Modulated One-dimensional Structure of $Cd(NH_3)_3Ni(CN)_4$

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Synopsis The structure of a crystal of $Cd(NH_3)_3Ni(CN)_4$ has been solved and refined as an incommensurate structure in four-dimensional superspace. The dominating feature of the modulation is the incommensurate alternation between octahedrally and tetrahedrally coordinated cadmium atom in the electroneutral chains [-$Cd(NH_3)_n$-NC-$Ni(CN)_2$-CN-]$_\infty$ (*n* alternates between 2 and 4) oriented along **a** axis, in which the $[Cd(NH_3)_n]^{2+}$ cations are linked by square $[Ni(CN)_4]^{2-}$ anions.

Abstract The structure of a crystal of $Cd(NH_3)_3Ni(CN)_4$ has been solved and refined as an incommensurate structure in four-dimensional superspace. The structure is monoclinic, superspace group $C2/c(\alpha,0,\gamma)0s$, cell parameters a=8.4867(14), b=15.951(3), c=7.604(3) Å, β=90.48(2)º, modulation vector 0.4365(11)$\mathbf{a}^*$+0.1307(9)$\mathbf{c}^*$. The Xcalibur point detector diffractometer has been used for the data collection up to the third order satellites. The structure was refined from 3496 observed reflections to final R=0.0371. The modulation strongly affects all atoms of the structure. The dominating feature of the modulation is the incommensurate alternation between octahedrally and tetrahedrally coordinated cadmium atom in the electroneutral chains [-$Cd(NH_3)_n$-NC-$Ni(CN)_2$-CN-]$_\infty$ (*n* alternates between 2 and 4) oriented along the **a** axis, in which the $[Cd(NH_3)_n]^{2+}$ cations are linked by square $[Ni(CN)_4]^{2-}$ anions. The modulations exhibit a switching character that can be described by the crenel and sawtooth functions.

Table 1 List of the orthogonalized functions used in the refinement: $Ortho_i(x_4) = B_{i0} + \sum_{n=1}^{m} A_{in} \sin 2\pi n x_4 + \sum_{n=1}^{m} B_{in} \cos 2\pi n x_4$

Atom	$Ortho_i$	B_{i0}	A_{i1}	B_{i1}	A_{i2}	B_{i2}	A_{i3}
Cd1	0	1.000	-	-	-	-	-
	1	-2.891	4.056	-	-	-	-
	2	0.000	0.000	1.523	-	-	-
	3	0.000	0.000	-3.788	3.572	-	-
	4	-5.072	6.380	0.000	0.000	-	2.598
Cd2	0	1.000	-	-	-	-	-
	1	1.501	2.699	-	-	-	-
	2	0.000	0.000	1.344	-	-	-
	3	0.000	0.000	1.374	2.131	-	-
	4	-5.143	-8.391	0.000	0.000	4.451	-
N4	0	1.000	-	-	-	-	-
	1	1.556	2.750	-	-	-	-
	2	0.141	0.189	1.355	-	-	-

In accordance with Schmidt's orhogonalization procedure the lower triangle of coefficients is used. Moreover, for the Cd1 atom the term $B_{42} \cos 4\pi x_4$ is skipped as it is already strongly involved in precedent terms (for more details see Petříček *et al.* ,1990).

Table 2 Final values of coordinates and Fourier amplitudes of the displacive modulation functions. The waves are sorted by the term (s for sinus, c for cosinus, o for orthogonalized and u for the slope of the sawtooth functions) and n.

	x_{40}	Δ	Wave	*x*	*y*	*z*	*Ueq/Uiso (Å²)*
Cd1[a]	0.25	0.4365		1	0.20155(4)	0.25	0.0247(2)
			o,1	0	-0.00045(9)	0	
			o,2	0.01174(8)	0	-0.00828(11)	
			o,3	0.0027(3)	0	0.0033(3)	
			o,4	0	-0.0008(2)	0	
Cd2[a]	0.75	0.5635		1	0.14519(4)	0.25	0.0367(2)
			o,1	0	0.00353(7)	0	
			o,2	0.01566(8)	0	-0.01343(11)	
			o,3	0.00418(12)	0	-0.00665(17)	
			o,4	0	0.00083(10)	0	
Ni[b]	0.75	1		0.5	-0.01073(3)	0.25	0.02530(17)
			s,1	0	-0.00952(5)	0	
			c,1	0.0079(3)	0	-0.0006(5)	
			s,2	-0.00727(19)	0	-0.0002(3)	
			c,2	0	0.00089(8)	0	
			u	0.0350(4)	0	0.0078(7)	
C1[b]	0.81740[c]	1		0.6550(4)	0.07102(18)	0.2481(4)	0.0282(9)
			s,1	0.0029(8)	-0.0110(4)	0.0001(10)	
			c,1	0.0079(13)	0.0009(7)	-0.0028(19)	
			s,2	-0.0056(8)	0.0012(5)	-0.0020(12)	
			c,2	0.0083(8)	0.0003(5)	0.0004(13)	
			u	0.0518(19)	-0.0037(11)	0.009(3)	
N1[b]	0.85981[c]	1		0.7525(3)	0.12053(17)	0.2469(4)	0.0371(9)
			s,1	0.0089(9)	-0.0112(5)	-0.0003(12)	
			c,1	0.0086(10)	0.0033(6)	-0.0062(15)	
			s,2	0.0004(6)	-0.0003(3)	-0.0035(9)	
			c,2	0.0129(9)	-0.0009(5)	0.0001(13)	
			u	0.0561(18)	-0.0072(10)	0.009(3)	
C2				0.6550(4)	-0.09278(19)	0.2478(4)	0.0311(10)
			s,1	0.0025(5)	-0.0132(3)	0.0019(5)	
			c,1	0.0173(5)	-0.0020(3)	0.0033(6)	
			s,2	0.0017(8)	-0.0008(4)	0.0019(11)	
			c,2	-0.0012(7)	0.0030(4)	-0.0015(10)	
			s,3	-0.0059(9)	0.0020(4)	0.0008(12)	
			c,3	0.0011(10)	0.0022(5)	0.0027(12)	
N2				0.7485(4)	-0.1440(2)	0.2471(4)	0.0455(11)

