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## Supramolecular Chemistry

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### **A new carboxylic chelate ligand and its supramolecular complexes formed with sodium ions and alcohol molecules**

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## A new carboxylic chelate ligand and its supramolecular complexes formed with sodium ions and alcohol molecules

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The new hydrazone ligand **1**, featuring a 2-carboxy group at the aromatic ring and a trifluoromethyl structural modification in the pentane-2,4-dione moiety, has been synthesised via the *Japp–Klingemann* route. The compound is shown to form binuclear multicomponent chelate complexes (**2** and **3**) composed of two sodium ions, two charge equalising carboxylates of the hydrazone molecule, two more carboxylic hydrazones and two alcohol solvent molecules, with the latter being either EtOH or *n*-BuOH. X-ray crystal structures of the free hydrazone ligand as well as of the complexes have been studied. They demonstrate for the free ligand a ribbon-type aggregation of carboxylic dimers, while the isomorphous complexes possess a remarkable binuclear structure with the two sodium ions in a distorted octahedral coordination geometry of six oxygen atoms coming, at the equatorial and apical sites, from the hydrazone carbonyl groups and the hydroxyl of the solvent molecules, respectively. The hydrogen bonds owing to the alcohol molecules give rise to the stack formation of the supramolecular cluster. Weak intermolecular contacts involving the fluorine atoms also contribute to the crystalline packing in the case of both the free ligand and the complexes.

**Keywords:** chelate ligand; sodium coordination; alcohol supramolecular complexes; X-ray crystal structures; hydrogen bonds

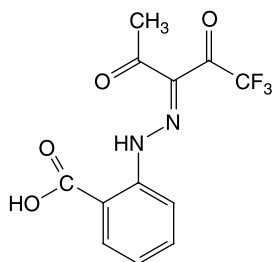
### Introduction

The binding and transport of the sodium and potassium metal ions are of vital importance to life (1). Naturally occurring substances, capable of performing these processes, are given by the well-known ionophores such as valinomycin and nonactin (2). The rapid development of the crown compounds (3), as an exemplary synthetic mimic, has presented us with an immense variety of macrocyclic ligands (4) that form complexes with alkali metal ions of different thermodynamics and kinetics (5), corresponding to their degree of preorganisation (6). In this connection, noncyclic analogues of the crown compounds, designated as podands (7), that form complexes with main group I metal ions, have also been prepared in a wide range (8, 9). Besides these noncyclic ligands of aprotic nature, the protic complexones are another important class of the ligands providing neutral chelate complexes of inner salt type with alkali and alkaline earth metal ions (7). Some of them are traditional tools in analytical chemistry (10). The others have been studied with regard to their biological activity (11–13) or specific coordination geometry (14, 15). Recent challenges arise from current topics of supramolecular chemistry (6) involving crystal engineering (16) and molecular recognition behaviour (17, 18),

aiming at the design of sorptive materials that may be used for compound storage (19, 20) or chemical sensing (21). Particular transition metal complexes, known as the MOF-type coordination polymers (22, 23), are currently a very active field of research in these respects, while corresponding complexes formed of main group metal ions, especially alkali and alkaline earth metal ions, are up for development.

In a previous paper (24), we reported on the complexes of 3-(arylhydrazono)pentane-2,4-diones with the transition metal ions copper(II) and nickel(II). Moreover, we found that fluorine substitution in the pentane-2,4-dione moiety of the hydrazone gave rise to a particular packing mode in the crystal structure (25), which could also have a favourable effect here. We now describe for the first time complexes of a respective hydrazone **1** with sodium ions, containing additional alcohol molecules in the coordination sphere, to yield an interesting new type of supramolecular aggregate structure. In terms of facts, the present complexes are composed of molecules of the hydrazone **1**, the carboxylate of **1**, sodium ions and ethanol (**2**) or *n*-butanol (**3**) solvent molecules in a stoichiometric ratio 2:2:2:2, respectively, considering the formed cluster unit (Scheme 1). The synthesis of the compounds (**1–3**) is presented and their X-ray crystal structures are discussed.

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- 1 (LH)  
 2  $[\text{Na}_2\text{L}_2(\text{LH})_2] \cdot 2 \text{ EtOH}$   
 3  $[\text{Na}_2\text{L}_2(\text{LH})_2] \cdot 2 n\text{-BuOH}$

Scheme 1. Compounds discussed.

## Results and discussion

### Synthesis of compounds

The free arylhydrazone ligand **1** was synthesised via the Japp–Klingemann reaction (26) between the diazonium salt of 2-aminobenzoic acid and 1,1,1-trifluoropentane-2,4-dione in a methanolic solution containing sodium acetate (27). The diazonium salt was prepared by the usual diazotation of 2-aminobenzoic acid (28). The complexes **2** and **3** were obtained by recrystallisation of crude **1** from ethanol and *n*-butanol, respectively, in the presence of sodium ions, coming from the reaction components.

### Structural study

The crystal data, experimental parameters and selected details of the refinement calculations are summarised in Table 1. The information regarding conformational features and possible non-covalent interactions in the crystal structures is presented in Tables 2–4. The molecular structures are depicted in Figures 1, 3 and 4, while packing illustrations are presented in Figures 2 and 5.

