ray powder diffraction data indicates that the space group is *Pn*2$_1$*a* (No. 33). The crystal structure results are discussed, the three models are compared, and the powder results are supported by the Rietveld agreement factors corresponding to the single-crystal and powder structures, as well as by the observation of the powder crystallites under the microscope to discard considerable preferred orientation effects. In addition, a search in the Cambridge Structural Database (Allen, 2002) was used to determine the validity of the bond distances and overall coordination complex geometry derived from powders.

II. EXPERIMENTAL

A. X-ray powder diffraction

The synchrotron X-ray powder diffraction data of [Co(NH$_3$)$_5$Cl]Cl$_2$ was collected at the X16C beamline of the N.S.L.S.-I, Brookhaven National Laboratory, USA. The pink [Co(NH$_3$)$_5$Cl]Cl$_2$ powder was loaded into a 0.7 mm diameter glass capillary, and the data were collected at room temperature using a capillary spinner. The wavelength 0.700 12 Å was selected with a Si(111) double monochromator. The wavelength calibration was carried out using an Al$_2$O$_3$ NIST standard. The incident parallel beam was monitored with an ion chamber, and a Ge(111) analyzer crystal was placed after the sample and before the detector to increase the angular resolution, whereas the out-of-plane resolution was given by slits. A NaI(Tl) scintillation detector was used to measure the diffracted radiation.

---
a)Author to whom correspondence should be addressed. Electronic mail: spagol@wm.edu

B. Crystal structure determination from powders

The X-ray powder diffraction data of $[Co(NH_3)_5Cl]Cl_2$ was indexed with TREOR (Werner *et al.*, 1985) leading to the unit-cell parameters $a = 13.287(5)$ Å, $b = 10.34(1)$ Å, $c = 6.718(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 923.39$ Å^3 ($M_{20} = 29$); and with DICVOL06 (Boultif and Louër, 2004) leading to the lattice parameters $a = 13.2704$ Å, $b = 10.3300$ Å, $c = 6.7098$ Å, $\alpha = \beta = \gamma = 90°$, $V = 919.81$ Å^3 ($M_{20} = 43.2$). The unit-cell parameters were refined through a Le Bail fit (Le Bail, 2005) in the space group $P222$ (No. 16) using GSAS (Larson and von Dreele, 2004). Those values ($a = 13.2665$ Å, $b = 10.3382$ Å, $c = 6.7087$ Å, $\alpha = \beta = \gamma = 90°$) were used for crystal structure determination. The Rietveld graph is shown in online Supplementary Figure S1, and the agreement factors were $R_{wp} = 5.07\%$, $\chi^2 = 2.26$, and $R_p = 3.98\%$.

The crystal structure was solved using direct methods as implemented in the software EXPO2013 (Altomare *et al.*, 2013), which also indexed the powder diffraction data, yielding basically the same unit-cell parameters, and it suggested two space groups. The largest figure of merit was 0.196 for $Pn2_1a$ (No. 33), followed by 0.113 for $Pnma$ (No. 62).

The Rietveld refinement of the crystal structure model in $Pn2_1a$ was carried out with the software GSAS (Larson and von Dreele, 2004). The atomic positions of the hydrogen atoms were calculated with SHELX (Sheldrick, 2008) as implemented through WinGX (Farrugia, 2012) and refined with soft bond-length and bond-angle restraints. The following parameters were refined in the Rietveld fits: scale factor, 36 cosine Fourier series coefficients for the background function No. 2, unit-cell parameters, 2θ zero-point error, fractional atomic coordinates, isotropic atomic displacement parameters, and asymmetry-corrected Pseudo-Voigt profile parameters (profile function No. 3). A constant term for X-ray absorption correction suitable for capillary transmission geometry, as implemented in GSAS (Larson and von Dreele, 2004), was used. Its value was calculated to be 0.636 Å^{-1}, assuming an absorption linear coefficient of 25.44 cm^{-1}, 0.035 cm capillary radius, 0.5 powder packing coefficient, and 0.700 12 Å radiation.

The scattering factors used were those of Co^{+3}, Cl^-, N, and H. The atomic displacement parameter of the hydrogen atoms was constrained to 1.2 times the value of that of the non-hydrogen atoms, both of which were refined subjected to a group constraint. The Rietveld-refined atomic coordinates were corrected following the procedure published in Scott (1983).

III. RESULTS AND DISCUSSION

The crystallographic parameters describing the crystal structure of $[Co(NH_3)_5Cl]Cl_2$ after Rietveld refinement, and the Rietveld agreement factors are summarized in Tables I and II. Figure 1 shows the coordination sphere around the Co(III) ions and the Co(III)—ligand interatomic distances. Figure 2 shows the Rietveld refinement graph.

