

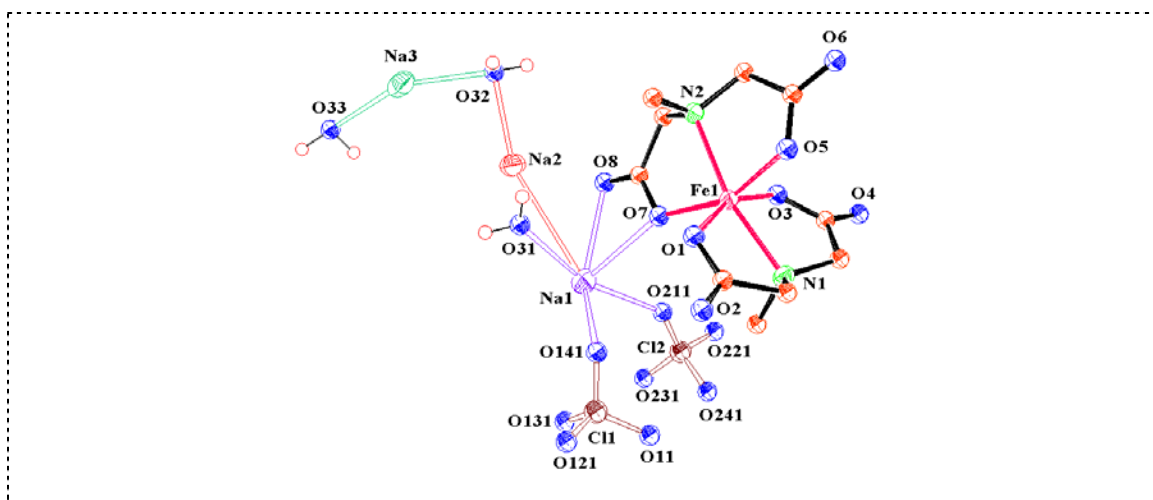
## Electronic Supporting Information (ESI) for MS b605056e

### Structure of sodium bis(N-methyl-iminodiacetato)iron(III). *Trans*-meridional N-coordination in the solid state and in solution

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*Packing patterns in the crystals of Na[Fe(mida)<sub>2</sub>].2NaClO<sub>4</sub>.3H<sub>2</sub>O (1).*

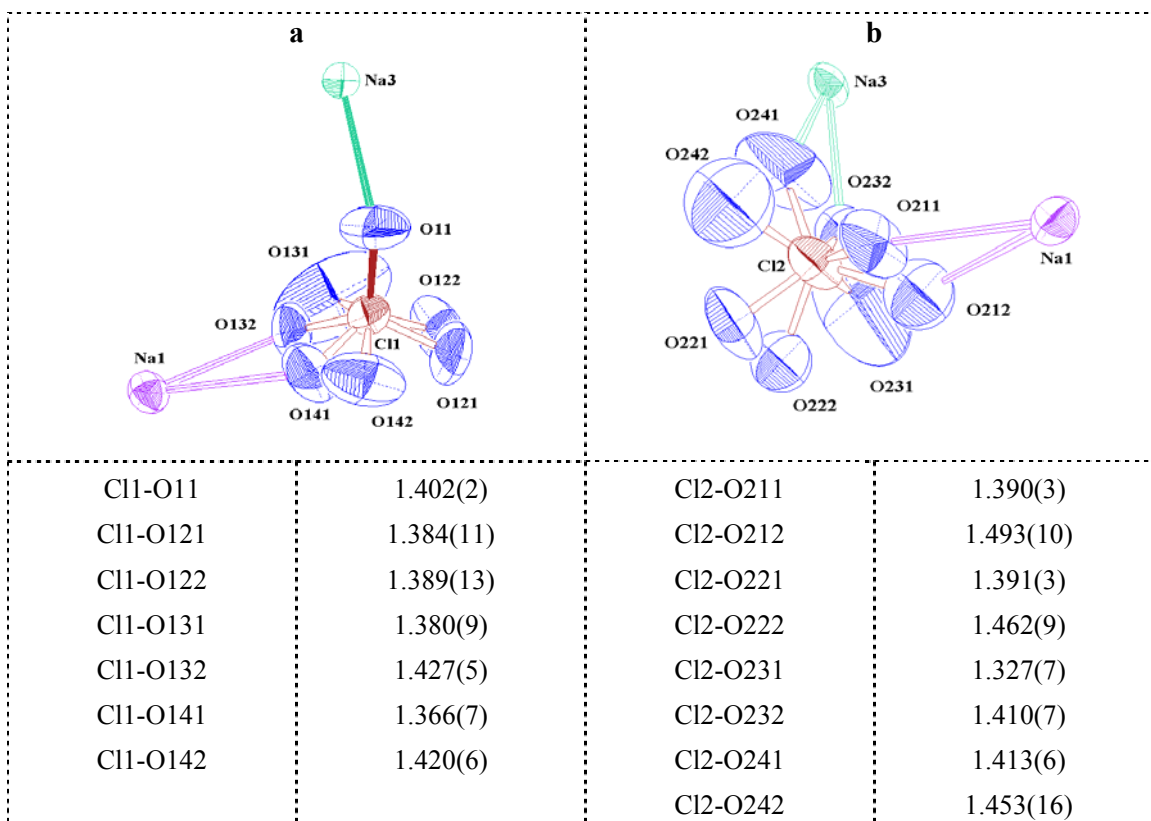
The crystals of **1** are made up from four major components (cf. Fig. S1) which are the [Fe(mida)<sub>2</sub>]<sup>-</sup> complex anions, the three crystallographically unique sodium counter ions Na1, Na2 and Na3, the waters of crystallization (O31, O32 and O33) and the auxiliary perchlorate anions (Cl1 and Cl2 with the surrounding perchlorate oxygens).



