Crystal engineering of chiral superstructures based on (*R*)-(+)-1,1′-bi-2-naphthol and the alkali derivatives of racemic (*R*,*S*)-1,1′-bi-2-naphthol

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Received (in Montpellier, France) 1st December 2000, Accepted 16th February 2001

(*R*)-(+)-1,1′-Bi-2-naphthol [(*R*)-(+)-($HOC_{10}H_6C_{10}H_6OH$)] has been used as a chiral building block in the construction of chiral organo-organometallic crystals. The reaction of the neutral molecule with [$Co(\eta^5\text{-}C_5H_5)_2$] in diethyl ether yields the supramolecular salts [$Co^{III}(\eta^5\text{-}C_5H_5)_2$][(*R*)-(+)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*)-(+)-($HOC_{10}H_6C_{10}H_6OH$)] (**1**) and [$Co^{III}(\eta^5\text{-}C_5H_5)_2$][(*R*)-(+)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*)-(+)-($HOC_{10}H_6C_{10}H_6OH$)]$_{0.5}$ (**2**), depending on the stoichiometric ratios between the binaphthol and the organometallic sandwich compound. Molecular aggregation is achieved *via* a combination of neutral and charge-assisted O–H···O bonds between the binaphthol and binaphtholate components and *via* weaker interactions of the C–H···O and C–H···π types involving the [$Co^{III}(\eta^5\text{-}C_5H_5)_2$]$^+$ cation. The same reaction with racemic 1,1′-bi-2-naphthol in diethyl ether, followed by recrystallisation from nitromethane, yields the solvate species [$Co^{III}(\eta^5\text{-}C_5H_5)_2$]-[(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)][$MeNO_2$]$_{1.5}$ (**3**). For comparison, the alkali salts Cs[(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] (**4**) and Rb[(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] (**5**) have also been prepared by treating [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] with the Cs and Rb hydroxides. Both organometallic and alkali salts show how the cations tend to be encapsulated within a niche formed by the folding of hydrogen-bonded naphthol–naphtholate chains.

Crystal engineering involves the planning, synthesis and characterisation of a crystalline material from its building blocks, whether molecules, ions or coordination complexes.[1] Since the interactions responsible for crystal cohesion are the same as those that hold together molecular aggregates in supermolecules, crystal engineering is logically connected to supramolecular chemistry.[2] The major problem behind the preparation of solid state materials is that of combining a very large number of ions or molecules, and their individual properties and structural characteristics, into a particular three-dimensional arrangement that may possess the required collective properties.[3] This is where crystal engineering may contribute: a knowledge of the way molecules or ions recognise each other (or self-recognise) and link by means of non-covalent interactions is crucial in the design of three-dimensional aggregates. Applications of this way of thinking are numerous and rapidly increasing thanks to the contributions of many important research groups. Some of the areas receiving the most intense investigation are: (i) nanoporous and meso-porous materials,[4] where building blocks are selected in order to leave large cavities and channels in crystal structures; (ii) materials for conductivity and magnetic applications,[5] by incorporating metal atoms with open-shell spin systems into the solid; (iii) crystal polymorphism,[6] with its enormous economic implications to the drug and food industries; and (iv) solids for non-linear optics,[7] by preparing materials with appropriate orientations of strongly dipolar molecules or ions.

A necessary, but not sufficient, condition for achieving appreciable second harmonic generation effects is that molecular dipoles in the crystal structures do not cancel each other, that is they do not adopt a centrosymmetric relative orientation.[8] Clearly, the utilisation of (enantiomerically pure) chiral building blocks leads to non-centrosymmetric crystals, a precondition for having non-centrosymmetric dipoles. As a part of our studies of organo-organometallic crystal engineering we are also preparing organometallic molecules and ions carrying delocalised π-conjugated systems, such as [$Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-}$stilbene)]$^+$,[9] that may act as push-pull systems while, on the other hand, investigating the use of chiral organic molecules that may form the desired chiral architectures.[10] The near future objective is to combine the two strategies, in order to obtain chiral host superstructures that can accommodate organometallic-based dipolar units.