It has been pointed out (Toby, 2006) that the best way to judge the correctness of a model from powders is: (1) graphically and carefully observing the experimental and calculated Rietveld profiles; and (2) confirming that the chemical bonding in the model is plausible. For this material, since powder and single-crystal diffraction give rise to crystal structure

TABLE I. Crystal data of $[Co(NH_3)_5Cl]Cl_2$ from synchrotron X-ray powder diffraction [space group $Pn2_1a$ (No. 33), orthorhombic (standard setting $Pna2_1$)].

Unit cell	Rietveld agreement factors
$a = 13.2648(3)$ Å	$R_{wp} = 6.01\%$
$b = 10.336\,93(17)$ Å	$R_I = 2.16\%$
$c = 6.708\,05(17)$ Å	$\chi^2 = 3.37$
$V = 919.79(3)$ Å^3	$R_p = 4.84\%$
$Z = 4$	Maximum and minimum in the Fourier difference map $= +0.30$ and -0.29 e^-/Å^3, respectively

descriptions in two space groups, $Pnma$ and $Pn2_1a$, respectively, and unresolved subtleties in the internal geometry of the coordination complex still remained after the work of Messmer and Amma (1968); the Rietveld method was also used to further assess the validity of the published models from single-crystal diffraction (Shigeta *et al.*, 1963; Messmer and Amma, 1968), comparing their Rietveld agreement factors and Rietveld graphs with those of the model from powders.

The unit-cell parameters reported in 1963 and 1968 are similar to those found from powders (after Rietveld refinement), and the values from the three models are compared in Table III. The unit-cell parameters determined in 1968 are the closest to those calculated from the powder pattern.

In order to first assess the validity of the model of Shigeta *et al.* (1963), the unit-cell parameters, 2θ zero-error, background coefficients, and peak profile parameters were refined in a model biased Le Bail fit replacing the space group $P222$ by $Pnma$, typing the published atomic coordinates and re-adjusting the $L_{i,j}$ coefficients of the profile function No. 3 (Larson and von Dreele, 2004).

In the Rietveld fit that followed, only the scale factor and the background coefficients were initially refined. The calculated pattern showed serious misfits for the most intense peaks and many others. After refining the published atomic coordinates (without bond-length restraints), and the isotropic atomic displacement parameters (subjected to a group constraint), the best agreement factors achieved were $R_{wp} = 10.24\%$, $\chi^2 = 9.22$, $R_I = 5.78\%$, $R_p = 7.67\%$ (in all cases significantly larger than those of our model from powders); and although diminished, the misfits persisted (see online Supplementary Figure S2). Moreover, the two nitrogen positions above and below the mirror plane in the unrefined single-crystal model (Shigeta *et al.*, 1963) split into four, rendering the refined model implausible. The Fourier difference map showed minimum and maximum values of -0.63 and $+0.86$ e^-/Å^3, respectively.

We point out that various factors could have contributed to an erroneous structure (with $R = 0.109$) reported by Shigeta *et al.* (1963), such as the visual determination of the reflection intensities, the lack of absorption correction, and that the material was simply assumed to be isostructural with a rhodium (III) salt. Individual atomic displacement parameters for each atomic coordinate and hydrogen positions were not reported either.

Towards facilitating the comparison of all three models and their Rietveld refinements, Figure 3 shows the crystal packing in the three models, and Figure 4 shows the reported coordination complex geometry using the labeling scheme of

TABLE II. Atom labels, fractional atomic coordinates, occupancy factors, and isotropic atomic displacement parameters of [Co(NH$_3$)$_5$Cl]Cl$_2$ from the analysis of synchrotron X-ray powder diffraction data.