**Fig. S1.** The asymmetric unit of **1** excluding the second set of disordered perchlorate oxygen atoms (thermal ellipsoids for iron and sodium ions at the 50% probability level; all other elements drawn without including thermal equivalents).

Three of the four perchlorate oxygens at Cl1 are disordered: **0121/0122**, **0131/0132**, **0141/0142** (occupation factor 0.5 in all cases) whereas all perchlorate oxygens at Cl2 show disorder: **0211/0212** (occupation 0.65/0.35), **0221/0222** (occupation 0.65/0.35), **0231/0232** (occupation 0.65/0.35), **0241/0242** (occupation 0.65/0.35). A full depiction of the both perchlorate anions is shown in Figs. S2(a) and S2(b). The Cl-O bond distances are typical for perchlorate anions in a crystal matrix of a metal complex.<sup>1-4</sup> Also, disorder of perchlorate oxygens is a phenomenon frequently observed in metal complex structures.<sup>1-4</sup> For the sake of

clarity, the disorder of the perchlorate oxygens has been removed from the figures and discussion below.



**Fig. S2.** Depiction of the Cl-O interactions of the both disordered perchlorate anions (**a**: perchlorate at Cl1, **b**: perchlorate at Cl2) in the structure of **1** (thermal ellipsoids for all elements at the 50% probability level).

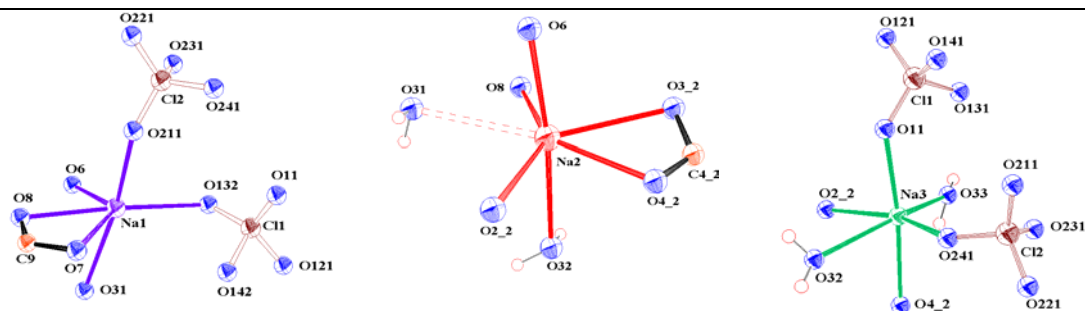
The Na-O interactions of the three sodium ions (excluding disorder of the perchlorate oxygens has been excluded from the drawings) is shown Figs. S3(a)-S3(c). Na1 (Fig. S3(a)) and Na2 (Fig. S3(b)) show an effective coordination number (CN) of seven while Na3 (Fig. S3(c)) is six-coordinate.

