

# The Crystal Structure of $N^1$ -Isopropyl-2-methyl-1,2-propanediammonium Malate

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The title compound crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in a cell of dimensions  $a=7.685(2)$  Å,  $b=9.122(2)$  Å,  $c=11.432(2)$  Å,  $\alpha=69.13(2)^\circ$ ,  $\beta=104.52(2)^\circ$  and  $\gamma=112.31(2)^\circ$ . The structure was solved by direct and Fourier techniques and refined by full-matrix least-squares calculations to  $R=0.090$  for 1683 independent reflections. The structure consists of  $(C_7H_{20}N_2)^{2+}$  cations and  $(C_4H_4O_5)^{2-}$  anions which form a hydrogen bonded network. The amine conformation is synclinal with N–N distance of  $3.139(8)$  Å and torsion angle N1–C1–C2–N2 of  $73.7(5)^\circ$  and the malate ion conformation is antiperiplanar with a torsion angle C8–C9–C10–C11 of  $178.3(5)^\circ$ .

Coordination compounds formed by different amines and carboxylate ions with transition metal ions are being widely investigated in this laboratory. During the crystallization of *bis*( $N^1$ -isopropyl-2-methyl-1,2-propanediamine)malatocopper(II) dihydrate-methanol<sup>1</sup> and *catena*-( $N^1$ -isopropyl-2-methyl-1,2-propanediamine)- $\mu$ -(malato-*O*, *O'*:*O''*)copper(II) pentahydrate,<sup>2</sup> colourless crystals of the presently investigated compound  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium malate were formed.

The molecular structure of the compound was determined to investigate the conformations of the protonated amine and the malate ions. The corresponding amine salts have shown that the conformation of uncoordinated ethylenediamine is either synclinal<sup>3,4</sup> or antiperiplanar.<sup>5–8</sup> The malate ion conformation, like succinate and tartrate ions, is mostly antiperiplanar, when uncoordinated<sup>4–7</sup> or when mono- or bidentately coordinated,<sup>1,2,9–10</sup> but a synclinal conformation has been found as well.<sup>11</sup> In tridentate coordination to the same cation the malate ion conformation can also be synclinal owing to the chelation.<sup>12–14</sup>

## EXPERIMENTAL

*Preparation of the crystals.* Ethanol solution of  $N^1$ -isopropyl-2-methyl-1,2-propanediamine (Aldrich Chemical Co. Inc.) and excess of a salt prepared from DL-lactic acid (Riedel de-Haen) and copper(II) carbonate (J.T. Baker) were stirred for several days and the excess salt filtered off. During slow evaporation of the filtrate solution colourless crystals formed amongst two different kinds of blue crystals. A well formed crystal ( $0.3 \times 0.4 \times 0.4$  mm) was selected for single crystal X-ray measurement.

*Unit cell determination.* Unit cell determination and intensity data collection were carried out on a Nicolet P3 four-circle diffractometer equipped with a Nova 3 computer and XTL-program system. Radiation was graphite monochromatized  $MoK_\alpha$  ( $\lambda=0.71069$  Å).

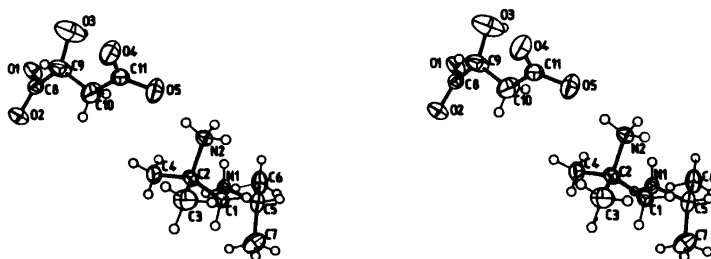


Fig. 1. ORTEP drawing with 50 % probability ellipsoids for non-hydrogen atoms of  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium malate.

