Rational Design, Synthesis and Crystal Structure Investigation of Hydrogen-Bonded Coordination Polymers of Bicyclic Bis-Lactam Dicarboxylates[‡]

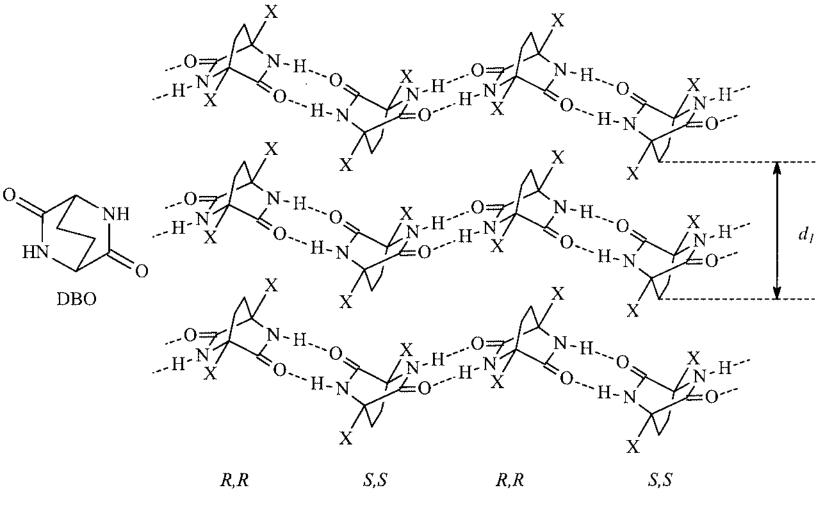
Denis A. Lenev,[a] Konstantin A. Lyssenko,[b] and Remir G. Kostyanovsky*[a]

Keywords: Carboxylate ligands / Chirality / Crystal engineering / Hydrogen bonding / Lactams

The crystal structures of the racemic coordination polymers (±)-**1** to (±)-**4** and the coordination dimers (±)-**6** and (±)-**7**, containing molecular "brick walls" with inorganic coatings and molecular "brick walls" with mixed organic-inorganic coatings, respectively, were predicted and verified on the basis of the zigzag $R_2^2(8)$ H-bonded tape columnar packing motif of the purely organic racemic dialkyl 3,6-dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylates.

Introduction

H-bonded supramolecular aggregation of metal ion-coordinated assemblies is a promising approach in crystal engineering, combining a variety of coordination types and well established organic motifs of H-bonding.[1−8] In a preceding paper[9] we have shown that functionalized derivatives of chiral C_2-symmetric bicyclic dipeptide, 2,5-diazabicyclo[2.2.2]octane-3,6-dione (DBO), viz. corresponding dialkyl 1,4-dicarboxylates, form predictable heterochiral zigzag tapes with lactamic $R_2^2(8)$ H-bonding, in which molecules of different chirality alternate strictly (Scheme 1), as in the crystal structures of (±)-DBO and other bislactams[10−14] (for other important works on lactamic H-bonded tapes, see refs.[15−17]). A new two-dimensional motif appears in all investigated crystals of the racemic and chiral quasi-racemic esters, with homochiral columns being formed by stacking of the heterochiral tapes orthogonally to their propagation axes. We refer to this two-dimensional motif as molecular "brick walls" with non-polar coating (Scheme 1) (compare ref.[18]). An attempt to extend the "brick walls" into the third dimension (and thus explain the design of the whole crystal structure) through H-bonding, involving carboxylic acid moieties (Scheme 1, X = CO_2H)



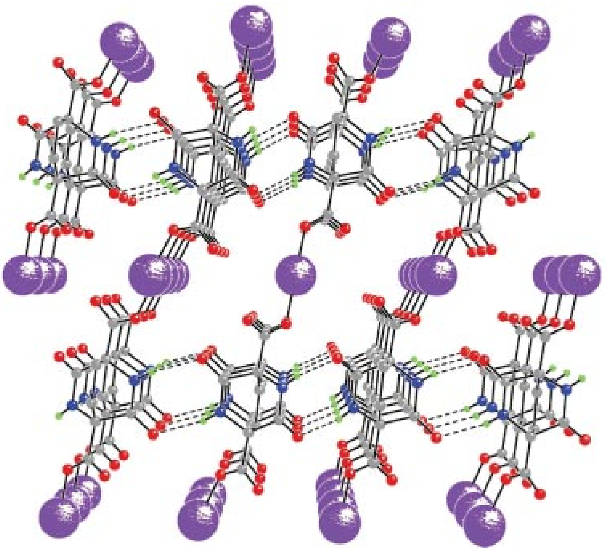
Scheme 1. Molecular "brick wall" with nonpolar coating (X = CO_2alkyl) observed in crystal structures of dialkyl DBO-1,4-dicarboxylates, where d_l is the distance between adjacent molecules in the column and is equal to the corresponding translation (crystal lattice parameter)