The arrangements of the sodium ions around a individual *mer*-[Fe(mida)<sub>2</sub>]<sup>-</sup> complex anion is shown in Fig. S4. Each complex anion is in contact with sodium ions Na1, Na2 and Na3 whereas eight Na-O bonds are formed. These interactions are realized by Na-O bonding to both iron coordinated as well as non-iron coordinated oxygen atoms of *mer*-[Fe(mida)<sub>2</sub>]<sup>-</sup>. Two three-membered rings are formed between the iron coordinated and non-iron coordinated carboxylato oxygens and a sodium ion with the members Na1, O7 and O8 as well as Na2, O3 and O4.

**a**

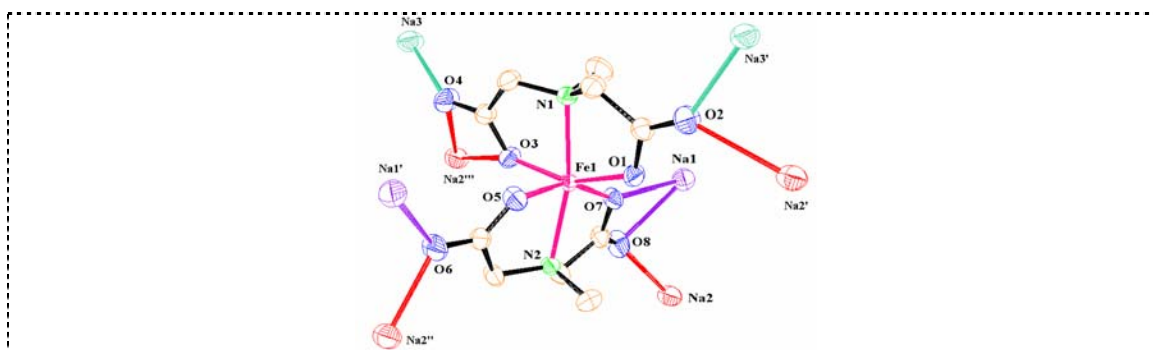
**b**

**c**



O atom	Na1–O	O atom	Na2–O	O atom	Na3–O
O6	2.3806(18)	O8	2.3608(18)	O4	2.3229(18)
O7	2.6266(16)	O2	2.692(2)	O2	2.3999(18)
O8	2.4838(19)	O3	2.7119(17)	O32	2.584(3)
O31	2.434(3)	O4	2.511(2)	O33	2.347(4)
<i>O141</i>	<i>2.443(8)</i>	O6	2.3356(18)	O11	2.406(3)
<i>O132</i>	<i>2.478(6)</i>	O32	2.379(2)	<i>O241</i>	<i>2.379(6)</i>
<i>O211</i>	<i>2.365(4)</i>	O31	2.827(3)	<i>O232</i>	<i>2.441(7)</i>
<i>O212</i>	<i>2.418(11)</i>				

