

# Structure of Alkali Metal Hydroxamates and their Lossen Rearrangement

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Neutral alkali metal salts of benzhydroxamic acids described in the literature are in fact acid salts; neutral salts rearrange to *N,N'*-diarylureas under mild conditions.

Hydroxamic acids **1** are both weak acids and bases.<sup>1</sup> During deprotonation they can behave either as O-acids or as N-acids, yielding the anions **2** or **3**, respectively.<sup>1,5,8</sup> The existence of the third possible structure of the anion, **4**, has never been proven.

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|---|--|
| <b>1</b> RC(O)NHOH  | <b>a</b> R = Ph, M = K   |
| <b>2</b> RC(O)NHO <sup>-</sup> M <sup>+</sup>                             | <b>b</b> R = 4-ClC <sub>6</sub> H <sub>4</sub> , M = K               |
| <b>3</b> [RC(O)N <sup>-</sup> OHM <sup>+</sup> ↔ RC(O <sup>-</sup> )=NOH] | <b>c</b> R = 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> , M = K |
| <b>4</b> RC(OH)=NO <sup>-</sup> M <sup>+</sup>                            | <b>d</b> R = Ph, M = Li  |
| <b>5</b> RC(O)NHO <sup>-</sup> M <sup>+</sup> · RC(O)NHOH                 | <b>e</b> R = Ph, M = K   |

The long-standing controversy about the correct structure of the anion (or about the position of the equilibrium **2** ↔ **3**) is the consequence of comparing different acids under different conditions.<sup>8–11</sup> The results were recently summarized<sup>8</sup> as follows. While the N-anion **3** prevails in the gas phase<sup>2,5</sup> or still more so in the presence of electron-attracting substituents, unsubstituted acids in polar solvents may yield considerable amounts<sup>8,11</sup> of the O-anion **2**. In the solid state, only two simple alkali metal salts have been investigated and both have the structure of the O-anion, e.g. **5d**.<sup>13</sup>

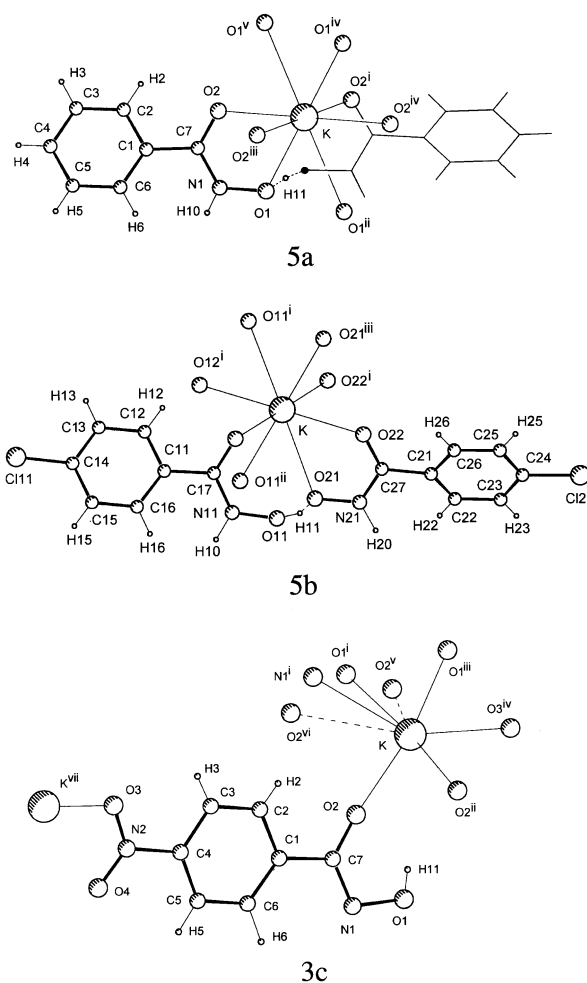
We have established by X-ray analysis that 4-nitrobenzhydroxamic acid forms the N-salt **3c** while benzhydroxamic acid and 4-chlorobenzhydroxamic acid give acid salts **5a** and **5b**.