| Atom label	Atom	x/a	y/b	z/c	Occupancy	U_{eq} (Å^2)
Co1	Co^{+3}	0.8943(6)	0.373(6)	0.1789(12)	1	0.0199(15)
Cl2	Cl$^-$	1.0238(10)	0.381(6)	−0.036(3)	1	0.0199(15)
Cl3	Cl$^-$	0.8588(19)	0.119(6)	0.654(7)	1	0.0199(15)
Cl4	Cl$^-$	0.8479(19)	0.623(6)	0.660(7)	1	0.0199(15)
N5	N	0.986(2)	0.375(11)	0.406(5)	1	0.0199(15)
N6	N	0.791(2)	0.370(12)	0.361(6)	1	0.0199(15)
N7	N	0.798(2)	0.354(8)	−0.034(5)	1	0.0199(15)
N8	N	0.890(5)	0.173(5)	0.157(11)	1	0.0199(15)
N9	N	0.906(5)	0.554(5)	0.188(11)	1	0.0199(15)
H10	H	1.019	0.449	0.415	1	0.0239
H11	H	0.9449	0.364	0.5094	1	0.0239
H12	H	1.031	0.311	0.396	1	0.0239
H13	H	0.889	0.5895	0.071	1	0.0239
H14	H	0.862	0.583	0.278	1	0.0239
H15	H	0.9678	0.5758	0.224	1	0.0239
H16	H	0.812	0.314	0.453	1	0.0239
H17	H	0.786	0.449	0.414	1	0.0239
H18	H	0.7328	0.348	0.305	1	0.0239
H19	H	0.9496	0.1414	0.194	1	0.0239
H20	H	0.843	0.1443	0.24	1	0.0239
H21	H	0.874	0.1465	0.035	1	0.0239
H22	H	0.8204	0.399	−0.138	1	0.0239
H23	H	0.793	0.2705	−0.065	1	0.0239
H24	H	0.7382	0.383	0.006	1	0.0239
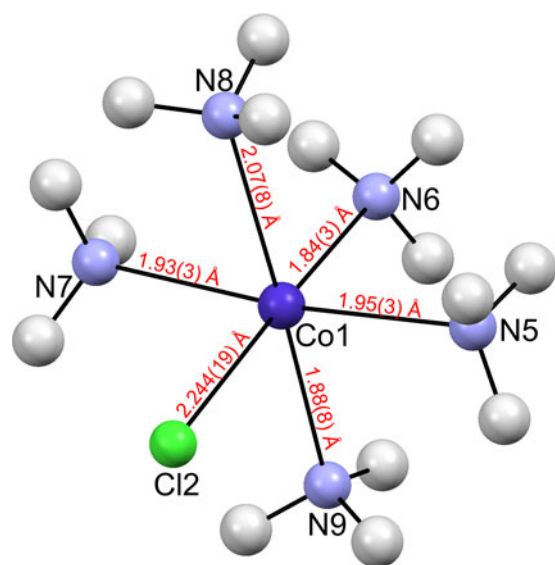
Figure 1. (Color online) The coordination sphere around the Co(III) ions in [Co(NH$_3$)$_5$Cl]Cl$_2$ showing the atom-labeling scheme and selected interatomic distances. Thermal ellipsoids are represented at the 50% probability level. Co^{3+} ions are shown in dark blue, N in light blue, Cl$^-$ in green, and H in light gray.

the respective publications (Shigeta *et al.*, 1963; Messmer and Amma, 1968). Table IV summarizes the Rietveld agreement factors, Fourier difference residuals, and the number of parameters refined in each fit, all of which were carried out using our synchrotron powder diffraction data (this work).

The number of restraints only refers to the bond-distance and -angle restraints to refine the positions of hydrogen atoms. Those were included in the powder model (neither single-crystal model reported H atoms), and in the Rietveld-refined model of Messmer and Amma (1968), for comparison

purposes. The number of constraints is one in all cases, and it corresponds to the isotropic atomic displacement parameters of non-H atoms and H atoms (when included).

Following the procedure described in Scott (1983) for the estimation of standard uncertainties from Rietveld fits, the number of crystallographic parameters (N_C) is the sum of the three lattice parameters, the number of refinable atomic coordinates, and the atomic displacement parameter. The number of profile parameters (N_P) is the sum of 36 background coefficients, the scale factor, the zero-point error, and peak profile parameters (when refined in the last GSAS cycles). The total number of parameters refined (N_T) is the sum of N_C and N_P. The entries in Table IV corresponding to the model from powders in $Pn2_1a$ were used in the calculation of the standard uncertainties following the procedure described in Scott (1983).

Furthermore, all three structural models are credible from the chemical-bonding point of view; however, the models describe subtleties in the geometry of the [Co(NH$_3$)$_5$Cl]$^{2+}$ coordination complex differently. The overall crystal packing in both single-crystal and powder structures is quite similar. The coordination sphere around the Co(III) ion is octahedral, and it is composed of five ammonia molecules and one chloride ion. Viewed approximately along the *c*-axis, the structures show two alternating horizontal layers, one layer is made of chloride ions, and the second of penta-ammonium cobalt (III) chloride complex ions [Co(NH$_3$)$_5$Cl]$^{2+}$, respectively. This is represented in Figure 3 for the single-crystal (Shigeta *et al.*, 1963; Messmer and Amma, 1968) and powder structures.

