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Simultaneous binding of boron and alkaline metal cations by a macrocyclic ligand bearing catechol units: structural analysis of borocryptates[†]

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Summary — A podand-type ligand based on the [22] diaza-tetraoxa macrocycle bearing two pendant catechol units was shown to bind simultaneously and in a inclusive fashion boron and alkaline metal cations. A detailed solid-state structural analysis of the potassium, rubidium and caesium complexes is reported.

boro-cryptand / alkaline cryptate / spiro-borate ester / macrobicycle / catechol

Résumé — Complexation simultanée de cations alcalins et du bore par un récepteur macrocyclique portant deux unités catéchol: études structurales de borocryptates. *La fonctionnalisation du [22] macrocycle au niveau des amines par deux résidus catéchol conduit à un récepteur capable de complexer simultanément un atome de bore et un cation alcalin. La nature inclusive des complexes au potassium, rubidium et au césium est discutée à partir des données structurales obtenues par diffraction des rayons X.*

boro-cryptand / borocryptate / spiroborate / macrobicycle / catéchol

Introduction

Boromycin (fig 1), an antibiotic produced by *Streptomyces antibioticus*, is the first known natural product containing a boron atom. The organic core of boromycin may be regarded as a tetradentate polyhydroxy macrolide capable of binding boron, which has a cleft composed of oxygen atoms. Boromycin was isolated by Hütter et al [1], and the structures of both the boron-free *des*-valine-boromycin and its rubidium salt have been elucidated by X-ray crystallography (fig 1) [2, 3]. Aplasmomycin, produced by *Streptomyces griseus*, is another antibiotic which contains a boron atom [4]. Its structure was also investigated [5] and showed that it differs from boromycin by having two chemically identical subunits surrounding the borate complex.

Inspired by structural and chemical features of the above-mentioned naturally occurring antibiotics and those of cryptands [6], we designed and synthesized the macrocyclic compound **1**-4H which is of the podand type (fig 2) [7].

The design of the **1**-4H was based on the combination of a macrocyclic framework and two bidentate dianionic ligands. For the preorganized macrocyclic core, the 18-membered ring diazatetraoxa macrocycle [8] was chosen because of its ability to bind hard cations [9]. By analogy, the macrocyclic moiety should act as the cleft of oxygen atoms in boromycin. As for the bidentate ligand, catechol seemed to be suitable for binding transition metal cations. The linkage of the catechol moieties to the macrocycle was achieved using either an amide bond or a methylene group [7]. A similar concept has been reported for podands and coronands bearing two catechol units linked by polyethylene glycol chains [10]. On the other hand, triaza- and tetraaza-macrocycles bearing three and four pendant catecholate units [11], as well as macrobicyclic tris-catecholate ligands serving as siderophore analogues, have also been reported [12].

The chemistry of binuclear complexes has been extensively studied over the past 20 years [13]. At an earlier period many homo- and heterobinuclear complexes reported were essentially of the same type, ie, two alkaline or two transition metal cations. It is only recently that considerable effort has been invested in the synthesis of heterobinuclear complexes bearing both a hard alkaline or alkaline-earth cation and a soft transition metal cation [14]. Compound **1**-4H may also be regarded as a binucleating ligand capable of binding two cations (fig 3). Indeed, the binding by $\mathbf{1}^{4-}$

[†] Dedicated to Prof Raymond Weiss.

* Correspondence and reprints.

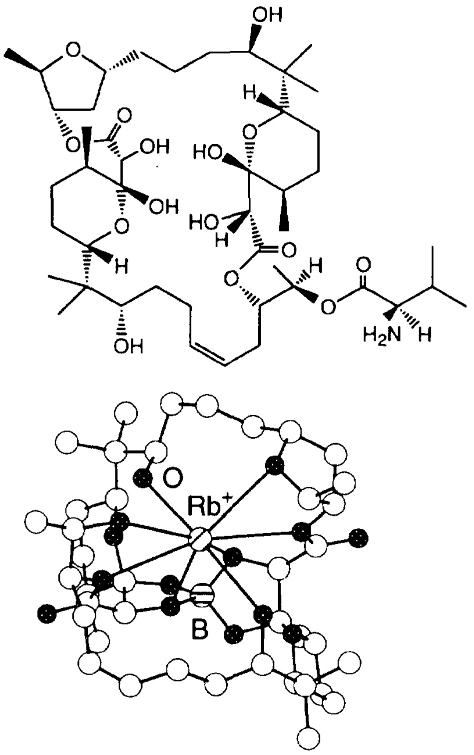

Fig 1. Chemical structure of boromycin (top) and the X-ray structure of the rubidium salt of *des*-valine-boromycin [3]. For the sake of clarity H atoms are not presented.