[‡] Self-assembly of Cage Structures, 15. Part 14: ref.[19]

[a] N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russia
Fax: (internat.) +7-095/938-2156
E-mail: kost@center.chph.ras.ru
[b] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991, Moscow, Russia
Fax: (internat.) +7-095/135-5085
E-mail: kostya@xrlab.ineos.ac.ru

DOI: 10.1002/ejic.200300115

failed because of hydrate formation.[9] In the case of competitive H-bonding carbamoyl substituents (X = $CONH_2$), either nanochannels or unbalanced chiral, triply interpenetrated, diamondoid networks form.[19] We therefore tried to use supramolecular forces from another field, metal−carboxylate ligand interactions, which it was hoped might direct self-assembly of the desired three-dimensional crystal structure (Scheme 2). In addition, we were also very interested in the senses of chirality of the assemblies formed. In this study we report the results of the initiated research. In fact, examples of coordination structures of cyclic dipeptides have already been published for Na and Tl^I salts of *cyclo*-(L-α-aspartyl-L-phenylalanine)[20,21] and in particular for a coordination polymer of Ag^I with *cyclo*-(L-methionyl-L-methionyl).[22] However, little attention is given in those papers to the supramolecular aspects of the structures.

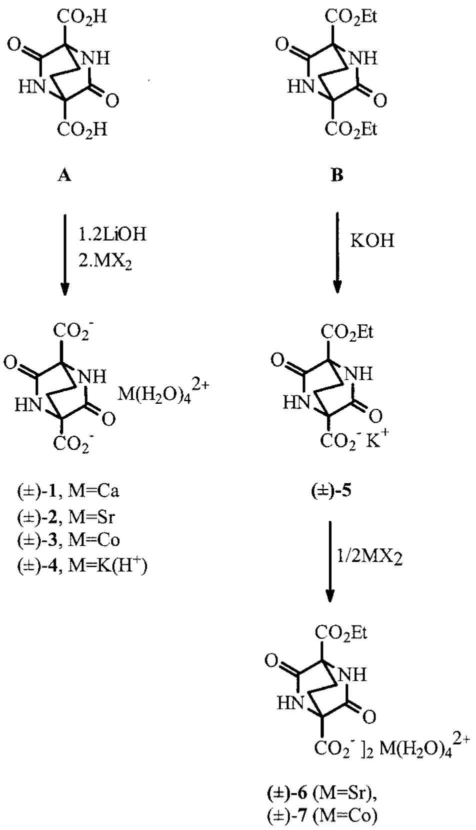


Scheme 2. Hypothetical three-dimensional self-assembly of H-bonded tapes of DBO-1,4-dicarboxylate dianions by coordination with metal cations (M lilac, C grey, N blue, O red, H green)

Results and Discussion

The synthesis of the metal DBO-1,4-dicarboxylates is depicted in Scheme 3. Metal salts of the diacid **(±)-A**[9] **(±)-1** to **(±)-3** were prepared in aqueous solution through exchange reactions. The potassium acid salt **(±)-4** was prepared by treatment of **A** with one equivalent of KOH. Monosaponification of diester **(±)-B**[9] gave compound **(±)-5**, which was converted into salts **(±)-6** and **(±)-7** through exchange reactions. All the salts were racemic. For the compounds **(±)-1** to **(±)-4**, **(±)-6** and **(±)-7**, single crystals were grown and X-ray diffraction investigation was undertaken (Table 1).

The molecular structures of the bis-lactam dicarboxylate anions in all structures studied remain practically unchanged, with variation of the bicyclic conformation from synchro- to asynchro-twist, as previously observed for the diester derivatives.[9] The dianion symmetry in **1** to **3** is close to C_2 (in **1**, the dianion occupies the special position on the twofold axis) with some deviation due to variations of the disposition of the CO_2^- groups and the bicyclic skeleton. In contrast, the symmetry of the monoanionic species in the compounds **4**, **6** and **7** cannot exceed C_1.