### Crystal structures of the free ligand (1)

The hydrazone **1** crystallises from toluene as yellow rods of the triclinic space group *P*-1. The molecular structure including the atom numbering scheme is presented in Figure 1. Being in conformity with the crystal structure analyses of the related compounds (24, 25, 29), the molecular structure of **1** shows the presence of an intramolecular six-membered hydrogen-bonded ring formed between the N-bound hydrogen H(2) and one of the oxygens of the pentane-2,4-dione fragment [ $\text{N}(2)\text{—H}(2)\cdots\text{O}(1)$  1.90 Å, 131.2°]. In addition, this hydrogen atom is bonded to O(3) of the carboxy substituent [ $\text{N}(2)\text{—H}(2)\cdots\text{O}(3)$  2.00 Å, 126.5°], giving rise to a bifurcated bonding situation for H(2). The fact that the oxygen of the  $\text{CH}_3\text{CO}$  moiety is used for strong intramolecular hydrogen bonding indicates the higher

Table 1. Crystal data, experimental parameters and selected details of the refinement calculations of compounds **1–3** (estimated standard deviations are in parentheses).

| Compound  | 1   | 2   | 3   |
|---|---|---|---|
| Formula unit  | $\text{C}_{12}\text{H}_9\text{F}_3\text{N}_2\text{O}_4$ | $\text{C}_{52}\text{H}_{44}\text{F}_{12}\text{N}_8\text{Na}_2\text{O}_{18}$ | $\text{C}_{56}\text{H}_{54}\text{F}_{12}\text{N}_8\text{Na}_2\text{O}_{18}$ |
| Formula weight  | 302.21  | 1342.93   | 1401.06   |
| Crystal system  | Triclinic   | Monoclinic  | Monoclinic  |
| Space group   | <i>P</i> -1   | <i>P</i> 2 <sub>1</sub> / <i>n</i>  | <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| Unit cell dimensions  |   |   |   |
| <i>a</i> (Å)  | 5.0637(2)   | 13.3812(9)  | 13.350(3)   |
| <i>b</i> (Å)  | 8.5278(4)   | 8.0093(6)   | 7.9930(2)   |
| <i>c</i> (Å)  | 14.596(1)   | 27.829(2)   | 28.931(6)   |
| $\alpha$ (°)  | 95.317(3)   | 90  | 90  |
| $\beta$ (°)   | 90.422(2)   | 97.126(3)   | 93.25(3)  |
| $\gamma$ (°)  | 106.144(2)  | 90  | 90  |
| <i>V</i> (Å <sup>3</sup> )  | 602.45(5)   | 2959.5(4)   | 3082.2(12)  |
| <i>Z</i>  | 2   | 2   | 4   |
| <i>D</i> <sub>c</sub> (m <sup>-3</sup> )  | 1.666   | 1.507   | 1.510   |
| Data collection   |   |   |   |
| Temperature (K)   | 93(2)   | 153(2)  | 93(2)   |
| No. of collected reflections within the $\theta$ -limit (°)                                 | 17252   | 30380   | 30443   |
| No. of unique reflections   | 3865  | 6522  | 6553  |
| <i>R</i> <sub>int</sub>   | 0.0379  | 0.0669  | 0.0671  |
| Refinement calculations full-matrix least-squares based on all <i>F</i> <sup>2</sup> values |   |   |   |
| No. of refined parameters   | 196   | 426   | 449   |
| No. of values used [ <i>I</i> > 2σ( <i>I</i> )]   | 2591  | 4243  | 3915  |
| <i>R</i> (= Σ Δ <i>F</i>  /Σ  <i>F</i> <sub>o</sub>  )                                      | 0.0432  | 0.0584  | 0.0494  |
| <i>wR</i> on <i>F</i> <sup>2</sup>  | 0.1334  | 0.1933  | 0.1745  |

Table 2. Selected structural parameters [distances (Å), angles (°)] involving the ligand molecules in compounds **1–3**.