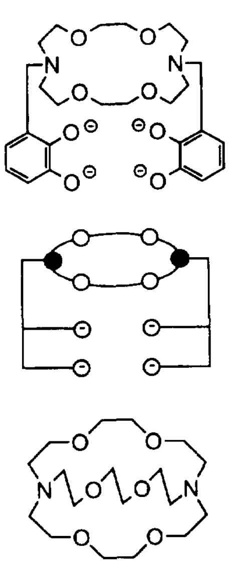

Fig 2. Compound 1^{4-} (top), its schematic representation (middle) and [222] cryptand (bottom).

of a main group element such as boron leads to the negatively charged pseudocryptand ($1^{4-}\cdot B^{3+}$), a complex of the Böeseken type [15] found in boromycin [2, 3] and aplasmomycin [5]. In turn, this complex binds an alkaline cation M^+ affording the neutral pseudocryptate ($1^{4-}\cdot B^{3+}\cdot M^+$). The driving force for the formation of these complexes is attractive charge-charge and charge-dipole interactions. The early design of cryptands consisted of the construction of cage molecules able to bind cationic substrates within their cavity thus leading to cryptates. Since the [222] cryptand is neutral, for the sake of charge neutrality, the cation cryptate is accompanied by a counteranion. As mentioned above, this aspect is avoided by the approach presented here. Furthermore, the formation of the borate ester ($1^{4-}\cdot B^{3+}$) bearing one negative charge increases the binding affinity of the ligand for mono-charged M^+ cations. It is worth noting that when a tetrahedrally coordinating metal cation such as boron is bound by both catecholate subunits of the achiral ligand 1^{4-}, a chiral pseudo cryptand is generated (fig 3). Other compounds composed of the [22] macrocycle and two bipyridine moieties and their ability to bind both transition and alkaline metal cations have been described [16].

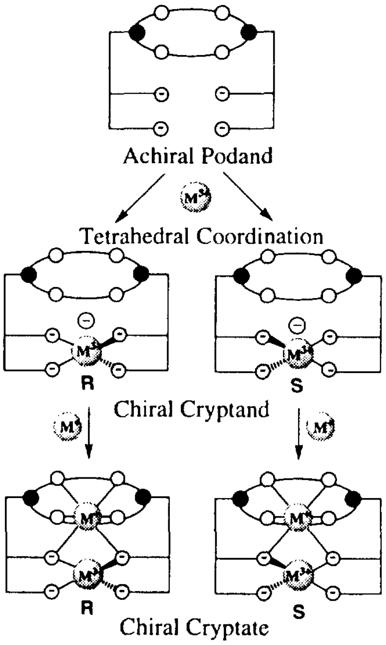

Fig 3. Schematic representation of the cascade-type formation of binuclear complexes between 1^{4-} and metal cations. The figure also schematically represents chiral aspects (see text).

Since upon coordination of boron, dramatic changes in the ^{1}H-NMR spectrum of **1** were observed in solution, the binding ability of ($1^{4-}\cdot B^{3+}$) towards alkaline [17] and NH_4^+ [18] cations was studied by NMR spectroscopy in $CDCl_3$ and CD_3OD. Based on competition experiments, the binding constant for ($1^{4-}\cdot B^{3+}\cdot K^+$) complex was estimated to be around $10^{12.5}$ mol L^{-1} in methanol, the highest ever observed for a synthetic complexing agent. On the other hand, selectivity factors between K^+ and both Na^+ and Cs^+ cations greater than 10^3 and 10^2 respectively were determined [17]. The ($1^{4-}\cdot B^{3+}\cdot K^+$) complex was also shown to be more stable by a factor of 10^2 than the ([222], K^+) complex. The

Table I.