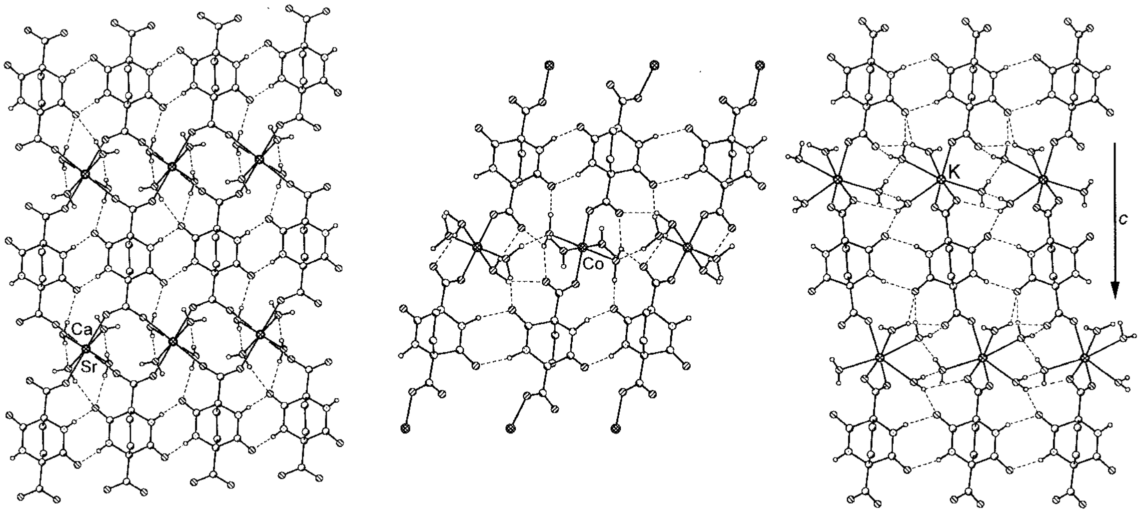
Scheme 3. Synthesis of metal DBO-1,4-dicarboxylates

It is remarkable that all the studied compounds **1** to **4**, **6** and **7** are tetrahydrates. X-ray diffraction investigation has shown that in **1** to **4** the bicyclic anions assemble in heterochiral zigzag tapes and form the expected "brick walls" (Scheme 1) with carboxylic groups on the outer surfaces. The carboxylic oxygen atoms of neighbouring "brick walls', together with four water molecules, form the coordination sphere of each metal ion. Metal ion coordination crosslinks the "brick walls', so the observed structures consist of alternating organic and inorganic layers (Figure 1). Consequently we may regard compounds **1** to **4** as coordination polymers. Their crystal structures differ in the building of the inorganic layers, but **1** and **2** are practically isostructural (if we do not take into account the crystallographic axis 2, which is present in **1** but missing in **2**). A change in the metal ion results only in slight deviations in lactam H-bond strength (N···O distance) and d_1 separation (Scheme 1). The N···O distance increases systematically from 2.854(4) Å in **4** to 3.042(5) Å in **2**. The same trend is observed for the d_1 separation, being 5.49 Å in **4** (even shorter than in the corresponding esters; see below) and going up to 6.12 Å in **2**. Thus, even bigger cations, such as Sr, although making lactam H-bonding weaker, do not change the observed molecular "brick wall" motif. The construction of the inor-

Table 1. X-ray diffraction data for the compounds **1** to **4**, **6** and **7**

	(±)-**1**	(±)-**2**	(±)-**3**	(±)-**4**	(±)-**6**	(±)-**7**
Formula	$C_8H_{14}CaN_2O_{10}$	$C_8H_{14}N_2O_{10}Sr$	$C_8H_{14}CoN_2O_{10}$	$C_8H_{15}KN_2O_{10}$	$C_{20}H_{30}N_4O_{16}Sr$	$C_{20}H_{30}CoN_4O_{16}$
T, K	110	298	110	298	110	110
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2/c$	Pc	$P\bar{1}$	$Pca2_1$	$C2/c$	$Pca2_1$
a, Å	10.851(2)	11.027(2)	5.804(1)[a]	11.429(2)	43.554(5)	10.326(2)
b, Å	5.987(1)[a]	6.117(1)[a]	10.261(2)	5.493(1)[a]	5.9568(7)[a]	5.586(1)[a]
c, Å	9.980(2)	10.191(2)	11.449(3)	20.021(4)	10.371(1)	44.179(9)
α, deg			77.582(4)			
β, deg	112.393(5)	112.88(3)	79.037(4)		99.047(3)	
γ, deg			75.162(4)			
V, Å^3	599.5(2)	633.3(2)	637.1(3)	1257.0(4)	2657.1(5)	2548.3(9)
Z	2	2	2	4	4	4
M	338.29	385.83	357.14	338.32	670.10	641.41
μ, cm^{-1}	5.85	43.16	14.05	4.82	21.35	7.62
$F(000)$	352	388	366	704	1376	1332
Absorption Correction[b]	A	B	A	none	A	A
ρ_{calcd}, g·cm^{-3}	1.874	2.023	1.862	1.788	1.675	1.672
$2\theta_{max}$, deg	60	60	57	64	52	58
Diffractometer	Smart CCD	Siemens P3	Smart CCD	Siemens P3	Smart CCD	Smart CCD
Scan mode	ω	θ/2θ	ω	θ/2θ	ω	ω
No. of reflections measured	4774	3185	6068	4459	7885	12426
R_{int}	0.0286	0.0171	0.0253	0.0033	0.0639	0.0351
No. of independent reflections	1751	1837	3137	3447	2637	5206
No. of reflections with $I > 2\sigma(I)$	1465	1668	2530	2855	1860	4436
No. of parameters	124	200	249	205	240	462
R_1	0.0465	0.0203	0.0467	0.0435	0.0524	0.0496
wR_2	0.1173	0.0513	0.1040	0.1210	0.1282	0.1277
GOF	0.930	1.018	1.074	1.069	0.934	1.031
Max./min peak, e·Å^{-3}	0.83/−0.35	0.33/−0.41	0.86/−0.56	0.38/−0.40	1.23/−0.68	1.13/−0.58

