M Miscellaneous crystals

No. M29 $H_2NCONHNH_2 \cdot HCl$, Semicarbazide hydrochloride

(M = 111.53; [D: 117.57])

1a Dielectric anomaly in $H_2NCONHNH_2 \cdot HCl$ was observed and the possibility of ferroelectric phase transition was mentioned by Rocaries and Boldrini in 1972. 72Roc

b

phase	IV [a])	III [a])	II [a])	I [a])
state			(F) [a])	P [a])
crystal system				orthorhombic [b])
space group				$P2_12_12_1 - D_2^4$ [b])
Θ [°C]		–230 [a])	19 [a])	21 [a])

[a]) 72Roc
[b]) 60Joh, 65Nar

Chemical decomposition and polymerization begin at about 30 °C. 72Roc
ρ = 1.594 · 10^3 kg m^{-3}, ρ_X = 1.592 · 10^3 kg m^{-3} at RT. 71Bol
ρ_X = 1.598 · 10^3 kg m^{-3} [D: 1.699 · 10^3 kg m^{-3}] at RT. 87Rou, 88Rou
Colorless. 65Nar

2a Crystal growth: slow evaporation of saturated aqueous solution. 76Faw
Solubility: see 71Bol

b Crystal form: prism elongated along [001]. 65Nar

3a Unit cell parameters at RT (phase I):
a = 7.545(1) Å, b = 13.215(3) Å, c = 4.668(1) Å. 71Bol
a = 7.53(1) Å, b = 13.18(2) Å, c = 4.67(1) Å 87Rou, 88Rou
[D: a = 7.55(1) Å, b = 13.21(2) Å, c = 4.68(1) Å].

b Z = 4 in phase I. 65Nar
Crystal structure: Table M29-001, Table M29-002, Table M29-003; Fig. M29-001, Fig. M29-002; see also 60Joh, 65Nar

5a Dielectric constant: Fig. M29-003.
$\kappa_{(110)} = C/(T - \Theta_p)$, $T > \Theta_p$ where $C = 7.2 \cdot 10^3$ K, Θ_p = 21 °C. 72Roc

9a Infrared spectra above 1.2 · 10^{13} Hz (400 cm^{-1}): see 78Sri

10a Raman scattering: Fig. M29-004.

14b X-ray diffuse scattering: see 72Roc

Table M29-001. $H_2NCONHNH_2 \cdot HCl$. Fractional coordinates at $T = 298$ K (phase I) [87Rou].

	x	*y*	*z*
Cl	0.2544(2)	0.1399(1)	0.9646(4)
O	0.7574(4)	0.0873(3)	0.8218(6)
N1	0.9276(3)	0.1608(2)	0.4795(7)
N2	0.6330(3)	0.1326(2)	0.39639(6)
N3	0.4914(3)	0.0659(2)	0.4576(6)
C	0.7756(3)	0.1251(2)	0.5813(6)
H1	1.0303(2)	0.1669(5)	0.6152(6)
H2	0.9344(2)	0.1917(7)	0.2874(1)
H3	0.6592(9)	0.1346(5)	0.1823(8)
H4	0.4319(9)	0.0836(5)	0.6550(6)
H5	0.3970(1)	0.0782(6)	0.3009(2)
H6	0.53489(9)	–0.0086(5)	0.4547(2)

Table M29-002. $D_2NCONDND_2 \cdot DCl$. Fractional coordinates and isotropic temperature parameters at $T = 298$ K (phase I) [88Rou]. B_{eq} is defined as $B_{eq} = (1/3)\Sigma_i\Sigma_j a_i a_j b_{ij}$, where b_{ij} is defined by Eq. (b) in Introduction.

	x	*y*	*z*	B_{eq} [Å^2]
Cl	0.2544(3)	0.1398(2)	0.9647(6)	2.5(1)
O	0.7565(5)	0.0877(3)	0.8205(9)	2.0(2)
N1	0.9277(5)	0.1608(3)	0.4792(9)	2.9(1)
N2	0.6328(4)	0.1329(2)	0.3969(7)	1.9(1)
N3	0.4910(4)	0.0660(2)	0.4584(7)	2.1(1)
C	0.7754(4)	0.1248(3)	0.5802(7)	1.4(1)
D1	0.0329(1)	0.1635(5)	0.5918(1)	5.9(8)
D2	0.9449(7)	0.1898(4)	0.2958(8)	6.4(11)
D3	0.6563(7)	0.1372(3)	0.1808(4)	5.3(10)
D4	0.4219(4)	0.0797(8)	0.6545(2)	5.7(14)
D5	0.3996(4)	0.0794(7)	0.3122(7)	5.5(11)
D6	0.5409(5)	–0.0165(1)	0.4838(8)	6.0(14)

Table M29-003. $H_2NCONHNH_2 \cdot HCl$, $D_2NCONDND_2 \cdot DCl$. Interatomic distances [Å], bond angles [°] and hydrogen bond geometry [Å, °] at $T = 298$ K (phase I) [88Rou].