| Atoms involved                               | <b>1</b>  | <b>2</b> (LH) | <b>2</b> (L) | <b>3</b> (LH) | <b>3</b> (L) |
|--|-----------|---------------|--------------|---------------|--------------|
| <b>Bond lengths</b>                          |           |               |              |               |              |
| N(1)—N(2)                                    | 1.303(3)  | 1.300(3)      | 1.290(3)     | 1.299(4)      | 1.299(4)     |
| N(1)—C(3)                                    | 1.322(3)  | 1.324(3)      | 1.327(3)     | 1.324(4)      | 1.338(4)     |
| N(2)—C(6)                                    | 1.411(2)  | 1.403(3)      | 1.417(3)     | 1.411(4)      | 1.414(4)     |
| C(2)—C(3)                                    | 1.484(2)  | 1.478(4)      | 1.467(4)     | 1.487(5)      | 1.472(4)     |
| C(3)—C(4)                                    | 1.464(2)  | 1.453(4)      | 1.461(4)     | 1.462(5)      | 1.463(5)     |
| C(2)—O(1)                                    | 1.230(2)  | 1.217(3)      | 1.461(4)     | 1.225(4)      | 1.223(4)     |
| C(4)—O(2)                                    | 1.211(2)  | 1.210(3)      | 1.206(3)     | 1.210(4)      | 1.211(4)     |
| C(7)—C(12)                                   | 1.479(2)  | 1.479(4)      | 1.519(3)     | 1.499(4)      | 1.508(4)     |
| <b>Bond angles</b>                           |           |               |              |               |              |
| C(3)—N(1)—N(2)                               | 121.6(1)  | 121.1(2)      | 121.7(2)     | 121.3(3)      | 121.0(3)     |
| N(1)—N(2)—C(6)                               | 118.7(1)  | 119.8(2)      | 119.5(2)     | 119.4(3)      | 119.7(3)     |
| N(1)—C(3)—C(2)                               | 124.8(1)  | 124.7(2)      | 124.7(2)     | 125.0(3)      | 124.1(3)     |
| N(1)—C(3)—C(4)                               | 112.3(1)  | 112.8(2)      | 112.7(2)     | 112.8(3)      | 113.2(3)     |
| C(2)—C(3)—C(4)                               | 122.9(1)  | 122.4(2)      | 122.6(2)     | 122.2(3)      | 122.7(3)     |
| C(3)—C(2)—O(1)                               | 118.5(1)  | 119.2(2)      | 118.4(2)     | 118.5(3)      | 119.6(3)     |
| C(3)—C(4)—O(2)                               | 125.6(1)  | 126.1(2)      | 125.9(3)     | 125.9(3)      | 125.2(3)     |
| <b>Torsion angles</b>                        |           |               |              |               |              |
| O(1)—C(2)—C(3)—N(1)                          | −4.6(2)   | −5.2(4)       | −0.17(4)     | −5.9(5)       | −3.4(5)      |
| C(2)—C(3)—N(1)—N(2)                          | 0.5(2)    | 1.1(3)        | 1.0(4)       | 0.1(5)        | 2.0(4)       |
| C(3)—N(1)—N(2)—C(6)                          | −175.7(1) | −180.0(2)     | −179.1(2)    | −178.8.2(3)   | −179.4(3)    |
| C(2)—C(3)—C(4)—O(2)                          | 13.8(2)   | 8.8(4)        | 2.7(5)       | 5.4(6)        | 2.6(5)       |
| <b>Dihedral angles</b>                       |           |               |              |               |              |
| mpla(1) <sup>a</sup> ···mpla(2) <sup>b</sup> | 7.24      | 4.98          | 11.37        | 3.00          | 7.51         |

<sup>a</sup>mpla(1): mean plane through the atoms C(6)—C(7)—C(8)—C(9)—C(10).<sup>b</sup>mpla(2): mean plane through the atoms H(2)—N(2)—N(1)—C(3)—C(2)—O(1).

acceptor ability compared to the CF<sub>3</sub>CO unit. The oxygen of this latter fragment is involved only in weak intermolecular hydrogen bonding. Two of the fluorine atoms of each molecule take part in molecular cross-linking by forming weak C—H···F and C—F···F contacts (30, 31) [H···F 2.69 Å; F···F 2.91(1) Å]. This may explain the distortion of the pentane-2,4-dione unit, which is reflected by the torsion angles that deviate significantly from the ideal values of 0 and 180° (Table 2).

Table 3. Bond lengths (Å) and angles (°) involving Na<sup>+</sup> in the complexes **2** and **3**.

|                     | <b>2</b> | <b>3</b> |
|---------------------|----------|----------|
| <b>Bond lengths</b> |          |          |
| Na(1)—Na(1')        | 3.402(2) | 3.346(2) |
| Na(1)—O(1)          | 2.341(2) | 2.344(2) |
| Na(1)—O(1A)         | 2.382(2) | 2.423(2) |
| Na(1)—O(3)          | 2.421(2) | 2.372(2) |
| Na(1)—O(3')         | 2.368(2) | 2.393(2) |
| Na(1)—O(3A)         | 2.284(2) | 2.284(2) |
| Na(1)—O(1GA)        | 2.463(2) | 2.291(2) |
| Na(1)—O(1G)         | 2.260(9) |          |
| <b>Bond angles</b>  |          |          |
| O(1GA)—Na(1)—O(3')  | 170.7(5) | 166.3(1) |
| O(1)—C(2)—O(3A)     | 163.6(1) | 161.0(1) |
| O(3)—C(4)—O(1A)     | 162.1(1) | 163.3(1) |

As displayed in Figure 2, in the crystal structure of **1**, molecules interact among each other by hydrogen bonding of their carboxylic acid groups [O(4)—H(4)···O(3) 1.81 Å, 174.5°], thus forming conventional centrosymmetric dimers. They are further linked by bifurcated C—H···O hydrogen bonds (32) [C(8)—H(8)···O(2) 2.58 Å, 121.7°, C(9)—H(9)···O(2) 2.53 Å, 123.2°], resulting in infinite supramolecular ribbons. Generally, the packing structure consists of 2D molecular sheets being linked among each other through C—H···F contacts.

#### Crystal structures of the sodium complexes **2** and **3**

Crystallisation of the aryl hydrazone **1** from ethanol or *n*-butanol in the presence of sodium ions from the crude product yields complexes of the composition [Na<sub>2</sub>L<sub>2</sub>(LH)<sub>2</sub>]<sub>2</sub>·2 ROH as yellow rods. For each of the two complexes, the asymmetric unit of the cell contains one half of the molecule, i.e. the complexes exhibit inversion symmetry. The structure of the Na<sup>+</sup>(LH)L<sup>−</sup> unit and the molecular structures of the complexes with the labelling of the relevant atoms are depicted in Figures 3 and 4, respectively. The space group symmetries (*P*2<sub>1</sub>/*n*) as well as the crystallographic parameters (Table 1) indicate that the structures of **2** and **3** are isomorphous. Hence, a detailed structural description can be confined to the crystal structure of **2**, being transferable to **3**.