In this paper, we focus our attention on the reaction between enantiomerically pure (*R*)-(+)-1,1′-bi-2-naphthol and cobaltocene. We report and discuss the synthesis and structural characterisation by single-crystal X-ray diffraction of the novel supramolecular salts [$Co^{III}(\eta^5\text{-}C_5H_5)_2$][(*R*)-(+)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*)-(+)-($HOC_{10}H_6C_{10}H_6OH$)] (**1**) and [$Co^{III}(\eta^5\text{-}C_5H_5)_2$][(*R*)-(+)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*)-(+)-($HOC_{10}H_6C_{10}H_6OH$)]$_{0.5}$ (**2**), as well as the product of the same reaction with racemic 1,1′-bi-2-naphthol, namely [$Co^{III}(\eta^5\text{-}C_5H_5)_2$][(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)][$MeNO_2$]$_{0.5}$ (**3**). (*R*,*S*)-1,1′-Bi-2-naphthol has also been used to prepare the alkali salts Cs[(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] (**4**) and Rb[(*R*,*S*)-($HOC_{10}H_6C_{10}H_6O$)] · [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] (**5**) by reaction with the corresponding hydroxides. These salts show some remarkable features that deserve to be described in the context of this paper.

The field of binaphthalene chemistry has developed into a

DOI: 10.1039/b009665m

large and diversified discipline in recent years and binaphthyl derivatives have been involved in many asymmetric processes with remarkable success.[11] Much activity in this field has been based on 1,1′-binaphthalene-2,2′-diol, which is readily available in enantiomerically pure form.[12,13] Atropisomeric derivatives have also been studied for NLO applications and properties.[14]

Experimental

As previously discussed in the case of polycarboxylic organic acids,[15] the reaction between the acidic species and [Co^{II}(η^5-C$_5$H$_5$)$_2$] proceeds essentially *via* three steps: (i) oxidation of the organometallic species [Co^{II}(η^5-C$_5$H$_5$)$_2$] by oxygen in the presence of the acidic organic species with the initial formation of the strongly basic $O_2^{\cdot-}$ anion and of the [Co^{III}(η^5-C$_5$H$_5$)$_2$]$^+$ cation, (ii) deprotonation of the binaphthol acid $HOC_{10}H_6C_{10}H_6OH$ by $O_2^{\cdot-}$ with formation of the partially deprotonated $HOC_{10}H_6C_{10}H_6O^-$ species, (iii) precipitation of the supramolecular salts and subsequent recrystallisation from polar solvents such as acetone or nitromethane.

Syntheses

[Co^{III}(η^5-C$_5$H$_5$)$_2$][(*R*)-(+)-(HOC$_{10}$H$_6$C$_{10}$H$_6$O)]·[(*R*)-(+)-(HOC$_{10}$H$_6$C$_{10}$H$_6$OH)] (1) and [Co^{III}(η^5-C$_5$H$_5$)$_2$]-[(*R*)-(+)-(HOC$_{10}$H$_6$C$_{10}$H$_6$O)] · [(*R*)-(+)-(HOC$_{10}$H$_6$-C$_{10}$H$_6$OH)]$_{0.5}$ (2). A solution of (*R*)-(+)-1,1′-bi-2-naphthol (30.3 mg, 0.10 mmol and 42.2 mg, 0.15 mmol, for synthesis of **1** and **2**, respectively) was prepared in diethyl ether and cobaltocene (10 mg, 0.05 mmol for **1**, 27.9 mg, 0.15 mmol for **2**) was added under argon atmosphere. The solutions turned yellow–brown upon oxidation of cobaltocene to cobaltocenium and a yellow–brown precipitate was formed on standing. The solution was exposed to air and the precipitate of **1** was dissolved in a 50 : 50 mixture of CH_3CN and CH_3NO_2, while **2** was dissolved in acetone. Slow evaporation of the solvent afforded crystals suitable for X-ray diffraction experiments.

[Co^{III}(η^5-C$_5$H$_5$)$_2$][(*R*,*S*)-(HOC$_{10}$H$_6$C$_{10}$H$_6$O)]·[(*R*,*S*)-(HOC$_{10}$H$_6$C$_{10}$H$_6$OH)][MeNO$_2$]$_{1.5}$ (3). (*R*,*S*)-1,1′-Bi-2-naphthol (64 mg, 0.22 mmol) was added to a solution of cobaltocene (21 mg, 0.11 mmol) in diethyl ether under argon atmosphere. The solution turned yellow–brown and a brown precipitate was formed, which was recrystallised from a 1 : 1 : 1 mixture of acetone, CH_3CN and CH_3NO_2.