However, both single-crystal models have been defined differently. In both cases, Co^{3+} and three N atoms sit on a mirror plane at $y = 1/4$, in a 4c special position (x, ¼, z), thus conferring partial planar symmetry to the coordination complex
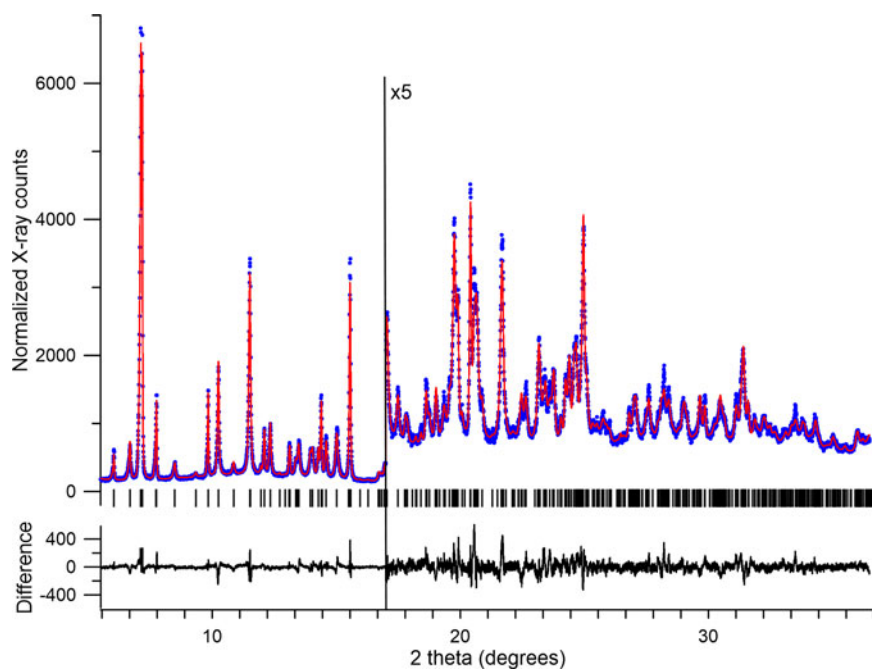
Figure 2. (Color online) Observed (blue circles), calculated (solid red line), and difference (bottom black line) X-ray powder diffraction patterns of [Co(NH$_3$)$_5$Cl]Cl$_2$ refined by the Rietveld method in the space group $Pn2_1a$ (No. 33), orthorhombic. Vertical bar symbols represent allowed peak positions.

ion [Co(NH$_3$)$_5$Cl]$^{2+}$ (see Figure 3). In the model of Shigeta *et al.* (1963), described with eight atomic coordinates and constructed by comparison with the structure of the analogous rhodium salt, N4 and N5 (above and below such mirror plane, respectively) are in 8d general positions [see Figure 3 (a)]; while in the model of Messmer and Amma (1968), described with seven atomic coordinates derived from a Patterson map, the N3 atom above the mirror plane in a 8d (x, y, z) general position generates N3′ (x, y−½, z) below the mirror plane, within the same complex ion [see Figure 3 (b)]. The atomic positions of both models above are summarized in Tables S.I and S.II (online Supplementary material).

Moreover, in both single-crystal structures, the layers of chloride ions are generated by only one crystallographically independent chloride. In the powder structure in $Pn2_1a$, the chloride layers are made of two crystallographically independent chloride ions (and a third chloride is coordinated to the cobalt ion). $Pn2_1a$ does not have inversion symmetry or mirror planes [see Figure 3(c)], and the [Co(NH$_3$)$_5$Cl]$^{2+}$ coordination complex does not show sections with planar symmetry.

In order to gather additional information to qualitatively assess the likelihood of observing planar symmetry within the coordination complex, and the credibility of the bond distances resulting from the three models, a search in the Cambridge Structural Database (Allen, 2002) version 5.38,

November 2016, was conducted to identify minimum, maximum, and average cobalt–NH$_3$ distances, for structures in which cobalt (this means Co^{2+} or Co^{3+} ions) was bonded to five ammonia molecules and one other residue of any kind. For $R < 5\%$, 69 entries were found resulting in 345 bond-distance observations. Those varied from 1.834 to 2.188 Å, and the average value was (1.966 ± 0.002) Å. Thus, in principle, the bond lengths shown in Figure 1 are deemed valid. Additionally, an analogous planar symmetry section of the coordination complex imposed by the crystal symmetry was not found in any of the above crystal structures. For the four entries hexa-ammine-cobalt(III) dichloride 3-carboxyprop-2-ynoate monohydrate (ASAWUM); (4-methylimidazole-N)-penta-ammine-cobalt(III) trichloride dihydrate (DUSDAW); hexa-ammine-cobalt(III) tris(methanesulfonate) (WEXRIB); and bis[(hexa-ammine)-cobalt(III)] trioxalate tetrahydrate (XEDNAV), in the space groups $Pnma$, $Pna2_1$, $Pnnm$, and $Pnnm$, respectively, only two of the six ligands in the coordination complex were placed on mirror planes for the three above cases in $Pnma$ and $Pnnm$. Thus, if the space group of the purpureo salt is actually $Pnma$, it would be the first structure (after the 69 published) wherein four ligands in [Co(NH$_3$)$_5$R]$^{2+}$ (for R = any residue) are on a mirror plane.

Figure 4 shows the coordination complex geometry reported in the three models, also using the labeling scheme from the publications cited. Messmer and Amma (1968) had identified two possible space groups, $Pnma$ and $Pn2_1a$; however, they chose to report the structure in $Pnma$ because of the observed correlation between the nitrogen atomic positions above and below the mirror plane (N3 and N3′) in $Pn2_1a$ refinements, which are symmetry-related in $Pnma$ but crystallographically independent in $Pn2_1a$.

One of the reasons for which this structure was revisited by Messmer and Amma (1968) was to further investigate the change in bond lengths that occur in metal complexes of this type resulting from *trans*-directing ligands, such as the electronegative chlorine atom. In the structural description of Shigeta *et al.* (1963), the Co–N1 distance *trans* to the

TABLE III. Space group symmetry and unit-cell parameters from the powder model, and the single-crystal models of Shigeta *et al.* (1963) and Messmer and Amma (1968).