Table 4. Structural parameters [distances (Å), angles (°)] of the non-covalent interactions in compounds **1**–**3**.

| Atoms involved<br>D—H···A | Symmetry                      | Distances |          |         | Angle<br>D—H···A |
|---------------------------|-------------------------------|-----------|----------|---------|------------------|
|                           |                               | D—H       | D···A    | H···A   |                  |
| <b>(1)</b>                |                               |           |          |         |                  |
| N(2)—H(2)···O(1)          | $x, y, z$                     | 0.92      | 2.598(2) | 1.90    | 131.2            |
| N(2)—H(2)···O(3)          | $x, y, z$                     | 0.92      | 2.655(2) | 2.00    | 126.5            |
| C(8)—H(8)···O(2)          | $-2 + x - 1 + y, z$           | 0.95      | 3.183(2) | 2.58    | 121.7            |
| C(9)—H(9)···O(2)          | $-2 + x, -1 + y, z$           | 0.95      | 3.153(3) | 2.53    | 123.2            |
| O(4)—H(4)···O(3)          | $-1 - x, 1 - y, 1 - z$        | 0.84      | 2.645(2) | 1.81    | 174.5            |
| C(9)—H(9)···F(2)          | $-1 + x, 1 - y, z$            | 0.95      | 3.381(3) | 2.69    | 130.3            |
| C(10)—H(10)···F(3)        | $1 - x, 1 - y, -z$            | 0.95      | 3.373(3) | 2.70    | 128.7            |
| C(5)—F(1)···F(1)          | $1 - x, 1 - y, -z$            | (C—F)     | (C···F)  | (F···F) | (C—F···F)        |
|                           |                               | 1.33      | 3.379(3) | 2.91    | 98.9             |
| <b>(2)</b>                |                               |           |          |         |                  |
| N(2)—H(2)···O(1)          | $x, y, z$                     | 0.89      | 2.591(3) | 1.94    | 128.8            |
| N(2)—H(2)···O(3)          | $x, y, z$                     | 0.89      | 2.616(3) | 1.92    | 134.0            |
| C(9A)—H(9A)···O(2)        | $-0.5 + x, 1.5 + y, -0.5 + z$ | 0.95      | 3.580(3) | 2.64    | 170.6            |
| C(8)—H(8)···O(4)          | $x, y, z$                     | 0.89      | 2.703(3) | 2.37    | 100.4            |
| N(2A)—H(2A)···O(1A)       | $x, y, z$                     | 0.89      | 2.588(3) | 1.90    | 133.0            |
| N(2A)—H(2A)···O(3A)       | $x, y, z$                     | 0.89      | 2.644(3) | 2.00    | 127.8            |
| O(1G)—H(1G)···O(4A)       | $-x, 2 - y, -z$               | 0.85      | 2.802(3) | 1.95    | 178.4            |
| O(1GA)—H(1GA)···O(4A)     | $-x, 2 - y, -z$               | 0.84      | 2.606(3) | 1.77    | 172.6            |
| O(4)—H(4)···O(4A)         | $x, y, z$                     | 0.84      | 2.536(3) | 1.72    | 164.4            |
| C(1)—H(1C)···F(1A)        | $1 - x, 1 - y, -z$            | 0.98      | 2.949(4) | 2.63    | 99.4             |
| C(1G)—H(1G2)···F(1)       | $0.5 - x, 0.5 + y, 0.5 - z$   | 0.99      | 3.204(4) | 2.57    | 121.6            |
| C(9)—H(9)···F(2)          | $-0.5 - x, 0.5 + y, 0.5 - z$  | 0.95      | 3.405(4) | 2.64    | 138.3            |
| C(1)—H(1A)···F(3)         | $0.5 - x, -0.5 + y, 0.5 - z$  | 0.98      | 3.389(4) | 2.62    | 135.2            |
| <b>(3)</b>                |                               |           |          |         |                  |
| N(2)—H(2)···O(1)          | $x, y, z$                     | 0.90      | 2.595(4) | 1.92    | 130.3            |
| N(2)—H(2)···O(3)          | $x, y, z$                     | 0.90      | 2.612(4) | 1.93    | 130.9            |
| C(9A)—H(9A)···O(2)        | $0.5 + x, 0.5 - y, 0.5 + z$   | 0.95      | 3.621(5) | 2.69    | 168.3            |
| C(8)—H(8)···O(4)          | $x, y, z$                     | 0.95      | 2.701(4) | 2.36    | 100.8            |
| N(2A)—H(2A)···O(1A)       | $x, y, z$                     | 0.90      | 2.576(4) | 1.89    | 131.2            |
| N(2A)—H(2A)···O(3A)       | $x, y, z$                     | 0.90      | 2.635(4) | 1.96    | 130.7            |
| O(1G)—H(1G)···O(4A)       | $2 - x, -y, 2 - z$            | 0.85      | 2.744(4) | 1.90    | 177.6            |
| O(4)—H(4)···O(4A)         | $x, y, z$                     | 0.84      | 2.544(4) | 1.73    | 163.9            |
| C(1)—H(1B)···F(1A)        | $1 - x, 1 - y, 2 - z$         | 0.98      | 3.219(5) | 2.61    | 120.6            |
| C(10)—H(10)···F(2A)       | $0.5 + x, 0.5 - y, -0.5 + z$  | 0.95      | 3.165(5) | 2.61    | 118.0            |
| C(9)—H(10)···F(2A)        | $2 - x, -y, 2 - z$            | 0.95      | 3.191(5) | 2.55    | 125.2            |