Cs[(*R*,*S*)-(HOC$_{10}$H$_6$C$_{10}$H$_6$O)]·[(*R*,*S*)-(HOC$_{10}$H$_6$-C$_{10}$H$_6$OH)] (4) and Rb[(*R*,*S*)-(HOC$_{10}$H$_6$C$_{10}$H$_6$O)]·[(*R*,*S*)-(HOC$_{10}$-H$_6$C$_{10}$H$_6$OH)] (5). CsOH monohydrate (23.5 mg, 0.14 mmol) was added to a solution of (*R*,*S*)-1,1′-bi-2-naphthol (39.0 mg, 0.14 mmol) in ethanol. The solution turned opaque and a white precipitate was formed. Slow evaporation of the solution afforded single crystals of **4**. (*R*,*S*)-1,1′-Bi-2-naphthol (61.3 mg, 0.21 mmol) was dissolved in ethanol and RbOH monohydrate (25.3 mg, 0.21 mmol) was added. The solution turned opaque and a white precipitate was formed. The solvent was then slowly evaporated to give colourless crystals of **5**.

Crystal structure determination

Diffraction intensities for compounds **1**–**3** were collected on a Bruker Smart CCD diffractometer, those for compounds **4** and **5** on a Nonius CAD4 diffractometer. Both diffractometers were equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.71073$ Å). All refinements were carried out on F^2 using all reflections. Crystal data and details of measurements are reported in Table 1. The computer program SHELX97[16] was used for structure solutions and refinements. All non-H atoms were refined anisotropically and hydrogen atoms bound to carbons were added in calculated positions (C–H = 0.95 Å). All binaphthol groups were refined as rigid groups. Except for the H atom bound to O(4) in **1**, which was added in a calculated position (O–H = 0.82 Å), all the other H atoms bound to oxygen were found in the Fourier maps and refined when possible. For all molecular representations the graphics program SCHAKAL99[17a] was used. The program PLATON[17b] was used to calculate the hydrogen bonding interactions of the O–H···O type reported in Table 2.

CCDC reference numbers 154549–154553. See http://www.rsc.org/suppdata/nj/b0/b009665m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Since the focus of this paper is on the supramolecular features of the crystalline materials, details of the structures of the ions will not be described, while some attention will be given to the conformational geometry of the anions derived from 1,1′-bi-2-naphthol. As will become apparent throughout the discussion, 1,1′-bi-2-naphthol is structurally very versatile, not only because it can participate in hydrogen-bonded networks as neutral and deprotonated species, but also because of the relative conformational freedom around the C–C bond joining the naphthol moieties.

Table 1 Crystal data and details of measurements for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{50}H_{37}CoO_4$	$C_{40}H_{30}CoO_3$	$C_{51.5}H_{41.5}CoN_{1.5}O_7$	$C_{40}H_{27}CsO_4$	$C_{40}H_{27}RbO_4$
MW	760.63	617.57	852.29	704.53	657.09
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal	Triclinic	Triclinic	Triclinic
Space group	$P4_32_12$	$P4_32_12$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	8	8	2	2	2
a/Å	14.3580(7)	13.2613(4)	10.446(2)	10.622(1)	10.682(1)
b/Å	14.3580(7)	13.2613(4)	14.850(2)	12.390(1)	12.214(1)
c/Å	37.944(2)	33.4406(15)	15.985(2)	12.590(1)	12.668(1)
α/°	90	90	68.894(5)	89.40(1)	90.00(1)
β/°	90	90	80.311(5)	112.13(1)	112.60(1)
γ/°	90	90	87.815(5)	100.14(1)	100.03(1)
U/Å^3	7822.3(2)	5880.9(4)	2279.7(6)	1508.1(2)	1498.5(2)
μ(Mo-Kα)/mm^{-1}	0.485	0.624	0.429	1.271	1.696
Measured reflects	99054	83597	32872	4689	4373
Unique reflects	15120	11365	16744	4428	4153
R_1 [on F, $I > 2\sigma(I)$]	0.0629	0.0331	0.0763	0.0476	0.0657
wR_2 (F^2, all data)	0.2076	0.0750	0.2554	0.1564	0.1998

All species discussed herein contain at least one mono-deprotonated binaphtholate anion, whether derived from chiral or racemic binaphthols. The presence of neutral molecules depends on the acid : base, *viz.* organic : organometallic, stoichiometric ratio. In all cases, self-aggregation of the binaphthol fragments yields networks formed *via* intermolecular and intramolecular O–H···O hydrogen bonds (see below). It is worth stressing the contribution to all crystalline systems of *ionic hydrogen bonds*, that is of interactions that combine hydrogen bond directionality with the strength of the Madelung field generated by the ionic charges.[18]