**5a**, KH(C<sub>6</sub>H<sub>5</sub>CONHO)<sub>2</sub>, monoclinic, *C2/c*, *a* = 32.982(3), *b* = 5.0784(5), *c* = 8.2664(4) Å, β = 104.041(7)°, *D*<sub>c</sub> = 1.545 g cm<sup>-3</sup> for *Z* = 4, direct methods (SHELXS86S)<sup>32</sup> and full-matrix least-squares (SHELXL93),<sup>33</sup> *R* = 0.036 for 1049 observed reflections, average e.s.d.s of bond lengths and angles between C, N and O atoms are 0.002 Å and 0.2°, respectively.

**5b**, ClC<sub>6</sub>H<sub>4</sub>CONHOK · ClC<sub>6</sub>H<sub>4</sub>CONHOH, orthorhombic, *Pna*2<sub>1</sub>, *a* = 8.1839(7), *b* = 5.0741(4), *c* = 38.203(2) Å, *D*<sub>c</sub> = 1.596 g cm<sup>-3</sup> for *Z* = 4, *R* = 0.047 for 1256 reflections; data treatment as above, average e.s.d.s 0.011 Å and 0.8°.

**3c**, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CONKOH, monoclinic, *Pc*, *a* = 9.9219(6), *b* = 3.9317(3), *c* = 11.5601(7) Å, β = 93.608(5)°, *Z* = 2, *D*<sub>c</sub> = 1.625 g cm<sup>-3</sup> for *Z* = 2, for 925 observed reflections; data treatment as above, *R* = 0.028, average e.s.d.s 0.005 Å and 0.4°.

The solid state structures conform with the behaviour of these acids in solution<sup>8</sup> if the crystalline phase is viewed as a very strongly polar medium: the O-anion **2** is present in **5**, not only from **1a** but even from the acid **1b** which is of medium strength. The stabilization of the N-anions in stronger benzhydroxamic acids was explained by the electron-attracting ability of the substituent, affecting the adjacent NH proton more effectively than the remote OH proton.<sup>8</sup> In the salts **5a,b** the geometry of the functional group is essentially unchanged compared with the free acids



**Fig. 1** Perspective view of molecules of potassium salts with atom labelling

**1**. In contrast, the C–N bond is shortened and the C=O bond lengthened in the anion **3c**, in agreement with the mesomeric formulae.

Numerous attempts to prepare neutral salts **2a** or **2b** were unsuccessful. Either acid salts **5a** or **5b** were obtained or Lossen rearrangement took place, yielding *N,N'*-diarylureas. The stability of **5** in the solid state is evidently supported by the coordination of eight oxygens around the potassium cation, involving both the carbonyl and hydroxylamino oxygens. In addition, the molecule of the acid is linked to the anion by a hydrogen bond between hydroxylamino oxygens. We believe that neutral potassium or sodium salts of acids **1**, **2** and of related derivatives have never been

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prepared; those reported in the literature<sup>23,24</sup> were certainly acid salts or the origin of the samples was not stated explicitly.<sup>14,15</sup> Of course, the composition of the salts used as intermediates in established syntheses of the acids has an influence on the yields reported.

Lossen rearrangement of **5** to the *N,N'*-diarylureas observed here is unique in terms of the mild conditions employed (yield up to 88% at room temperature). All reactions of hydroxamic acid derivatives in which the functional group rearranges from C- to N-bonded are classified as Lossen rearrangements, irrespective of the variety of isolated products.<sup>1,29</sup> In the generally assumed mechanism the electron sextet on nitrogen is essential. The narrow definition of Lossen rearrangement as the conversion of the salts of *N,O*-diacylhydroxylamines into *N,N'*-diarylureas has been proposed.<sup>29</sup> For the rearrangement of other derivatives, forcing conditions are needed: *e.g.* **1a** gives *N,N'*-diphenylurea when boiled in dioxan for 24 h.<sup>31</sup> As far as we are aware, the rearrangement of alkali metal salts of simple hydroxamic acids observed here is unprecedented.

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Techniques used: Single crystal X-ray diffraction

References: 34

Tables 1–10: Crystal structure data

Fig. 2: Crystal packing of **5a**, **5b** and **3c**

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