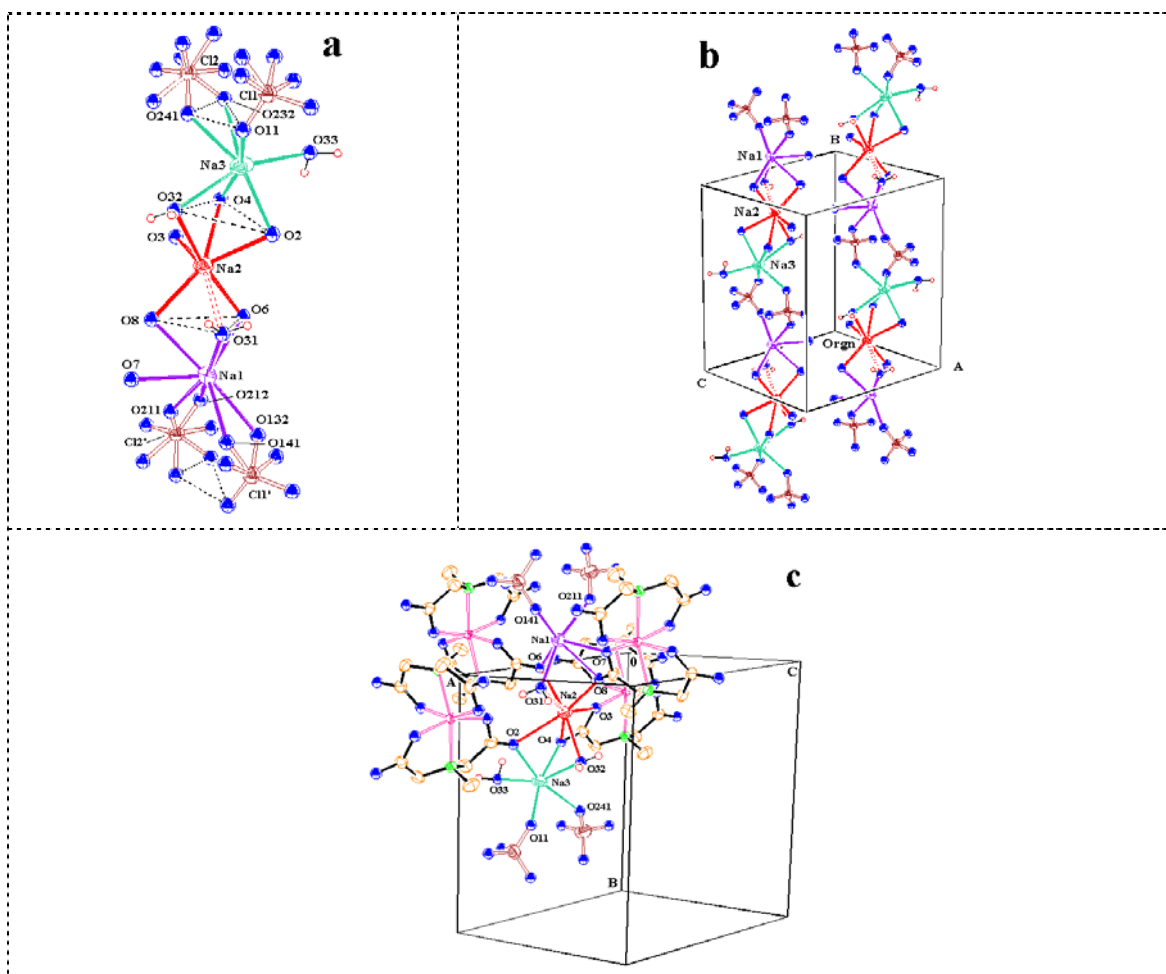
**Fig. S3.** Depiction of the Na–O interactions of the three sodium counter cations in the structure of **1** (a: Na1, b: Na2, c: Na3). Na–O distances to disordered perchlorate oxygens are expressed in italics. Because of the somewhat extended Na–O distance of Na2 to crystal water oxygen O31, this bond was drawn as dotted line (thermal ellipsoids for sodium at the 50% probability level, other elements are drawn without including thermal equivalents).



**Fig. S4.** Next neighbour Na–O contacts to a single  $[\text{Fe}(\text{mida})_2]^-$  complex in **1** (thermal ellipsoids at the 50% probability level).

As shown in Fig. S5(a), the sodium counter ions Na1, Na2 and Na3 form trimeric oxygen-bridged clusters. The central member of such a trimer is the counter cation Na2 which is triple bridged to the both terminal sodium ions Na1 and Na3. Each triple bridge consist of two  $\mu$ -

carboxylato bridges (bridging mode  $\mu\text{-}\eta^1\text{-carboxylato}$ )<sup>1</sup> and one  $\mu\text{-aqua}$  bridge to the terminal trimer members Na1 and Na3. The following oxygens act as  $\mu\text{-carboxylato}$  bridge heads in the sodium trimers: O2 and O4 each form a double  $\mu\text{-carboxylato}$  bridge between Na2 and Na3 while O6 and O8 form a double  $\mu\text{-carboxylato}$  bridge between Na1 and Na2. By linking of the individual trimer units with the perchlorate ions, infinite chains along vector *b* are formed (cf. Fig. S5(b)). Intercalated into these chains are the *mer*-[Fe(mida)<sub>2</sub>]<sup>-</sup> complex anions (cf. Fig. S5(c)).