Relevant intra- and intermolecular hydrogen bond parameters are listed in Table 2. The binaphtholate anions in **1** and **2** present an intramolecular hydrogen bond between the protonated and deprotonated oxygen atoms; the O···O separation is in the range 2.420–2.534 Å, which is comparable to that usually observed in charge-assisted O–H···$O^{(-)}$ interactions.[18a] This is interesting for two reasons: (i) the charge appears to remain localised on the deprotonated O atom without further delocalisation onto the whole anion (this observation is in keeping with previous observations on the behaviour of carboxylate groups in anions derived from polycarboxylic acids and in neutral zwitterions[19]); (ii) in terms of distances, the interaction is very similar to that found in both inter- and intramolecular hydrogen bonds involving both carboxylic and carboxylate groups.

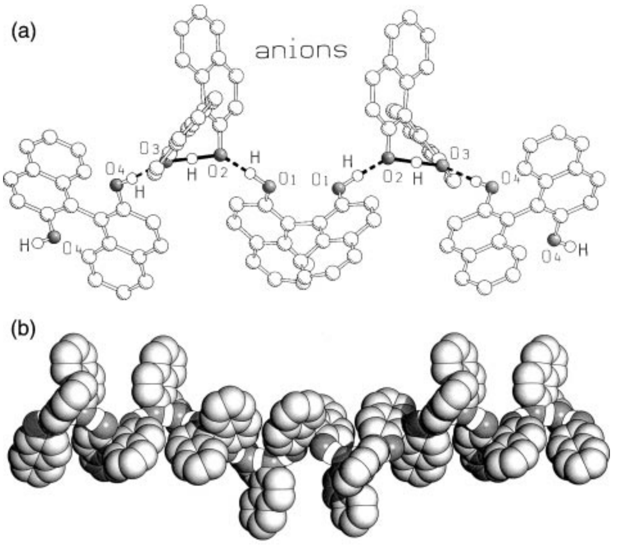

Fig. 1 (a) Ball-and-stick representation of the chain in **1**. The O–H···O hydrogen bonds along the chain are of two types: the intermolecular O–H···$O^{(-)}$ bond between the neutral spacer and the anion (broken lines) and the intramolecular hydrogen bond between the –OH group of the anion and the deprotonated oxygen atom (solid lines). (b) Space-filling representation of the spacer–anion chain in crystalline **1**.

The structures of 1 and 2

Crystalline **1** and **2** show similar structural features and will be discussed together. The main difference between the two species arises from the stoichiometric ratio between the binaphtholate anion and the neutral molecules of binaphthol: compound **1** contains one neutral molecule and one mono-deprotonated unit, while crystalline **2** contains half a neutral molecule per anion. The different stoichiometric ratios have consequences on the supramolecular organisation in the solid state. The most relevant features of the two compounds are summarised in the following discussion.

In **1** the neutral molecules act as bridges between mono-anions, thus forming a chain system in which anions and neutral molecules alternate [see Fig. 1(a)]. The O–H···O hydrogen bonds along the chain are of two types: the intermolecular O–H···$O^{(-)}$ bond between the neutral spacer and the anion [2.667(7) and 2.612(7) Å, respectively, see Table 2], and the intramolecular hydrogen bond between the –OH group of the anion and the deprotonated oxygen atom [2.427(7) Å]. Because of the enantiomerically pure nature of the component, the chain is chiral [see Fig. 1(b)]. The interaction between the spacer–anion chain and the cations is based on charge-assisted C–H···O hydrogen bonds as well as on C–H···π interactions. The cations lie nestled between the wings of pairs of binaphthol molecules; where two chains come together the cation is totally encapsulated by a total of two binaphthol molecules and two binaphtholate anions (one each from each hydrogen-bonded chain), as shown in Fig. 2.

Table 2 Intra- and (when not specified) intermolecular O(H)···O hydrogen bonding distances in compounds **1**–**5**

	O(H)···O/Å
1	Intra O(3)···O(2) = 2.427(7)
	O(4)···O(3) = 2.667(7)
	O(1)···O(2) = 2.612(7)
2	Intra O(1)···O(2) = 2.534(2)
	O(1)···O(3) = 2.555(2)
3	O(3)···O(5) = 2.598(5)
	O(4)···O(5) = 2.715(5)
	O(6)···O(1) = 2.568(5)
4	O(1)···O(2) = 2.652(4)
	O(1)···O(4) = 2.424(4)
	O(3)···O(4) = 2.556(4)
5	O(1)···O(2) = 2.650(4)
	O(1)···O(4) = 2.409(4)
	O(3)···O(4) = 2.554(4)

Compound **2** does not show the presence of infinite chains, rather, the neutral binaphthol molecule acts as a bridge between two mono-deprotonated anions as shown in Fig. 3(a). Interestingly, the intra- and the intermolecular O–H···O interactions do not differ very much in length [$d_{(O\cdots O)}$ = 2.534(2) *vs.* 2.555(2) Å]. The supramolecular trimeric unit, which carries a total charge of −2, *embraces* two cations as shown in Fig. 3(b). We shall see below that this type of "embrace" is found again in the alkali salts **4** and **5**.