Complex	$(1^{4-}\cdot B^{3+}\cdot K^+)$	$(1^{4-}\cdot B^{3+}\cdot Rb^+)$	$(1^{4-}\cdot B^{3+}\cdot Cs^+)$
Formula	$C_{26}H_{34}BN_2O_8K\cdot CH_2Cl_2$	$C_{26}H_{34}BN_2O_8Rb\cdot CH_2Cl_2$	$C_{26}H_{34}BN_2O_8Cs\cdot CH_2Cl_2$
Molecular weight	637.4	683.8	731.2
Color	Without	Without	Without
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	11.813(3)	11.780(3)	11.785(3)
b (Å)	15.576(4)	15.621(4)	15.825(4)
c (Å)	17.205(5)	17.311(5)	17.475(5)
β (deg)	106.12(2)	106.16(2)	106.33(2)
Volume (Å^3)	3041.2	3059.6	3127.5
Z	4	4	4
Dcalc (gcm^{-3})	1.392	1.484	1.553
Wavelength (Å)	1.5418	1.5418	0.7107
μ (cm^{-1})	36.177	43.088	13.929
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Crystal dim (mm)	0.2 x 0.2 x 0.12	0.06 x 0.20 x 0.26	0.25 x 0.20 x 0.20
Temperature	−100 °C	−100 °C	20 °C
Radiation	Cu$K\alpha$	Cu$K\alpha$	Mo$K\alpha$
θ min/max (deg)	3/52	3/52	2/25
Number of data	3 646	3 644	6 098
Number of data	2 410	2 612	3 625
Number of variable	370	370	370
Abs min/max	0.74/1.36	0.90/1.19	0.91/1.10
R(F)	0.032	0.026	0.032
Rw(F)	0.050	0.038	0.043
p	0.08	0.06	0.06
GOF	1.113	1.075	1.035

same experiments repeated with NH_4^+ gave the following selectivity sequence $NH_4^+ > Na^+ > Cs^+$. Furthermore, the $(1^{4-}\cdot B^{3+}\cdot NH_4^+)$ inclusive complex appeared to be more stable, at least by a factor of 10^3, than the ([222], NH_4^+) complex [18].

In the solid state, a detailed structural investigation of ([222], M^+) complexes was reported by Weiss et al [19]. Some 23 years later, in this contribution, we use X-ray studies to describe the structural features of the rubidium $(1^{4-}\cdot B^{3+}\cdot Rb^+)$ and caesium $(1^{4-}\cdot B^{3+}\cdot Cs^+)$ complexes of the pseudocryptand $(1^{4-}\cdot B^{3+})$. For comparison purposes, we include some of the data previously obtained for $(1^{4-}\cdot B^{3+}\cdot K^+)$ complex [17].

Experimental section

Compound **1**-4H was prepared according to published procedure [7]. Treatment of **1**-4H in EtOH with 1 equiv of $B(OH)_3$ and 1 equiv of MOH (M = Na, K, Rb, Cs) in H_2O/EtOH mixture at room temperature and under argon leads exclusively to the formation of $(1^{4-}\cdot B^{3+}\cdot M^+)$ complex. A single recrystallization of the raw material afforded the pure desired complex. For the $(1^{4-}\cdot B^{3+}\cdot K^+)$ complex, complete assignment of both proton and carbon signals could be performed using ^1H-^{13}C correlation experiments, and we assumed that the same assignment would hold for other complexes. Both rubidium and caesium complexes were chemically stable. Indeed, even in a solvolysing solvent such as CD_3OD, no alteration of their ^1H spectrum was detected over several weeks.

X-ray analysis

Suitable crystals of $(1^{4-}\cdot B^{3+}\cdot Rb^+)$ and $(1^{4-}\cdot B^{3+}\cdot Cs^+)$ were obtained from a CH_2Cl_2/hexane mixture. Both complexes were isostructural and contained a CH_2Cl_2 molecule of crystallization. Data for $(1^{4-}\cdot B^{3+}\cdot Rb^+)$ were collected at 173 K using a Philips PW1100/16 automatic diffractometer. The resulting data set was analyzed using the Enraf-Nonius SDP/VAX package. Data for $(1^{4-}\cdot B^{3+}\cdot Cs^+)$ were collected at 293 K using a Enraf-Nonius CAD 4F automatic diffractometer. The structure was solved by heavy atom method and refined anisotropically using absorption corrected data. Selected data dealing with both structures are given in table I. For comparison purposes, data obtained for $(1^{4-}\cdot B^{3+}\cdot K^+)$ [17] are also included. Positional parameters and their ESD values for the rubidium (table II) and caesium complexes (table III) are given below.

