

Table S1. Selected bond lengths (Å) and angles (°) of Zn(NH₃)₂Cl₂ at different temperatures.

Atom	Atom	Length	Atom	Atom	Atom	Angle
-173 °C						
Zn1	Cl1	2.2706(9)	Cl1	Zn1	Cl1 ¹	108.21(5)
Zn1	Cl1 ¹	2.2706(9)	N1	Zn1	Cl1	108.86(6)
Zn1	N1	2.014(4)	N1 ¹	Zn1	Cl1 ¹	108.86(6)
Zn1	N1 ¹	2.014(4)	N1	Zn1	Cl1 ¹	108.86(6)
			N1 ¹	Zn1	Cl1	108.86(6)
			N1	Zn1	N1 ¹	113.1(2)
-123 °C						
Zn1	Cl1	2.2706(9)	Cl1	Zn1	Cl1 ¹	108.43(5)
Zn1	Cl1 ¹	2.2707(9)	N1	Zn1	Cl1	108.94(6)
Zn1	N1	2.014(4)	N1 ¹	Zn1	Cl1 ¹	108.94(6)
Zn1	N1 ¹	2.014(4)	N1	Zn1	Cl1 ¹	108.94(6)
			N1 ¹	Zn1	Cl1	108.94(6)
			N1	Zn1	N1 ¹	112.6(2)
-73 °C						
Zn1	Cl1	2.2694(10)	Cl1	Zn1	Cl1 ¹	108.75(5)
Zn1	Cl1 ¹	2.2695(10)	N1	Zn1	Cl1	108.89(6)
Zn1	N1	2.008(4)	N1 ¹	Zn1	Cl1 ¹	108.89(6)
Zn1	N1 ¹	2.008(4)	N1	Zn1	Cl1 ¹	108.89(6)
			N1 ¹	Zn1	Cl1	108.89(6)
			N1	Zn1	N1 ¹	112.5(2)
-23 °C						
Zn1	Cl1	2.2700(10)	Cl1	Zn1	Cl1 ¹	108.91(6)
Zn1	Cl1 ¹	2.2700(10)	N1	Zn1	Cl1	108.84(7)
Zn1	N1	2.016(4)	N1 ¹	Zn1	Cl1 ¹	108.85(7)
Zn1	N1 ¹	2.016(4)	N1	Zn1	Cl1 ¹	108.84(7)
			N1 ¹	Zn1	Cl1	108.84(7)
			N1	Zn1	N1 ¹	112.5(3)
27 °C						
Zn1	Cl1	2.2703(11)	Cl1	Zn1	Cl1 ¹	109.06(6)
Zn1	Cl1 ¹	2.2703(11)	N1	Zn1	Cl1	108.87(8)
Zn1	N1	2.018(5)	N1 ¹	Zn1	Cl1 ¹	108.87(8)
Zn1	N1 ¹	2.018(5)	N1	Zn1	Cl1 ¹	108.87(7)
			N1 ¹	Zn1	Cl1	108.87(7)
			N1	Zn1	N1 ¹	112.2(3)
77 °C						
Zn1	Cl1	2.2679(13)	Cl1	Zn1	Cl1 ¹	109.40(8)
Zn1	Cl1 ¹	2.2679(13)	N1	Zn1	Cl1	108.81(10)
Zn1	N1	2.016(5)	N1 ¹	Zn1	Cl1 ¹	108.81(10)
Zn1	N1 ¹	2.016(5)	N1	Zn1	Cl1 ¹	108.81(10)
			N1 ¹	Zn1	Cl1	108.81(10)
			N1	Zn1	N1 ¹	112.2(4)

¹1-X,1/2-Y,+Z.

Table S2. The comparison of the main Raman bands for $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ and ammineite, $\text{CuCl}_2(\text{NH}_3)_2$.

	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ (our data)	ammineite $\text{CuCl}_2(\text{NH}_3)_2$ (Košek et al., 2023)
$\nu(\text{X}^1\text{-Cl})$	281 vs	230 vs
$\nu(\text{X-N})$	417 vs	424 vs
$\rho(\text{NH}_3)$	633 m	-
$\rho(\text{NH}_3)$	682 m	677 m
?	-	975 m
$\delta_s(\text{NH}_3)$	1333 w	1292 m
$\delta_{as}(\text{NH}_3)$	1457 m	-
$\delta_{as}(\text{NH}_3)$	1594 m	1594 w
$\nu(\text{N-H})$	-	3078 s
$\nu(\text{N-H})$	3170 m	3164 m
$\nu(\text{N-H})$	3255 vs	3247 vs
$\nu(\text{N-H})$	3332 s	3323 s
?	-	3587 w

¹X = Zn (for $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$) or Cu (for ammineite, $\text{CuCl}_2(\text{NH}_3)_2$).

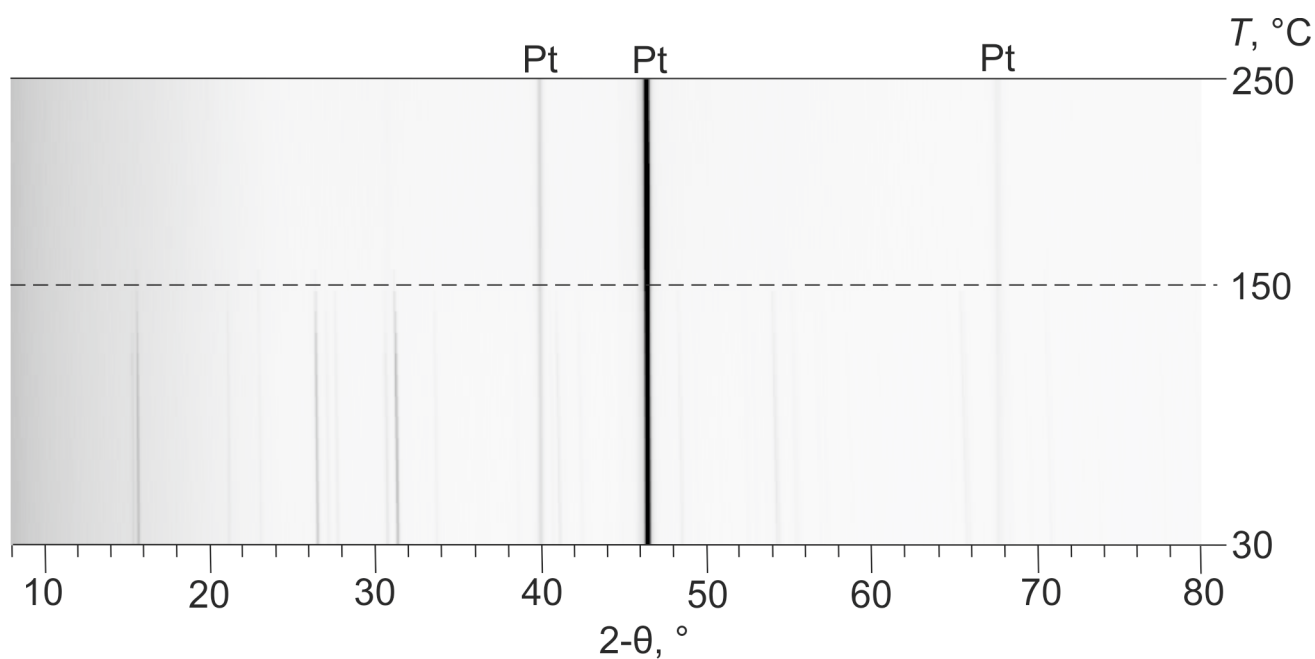


Figure S1. Powder X-ray diffraction patterns at different temperatures of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$.