There is a feature worth noting in the way anions and cations interact in crystalline **1** and **2**: the cobaltocenium cation is placed *side-on* with respect to the arene systems, thus optimising the number of C–H···π interactions. These interactions, though weak,[20] are enhanced by charge-assistance due to the presence of a cationic charge on the system carrying the C–H donors and of a negative charge on the supramolecular π-acceptor.[21]

The structure of 3 and a comparison with the structures of the alkali derivatives 4 and 5

Compound **3** is the only product obtained on treating cobaltocene with racemic [(*R*,*S*)-($HOC_{10}H_6C_{10}H_6OH$)] in a 1 : 2 stoichiometric ratio. Compound **3** crystallises with 1.5 molecules of nitromethane, which are hydrogen bonded to the naphthol units. As noted before,[16] the inclusion of solvent is often an unpredictable (and most often undesired) event in crystal engineering. Fig. 4(a) shows a ball-and-stick representation of the organic network formed by the mono-deprotonated anions and neutral molecules in crystalline $[Co^{III}(\eta^5\text{-}C_5H_5)_2][(R,S)\text{-}(HOC_{10}H_6C_{10}H_6O)] \cdot [(R,S)\text{-}(HOC_{10}H_6C_{10}H_6OH)] \cdot [MeNO_2]_{1.5}$ (**3**). The Cs and Rb derivatives **4** and **5** are isomorphous and the two systems isostructural. Because of the structural analogy with the cobaltocenium salt **3**, the three systems will be discussed together. The most relevant features are presented below.

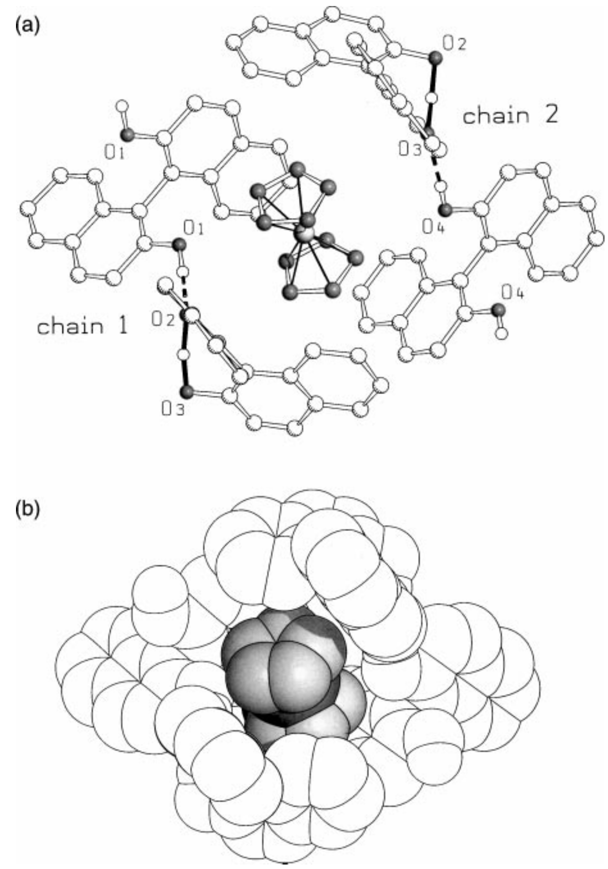

Fig. 2 (a) Ball-and-stick representation of the cation environment in crystalline **1**. The cation is encapsulated by a total of two binaphthol molecules and two binaphtholate anions, belonging to two hydrogen-bonded chains (here indicated as chains 1 and 2). (b) A space-filling representation of the same binaphthol/binaphtholate "embrace" around the cation in **1**.