			s,1	-0.0083(5)	-0.0207(3)	0.0018(6)	
			c,1	0.0134(5)	0.0008(3)	0.0007(5)	
			s,2	0.0009(7)	-0.0001(4)	0.0007(10)	
			c,2	0.0059(7)	0.0046(3)	-0.0022(8)	
			s,3	0.0030(8)	0.0064(4)	0.0010(10)	
			c,3	0.0022(8)	0.0003(5)	0.0011(10)	
N3				0.9982(4)	0.23658(17)	-0.0019(4)	0.0381(9)
			s,1	-0.0016(4)	-0.0023(3)	-0.0308(5)	
			c,1	0.0048(4)	0.0048(2)	-0.0151(5)	
			s,2	-0.0041(7)	0.0004(3)	-0.0023(7)	
			c,2	-0.0036(7)	0.0000(3)	0.0003(8)	
			s,3	-0.0025(7)	-0.0004(3)	-0.0064(9)	
H31[d]				0.921(4)	0.209(3)	-0.036(7)	0.149(16)
			s,1	0.000(5)	-0.008(4)	-0.015(8)	
			c,1	-0.005(5)	0.014(4)	-0.039(9)	
			s,2	-0.004(2)	0.002(2)	-0.009(4)	
			c,2	-0.001(2)	-0.005(2)	0.007(4)	
			s,3	-0.0013(12)	-0.0006(11)	-0.0004(16)	
			c,3	-0.0026(12)	0.0006(11)	-0.0071(16)	
H32[d]				1.081(4)	0.217(3)	-0.046(7)	0.149(16)
			s,1	0.000(4)	-0.009(4)	-0.018(8)	
			c,1	0.001(4)	0.001(4)	-0.011(8)	
			s,2	-0.0058(17)	0.0014(16)	-0.004(2)	
			c,2	0.0004(17)	0.0013(16)	0.001(2)	
			s,3	-0.0015(11)	0.0013(6)	-0.0080(12)	
			c,3	0.0013(11)	0.0026(6)	-0.0010(12)	
H33[d]				0.987(7)	0.2854(14)	-0.032(7)	0.149(16)
			s,1	0.003(8)	-0.0057(15)	-0.056(9)	
			c,1	0.026(8)	0.010(2)	-0.001(9)	
			s,2	-0.003(4)	0.0018(12)	0.001(4)	
			c,2	-0.014(4)	-0.0019(13)	-0.009(4)	
			s,3	-0.0020(19)	-0.0014(6)	-0.0053(19)	
			c,3	-0.0025(19)	0.0027(6)	-0.0087(19)	
N4[a]	0.7395(19)	0.5		0.9962(6)	0.0300(3)	0.4583(7)	0.0480(16)
			s,1	-0.0042(9)	-0.0014(5)	-0.0043(12)	
			c,1	0.0044(7)	-0.0007(3)	0.0021(8)	

[a] Crenel function

[b] Sawtooth function

[c] fixed in such a way that the discontinuity of the relevant atoms appears mutually with that for Ni atom

[d] restrained to form an ideal tetrahedron with central atom N3

Table 3 Final values of thermal parameters

	Wave	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd1		0.0283(6)	0.0237(3)	0.0221(3)	0	0.0006(3)	0
	o,1	0.0027(8)	0.0026(6)	0.0029(7)	0	0.0023(6)	0
	o,2	0	0	0	-0.0019(3)	0	0.0021(3)
	o,3	0	0	0	0.0055(7)	0	-0.0046(8)
	o,4	-0.0159(15)	0.0058(15)	-0.0008(18)	0	0.0005(11)	0
Cd2		0.0253(3)	0.0415(4)	0.0434(4)	0	-0.0008(2)	0
	o,1	0.0017(5)	0.0122(7)	0.0144(7)	0	-0.0014(4)	0
	o,2	0	0	0	0.0032(3)	0	-0.0186(4)
	o,3	0	0	0	0.0023(4)	0	-0.0103(6)
	o,4	-0.0035(9)	0.0148(12)	0.0007(11)	0	-0.0017(7)	0
Ni		0.0195(3)	0.0215(3)	0.0350(3)	0	0.0007(2)	0
	s,1	-0.0027(5)	-0.0007(4)	-0.0003(5)	0	-0.0004(4)	0
	c,1	0	0	0	-0.0021(3)	0	0.0015(3)
C1		0.0249(14)	0.0247(15)	0.0350(17)	0.0026(12)	-0.0009(13)	-0.0001(12)
N1		0.0316(14)	0.0337(16)	0.0461(18)	-0.0038(12)	0.0002(12)	0.0000(12)
C2		0.0272(17)	0.0325(17)	0.0337(18)	-0.0003(13)	0.0004(13)	-0.0006(12)
N2		0.0404(17)	0.045(2)	0.0507(19)	0.0115(15)	0.0001(14)	0.0012(15)
N4		0.050(3)	0.047(2)	0.047(3)	-0.0017(19)	0.001(2)	0.0165(19)
N3		0.0392(17)	0.0393(15)	0.0358(16)	0.0007(12)	0.0003(13)	0.0026(12)