[a] The translation corresponding to the d_1 distance between the DBO molecules in columns. [b] A, semiempirical absorption correction from equivalent reflections; B, ψ-scan absorption correction.



(a) (b) (c)

Figure 1. Projections of the crystal structures of **1** and **2** (practically isostructural) (a), **3** (b) and **4** (c), showing H-bonded heterochiral tapes of bicyclic anions united by metal ions coordination on the *ac*, *bc* and *ac* crystallographic planes, respectively

ganic layer is dictated solely by the nature of the metal cation (compare ref.[23]). The coordination numbers are 7 for K, 8 for Sr and Ca, and 6 for Co. Metal−oxygen distance ranges in the coordination polyhedra of **1** to **4**, **6** and **7** are shown in Table 2. The observed distances are not unusual, with the shortest being found in the cases of the Co complexes **3** and **7**. The inorganic layer is reinforced by H-bonds involving water molecules and carboxylic or amide carbonyl

Table 2. Metal ion − carboxylate O_{carb} or water O_w oxygen distance ranges in coordination polyhedra of **1** to **4**, **6** and **7**

	1	**2**	**3**	**4**	**6**	**7**
$M-O_{carb}$	2.371(1)−2.480(1)	2.498(6)−2.615(5)	2.056(2)−2.084(2)	2.357(2)−2.437(2)	2.491(3)−2.582(3)	2.057(3)−2.092(3)
$M-O_w$	2.466(1)−2.497(1)	2.584(6)−2.645(6)	2.041(2)−2.125(2)	2.426(3)−2.571(3)	2.601(3)−2.604(3)	2.083(3)−2.096(3)

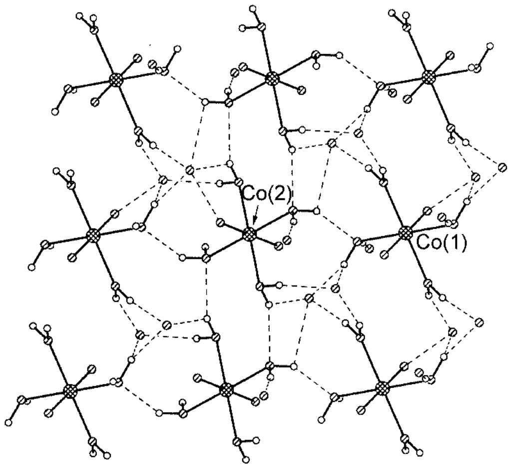
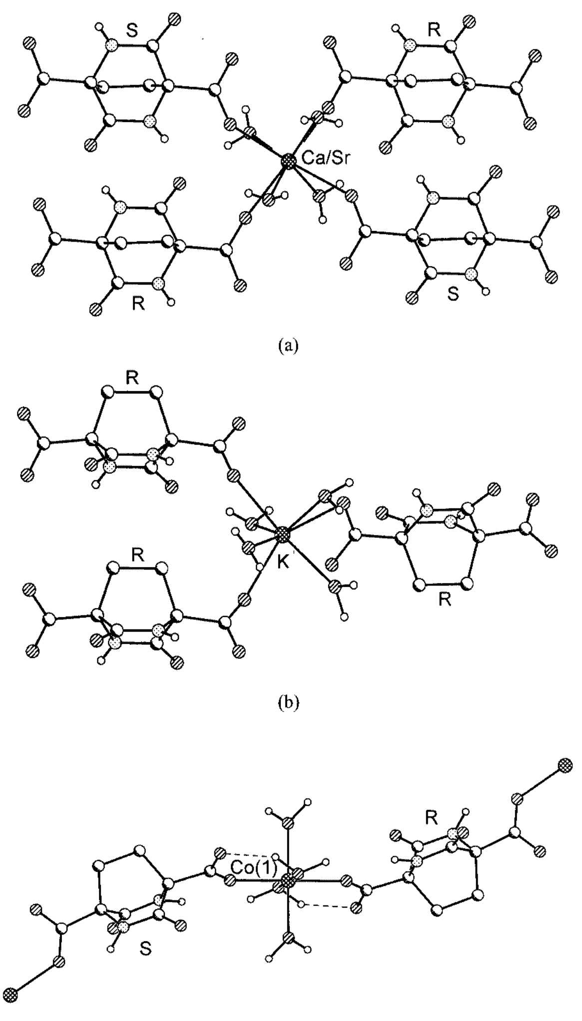