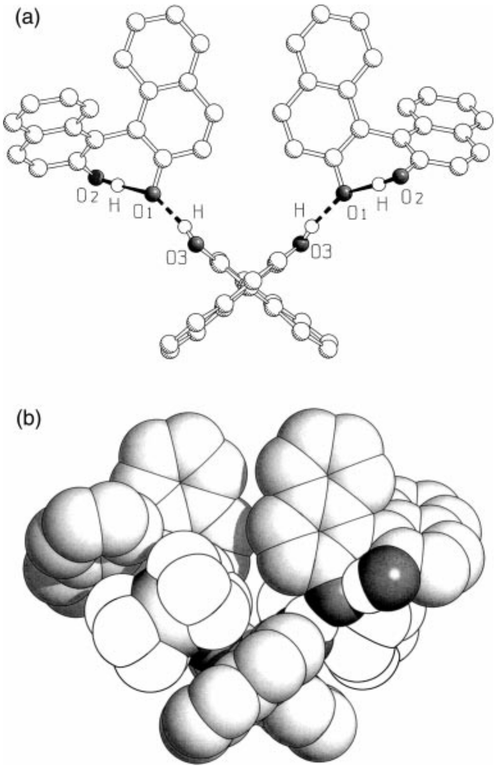

Fig. 3 (a) The neutral binaphthol molecule acts as a bridge between two mono-deprotonated anions in crystalline **2**. (b) Space-filling representation showing how the supramolecular dianion *embraces* two cations, thus optimising C–H$\cdots\pi$ interactions.

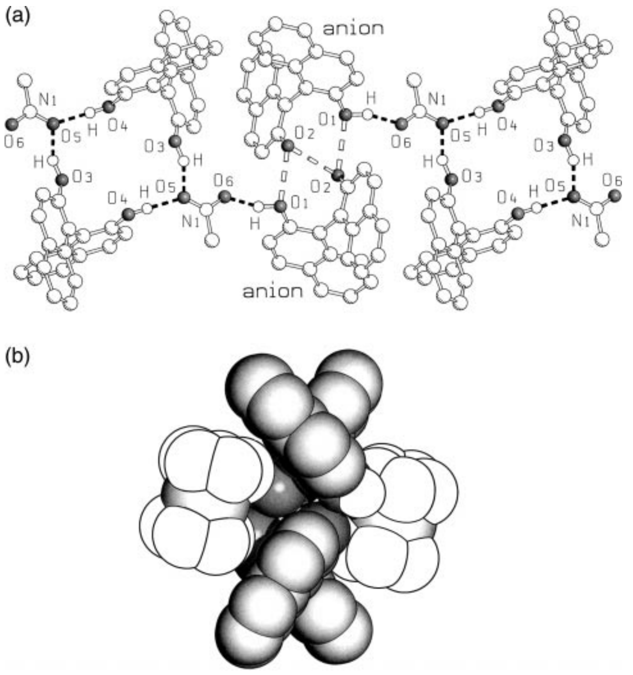

Fig. 4 (a) Ball-and-stick representation of the organic network formed by the mono-deprotonated anions and neutral molecules in crystalline **3**. Dashed open lines represent $O_{anion}\cdots O_{anion}$ short contacts, which do not correspond to hydrogen bonds. (b) The ion pair dimer constituted of two anions and two cations, $\{[Co^{III}(\eta^5\text{-}C_5H_5)_2]\cdot[(R,S)\text{-}(HOC_{10}H_6C_{10}H_6O)]\}_2$.

The three crystals obtained from the racemic compound all contain one molecule of binaphthol and one mono-deprotonated binaphthol anion. In **3**, contrary to what is observed for **1** and **2**, the neutral molecule does not interact directly with the anions. It is helpful to describe the crystal of **3** as formed by ion-pair dimers constituted of two anions and two cations, $\{[Co^{III}(\eta^5\text{-}C_5H_5)_2]\cdot[(R,S)\text{-}(HOC_{10}H_6C_{10}H_6O)]\}_2$, shown in Fig. 4(b), *joined* by nitromethane and neutral binaphthol molecules. This dimeric unit contains an intriguing pattern of O$\cdots$O contacts. There are two O$\cdots$O contacts [2.876(5) Å for O(2)$\cdots$O(2), 2.760(5) Å for O(1)$\cdots$O(2)], much shorter than the van der Waals distance, that do not correspond to hydrogen bonds. In fact, the only O–H group "left" on the mono-anion serves as a donor towards the nitromethane molecule, which also receives hydrogen bond donation from the neutral binaphthol molecules. The presence of O$\cdots$O contacts comparable in length to hydrogen bonds, but which cannot form this type of interaction, is another manifestation of the charge compression arising from the presence of ions in the crystal structure.[22] Besides the Coulombic interaction between ions, the supramolecular dianion shows a plethora of weaker C–H$\cdots$O and C–H$\cdots\pi$ interactions with the cobaltocenium cations, which confer directionality to the folding around the cations.