Table II. Positional parameters and their ESD for $(1^{4-}\cdot B^{3+}\cdot Rb^+)$.

Atom	x	y	z
RB	0.88270(3)	0.18364(2)	0.39920(2)
N1	0.6336(2)	0.1902(2)	0.4287(2)
C2	0.6106(3)	0.2809(3)	0.4383(2)
C3	0.6386(3)	0.3381(2)	0.3766(2)
O4	0.7632(2)	0.3453(2)	0.3916(1)
C5	0.7958(4)	0.4023(2)	0.3380(2)
C6	0.9266(4)	0.4141(2)	0.3638(2)
O7	0.9825(2)	0.3363(2)	0.3519(1)
C8	1.1078(3)	0.3437(2)	0.3758(2)
C9	1.1617(3)	0.2688(2)	0.3453(2)
N10	1.1405(2)	0.1859(2)	0.3793(2)
C11	1.2175(3)	0.1759(3)	0.4604(2)
C12	1.1810(3)	0.1094(3)	0.5109(2)
O13	1.0779(2)	0.1378(2)	0.5311(1)
C14	1.0535(3)	0.0885(2)	0.5933(2)
C15	0.9514(3)	0.1276(2)	0.6165(2)
O16	0.8469(2)	0.1217(2)	0.5513(1)
C17	0.7468(3)	0.1559(3)	0.5702(2)
C18	0.6380(3)	0.1420(3)	0.5020(2)
C19	0.5371(3)	0.1559(3)	0.3608(2)

C20	0.5565(3)	0.0663(2)	0.3362(2)
C21	0.6346(3)	0.0501(2)	0.2912(2)
C22	0.6551(3)	−0.0328(2)	0.2679(2)
C23	0.5970(3)	−0.1021(2)	0.2870(2)
C24	0.5150(3)	−0.0866(2)	0.3306(2)
C25	0.4969(3)	−0.0043(3)	0.3546(2)
O26	0.7001(2)	0.1075(1)	0.2637(1)
O27	0.7368(2)	−0.0321(1)	0.2267(1)
B	0.7785(3)	0.0572(3)	0.2263(2)
O28	0.9035(2)	0.0682(1)	0.2753(1)
O29	0.7760(2)	0.0856(2)	0.1452(1)
C30	0.9638(3)	0.0987(2)	0.2244(2)
C31	0.8891(3)	0.1065(2)	0.1466(2)
C32	0.9311(3)	0.1306(2)	0.0837(2)
C33	1.0510(3)	0.1475(3)	0.1012(2)
C34	1.1251(3)	0.1429(2)	0.1788(2)
C35	1.0822(3)	0.1185(2)	0.2429(2)
C36	1.1599(3)	0.1154(2)	0.3275(2)
C37	0.4705(4)	0.0897(3)	0.0947(3)
Cl1	0.4348(1)	0.19097(8)	0.12140(8)
Cl2	0.3664(1)	0.05221(9)	0.00775(8)
H1	0.6571	0.2985	0.4898
H2	0.5292	0.2873	0.4350
H3	0.6058	0.3932	0.3794
H4	0.6055	0.3146	0.3245
H5	0.7580	0.4559	0.3386
H6	0.7722	0.3793	0.2851
H7	0.9513	0.4292	0.4191
H8	0.9479	0.4583	0.3328
H9	1.1353	0.3452	0.4328
H10	1.1299	0.3949	0.3543
H11	1.2446	0.2776	0.3580
H12	1.1297	0.2661	0.2885
H13	1.2210	0.2293	0.4870
H14	1.2939	0.1612	0.4564
H15	1.2430	0.1004	0.5587
H16	1.1642	0.0572	0.4816
H17	1.1211	0.0876	0.6385
H18	1.0340	0.0316	0.5748
H19	0.9681	0.1860	0.6300
H20	0.9399	0.0979	0.6617
H21	0.7580	0.2155	0.5800
H22	0.7374	0.1284	0.6170
H23	0.6332	0.0827	0.4890
H24	0.5715	0.1580	0.5196
H25	0.5293	0.1922	0.3156
H26	0.4658	0.1568	0.3763
H27	0.6116	−0.1584	0.2713
H28	0.4714	−0.1328	0.3437
H29	0.4417	0.0042	0.3848
H30	0.8804	0.1354	0.0305
H31	1.0835	0.1627	0.0586
H32	1.2064	0.1565	0.1885
H33	1.1459	0.0627	0.3508
H34	1.2398	0.1175	0.3259
H35	0.4730	0.0513	0.1377
H36	0.5459	0.0918	0.0849

Table III. Positional parameters and their ESD for ($1^{4-}\cdot B^{3+}\cdot Cs^{+}$).