Figure 2. Projection of the H-bonded inorganic layer in **3** on the *ac* crystallographic plane



(a)

(b)

(c)

Figure 3. Coordination polyhedra and ligand chirality in **1** and **2** (a), **4** (b) and **3** (c)

oxygens (Figure 2 shows an example of H-bonded inorganic layer in **3**). The $O\cdots O$ distance, which characterizes the strength of the $O-H\cdots O$ bonds in the inorganic layer, varies between 2.732 and 3.034 Å and is practically unaffected by the nature of the cation. If one takes only the H-bonded network into consideration, the water molecules interconnect the H-bonded tapes in **1** to **4** in a three-dimensional framework.

The number and the chirality of bicyclic bis-lactam anions coordinated by metal ions vary, thus giving rise to differences in the structures of the inorganic layers and the positioning of the "brick walls'. In the cases of **1** and **2**, the alkaline earth metal ion is surrounded by four aqua ligands and four carboxylate oxygens. Each carboxylate group of the bis-lactams in these compounds is bound to two cations and thus serves as a bridging ligand. It is noteworthy that the coordination spheres of Ca and Sr in **1** and **2** both contain two (*R*,*R*) and two (*S*,*S*) enantiomers (Figure 3, a). In contrast, in the potassium complex **4** the bicyclic monoanions have two different kinds of carboxylate groups. In the first, only one of the carboxylate oxygen atoms is coordinated by metal ion, in the second both oxygen atoms are coordinated. This molecular asymmetry is not cancelled and propagates along the screw axis 2_1, so the acentric crystal structure (space group $Pca2_1$) has a polar axis in the *c* direction (Figure 1, c). In addition, the coordination polyhedron of K is homochiral (three bicyclic ligands are characterized by the same chirality; Figure 3, b). The observed difference in the chirality of the ligands is due to the fact that potassium forms bonds with anions from three separate H-bonded tapes: one from one "brick wall' and the two others from another. The latter two anions lie in the same column, one under the other, so that coordination causes a pronounced contraction of the d_1 distance (5.49 Å) in relation to the 5.57 Å in the crystal structure of the ester (±)-**B**.[9] Finally, in the crystal structure of the cobalt(II) salt **3** the metal ion (two independent cations each in the centre of symmetry) is characterized by the usual octahedral coordination with a *trans* arrangement of the monodentate ligands of opposite chirality (Figure 3, c).

If we take only the coordination connectivity into account, cations interconnect the anions, depending on the nature of the metal, in corrugated heterochiral layers (**1** and **2**) in the plane orthogonal to the axes of homochiral columns, or in the homochiral layers orthogonal to the axes of the heterochiral tapes (**4**), or in heterochiral chains (**3**) orthogonal to the "brick walls'.

All the coordination polymers obtained thus possessed the same general structure regardless of the type of metal (alkali, alkaline earth or transition), so that any desired property (e.g., magnetic) of the resulting material should be fine-tuneable simply by a change in the cation (compare ref.[2]).

Using the distinct and stable supramolecular organization of the "brick walls' in the crystal structures of covalent[9] (for example, (±)-**B**) and ionic DBO-1,4-dicarboxylates **1** to **4**, and also the well known analogy of the structure of biological membranes, we also tried to obtain coordination dimers **6** and **7**. In these structures, polar ionic and nonpolar alkyl residue regions should alternate, similarly to what has been observed in, for example, the structure of the monohydrate of the diketopiperazine *cyclo*-(L-leucyl-L-hystidyl).[24] Indeed, X-ray analysis has shown that the main features of packing remain unchanged, and we observe coordination dimerization of carboxylic ions. Strongly polar inorganic water-containing layers and nonpolar alkyl regions alternate as anticipated (Figure 4 shows the crystal structure of **7**). Comparison of the structures of organic and inorganic layers with those of the corresponding coordination polymers **2** and **3** has shown that the structure remains practically unchanged in the case of Sr, except for insignificant variations in the H-bonding in the inorganic layer. In **7** these changes are much more pronounced, and this is reflected in the homochirality of the coordination octahedron (Figure 5). The example of the Co complexes **3** and **7** thus implies that the chiralities of the ligands are practically independent of each other ((*RR*,*SS*) in one case and (*RR*,*RR*) in the other) and, unfortunately, are defined by peculiarities of crystal symmetry (centrosymmetric arrangement in **3** and acentric structure of **7**) and packing. It is noteworthy that the d_1 distances in **6** and **7** are approximately the average of those in the structures of (±)-**B** and **2** and **3**, respectively: in **6** d_1 equals 5.96 Å, in **7** 5.59 Å, whereas in **2** it is 6.12 Å, in **3** 5.80 Å, and in **B** 5.57 Å.