	$D_2NCONDND_2 \cdot DCl$	$H_2NCONHNH_2 \cdot HCl$
Bond lengths [Å]		
N1–C	1.329(6)	1.326(4)
C–N2	1.380(5)	1.382(4)
C–O	1.236(6)	1.234(4)
N2–N3	1.417(4)	1.412(3)
Cl–H1	2.437(1)	2.375(8)
N1–H1	0.952(1)	1.003(10)
N1–H2	0.951(8)	0.987(11)
N2–C	1.380(5)	1.382(4)
N2–H3	1.029(6)	1.020(10)
N3–H6	1.160(8)	1.036(9)
N3–H4	1.071(1)	1.051(9)
N3–H5	0.988(3)	1.033(11)
Bond angles [°]		
N2–N3–H4	115.9(7)	111.2(4)
N2–N3–H5	101.0(0)	106.1(4)
N2–N3–H6	111.2(6)	110.4(4)
H4–N3–H5	102.9(4)	107.1(5)
H4–N3–H6	103.2(2)	110.9(6)
H5–N3–H6	117.7(2)	110.9(6)
N3–N2–C	114.5(3)	114.5(2)
C–N2–H3	118.8(3)	117.7(4)
N2–C–N1	115.2(4)	114.9(3)
N2–C–O	120.4(4)	129.7(3)
N1–C–O	124.3(4)	124.4(3)
C–N1–H2	125.6(1)	121.2(5)
C-N1–H1	122.6(1)	117.8(5)
H1–N1–H2	111.7(4)	120.1(7)
N3–N2–H3	125.7(4)	111.1(4)

Hydrogen-bond geometry [Å, °]

X–H…*Y*		*X*–H	H…*Y*	*X*–*Y*	*X*–H…*Y*
N1–H1...Cl	*a*	0.952(1)	2.437(4)	3.363(7)	164.1(27)
	b	1.003(1)	2.375(8)	3.356(8)	166.1(5)
N1–H2...Cl	*a*	0.951(8)	2.879(4)	3.363(9)	128.4(37)
	b	0.987(11)	2.856(10)	3.356(8)	132.1(6)
N2–H3...O	*a*	1.029(6)	1.965(4)	2.272(8)	153.3(57)
	b	1.020(10)	1.946(11)	2.276(9)	156.6(6)
N3–H4...Cl	*a*	1.071(1)	2.115(4)	3.123(7)	163.2(31)
	b	1.051(9)	2.106(9)	3.121(9)	162.1(5)
N3–H5...Cl	*a*	0.988(3)	2.117(6)	3.123(8)	164.0(42)
	b	1.033(11)	2.070(10)	3.121(9)	163.1(6)
N3–H6...O	*a*	1.066(8)	2.028(7)	2.640(8)	131.9(6)
	b	1.036(9)	1.978(9)	2.643(7)	138.7(5)

Notes: (*a*) $H_2NCONHNH_2 \cdot HCl$
(*b*) $D_2NCONDND_2 \cdot DCl$

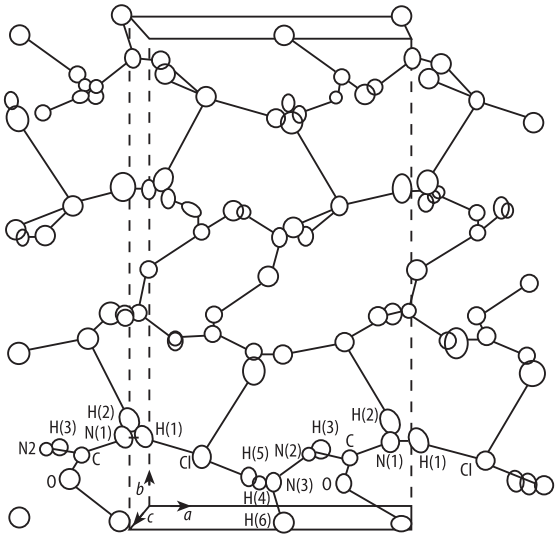

Fig. M29-001. $H_2NCONHNH_2 \cdot HCl$. Atomic arrangements in the unit cell [87Rou].