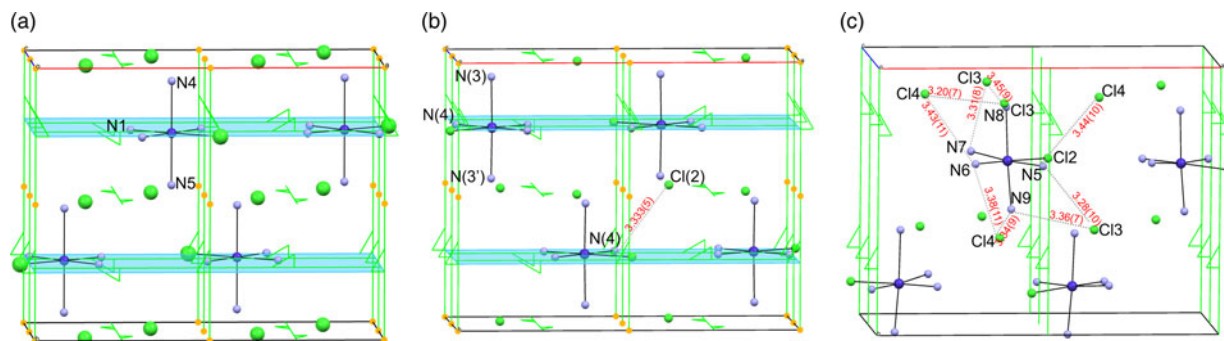| Model	Space group	a (Å)	b (Å)	c (Å)
Powder model (this work)	$Pn2_1a$	13.2648(3)	10.336 93(17)	6.708 05(17)
Shigeta *et al.* (1963)	$Pnma$	13.34(3)	10.33(3)	6.73(2)
Messmer and Amma (1968)	$Pnma$	13.26(1)	10.34(1)	6.720(5)

Figure 3. (Color online) The crystal structure of $[Co(NH_3)_5Cl]Cl_2$ approximately along the c-axis, with inversion centers shown in orange, 2_1 screw axes in green, and mirror planes in cyan. Glide planes are not shown for clarity; (a) the model of Shigeta *et al.* (1963) in *Pnma*, (b) the model of Messmer and Amma (1968) also in *Pnma*, and c) the model obtained from powder diffraction in *Pn2₁a* (H atoms are not shown for clarity). Co^{3+} ions are shown in dark blue, N in light blue, Cl^- in green. The atom labeling shown is that of the original publications (Shigeta *et al.*, 1963; Messmer and Amma, 1968). Selected hydrogen bonding is indicated with dashed gray lines and the distances are in Å.
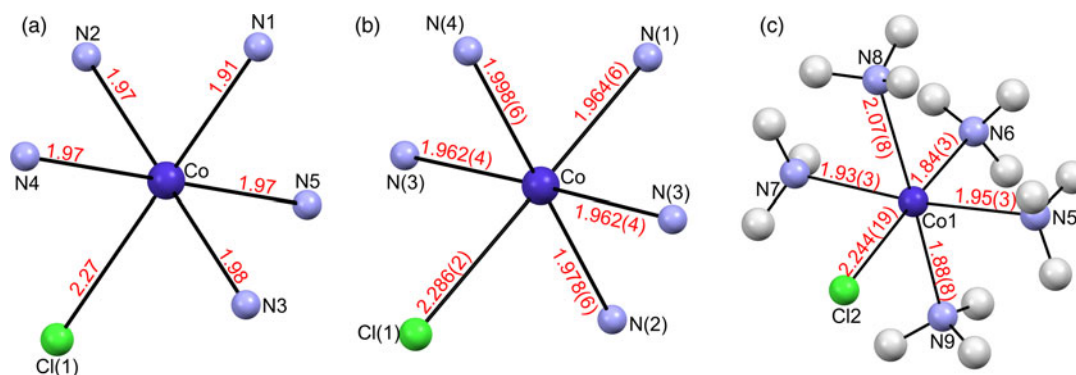

Figure 4. (Color online) The internal geometry of the coordination complex $[Co(NH_3)_5Cl]^{2+}$ with reported interatomic distances in Å and the original labeling scheme in the publications cited. (a) The model of Shigeta *et al.* (1963) in *Pnma*, (b) the model of Messmer and Amma (1968) also in *Pnma*, and (c) the model obtained from powder diffraction in *Pn2₁a* (this work). Co^{3+} ions are shown in dark blue, N in light blue, Cl^- in green, and H in light gray (only reported for the model in *Pn2₁a*).

TABLE IV. Summary of the equally weighted Le Bail fit in *P*222 and Rietveld refinement agreement factors for the model from powders in *Pn2₁a* (this work), and the single-crystal models of Shigeta *et al.* (1963) and Messmer and Amma (1968) [the latter was refined without and with calculated hydrogen positions; N_r is the number of restraints and N_{Cons} is the number of constraints; N_{Crys} is the number of crystallographic parameters, N_P the number of profile parameters, and N_T the total number of parameters refined, as defined in Scott (1983)].