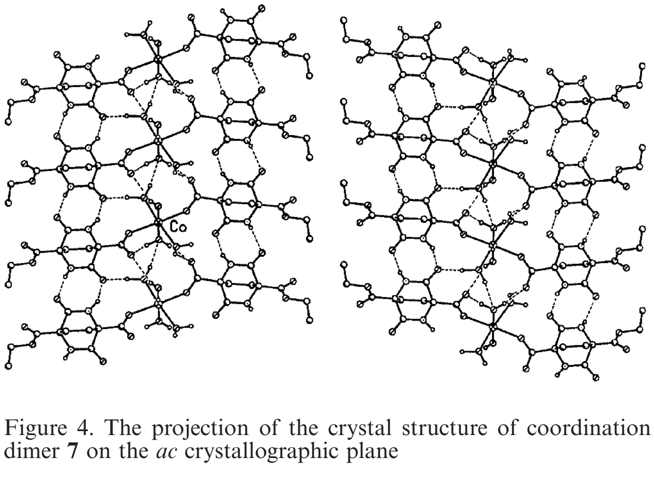


Figure 4. The projection of the crystal structure of coordination dimer **7** on the *ac* crystallographic plane

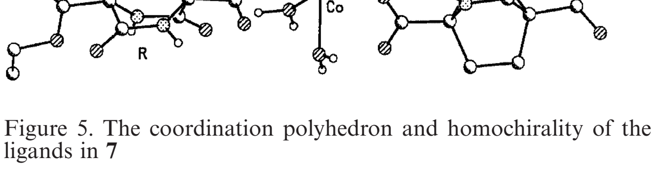


Figure 5. The coordination polyhedron and homochirality of the ligands in **7**

Compounds **6** and **7** thus represent hybrid-type materials. Firstly, the organic part makes the introduction of substituents with various functionalities possible; secondly, the nature of the cation itself may be varied. Moreover, the structures of these complexes are similar to those of biological membranes and offer perspectives for construction of ionoactive monolayers on that basis.

Conclusion

In this paper we have used a productive approach to crystal engineering − rational design of metal-organic H-bonded solids by combining a well defined H-bonded motif derived from pure organic crystal structures with the well known geometries of carboxylate metal complexes. Metal ion-assisted assembly of the bicyclic bis-lactam-dicarboxylate ions results in the predicted coordination polymers **1** to **4**, in which the molecular "brick wall" motif, found previously in dialkyl dicarboxylates (now with an inorganic ionic coating), is preserved. Formation of layers, stabilized by H-bonding of aqua ligands, is also observed. The salts' structures differ insignificantly as the coordinating centre changes. Monocarboxylate ion coordination results in other types of predicted structures, represented in the paper by coordination dimers **6** and **7**. In these compounds, "brick wall" formation is "coordinationally doubled", resulting in alternation of polar and non-polar layers (wall coatings) in the crystal.

We should also underline the limitations of our approach. Although we control the chirality of bis-lactam anions in the "brick walls", the examples of Co coordination polymer **3** and coordination dimer **7** imply that the chiralities of two anions coordinated by metal in a spatially distinct *trans* arrangement are independent of each other and depend only on the crystal symmetry and packing. Moreover, taking the strength of ionic interactions in comparison to hydrogen bonds into account, we believe that *both* organic dipole−dipole and van der Waals interaction-stabilized "brick walls" *and* inorganic H-bonded layers are responsible for the three-dimensional structure as a whole, their dimensionalities fortunately being complementary.

Finally, it should be mentioned that in the overall series of **1** to **4**, **6** and **7**, three crystal structures (**2**, **4**, **7**) are non-centrosymmetric (though achiral) and therefore offer perspectives for pyroelectric, piezoelectric and NLO applications.

Experimental Section

General Method for Preparation of Salts of (±)-A: A solution of LiOH in H_2O (2 mL, 0.2 M) was added to diacid (±)-**A** (25 mg, 0.1 mmol), and the mixture was heated until it became clear, was filtered through cotton wool, and 1 mol equiv. of solution of metal salt [$CaCl_2$, $Sr(NO_3)_2$ or $CoCl_2$] in H_2O (1 mL) was added. On standing at ambient temperature a fine powder usually crystallized. This was filtered off, dried in air, weighed and then suspended in H_2O (2 mL). The suspension was heated at reflux with slow addition of water until complete dissolution of the precipitate (5−15 min). The clear solutions were left to cool down and were kept at ambient temperature under the conditions suitable for slow evaporation of the solvent. Separate crystals formed over several days. Besides the complexes **1** to **4**, well defined crystals also formed in the cases of Zn, Mn^{II}, Ni^{II} and Cu^{II}. The Ba and Ag^{I} salts were insoluble in hot H_2O.