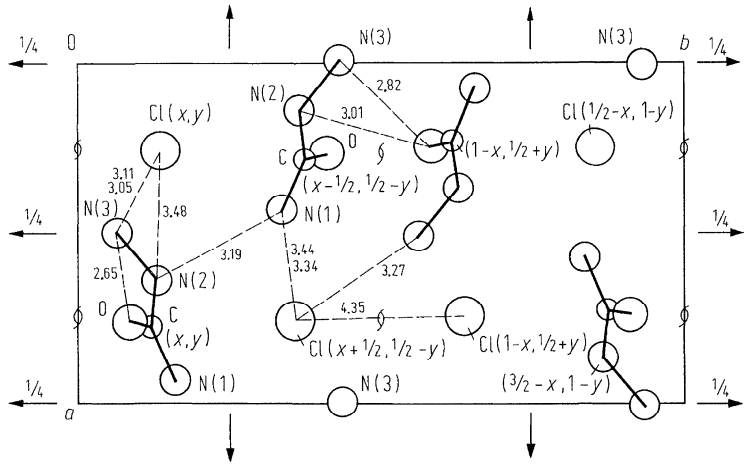

Fig. M29-002. $H_2NCONHNH_2 \cdot HCl$. Crystal structure [65Nar]. Projection on (001). Interatomic distances [Å] are indicated.

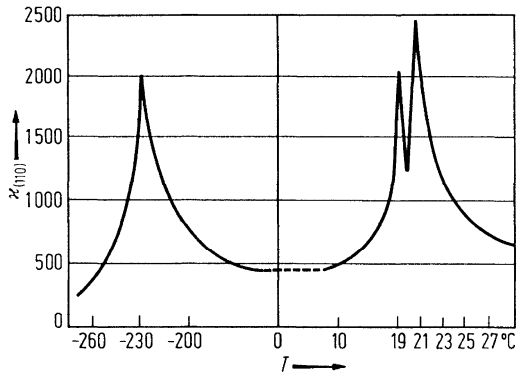

Fig. M29-003. $H_2NCONHNH_2 \cdot HCl$. $\varkappa_{(110)}$ vs. T [72Roc].

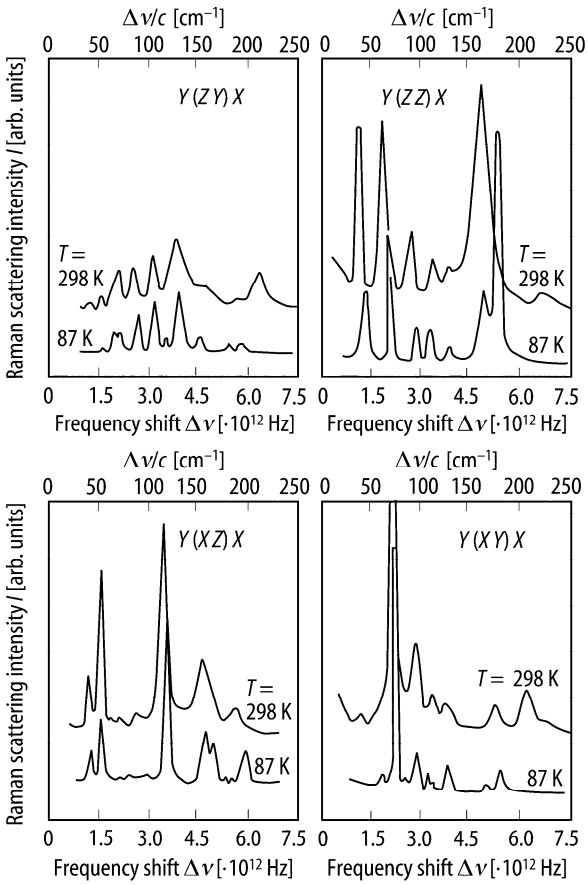

Fig. M29-004. $H_2NCONHNH_2 \cdot HCl$. I vs. $\Delta\nu$ [76Faw]. Parameter: T. I: Raman scattering intensities for different scattering geometries.

References

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