The organic network in crystalline **4** and **5** is reminiscent of that discussed for **3**, the main difference being the absence of the nitromethane bridge between the neutral molecules and the anions. This absence implies a different distribution of O–H$\cdots$O interactions. While in **3** the mono-deprotonated binaphthol anion donates a hydrogen bond to the nitromethane molecule, which then bridges the neutral moieties, in **4** and **5**, the mono-anions are hydrogen bonded *via* O–H$\cdots$O$^{(-)}$ interactions [see Fig. 5(a)], forming a tight supramolecular dianionic unit that embraces the alkali cations, as shown in Fig. 5(b). The similarity between the folding around the cations in **4**/**5** and in **3** is remarkable [compare Fig. 5(b) with Fig. 4(b)]. The neutral molecules bridge the dianion units *via* short O–H$\cdots$O$^{(-)}$ interactions [2.424(4) and 2.409(4) Å for Cs and Rb,

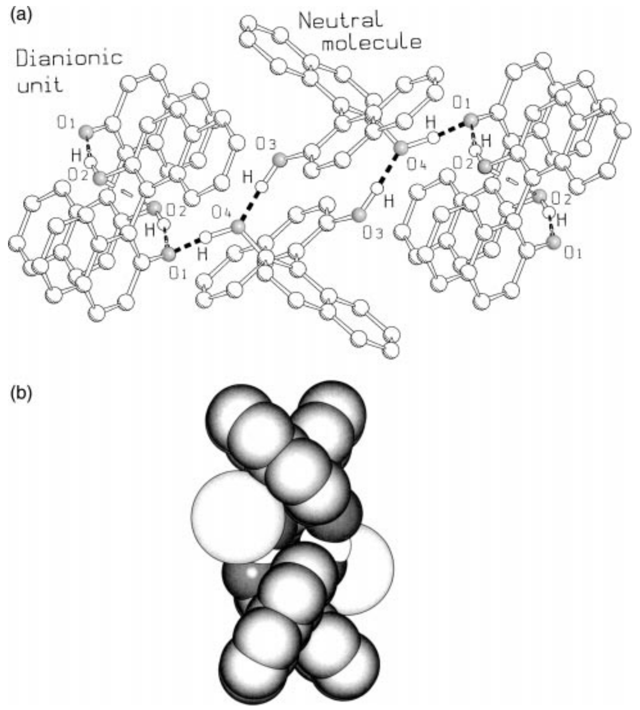

Fig. 5 (a) Neutral molecules bridge the dianionic units in **4** and **5** *via* short O–H···O$^{(-)}$ interactions, forming extended chains. The dashed open lines represent $O_{anion}\cdots O_{anion}$ short contacts, which do not correspond to hydrogen bonds. (b) In **4** and **5** the mono-anions are hydrogen bonded *via* O–H···O$^{(-)}$ interactions, forming a tight supramolecular dianionic unit that embraces the alkali cations. Note the close structural analogy with the dimers in **3**.

respectively]. The analogy of **3** with **4** and **5** can be extended further, if one considers the neutral dimer (binaphthol)$_2$(Me$_3$NO$_2$), shown in Fig. 4(a), as the counterpart of the neutral dimer present in **4** and **5**, shown in Fig. 5(a). Both crystalline **3** and the pair **4**/**5** can then be seen as containing chains of dimers, alternately neutral and dianionic, which are able to tightly "grip" the cations. The pattern of O···O separations within the dianionic unit in **4** and **5** differs from that within the same unit in **3**: while the O(2)···O(2) contact extends from 2.876(5) Å in **3** to 2.916(4) and 2.962(4) Å in **4** and **5**, respectively, the O(1)···O(2) distance shortens appreciably [2.760(5) Å for **3** *vs.* 2.652(4) and 2.650(4) Å for **4** and **5**, respectively]; while the O(2)···O(2) contact is not a hydrogen-bonding interaction in all three systems, the O(1)···O(2) interaction is an O–H···O interaction in **4** and **5**, as is also confirmed by the presence of hydrogen atom electron density along the contact and by the different distribution of hydrogen bonds involving the neutral system.