Calcium 3,6-Dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylate Tetrahydrate (±)-(1): Yield 30 mg (88%). Colourless needles, becoming turbid in air. $C_8H_{14}CaN_2O_{10}$ (338.3): calcd. C 28.4, H 4.2, N 8.3, Ca 11.6; found C 28.7, H 3.9, N 8.1, Ca 12.0.

Strontium 3,6-Dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylate Tetrahydrate [(±)-2]: Yield 15 mg (40%). Colourless prisms. $C_8H_{14}N_2O_{10}Sr$ (385.8): calcd. C 24.9, H 3.7, N 7.3; found C 25.0, H 3.8, N 7.3.

Cobalt(II) 3,6-Dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylate Tetrahydrate [(±)-3]: Yield 21 mg (58%). Transparent pink prisms, becoming blue and turbid in air. $C_8H_{14}CoN_2O_{10}$ (357.1): calcd. C 26.9, H 4.0, N 7.8; found C 28.0, H 4.0, N 8.1 (the significant deviation of the amount of C found from the calculated value may be attributed to water loss).

Potassium 3,6-Dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylate Tetrahydrate [(±)-4]: For preparation of this acid salt, 1 mol equiv. of KOH was taken per mol of (±)-**A**. Yield 18 mg (52%). Colourless blocks. $C_8H_{15}KN_2O_{10}$ (338.3): calcd. C 28.4, H 4.5, N 8.3; found C 28.0, H 4.3, N 8.3.

Potassium 3,6-Dioxo-4-(ethoxycarbonyl)-3,6-dioxo-2,5-diazabicyclo[2.2.2]octane-1-carboxylate [(±)-5]: A solution of KOH in EtOH (0.0546 M, 20 mL) was slowly (10 min) added, with heating and vigorous stirring, to a boiling solution of (±)-**B** (1.551 g, 5.456 mmol) in 96% EtOH (130 mL). As soon as the mixture started to become turbid (≈ 15−20 min after the start of addition), heating was stopped, the mixture was cooled to 40 °C, and, with this temperature being maintained, KOH (0.0546 M, 80 mL) was added (slowly, 2 h). The mixture was cooled to 0°C and left for 24 h. The white precipitate of a mixture of mono- and disalts was filtered off, washed with EtOH and dried in vacuo. It was then recrystallized from the minimum possible amount of boiling water. The product crystallized as thin plates, which were filtered off, washed with cold H_2O and dried in air. Yield is 977 mg (61%), m.p. 380−390° C(dec.). ^1H NMR (400 MHz, D_2O, 60° C): $\delta = 1.32$ (t, $^3J = 7$ Hz, 3 H, CH_3,), 2.2−2.35 (m, 4 H, CH_2CH_2,), 4.38 (m, 2 H, CH_2Me) ppm. $C_{10}H_{11}KN_2O_6$ (294.3): calcd. K 13.3, C 40.8, H 3.7, N 9.5; found K 13.7, C 39.7, H 4.0, N 9.5.

Preparation of Salts (±)-6 and (±)-7: A solution of $CoCl_2$ (6.5 mg, 0.05 mmol) or $Sr(NO_3)_2$ (10.6 mg, 0.05 mmol) in H_2O (0.5 mL) was added to a hot solution of (±)-**5** (30 mg, 0.10 mmol) in H_2O (1 mL). After 1 h the precipitate was filtered off, dried in air and recrystallized from water in the same manner as for the coordination polymers.

Strontium Bis{4-(Ethoxycarbonyl)-3,6-dioxo-2,5-diazabicyclo[2.2.2]-octane-1-carboxylate} tetrahydrate [(±)-6]: Yield 8 mg (25%). Very thin colourless plates. $C_{20}H_{30}N_4O_{16}Sr$ (670.1): calcd. C 35.9, H 4.5, N 8.4; found C 36.0, H 4.3, N 8.2.

Cobalt(II) Bis{4-(Ethoxycarbonyl)-3,6-dioxo-2,5-diazabicyclo[2.2.2]-octane-1-carboxylate} Tetrahydrate (±)-7: Yield 8 mg (27%). Transparent pink prisms. $C_{20}H_{30}CoN_4O_{16}$ (641.4): calcd. C 37.5, H 4.7, N 8.7; found C 37.5, H 4.5, N 8.9.