Cell parameters were obtained by reading seven reflections on the film and rapidly collecting from the thus fixed cell a short run of intensity data with  $15^\circ > 2\theta > 25^\circ$ . From the recorded reflections, 25 were selected for the least squares refinement of cell dimensions. Crystal data:  $a=7.685(2)$  Å,  $b=9.122(2)$  Å,  $c=11.4323(2)$  Å,  $\alpha=69.13(2)^\circ$ ,  $\beta=104.52(2)^\circ$ ,  $\gamma=112.31(2)^\circ$ ,  $V=686.6(3)$  Å<sup>3</sup>,  $Z=2$ ,  $M=264.40$ ,  $D_c=1.283$  g cm<sup>-3</sup>, space group  $P1$ ,  $\mu(\text{MoK}\alpha)=1.1$  cm<sup>-1</sup>.

**Data collection.** Intensity data were collected at room temperature ( $5^\circ < 2\theta < 50^\circ$ ) with variable speed ( $2.0\text{--}29.3$  °min<sup>-1</sup>)  $\omega$ -scan technique. A total of 2423 reflections were measured, of which 1683 had  $I > 2\sigma(I)$ , where  $\sigma$  is the standard deviation estimated from counting statistics. These were regarded as observed and used in the structure refinement.

The data were corrected for Lorentz and polarization factors but not for absorption due to the small variation of intensities during the  $\phi$ -axis rotation.

**Structure determination.** The structure was solved by direct methods with the MULTAN 80<sup>15</sup> program and further refinement and other structural calculations were done with the X-RAY 76<sup>16</sup> program. Scattering factors were those contained in the program systems. Refinement done by minimizing the function  $\sum(|F_o| - |F_c|)^2$  using unit weights and isotropic temperature factors converged to the  $R$  value of 0.132 ( $R = \sum||F_o| - |F_c|| / \sum|F_o|$ ). Subsequent difference Fourier syntheses with anisotropic thermal parameters revealed all hydrogen atoms of the amine. These were included in the refinement for two cycles with isotropic thermal parameters while the hydrogen atoms of the malate ion were positioned at the calculated sites with a tetrahedral geometry, with the distance of 1.0 Å and fixed ( $U_{\text{iso}}=0.07$  Å<sup>2</sup>) thermal parameters. H(O3) was located in the middle of a broad electron density maxima. All hydrogen atom parameters were then fixed and three full-matrix refinement cycles gave the final  $R$  value of 0.090. The average and maximum shift/error ratios in the last cycle were 0.0065 and 0.045, respectively. Lists of structure factors and anisotropic thermal parameters are obtainable from the author.

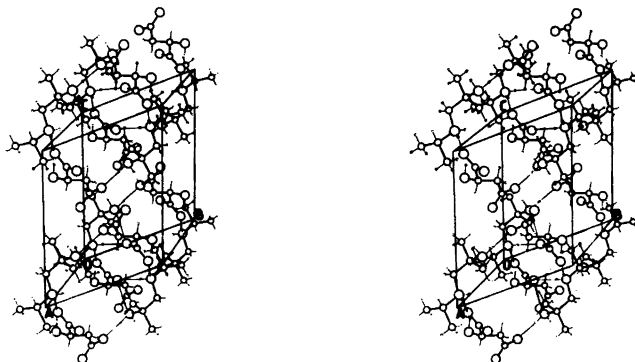


Fig. 2. PLUTO drawing showing the molecular packing of  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium malate with some hydrogen bonds.