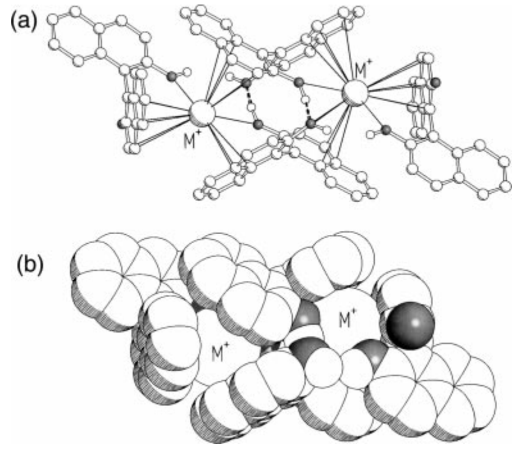

Fig. 6 (a) The Rb and Cs cations in **4** and **5** interact simultaneously with three surrounding arene systems and the related O atoms (M = Cs, Rb). (b) A space-filling representation of the dianionic pair embracing the alkali cations.

Another remarkable feature of the structures of **4** and **5** is the marked presence of π-interactions between the alkali cations and the arene systems. Fig. 6(a) shows how both Cs and Rb cations interact simultaneously with three surrounding arene systems [Cs···C and Rb···C shortest distances are 3.457(4) and 3.398(4) Å, respectively]. This type of interaction is well established and has been observed and commented upon in a number of alkali salts.[23] The coordination sphere of the alkali cations is completed by O···Cs/Rb interactions [2.936(4), 3.038(4) and 2.794(4), 2.880(4) Å in **4** and **5**, respectively]. A space-filling representation of the dianionic pair embracing the alkali cations is shown in Fig. 6(b).

Conclusions

With this study we have discovered some interesting analogies between otherwise very different chemical systems. Both the cobaltocenium salt **3** and the alkali salts **4** and **5** show the presence of dimeric anionic units. These units are *topologically* identical and both form tight ion pairs, folding around the respective cations, but are held together by different types of interactions. **4** and **5** show hydrogen-bonding interactions, which are absent in **3**. On the other hand, the dianions in **3** form hydrogen bonds with the neutral nitromethane units, which, in turn, bridge neutral binaphthol molecules. This comparison seems to suggest that the hydrogen-bonding interactions in **4** and **5** are *not essential* to the stability of the supramolecular dianion, and that the O–H donors can be used for other tasks such as linking neutral molecules. This is in keeping with the results of theoretical *ab initio* calculations carried out on several crystalline systems containing hydrogen acid anions[24] (hydrogen carbonates, hydrogen oxalates, hydrogen squarates and hydrogen croconates), which have demonstrated that hydrogen-bonding interactions constitute small stabilising contributions to the much more relevant balance of electrostatic interactions due to the presence of ions. Furthermore, the comparison between **3** and **4**/**5** shows that C–H···π interactions can play the same role as $M^+\cdots\pi$ interactions between the alkali cations and the arenes. Clearly, in these crystals there is a plethora of pairwise interactions that are simultaneously optimised. In this respect, one may argue that it is somewhat meaningless to try to pry apart all different contributions, since what really matters in the end is the optimisation of the *global* (free) energy, which is responsible for the cohesion of the crystalline materials.[25]

This work has provided further evidence that the utilisation of enantiomerically pure chiral building blocks is a good route towards chiral crystals. Enantiopure binaphthol can be successfully used to prepare chiral crystalline architectures in which organometallic cations can be accommodated. The next step is to include dipolar organometallics into the chiral framework. This strategy has been used by several research groups in the solid state chemistry field to produce materials for NLO applications.[7]

Also of some importance is the notion that the stoichiometric ratios can be used to modify the supramolecular assembly, from discrete entities, as in **2**, to extended hydrogen-bonded networks, as in **1**. It is true, however, that our control of the supramolecular arrangement is hampered by the lack of precise structural information on all those systems that do not yield crystals suitable for single-crystal X-ray diffraction, as in the cases of all other stoichiometric ratios employed. Clearly, one can *always* obtain a crystalline salt material *via* solvent evaporation. Powder diffraction shows that amorphous species are very rare, but whether the solid residue is a single new phase or a mixture of phases of different compositions is almost impossible to determine in the absence of information from single-crystal experiments. Indeed, only the full development of *ab initio* structural determination from powder diffraction data will allow us to overcome this major problem in the characterisation of crystal engineering products.

Acknowledgements

Financial support by MURST (projects: Supramolecular Materials 1999–2000, Solid Supermolecules 2000–2001) and by the Universities of Bologna (project: From Molecules to Materials, 2000–2001) and Sassari is acknowledged.

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