Atom	x	y	z
CS	0.88079(2)	0.17880(2)	0.39519(2)
N1	0.6320(3)	0.1898(3)	0.4250(2)
C2	0.6082(4)	0.2803(4)	0.4317(3)
C3	0.6379(5)	0.3356(4)	0.3712(4)
O4	0.7624(3)	0.3466(2)	0.3901(2)
C5	0.7976(6)	0.4001(4)	0.3365(4)
C6	0.9289(5)	0.4110(4)	0.3623(3)
O7	0.9841(3)	0.3341(2)	0.3477(2)
C8	1.1091(5)	0.3390(3)	0.3752(3)
C9	1.1621(4)	0.2642(3)	0.3449(3)
N10	1.1399(3)	0.1823(3)	0.3775(2)
C11	1.2178(4)	0.1698(4)	0.4589(3)
C12	1.1771(4)	0.1080(4)	0.5101(3)
O13	1.0824(3)	0.1420(2)	0.5348(2)
C14	1.0527(4)	0.0929(3)	0.5944(3)
C15	0.9501(4)	0.1319(4)	0.6161(3)
O16	0.8459(3)	0.1216(2)	0.5519(2)
C17	0.7460(4)	0.1611(4)	0.5665(3)
C18	0.6369(4)	0.1444(4)	0.4983(3)
C19	0.5389(4)	0.1535(4)	0.3573(3)
C20	0.5600(4)	0.0654(3)	0.3353(3)
C21	0.6337(3)	0.0450(3)	0.2893(2)
C22	0.6529(4)	−0.0377(3)	0.2685(3)
C23	0.5966(4)	−0.1047(3)	0.2906(3)
C24	0.5188(4)	−0.0861(4)	0.3366(3)
C25	0.5021(4)	−0.0054(4)	0.3574(3)
B	0.7741(4)	0.0474(4)	0.2223(3)
O26	0.6968(2)	0.1004(2)	0.2575(2)
O27	0.7314(2)	−0.0389(2)	0.2245(2)
O28	0.9001(2)	0.0571(2)	0.2713(2)
O29	0.7745(3)	0.0734(2)	0.1421(2)
C30	0.9607(3)	0.0916(3)	0.2226(2)
C31	0.8858(4)	0.0985(3)	0.1453(2)
C32	0.9285(5)	0.1250(4)	0.0841(3)
C33	1.0467(5)	0.1458(4)	0.1024(3)
C34	1.1187(4)	0.1421(3)	0.1792(3)
C35	1.0780(3)	0.1151(3)	0.2432(2)
C36	1.1558(4)	0.1122(3)	0.3261(3)
C37	0.4658(6)	0.0896(5)	0.0937(4)
Cl1	0.4316(2)	0.1891(1)	0.1181(1)
Cl2	0.3643(2)	0.0499(2)	0.0104(1)
H1	0.6530	0.2989	0.4830
H2	0.5262	0.2867	0.4268
H3	0.6010	0.3890	0.3707
H4	0.6100	0.3101	0.3201
H5	0.7607	0.4536	0.3354
H6	0.7742	0.3759	0.2846
H7	0.9541	0.4238	0.4176
H8	0.9504	0.4558	0.3330
H9	1.1333	0.3389	0.4318
H10	1.1350	0.3896	0.3561
H11	1.2451	0.2724	0.3579
H12	1.1302	0.2621	0.2885
H13	1.2268	0.2229	0.4852
H14	1.2923	0.1511	0.4545
H15	1.2408	0.0953	0.5556
H16	1.1517	0.0576	0.4805
H17	1.1188	0.0904	0.6403
H18	1.0321	0.0374	0.5746
H19	0.9648	0.1904	0.6265
H20	0.9400	0.1049	0.6623
H21	0.7592	0.2202	0.5718
H22	0.7343	0.1391	0.6143
H23	0.6338	0.0856	0.4869
H24	0.5697	0.1600	0.5149
H25	0.5324	0.1883	0.3119
H26	0.4663	0.1545	0.3709
H27	0.6092	−0.1609	0.2759
H28	0.4772	−0.1307	0.3531
H29	0.4489	0.0042	0.3885
H30	0.8786	0.1288	0.0310
H31	1.0790	0.1630	0.0609
H32	1.1991	0.1584	0.1893
H33	1.1407	0.0607	0.3496
H34	1.2355	0.1129	0.3241
H35	0.4689	0.0530	0.1374
H36	0.5411	0.0911	0.0839