**Table 1.** Fractional atomic coordinates with estimated standard deviations in parentheses and equivalent isotropic thermal parameters of the form  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_j^*$  ( $\times 10^2$ ) for *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediammonium malate.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N1	0.5029(6)	0.2438(5)	0.1849(4)	2.8
N2	0.4593(6)	0.4256(5)	0.3577(4)	3.1
O1	-0.2033(5)	0.8197(5)	0.0109(4)	4.5
O2	-0.3581(5)	0.5872(5)	0.1421(4)	4.4
O3	0.0457(8)	0.9272(6)	0.1959(5)	8.7
O4	0.1602(7)	0.7422(6)	0.4692(4)	6.1
O5	0.3015(6)	0.6048(6)	0.4237(4)	5.4
C1	0.4369(7)	0.1729(6)	0.3122(5)	2.9
C2	0.3260(7)	0.2651(7)	0.3365(5)	3.1
C3	0.2420(10)	0.1598(8)	0.4586(7)	5.3
C4	0.1765(8)	0.3049(8)	0.2270(6)	4.7
C5	0.6447(8)	0.1733(7)	0.1730(5)	3.7
C6	0.7314(8)	0.2806(9)	0.0518(6)	4.9
C7	0.5843(10)	-0.0073(8)	0.1760(6)	5.3
C8	-0.2209(7)	0.7195(7)	0.1169(5)	3.2
C9	-0.0731(9)	0.7610(7)	0.2273(6)	5.4
C10	0.0256(10)	0.6397(9)	0.2894(7)	6.7
C11	0.1725(8)	0.6669(7)	0.4034(5)	3.7

**Table 2.** Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediammonium malate.

N1-C1	1.498(7)	C1-N1-C5	113.6(4)	C8-O1	1.233(6)	O1-C8-O2	124.6(5)
N1-C5	1.513(9)	N1-C1-C2	114.9(4)	C8-O2	1.261(6)	O1-C8-C9	118.4(4)
N2-C2	1.497(7)	N1-C5-C6	108.1(5)	C11-O4	1.225(10)	O4-C11-O5	124.2(5)
C1-C2	1.530(10)	N1-C5-C7	110.0(5)	C11-O5	1.255(9)	O4-C11-C10	121.1(7)
C2-C3	1.521(9)	N2-C2-C1	109.6(4)	C9-O3	1.410(7)	C8-C9-C10	112.9(6)
C2-C4	1.513(8)	N2-C2-C3	107.2(5)	C8-C9	1.524(8)	C8-C9-O3	112.4(5)
C5-C6	1.519(9)	N2-C2-C4	107.5(4)	C9-C10	1.453(11)	C10-C9-O3	114.9(6)
C5-C7	1.524(8)	C3-C2-C4	112.4(5)	C10-C11	1.522(9)	C9-C10-C11	117.1(7)
		C6-C5-C7	112.9(6)				

**Table 3.** Hydrogen bond lengths (Å) and angles (°) with estimated standard deviations in parentheses when refined for *N*<sup>1</sup>-isopropyl-2-methyl-1,2-propanediammonium malate.<sup>a</sup>

A	H	B	sym	A-H	B-H	A-B	LAHB
N1	H	O1	i	0.81	2.02	2.824(5)	173
N1	H'	O2	ii	0.86	1.94	2.797(6)	175
N2	H	O2	ii	0.94	1.90	2.791(6)	158
N2	H'	O5	iii	1.01	1.71	2.701(6)	166
N2	H''	O5		0.97	1.78	2.749(9)	175
O3	H	O1	iv	0.97	2.16	2.794(6)	129

<sup>a</sup> Symmetry codes refer to equivalent positions: i: -*x*, 1-*y*, -*z*. ii: *x*+1, *y*, *z*. iii: 1-*x*, 1-*y*, 1-*z*. iv: -*x*, 2-*x*, -*z*.