Model	Agreement factors										
	R_{wp} (%)	χ^2	R_I (%)	R_p (%)	Fourier difference $(e^-/Å^3)$		N_r	N_{Cons}	N_{Crys}	N_P	N_T
Le Bail	5.07	2.26	–	3.98	–	–	0	0	3	43	46
Powder model	6.01	3.37	2.16	4.84	−0.29	0.30	45	1	76	38	114
Shigeta *et al.*	10.24	9.22	5.78	7.67	−0.71	1.08	0	1	23	38	61
Messmer and Amma	8.48	6.65	3.50	6.94	−0.47	0.49	0	1	23	38	58
Messmer and Amma with H	6.67	4.14	3.15	5.35	−0.37	0.49	36	1	53	38	91

Co–Cl bond [see Figures 3(a) and 4(a)] is significantly shorter than the four remaining Co–N distances; this is 1.91 vs. 1.97 (×3) and 1.98 Å. On this issue, Messmer and Amma (1968) concluded that a significant *trans* distortion was not observed within the limitations of their data; however, it was confidently determined that one of the Co–N distances [Co–N(4)] was larger than the remaining four; this is 1.998(6) vs. 1.962(4) (×2), 1.946(6), and 1.987(6) Å [see Figures 3(b) and 4(b)]; and that such N atom is likely involved in hydrogen bonding to a chlorine atom [Cl(2)] [see Figure 3(b)], and this likely

gives rise to the longest distance observed for Co–N(4), and the shortest N(4)–Cl(2) distance of 3.333(5) Å, among all N–Cl distances.

Thus, three questions to answer using our synchrotron X-ray powder diffraction data have been identified in our work: (1) Is the space group *Pnma* correct, or the crystal structure is a pseudosymmetry case and it is better described in *Pn2₁a*?; (2) Is there a Co–N distance significantly larger than the remaining four, such as Messmer and Amma (1968) reported?; and (3) Can a significant *trans* effect be

observed in this compound such as Shigeta *et al.* (1963) did, within the limitations of our powder diffraction data?

Toward answering these questions and further compare the models, we also Rietveld-refined the results of Messmer and Amma (1968) using our synchrotron powder pattern. The Rietveld fit obtained is shown in online Supplementary Figure S3, and the agreement factors and other Rietveld refinement details are summarized in Table IV. In this case, the Rietveld refinement renders a chemically plausible model; however, the graphical observation of the Rietveld fit again points to serious model deficiencies (see online Supplementary Figure S3).

One could think that considerable preferred orientation effects could explain why the calculated intensities of a few low-angle peaks [this is (011) around $2\theta = 7.129°$ and (210) at $2\theta = 7.186°$] are below their observed values. Thus, we observed the powder crystallites under the microscope. The micrographs are shown in Figure 5, and they indicate that the powder crystallites are very small (estimated in the order of 1–10 μm) and of a rather spherical shape; thus, preferred orientation corrections are unlikely to be required.

To further test the model of Messmer and Amma (1968), the hydrogen positions were added with SHELX (Sheldrick, 2008) as implemented through WinGX (Farrugia, 2012), leading to a considerable improvement of the Rietveld fit (online Figure S4); however, the agreement factors (shown in Table IV) remained higher than those obtained in $Pn2_1a$. We must note that Messmer and Amma (1968) did not report hydrogen positions, and absorption corrections were not carried out.

Thus, considering all above results, in particular, the lowest agreement factors and Fourier difference residuals

Figure 5. (Color online) Micrographs of the powder crystallites in the [Co(NH$_3$)$_5$Cl]Cl$_2$ specimen used for X-ray powder diffraction data collection. (a) View at 1 μm resolution showing the absence of large needles or plates, and small microcrystallites (estimated 1–10 μm size); (b) one microcrystallite.

obtained for the model from powders in $Pn2_1a$, in principle such model seems physically meaningful to us. We believe the analysis of the synchrotron powder diffraction data rather indicates the validity of the $Pnma$ space group choice reported in Messmer and Amma (1968) is questionable, and we note that it has been already an arguable choice in 1968, as the authors mentioned. An additional hint toward the structural description in $Pn2_1a$ is given by evaluating the possibilities of formation of energetically favorable hydrogen-bonding motifs in the crystal packing adopted. It seems reasonable that the partial planarity of the [Co(NH$_3$)$_5$Cl]$^{2+}$ coordination complex, as well as bond distances and angles in the $Pnma$ description, can be slightly distorted because of the bonding energy gains resulting from hydrogen bonding of the −NH groups of ammonia to other nitrogen and chloride ions.