Crystallographic data and parameters of the refinement for complexes **1** to **4**, **6** and **7** are presented in Table 1. The data collection was carried out by use of the θ/2θ scan mode for the 4-circle diffractometer (Siemens P3) and the ω-scan mode with 0.3° step in ω and 10 s (for **1** and **3**) or 20 s (**6** and **7**) exposure for SMART CCD diffractometer. The X-ray diffraction data for SMART CCD were processed by use of the SAINT PLUS program package. All structures were solved by direct methods and refined by full-matrix, least-squares against F^2 in the anisotropic (H atoms isotropic) approximation, by use of the SHELXTL-97 package. The positions of hydrogen atoms were located from the Fourier electron density synthesis and included in refinement in isotropic or riding model approximation. The hydrogen atom of the CO_2H groups in the monohydropotassium salt **4** was not located, probably due to the superposition of the CO_2^- and CO_2H groups, reflected in the equalization of the corresponding C−O bond lengths. The absolute structures in the cases of **2**, **4** and **7** were determined on the basis of the Flack parameter.
CCDC entries 204270−204275 (**1** to **4**, **6** and **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank Prof. Dr. V. Buß (University of Duisburg) for helpful discussions. This work was supported by INTAS (grant No. 99−00157), the Russian Academy of Sciences (academician N. T. Kuznetsov programme) and the Russian Foundation for Basic Research (grant Nos. 00-03-32738, 00-03-81187 Bel, 03-03-32019 and 03-03-06525 MAS).

[1] M. Munakata, L. P. Wu, M. Yamamoto, K.-S. Takayoshi, M. Maekawa, *J. Am. Chem. Soc.* **1996**, *118*, 3117−3124.

[2] J. C. MacDonald, P. C. Dorrestein, M. M. Pilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Schultz, J. L. Manson, *J. Am. Chem. Soc.* **2000**, *122*, 11692−11702.

[3] E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius, K. Rissanen, *Eur. J. Inorg. Chem.* **2001**, 1515−1521.

[4] A. D. Burrows, C.-W. Chan, M. M. Chowdhry, J. E. McGrady, D. M. P. Mingos, *Chem. Soc. Rev.* **1995**, *24*, 329−337.

[5] I. Goldberg, *Chem. Eur. J.* **2000**, *6*, 3863−3870.

[6] C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *Angew. Chem.* **1999**, *111*, 1932−1936; *Angew. Chem. Int. Ed.* **1999**, *38*, 1815−1819.

[7] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375−1405.

[8] S. Ferlay, O. Felix, M. W. Hosseini, J. M. Planeix, N. Kyritsakas, *Chem. Commun.* **2002**, 702−703.

[9] K. A. Lyssenko, D. A. Lenev, R. G. Kostyanovsky, *Tetrahedron* **2002**, *58*, 8525−8537.

[10] M.-J. Brienne, J. Gabard, M. Leclercq, J.-M. Lehn, M. Cesario, C. Pascard, M. Cheve, G. Dutruc-Rosset, *Tetrahedron Lett.* **1994**, *35*, 8157−8160.

[11] D. N. J. White, J. D. Dunitz, *Isr. J. Chem.* **1972**, *10*, 249.

[12] M. Tichy, L. Ridvan, P. Holy, J. Zavada, J. Cisarova, J. Podlaha, *Tetrahedron: Asymmetry* **1998**, *9*, 227−234.

[13] C. Altomare, S. Cellamare, A. Carotti, G. Casini, M. Ferappi,

E. Gavuzzo, F. Mazza, P.-A. Carrupt, P. Gaillard, B. Testa, *J. Med. Chem.* **1995**, *38*, 170−179.

[14] M. Czugler, A. Kalman, B. Oleksyn, M. Kajtar, *Cryst. Struct. Commun.* **1980**, 791−794.

[15] J. C. MacDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383−2420.

[16] G. T. R. Palmore, M. T. McBride, *Chem. Commun.* **1998**, 145−146.

[17] S. Palacin, D. N. Chin, E. E. Simanek, J. C. MacDonald, G. M. Whitesides, M. T. McBride, G. T. R. Palmore, *J. Am. Chem. Soc.* **1997**, *119*, 11807−11816.

[18] H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **1998**, *120*, 10622−10628.

[19] R. G. Kostyanovsky, K. A. Lyssenko, D. A. Lenev, I. A. Bronzova, *Tetrahedron: Asymmetry* **2002**, *13*, 2697−2701.

[20] P. Mikulcik, J. Riede, H. Schmidbaur, *Chem. Ber.* **1991**, *124*, 2743−2746.

[21] P. Mikulcik, P. Bissinger, J. Riede, H. Schmidbaur, *Z. Naturforsch., Teil B* **1992**, *47*, 952−956.

[22] Y. Kojima, T. Yamashita, Y. Ishino, T. Hirashima, K. Hirotsu, *Chem. Lett.* **1983**, 453−454.

[23] E. G. Bakalbassis, M. Korabik, A. Michailides, J. Mrozinski, C. Raptopoulou, S. Skoulika, A. Terzis, D. Tsaousis, *J. Chem. Soc., Dalton Trans.* **2001**, 850−857.

[24] I. Tanaka, T. Iwata, N. Takahashi, T. Ashida, *Acta Crystallogr., Sect. B* **1977**, *33*, 3902.

Received February 27, 2003