Table 4. Anisotropic temperature parameters ( $\times 10^2$ ) with estimated standard deviations in parentheses for  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium malate.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
N1	2.5(2)	3.2(2)	2.6(2)	1.3(2)	-0.4(2)	-1.1(2)
N2	3.0(2)	3.2(2)	3.0(2)	0.6(2)	0.1(2)	-1.2(2)
O1	3.5(2)	4.4(2)	3.5(2)	0.1(2)	-0.0(2)	-0.5(2)
O2	3.9(2)	3.6(2)	4.0(2)	-0.2(2)	0.4(2)	-0.8(2)
O3	9.7(4)	5.6(3)	6.6(4)	-0.6(3)	-0.6(3)	-1.3(3)
O4	6.2(3)	7.6(3)	6.6(3)	4.1(3)	-1.7(2)	-4.0(3)
O5	5.2(3)	7.3(3)	5.5(3)	4.0(3)	-1.5(2)	-3.4(2)
C1	2.7(3)	2.8(3)	2.7(3)	0.7(2)	0.0(2)	-0.7(2)
C2	2.4(3)	3.1(3)	3.6(3)	0.4(2)	0.1(2)	-1.5(2)
C3	4.5(4)	6.5(5)	1.0(3)	3.2(3)	-1.7(3)	-1.7(3)
C4	3.0(3)	5.0(4)	7.0(4)	1.7(3)	-0.9(3)	-3.5(3)
C5	3.3(3)	5.4(4)	3.2(3)	2.5(3)	-0.1(2)	-1.3(3)
C6	3.9(3)	7.3(5)	4.0(3)	2.5(3)	0.9(3)	-1.3(3)
C7	7.6(5)	5.2(4)	4.5(4)	3.4(4)	1.2(3)	-1.3(3)
C8	3.3(3)	2.9(3)	3.3(3)	1.1(3)	0.0(2)	-1.0(3)
C9	5.3(4)	3.0(3)	5.0(4)	0.3(3)	-0.8(3)	-0.2(3)
C10	6.2(5)	5.8(5)	8.1(5)	3.4(4)	-3.7(4)	-3.8(4)
C11	3.7(3)	2.9(3)	3.9(3)	1.1(3)	-0.3(3)	-1.0(3)

## RESULTS AND DISCUSSION

The structure consists of separate  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium cations and malate anions held together by hydrogen bonds. Atomic labelling is seen in Fig. 1 and fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1. Bond lengths and angles are given in Table 2. A PLUTO<sup>17</sup> drawing shows the molecular packing in Fig. 1.

*The  $N^1$ -isopropyl-2-methyl-1,2-propanediammonium ion.* The torsion angle N1-C1-C2-N2 of  $-73.7(5)^\circ$  is comparable to those of  $71.4(2)$  and  $-71^\circ$  found for ethylenediamine in Refs. 3 and 4, respectively. Bond lengths and angles are normal. Observed N-H bond lengths vary between 0.81 and 1.01 Å and C-H bond lengths between 0.78 and 1.10 Å with means 0.92 and 0.98 Å, respectively.

*The malate ion.* Bond lengths and angles are normal. The conformation of the ion is similar to that of most other dicarboxylates with four aliphatic carbon atoms lying in a plane. Both carboxylic groups are nearly planar and the oxygen atom of the  $\alpha$ -hydroxy group deviates 0.316 Å and H(O3)  $-0.38$  Å from the plane determined by the adjacent carboxylic group. The torsion angle C8-C9-C10-C11 is  $178.3(5)^\circ$ . The dihedral angles between the least-squares planes through atoms O1, O2, C8, C9 and O3 (plane 1), atoms O4, O5, C10 and C11 (plane 2) and C8, C9, C10 and C11 (plane 3) are (planes 1,2)  $89.0^\circ$ , (planes 1,3)  $61.7^\circ$  and (planes 2,3)  $27.4^\circ$ . The corresponding angles in malates crystallized from the same solution are  $82.5$ ,  $68.5$  and  $29.3^\circ$  (Ref. 1) and  $72.7$ ,  $52.5$  and  $54.9^\circ$  (Ref. 2.).

*Molecular packing.* The structure forms a three-dimensional hydrogen bonded network. The hydrogen atoms of the protonated nitrogen atoms and the hydrogen atom of the hydroxyl group each form a two-centered hydrogen bond to a carboxylic oxygen atom. Two different hydrogen atoms are bonded to each oxygen atoms. The hydrogen bond system is described in Table 3. The bond O3-H-O1 deviates substantially from the usual approximate linearity.

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