In the binuclear complex of **2**, which is constructed of two anionic ( $L^-$ ) and two uncharged ligands (LH), the sodium ions adopt a distorted octahedral coordination environment [Figure 4(a)]. The equatorial positions within the coordination polyhedron are occupied by the oxygens of two ligands with the Na—O distances ranging between 2.284(2) and 2.382(2) Å. The axial positions are occupied by the oxygen of the disordered ethanol molecule (SOF: 0.67, 0.33) and the carboxylate oxygen which is simultaneously bonded to both the sodium ions. The corresponding Na—O distances are 2.463(2) [2.260(2)] and 2.421(2) Å, respectively; the Na···Na distance is 3.402(2) Å. A conformational analysis of the complex ligands LH and  $L^-$  reveals less differences regarding their bond lengths, but shows different degrees of distortion of their pentane-2,4-dione fragments (Table 2), which can be ascribed to an asymmetric

coordinating behaviour of the fluorine atoms of the respective  $CF_3CO$  moiety. Only one fluorine atom of the anionic ligand is involved in the intermolecular association via C—H···F hydrogen bonding (30, 31), whereas in the protonated ligand, all the fluorine atoms take part in this kind of interaction. Another striking difference between the ligands is the inclination of the carboxylate group with respect to the aromatic ring to which it is attached [20.4(2)°], whereas the benzoic acid element of the uncharged ligand hardly deviates from planarity. As in the crystal structure of **1**, the almost planar geometry of the ligands is stabilised by a tight network of intramolecular hydrogen bonds comprising bifurcated N—H···O contacts between the N-bound hydrogens H(2) [H(2A)] and the carbonyl oxygens O(1) [O(1A)] as well as the carboxy and carboxylate oxygens [O(3) and O(3A)]. Moreover, the *ortho*-substituents of pairs of ligand molecules are

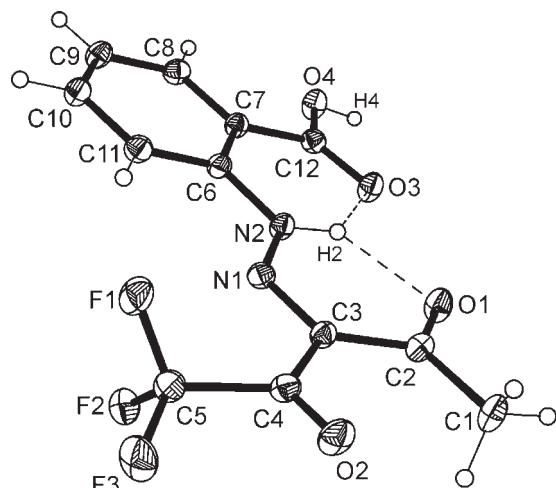


Figure 1. A perspective view of the molecular structure of **1** (LH) including the atom numbering scheme of the non-hydrogen atoms. Thermal ellipsoids are drawn at a 50% probability level. The broken lines represent the hydrogen bonds.

connected by a strong  $\text{O}-\text{H}\cdots\text{O}^-$  hydrogen bond [ $\text{O}(4\text{A})-\text{H}(4\text{A})\cdots\text{O}(4)$  1.72 Å, 164.4°]. The distance of 3.45 Å between the aromatic rings and the six-membered hydrogen-bonded rings suggests the presence of intermolecular  $\pi\cdots\pi$  interactions. The stacking interactions between the aromatic building blocks are also evident in the overall crystal structure of **2**, being characteristic of a columnar packing mode which shows an offset arrangement between the consecutive molecules (Figure 5). Within a given stack, the complex molecules are linked via the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the alcohol

molecules and the carboxylate groups of the complex ligands [ $\text{O}(1\text{GA})-\text{H}(1\text{GA})\cdots\text{O}4$  1.77 Å, 172.6°]. An inter-stack association is realised by the  $\text{C}-\text{H}\cdots\text{F}$  hydrogen bonding ( $\text{H}\cdots\text{F}$  2.57–2.63 Å).

The increased spatial demand of the alcohol component (*n*-BuOH) of the complex **3** induces an elongation of the crystallographic *c*-axis and lowers the monoclinic angle. However, the molecular structure as well as the packing behaviour of the complex **3** deviates only insignificantly from **2**, which is also evident from Figure 4. Both the crystal structures show approximately identical patterns of non-covalent interactions.

### Comparative reflection and conclusions

The new carboxylic hydrazone ligand **1** and its uncharged supramolecular complexes, containing besides sodium ions EtOH (**2**) or *n*-BuOH (**3**) solvent molecules, were studied by the X-ray crystal structure technique, giving rise to the following statement.