Table V shows the hydrogen-bonding distances calculated by PLATON (Spek, 2002) and most of the N–Cl distances leading to hydrogen bonding are also shown in Figure 3(c) (a few were omitted for clarity). It is interesting to note that rather than a considerable deviation from planar symmetry for the atoms Cl2, N5, N6, and N7 [see Figure 3 (c)], it rather seems that the angles of N9 and N8 with the above atoms considerably deviate from the $(90 ± 1)°$ values observed for the corresponding N3 and N3′ atoms in Figure 3(b), in $Pnma$. In $Pn2_1a$, such angles are not related by mirror symmetry, and their values range from 80 to 100° instead. Since these irregular features in the internal geometry of the coordination complex could be explained by the maximization of lattice energy gains by hydrogen bonding within the crystal, we believe that this is a reasonable chemical reason leading to a better description of the structure in $Pn2_1a$, and the structure is a pseudosymmetry case (approximation to a higher symmetry). It must be also mentioned that *ADDSYM* in the software PLATON (Spek, 2002) suggested a space group change to $Pnma$. However, Spek (2002) indicates that approximations to pseudosymmetry frequently occur in crystal structures; for this reason, the missed symmetry alerts might be false in some cases, and they require careful consideration by the crystallographer analyzing "by hand" the diffraction data.

Thus, our answer to the first question above is that the comparison of the three models using the modern synchrotron powder pattern, including X-ray absorption corrections, calculated hydrogen atom positions, and discarding preferred orientation effects, indicates the correct space group choice is $Pn2_1a$, not $Pnma$. This choice is further supported by the possibilities of formation of energetically more favorable hydrogen-bonding motifs in the lower symmetry space group, leading to a pseudosymmetry.

To answer questions 2 and 3, we must analyze in detail the standard uncertainties of the atomic coordinates from powders, keeping also in mind that the hydrogen positions are only calculated since in the general case, powder diffraction data do not afford their experimental determination. Referring to Figure 4(c), we note that the Co–N8 distance, 2.07(8) Å, is larger than the remaining four, 1.84(3), 1.88 (8), 1.93(3), and 1.95(3) Å. Thus, using the calculated standard uncertainties and assuming uncorrelated errors, within two standard deviations (95% confidence level), we cannot say from the powder data that this distance is *statistically significantly* longer than the rest. However, within one standard deviation (68% confidence level), we could affirm it is
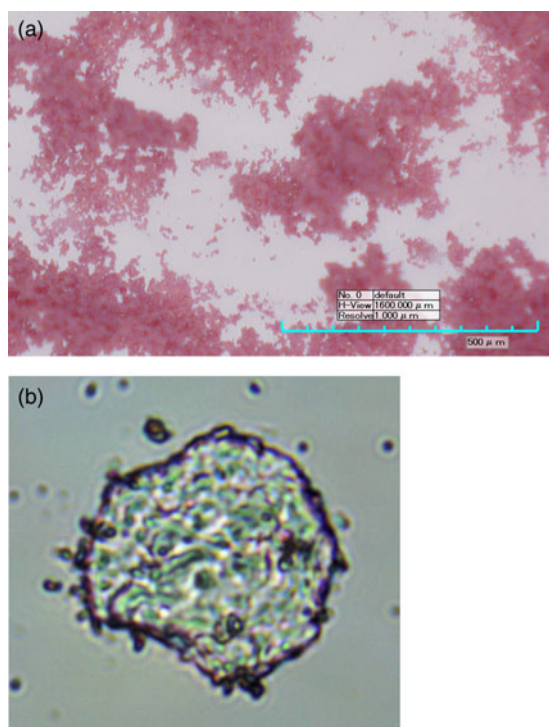
TABLE V. Hydrogen-bonding distances (in Å) and angles (in °) calculated by PLATON (Spek, 2002) for the crystal structure of [Co(NH₃)₅Cl]Cl₂ from synchrotron X-ray powder diffraction [space group $Pn2_1a$ (No. 33), orthorhombic].

Donor	H	Acceptor	Donor–H	H acceptor	Donor acceptor	Donor–H acceptor
N5	H10	Cl3	0.880	2.440	3.28(10)	160.00
N5	H12	Cl4	0.890	2.550	3.44(10)	175.00
N6	H18	Cl4	0.890	2.740	3.43(11)	135.00
N6	H17	Cl4	0.890	2.580	3.38(11)	150.00
N7	H22	Cl4	0.890	2.710	3.52(9)	152.00
N7	H23	Cl3	0.890	2.600	3.31(8)	137.00
N8	H20	Cl3	0.890	2.800	3.41(9)	127.00
N8	H20	Cl4	0.890	2.600	3.20(7)	126.00
N8	H21	Cl3	0.890	2.580	3.45(9)	165.00
N9	H14	Cl4	0.890	2.600	3.34(9)	140.00
N9	H15	Cl3	0.880	2.480	3.36(7)	175.00

(additional details are in the online Supplementary material). This result agrees with the analysis of Messmer and Amma (1968), who confidently concluded that one of the distances is longer than the other four.

