Crystal data for bis(1,10-phenanthroline)-hydrobromic acid 2·5 hydrate, \((C_{12}H_{8}N_2)_2\cdot HBr\cdot 2·5\ H_2O\). By M. Montagu-Bourin, P. Levillain and R. Ceolin, Laboratoires de Chimie Minérale et de Chimie Analytique, Faculté de Pharmacie, 37032 Tours, France and G. Thevenet and C. Souleau, Laboratoire de Chimie Minérale II, Faculté de Pharmacie, 92290 Chatenay-Malabry, France

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Abstract

Powder data for bis(1,10-phenanthroline)-hydrobromic acid 2·5 hydrate are reported. Crystals are monoclinic, \(Pb\) or \(P2_1/b\), with \(a = 12.37\ (2), b = 26.41\ (4), c = 7.496\ (8) \(\text{Å}, \gamma = 115.2\ (1)^\circ\), \(U = 2216\ \text{Å}^3\). \(M = 486.37\). \(Z = 4\). \(D_{\text{m}} = 1.43\ (3)\), \(D_\text{a} = 1.46\ Mg\ m^{-3}\).

Origin of specimen

The molar solubility \(S\) of 1,10-phenanthroline (phen) in water at 298 K, as a function of the HBr concentration, \(C\), in a saturated solution may be expressed by \(S = AC + S_0\). We have found \(A = 2.234\) and \(S_0 = 0.0154\) with \(r^2 = 0.995\). The slope \(A\), close to 2 as previously reported for bis(1,10-phenanthroline)-HCl (Thevenet, Souleau, Montagu-Bourin & Ceolin, 1980), could indicate the existence of a compound with a 2:1 ratio between phen and HBr. White needles were grown from an aqueous solution prepared with this ratio. Analysis gave the following results:

<table>
<thead>
<tr>
<th>C%</th>
<th>H%</th>
<th>N%</th>
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<tbody>
<tr>
<td>59.27</td>
<td>4.56</td>
<td>11.52</td>
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Theoretical:

<table>
<thead>
<tr>
<th>C%</th>
<th>H%</th>
<th>N%</th>
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<tbody>
<tr>
<td>59.11</td>
<td>4.46</td>
<td>11.66</td>
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Crystal geometry

The monoclinic space group, \(Pb\) or \(P2_1/b\) (systematic extinctions: \(hk0\) absent for \(k\) odd) and the cell parameters were determined from oscillation and Weissenberg photographs with Cu K\(\alpha\) radiation (\(\lambda = 1.5418\ \text{Å}\)).

Powder data

The powder data reported in Table 1 were obtained with a 114.6 mm diameter Guinier camera \([\lambda(Cu K\alpha) = 1.54051\ \text{Å}]\). Intensities were estimated visually.

Crystal physics

DTA curves show that the water is evolved in three steps during the spontaneous rehydration at 297 K of the quenched anhydrous compound which melts congruently at 479 K. This result was confirmed by measuring the weight variation during the spontaneous rehydration at 297 K of the quenched anhydrous compound which melts congruently at 479 K.

Comparison with other results

\((\text{phen})_2\cdot HBr\cdot 2·5\ H_2O\) (\(A\)) differs from \((\text{phen})_2\cdot \text{HCl}\cdot 2H_2O\) (\(B\)) (Thevenet et al., 1980) by the hydration and the parameter \(c\) \((c_A > 2c_B)\), though they remain in the same translation symmetry. It was not possible to determine if they belong to the same point symmetry and therefore to the same space group.

The experimental difference \(\Delta U = U_A - 2U_B\) is 60 Å\(^3\). This value may be connected both to the nature of the anion and to the hydration since the calculated \(\Delta U\) is 57 Å\(^3\), assuming a van der Waals volume of 30 Å\(^3\) for \(2\ H_2O\) and a difference of 27 Å\(^3\) between the volumes of the four halogen anions in the largest cell \((U_{\text{Cl}} = 24.4\ Å^3, U_{\text{Br}} = 31.1\ Å^3)\).

This work was undertaken to obtain the configuration of the \((\text{phen})_2^2 H^+\) cation isolated by Marzocchi & Paoletti (1968) and Rund & Keller (1970) as a perchlorate salt. Unfortunately, since the crystals were needles of poor quality, it was not possible to carry out a complete structural analysis.

References