The molecular geometry of **1** is virtually the same as found for the other previously studied fluorine-free and fluorine-containing examples of this compound class, showing the intramolecular six-membered hydrogen-bonded ring and the overall planar geometry due to the extensive conjugation of the  $\pi$ -electron system (24, 25, 29). Also, the fact that the acetyl unlike the trifluoroacetyl oxygen of the pentane-2,4-dione moiety forms the intramolecular hydrogen bond is revealed in the structure of compound **1**. Hence, a constitutional modification by an *ortho*-substituted carboxylic group does not markedly affect the conformational

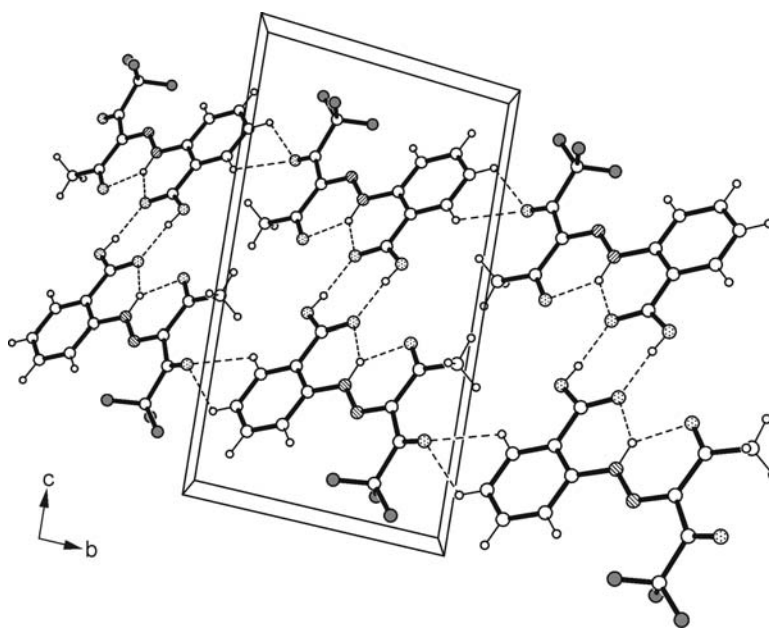


Figure 2. An excerpt of the packing structure of **1** (LH) showing the mode of intermolecular interactions. The heteroatoms are distinguished by a different shading. The broken lines represent hydrogen-bond-type interactions.

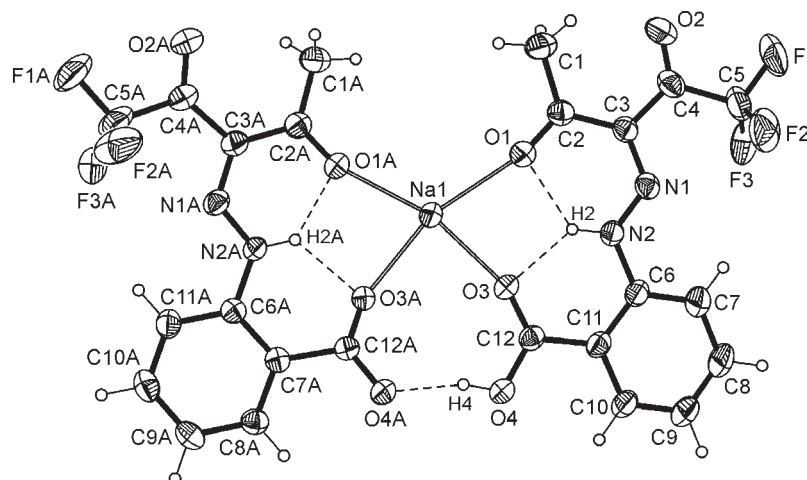


Figure 3. A perspective view of the equatorial coordination plane (open lines) around a sodium ion in the complexes **2** and **3**. The broken lines represent the hydrogen bonds.

solid-state structure inherent of the hydrazone framework but actually helps to stabilise the planar geometry of the molecule by additional intramolecular hydrogen bonding. A rather comparable situation with the involvement of an additional oxygen atom in the intramolecular hydrogen bonding was found for a related hydrazone featuring two *ortho*-positioned nitro substituents (29). By contrast, the carboxylic function of **1** has a strong bearing on the packing structure in that hydrogen-bonded dimers are formed, leading to the supramolecular ribbons which determine the lattice structure.

An almost planar geometry of the hydrazone molecule(s) stabilised by an analogous network of intramolecular hydrogen bonds, incorporating the carboxyl and carboxylate oxygens, respectively, is also shown in the isomorphous structures of the sodium complexes **2** and **3**. In other words, the conformational structure of the hydrazone molecules is only little affected by the formation of the carboxylate group and binding to the sodium ion, unlike the packing in the crystal, leading to the specific formation of a binuclear alcohol-containing cluster around the sodium ions. That is, the carboxylic dimers in **1** are broken at a single site of the hydrogen-bonded ring by the deprotonation followed by an insertion of the sodium ion. The binuclear complexes associate in a stack stabilised via hydrogen bonding through the alcohol molecules, whereas the contact between the neighbouring stacks is only of the weak C—H...F type of interaction. Therefore, the overall supramolecular packing motif is ribbon-type for **1** and stack-like for **2** and **3**, in each case being involved in a weak interconnection through the intermediary of fluorine atoms.

In summary, we have shown that this particular compound class of arylhydrazones not only yields complexes with soft transition metal ions such as Cu<sup>2+</sup> and Ni<sup>2+</sup>, but also is capable of forming chelate-type

complexes with the hard alkali metal ion Na<sup>+</sup>. This gives rise to an interesting supramolecular aggregate, comprising in addition to the two metal ions and the two charge equalising carboxylates of the hydrazone two more carboxylic hydrazones and two alcohol solvent molecules for the construction of the supramolecular cluster. A challenging idea for a future structural design is to exchange the simple alcohol molecules for multivalent alcohols or more specific tectones (33) featuring other coordinative functions. Investigations into this direction are the aim of our group.