Concerning the *trans* effect reported in Shigeta *et al.* (1963), and referring again to Figure 4(c), we see that the Co–N6 distance of 1.84(3) Å is indeed the shortest among the five Co–N distances leading to a *trans* effect. However, through the same analysis and assuming uncorrelated errors, we cannot affirm from our powder data that the Co–N6 distance is the shortest distance among the five, giving rise to a *statistically significant trans* effect with 68% confidence level (additional details are in the online Supplementary material).

In qualitative terms, we assert that the powder data point to the presence of both effects, but the *trans* effect is less likely than the one reported by Messmer and Amma (1968).

IV. CONCLUSION

This article reports the crystal structure of the purpureo salt, [Co(NH₃)₅Cl]Cl₂, recently re-determined from its synchrotron powder diffraction data in the lower symmetry space group $Pn2_1a$ (No. 33). This particular case reminds us that crystal structures solved from single-crystal X-ray diffraction are not always "indisputable."

Furthermore, a disadvantage of the powder diffraction technique is that there is not an absolute scale to distinguish between good and poor Rietveld agreement factors (R_{wp}, χ^2, R_I, R_p). However, this work also shows that in addition to carefully evaluating the graphical representation of the Rietveld fit and the overall credibility of the chemical bonding, the comparison of the Rietveld agreement factors of alternative models fitting the same diffraction data, the use of error analysis, the comparison of the crystallographic parameters determined with those of similar structures in the Cambridge Structural Database (Allen, 2002), and the observation of the powder crystallites under the microscope are valuable resources to evaluate the validity of models derived from powders.

In summary, we conclude that the crystal structure of the purpureo salt is a pseudosymmetry case, and it should be described using the space group $Pn2_1a$, rather than *Pnma*. This is likely because of the formation of energetically more favorable hydrogen-bonding motifs in $Pn2_1a$, afforded by a slight distortion of the coordination complex geometry previously reported in *Pnma* (Messmer and Amma, 1968).

Additional details of the internal geometry of the [Co(NH₃)₅Cl]²⁺ coordination complex have been described. We can affirm that most likely the effect reported in Messmer and Amma (1968) (one longest Co–N distance among the five) is real. Furthermore, although probably the *trans* effect also exists, our confidence level is lower than that the above because of the limitations of our data. To further elucidate these structural details, a modern single-crystal structure determination would be certainly advantageous, although a carefully performed data collection and Rietveld analysis from synchrotron powder diffraction would also lead to such results.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715617000677.

Allen, F. H. (2002). "The Cambridge structural database: a quarter of a million crystal structures and rising," Acta Crystallogr. B **58**, 380–388.

Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N., and Falcicchio, A. (2013). "EXPO2013: a kit of tools for phasing crystal structures from powder data," J. Appl. Crystallogr. **46**(4), 1231–1235.

Boultif, A. and Louër, D. (2004). "Powder pattern indexing with the dichotomy method," J. Appl. Crystallogr. **37**(5), 724–731.

Farrugia, L. (2012). "WinGX and ORTEP for windows: an update," J. Appl. Crystallogr. **45**(4), 849–854.

Larson, A. C. and vonDreele, R. B. (2004). *General Structure Analysis System (GSAS)* (Los Alamos National Laboratory Report 86–748). New Mexico, USA.

Le Bail, A. (2005). "Whole powder pattern decomposition methods and applications: a retrospection," Powder Diffr. **20**(4), 316–326.

Le Bail, A., Cranswick, L. M. D., Adil, K., Altomare, A., Avdeev, M., Cerny, R., Cuocci, C., Giacovazzo, C., Halasz, I., Lapidus, S. H., Louwen, J. N., Moliterni, A., Palatinus, L., Rizzi, R., Schilder, E. C., Stephens, P. W., Stone, K. H., and van Mechelen, J. (**2009**). "Third structure determination by powder diffractometry round robin (SDPDRR-3)," Powder Diffr. **24** (3), 254–262.

Messmer, G. G. and Amma, E. L. (**1968**). "Redetermination of the crystal structure of chloropentamminecobalt(III) dichloride," Acta Crystallogr. B **24**, 417–422.

Scott, H. G. (**1983**). "The estimation of standard deviations in powder diffraction Rietveld refinements," J. Appl. Crystallogr. **16**, 159–163.

Sheldrick, G. M. (**2008**). "A short history of SHELX," Acta Crystallogr. A **64**, 112–122.

Shigeta, Y., Komiyama, Y., and Kuroya, H. (**1963**). "The crystal structure of purpureo salt, $[Co(NH_3)_5Cl]Cl_2$," Bull. Chem. Soc. Jpn. **36**(9), 1159–1162.

Spek, A. L. (**2002**). "Single-crystal structure validation with the program PLATON," J. Appl. Crystallogr. **36**, 7–13.

Toby, B. H. (**2006**). "R factors in Rietveld analysis: how good is good enough?" Powder Diffr. **21**(1), 67–70.

Werner, P. E., Erikson, L., and Westdahl, M. (**1985**). "TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries," J. Appl. Crystallogr. **18**, 367–370.