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Selected bond angles (°) and distances (Å).

Complex	*N1MN10*	*N1N10*	*N1M*	*MN10*	*MO4*	*MO7*	*MO13*	*MO16*	*MO26*	*MO28*
1-K	177.7	6.30	3.14	3.16	2.79	2.80	2.77	2.89	2.90	2.79
1-Rb	176.0	6.26	3.14	3.12	2.87	2.87	2.84	2.94	2.95	2.86
1-Cs	174.3	6.27	3.15	3.12	2.99	2.96	2.94	3.02	3.01	2.95

For numbering see figure 4. For ($\mathbf{1}^{4-}\cdot B^{3+}\cdot K^+$) see [17].

Further details of the crystal structure investigation are available on request from British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90429.

Results

In all three cases, as expected because of the tetrahedral coordination around boron, both *R* and *S* isomers are present in the unit cell. The cation M^+ (K^+, Rb^+, Cs^+) is located within the cavity formed by the negatively charged pseudocryptand ($\mathbf{1}^{4-}\cdot B^{3+}$).

For each complex, the lone pairs of both nitrogen atoms are oriented towards the interior of the cavity (in/in conformation). The N1-N10 (for numbering of selected atoms see fig 4) distances are almost the same for all three complexes (table IV). The observed average distance of ca 6.27 Å is considerably longer than the N-N distances of 5.75 Å, ca 6.00 Å and ca 6.06 Å obtained for ([222], K^+), ([222], Rb^+) and ([222], Cs^+) complexes, respectively [19]. The cation M^+ is almost located at equal distances from the two bridgehead nitrogen atoms. In marked contrast with the ([222], M^+) cryptate, for ($\mathbf{1}^{4-}\cdot B^{3+}\cdot M^+$); (M = K, Rb, Cs) the N-M^+ distance varies only slightly from an average distance of ca 3.15 Å (table IV). This distance is considerably longer than the N-M^+ distances of 2.87 Å, ca 3.00 Å and ca 3.03 Å observed for ([222], K^+), ([222], Rb^+) and ([222], Cs^+) complexes respectively [19].

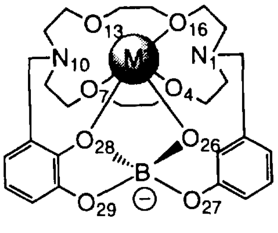

Fig 4. Schematic representation of ($\mathbf{1}^{4-}\cdot B^{3+}\cdot M^+$, M = K, Rb, Cs) complexes and the numbering of selected atoms.

Among the eight oxygen atoms present in **1**-4H, only six, the four ether junctions (O4, O7, O13, O16) and two borate oxygen atoms (O26, O28), are localized within a bonding distance of M^+ (average distance of ca 2.82 Å for K^+, ca 2.89 Å for Rb^+, ca 2.98 Å for Cs^+). For all three complexes, the metal cation M^+ is surrounded by six oxygen and two nitrogen atoms with irregular coordination polyhedrons around M^+. In contrast with the ([222], M^+) complexes in which the cation interacts with all heteroatoms and is located almost in the center of the cage, in the case of ($\mathbf{1}^{4-}\cdot B^{3+}\cdot M^+$), the average M^+-O distances are considerably shorter than the average M^+-N distances (table IV). This is an indication of stronger attractive interactions between the metal cation and oxygen atoms