## Experimental

### General

Elemental analysis: Heraeus CHN rapid analyser; MS (EI): Finnigan MAT 8200; FT-IR: KBr disc, Nicolet 510; NMR (internal standard TMS): Bruker Avance DPX 400. The starting compounds (2-aminobenzoic acid and 1,1,1-trifluoropentane-2,4-dione) were purchased from Aldrich (St Louis, MO, USA).

### Synthesis

#### 3-[(2-Carboxyphenyl)hydrazone]-1,1,1-trifluoropentane-2,4-dione, LH (**1**)

A solution of the diazonium salt was prepared under cooling (0–5°C) from 2-aminobenzoic acid (2.6 g, 19 mmol) in hydrochloric acid (3 N, 40 ml) and a concentrated aqueous solution of sodium nitrite (1.3 g, 19 mmol), according to the standard procedure (28). The cold solution of the diazonium salt was added under cooling (0°C) and stirring to a mixture being composed of 1,1,1-trifluoropentane-2,4-dione (2.28 ml, 2.93 g, 19 mmol), NaOH (1.0 g, 25 mmol), sodium acetate (7.5 g,

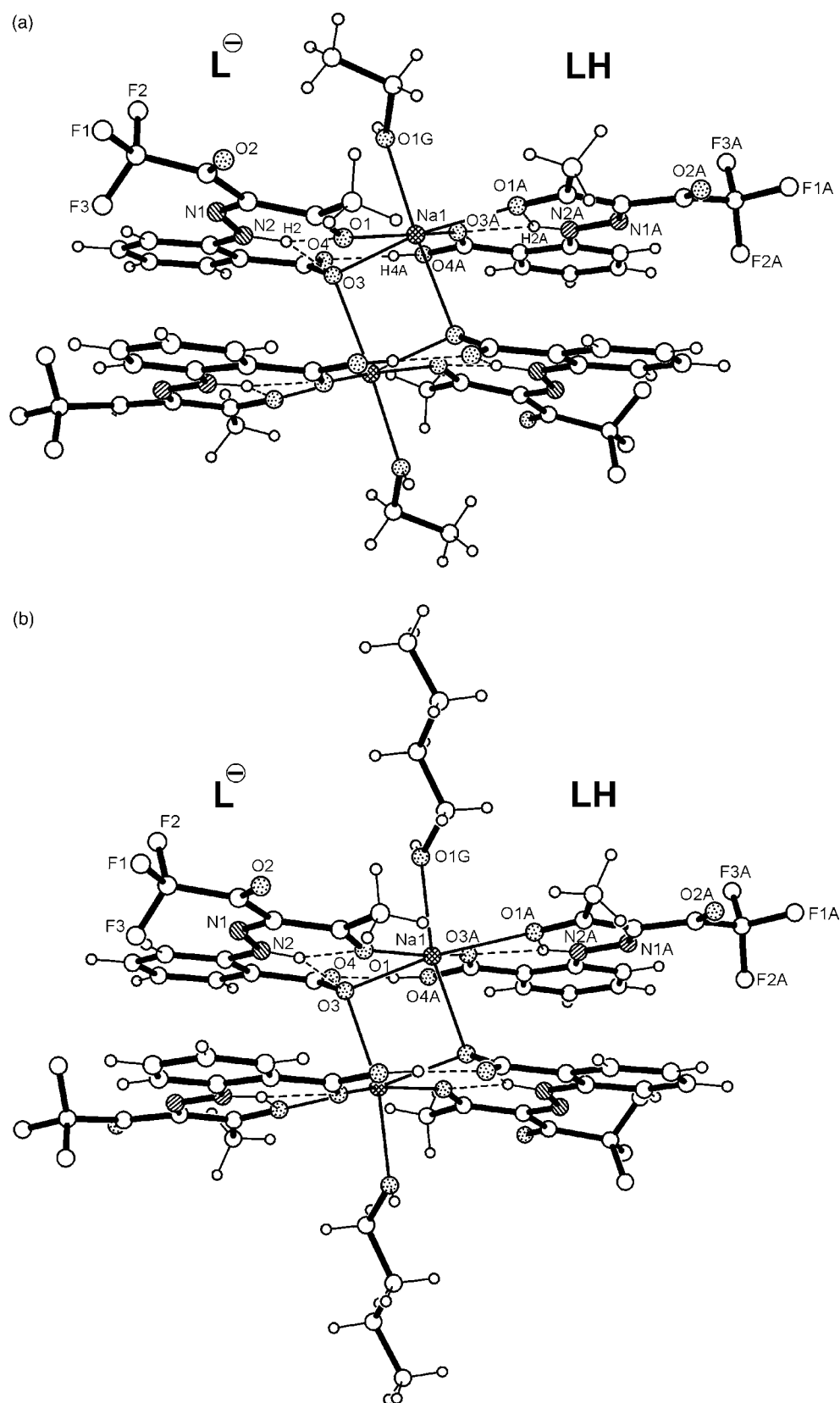


Figure 4. A perspective view of the complexes (a) **2** and (b) **3**. The heteroatoms are distinguished by a different shading. The thin lines around the sodium ions represent the coordinative bonds; the broken lines represent the hydrogen bonds. Only one of the disordered positions of the ethanol molecule in (a) is displayed for clarity.