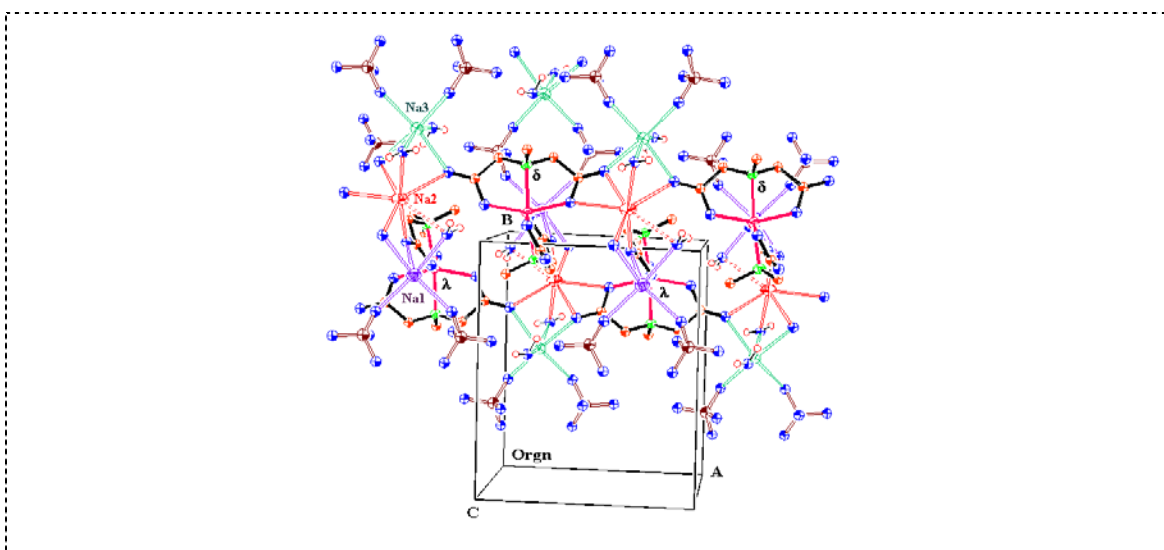


**Fig. S5(a).** View on the trimeric,  $\mu\text{-carboxylato}$ ,  $\mu\text{-aqua}$  bridged sodium cluster in the structure of **1**.

**Fig. S5(b).** Location of adjacent chains of the trimeric sodium cluster in the structure of **1** along *b* including the linking of the trimers by the perchlorate ions. (Thermal ellipsoids sodium at the 50% probability level, other elements are drawn without including thermal equivalents).

**Fig. S5(c).** Interaction of the tri-bridged trimeric sodium clusters with four adjacent complex anions. (thermal ellipsoids at the 50% probability level for all atoms except oxygen which was drawn without considering thermal equivalents).

Eventually, the way along which the  $[\text{Fe}(\text{mida})_2]^-$  complex anions are packed in the crystals of **1** is depicted in Fig. S6. By definition, the triclinic space group  $P-1$  has a fixed origin caused by the inversion operation. As a consequence, both mirror images of **1**, i.e. the *trans*  $\delta$ -NCH<sub>3</sub>- and *trans*  $\lambda$ -NCH<sub>3</sub> enantiomers are related to each other by the inversion operation where, for the case shown in Fig. S6, the inversion centers are located at the four end points of the *ab* plane. Only one slice of the whole packing is shown in Fig. S6. Extension into the direction of vector *c* (not shown) generates layers of complex anions in the *ac* plane piled one above another into the direction of *b*.



**Fig. S6.** Packing of the *trans*  $\delta$ -NCH<sub>3</sub>- and *trans*  $\lambda$ -NCH<sub>3</sub> enantiomers of *mer*- $[\text{Fe}(\text{mida})_2]^-$  in the crystal of **1**. (Thermal ellipsoids for iron and sodium at the 50% probability level, other elements are drawn without including thermal equivalents).

## References

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