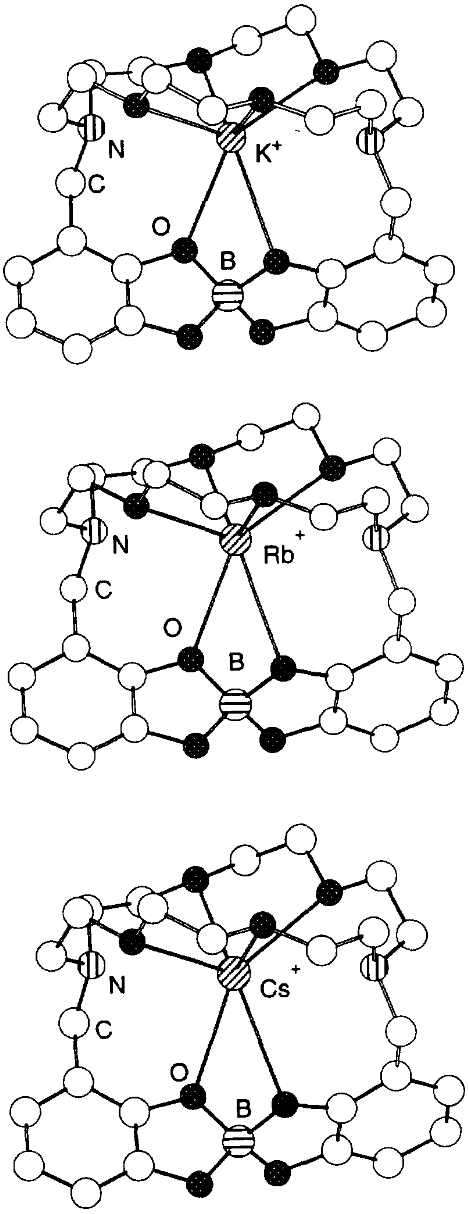

Fig 5. X-ray structures of ($\mathbf{1}^{4-}\cdot B^{3+}\cdot M^+$) complexes: M = K (top), M = Rb (middle), M = Cs (bottom). For the sake of clarity H atoms are not presented.

Table V. Selected distances (Å) and angles (°).

Complex	*BO26*	*BO27*	*BO28*	*BO29*	*O26BO27*	*O26BO28*	*O26BO29*	*O27BO28*	*O27BO29*	*O28BO29*
1-K	1.478	1.491	1.481	1.472	104.4	109.5	114.5	112.7	110.3	105.6
1-Rb	1.490	1.480	1.491	1.466	104.4	109.0	114.1	112.5	111.8	105.3
1-Cs	1.493	1.460	1.500	1.462	105.0	109.2	113.8	112.0	112.5	104.5
Average	1.487	1.477	1.490	1.466	104.6	109.2	114.1	112.4	111.5	105.1

For numbering see figure 4. Data for (**1**-K) from [17].

within bonding distances than with the two nitrogen atoms. Whereas for ([222], M^+) complexes [19] the N-M-N angle is almost 180°, in the case of ($1^{4-}{\cdot}B^{3+}{\cdot}M^+$), this value drops from 177° for K^+ to 176° for Rb^+ and 174° for Cs^+.

The coordination geometry around boron is indeed tetrahedral (table V). The B-O distances are close to 1.48 Å. Due to the rather rigid structure of the catecholate units, the O-B-O angles vary from 104° to 114° indicating a slight deformation of the tetrahedron, and the average values for all three structures remains almost identical.

As expected, the increase from 2.82 Å for K^+ to 2.89 Å for Rb^+ and to 2.98 Å for Cs^+ in the average M-O distance parallels the enhancement of the ionic radii of the alkaline cations (table IV). The N1-N10 distance decreases slightly from 6.30 Å in case of K^+ to 6.26 Å for Rb^+ and to 6.27 Å for Cs^+. The average $N{-}M^+$ distance follows the same trend (3.15 Å for K^+, 3.14 Å for Rb^+ and 3.135 Å for Cs^+).

In conclusion, we have demonstrated that the pseudocryptand compound **1**-4H participates in a cascade-type complexation process. Indeed, upon the binding of boron by both its catecholate subunits, compound $\mathbf{1}^{4-}$ leads to the spiroborate ester ($1^{4-}{\cdot}B^{3+}$), a preorganized cavity bearing one negative charge. The latter acts as a pseudo cryptand and binds in turn alkaline cations thus leading to the neutral ($1^{4-}{\cdot}B^{3+}{\cdot}M^+$) complexes. The inclusive nature of these complexes in the solid state is demonstrated by X-ray analysis.