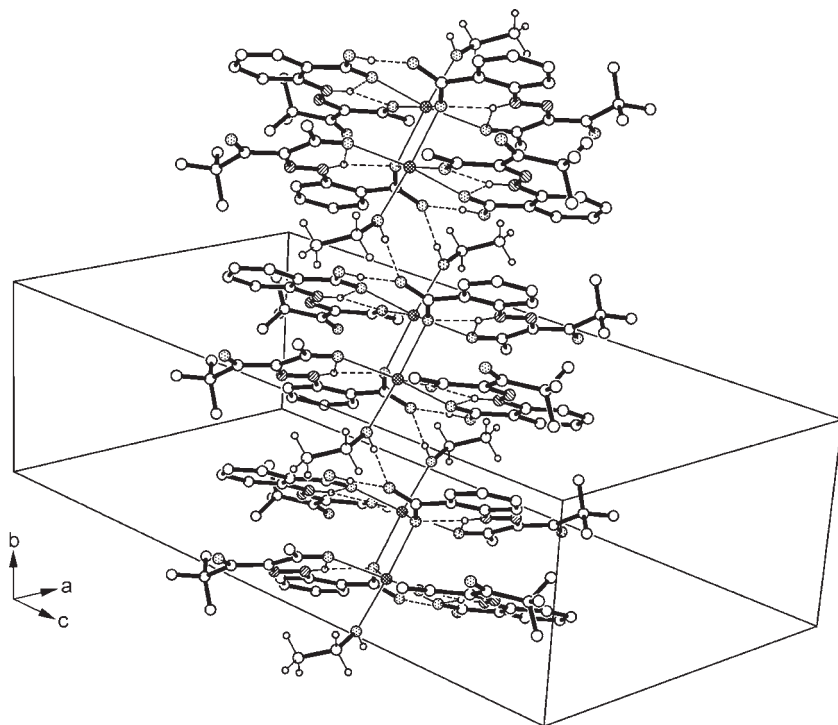


Figure 5. The packing motif of the complex **2**. The heteroatoms are distinguished by a different shading; the non-relevant hydrogen atoms are omitted. The thin lines around the sodium ions represent the coordinative bonds; the broken lines mean the hydrogen bonds. Only one of the disordered positions of the ethanol molecule is displayed for clarity.

92 mmol), methanol (160 ml) and water (160 ml). The mixture was allowed to warm to room temperature and stirred for 1 h. The precipitate that had formed was collected, washed with water, dried and recrystallised from toluene to afford 5.3 g (92%) yellow crystals; mp 249–251°C (dec.). IR (KBr,  $\text{cm}^{-1}$ ): 3336 (s, N–H), 1677 (s, C=O), 1639 (s, C=O), 1591 (s, C=N), 1380–1356 (s, CO=CH<sub>3</sub>), 758 (s, Ar-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.49 (s, 3H, CH<sub>3</sub>), 7.32 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, *p*-Ar-H), 7.67 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, *m*-Ar-H), 7.83 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, *o*-Ar-H), 8.03 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, *m*-Ar-H), 11.94 (s, 1H, COOH), 16.32 (s, 1H, NH); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  30.84 (CH<sub>3</sub>), 105.30 (CF<sub>3</sub>), 115.04 (*o*-Ar-C), 121.01 (C–COOH), 125.74 (*p*-Ar-C), 129.59 (C=N), 131.53 (*m*-Ar-C), 133.49 (*m*-Ar-C), 145.19 (C–N), 167.84 (COOH), 176.03 (CF<sub>3</sub>–C=O), 193.45 (C=O); MS (ED): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>: 302.05. Found: 302 ([M<sup>+</sup>], 100%). Anal. calcd for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>: C, 56.26; H, 5.04; N, 8.75. Found: C, 56.38; H, 4.96; N, 8.75.

#### Complex [Na<sub>2</sub>L<sub>2</sub>(LH)<sub>2</sub>] $\cdot$ 2 EtOH (**2**)

The crude product **1** of the above synthetic procedure was recrystallised from ethanol instead of toluene to yield compound **2** as yellow crystals that become opaque on

storage out of the mother liquor and rapidly decompose on heating to 86–88°C with the release of the solvent.

#### Complex [Na<sub>2</sub>L<sub>2</sub>(LH)<sub>2</sub>] $\cdot$ 2 *n*-BuOH (**3**)

The crude product **1**, as provided from synthesis, was recrystallised from *n*-butanol to yield on storage at 0–5°C during a period of 2 weeks compound **3** as yellow crystals that are rather unstable out of the mother liquor and rapidly decompose at 125–127°C with the release of the solvent.

#### X-ray crystallography

The single crystals of the compounds **1–3**, suitable for X-ray diffraction study, were obtained on recrystallisation from the solvents as given with the synthetic procedures. The intensity data were collected on a Kappa APEX II diffractometer (Bruker-AXS) with graphite monochromated CuK $\alpha$ -radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using  $\omega$ - and  $\phi$ -scans. The reflections were corrected for background, Lorentz and polarisation effects. The preliminary structure models were derived by the application of direct methods (34) and were refined by the full-matrix least-squares calculation based on  $F^2$  for all the reflections (35). For the metal complexes, an empirical absorption correction based on multi-scans was applied by using the SADABS

program (36). All non-hydrogen atoms were refined anisotropically. With the exception of the amino hydrogen atom H(2) in structures **1–3** and the hydroxy hydrogen atom of the alcohol component in **2**, all the hydrogen atoms were included in the models in the calculated positions and were refined as constrained to the bonding atoms. The crystal data and experimental parameters are summarised in Table 1. The crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication numbers CCDC-720739 (**1**), CCDC-720740 (**2**) and CCDC-720738 (**3**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, Email: deposit@ccdc.cam.ac.uk).

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