Although only the binding of boron (III) has been investigated so far, one may extend the same type of behavior to transition metals in oxidation state II (M^{2+}). Indeed, the complexation of M^{2+} cations by $\mathbf{1}^{4-}$ would lead to a dianionic pseudocryptand ($1^{4-}{\cdot}M^{2+}$). The latter would then bind an M'^{2+} alkaline-earth cation affording again a neutral complex of the type ($1^{4-}{\cdot}M^{2+}{\cdot}M'^{2+}$). Work along these lines, in particular the simultaneous binding of alkaline-earth cations such as Mg^{2+}, Ca^{2+}, Ba^{2+} and transition metals such as Ni^{2+}, Cu^{2+}, Zn^{2+}, is currently under investigation.

References

1 Hütter R, Keller-Schierlein W, Knüsel F, Prelog V, Rodgers GC, Sutter P, Vogel G, Voser W, Zähner H, *Helv Chim Acta* (1967) 50, 1533

2 Dunitz JD, Hawley DM, Miklos D, White D.NJ, Berlin Y, Marusic R, Prelog V, *Helv Chim Acta* (1971) 54, 1709

3 Marsh W, Dunitz JD, White DNJ, *Helv Chim Acta* (1974) 57, 10

4 Okazaki T, Kitahara T, Okami Y, *J Antibiotics* (1975) 28, 176

5 Stout TJ, Clardy J, Pathirana IC, Fenical W, *Tetrahedron* (1991) 47, 3511

6 Dietrich B, Lehn JM, Sauvage JP, *Tetrahedron Lett* (1969) 2889

7 Graf E, Hosseini MW, Ruppert R, *Tetrahedron Lett* (1994) 35, 7779

8 Dietrich B, Lehn JM, Sauvage JP, *Tetrahedron Lett* (1969) 2885

9 Izatt RM, Pawlak K, Bradshaw JS, *Chem Rev* (1991) 91, 172

10 Kobuke Y, Sumida Y, Hayashi M, Ogoshi H, *Angew Chem Int Ed Engl* (1991) 30, 1496

11 Weitl FL, Raymond KN, *J Am Chem Soc* (1980) 102, 2289; Raymond KN, Müller G, Matzanke BF, *Top Current Chem* (1984) 123, 49

12 Wolfgang K, Vögtle F, *Angew Chem, Int Ed Engl* (1984) 23, 714; Stutte P, Kiggen W, Vögtle F, *Tetrahedron* (1987) 43, 2065; McMurry TJ, Rodgers SJ, Raymond KN, *J Am Chem Soc* (1986) 108, 3451; McMurry TJ, Hosseini MW, Garrett TM, Hahn FE, Reyes ZE, Raymond KN, *ibid* (1987) 109, 7196; Garrett TM, McMurry TJ, Hosseini MW, Reyes ZE, Hahn FE, Raymond KN, *ibid* (1991) 113, 2965

13 Lehn JM, in *Frontiers of Chemistry*, IUPAC, Laidler KJ Ed, Pergamon, 1982; Fenton DE, Casellato U, Vigato PA, Vidali M, *Inorg Chim Acta* (1982) 62, 57; Zanello P, Tamburini S, Vigato PA, Mazzocchin GA, *Coord Chem Rev* (1987) 77, 165; Smith DC, Gray HB, *Chem Rev* (1990) 100, 169

14 Van Veggel FCJM, Verboom W, Reinhoudt DN, *Chem Rev* (1994) 94, 279 and references therein

15 Böeseken J, *Adv Carbohydr Chem* (1949) 4, 189

16 Nabeshima T, Inaba T, Sagae T, Furukawa N, *Tetrahedron Lett* (1990) 31, 3919

17 Graf E, Hosseini MW, Ruppert R, Kyritsakas N, De Cian A, Fischer J, Estournès C, Taulelle F, *Angew Chem, Int Ed Engl* (1995) 34, 1115

18 Graf E, Hosseini MW, Ruppert R, De Cian A, Fischer J, *J Chem Soc, Chem commun* (1995) 1505

19 Moras D, Metz B, Weiss R, *Acta Crystallogr Sect B* (1973) 29, 383