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Thermodynamics and mechanisms of the formation of supramolecules and supramolecular assemblies of s, p, d and f elements: problems and prospects

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Abstract. The experimental results concerning the mechanism and thermodynamics of formation of three classes of supramolecular systems, namely, polymers, discrete ring nanostructures and macrocyclic complexes (with crown ethers, cryptands, *etc*.) are surveyed. The thermodynamic factors, in particular, the bond energy between the 'building blocks', determining the stability of supramolecular assemblies are analysed. The energy contributions of the metal – ligand and metal – metal interactions and hydrogen bonds to the thermodynamics and mechanism of self-assembly are compared. The principles of design of new polynuclear assemblies of s, p, d and f elements are considered. The bibliography includes 165 references.

I. Introduction

The subject of supramolecular chemistry (SMCh) is the formation of new chemical structures upon self-assembly of molecules and molecular aggregates into supramolecular assemblies (SMA). A founder of this new scientific trend, J-M Lehn proposed [1,2] the following definition: 'Beyond molecular chemistry based on the covalent bond, there lies the field of supramolecular chemistry, whose goal it is to gain control over the intermolecular bond'.

Initially, the task of SMCh was formulated (according to Lehn's views) as the study of 'non-covalent interaction of two or more subunits' [3] or 'spontaneous interaction of molecules to give structured, stable, non-covalently bound aggregates'.[4] However, as experimental data on the synthesis of SMA such as supramacrocycles (SMC), macrocyclic complexes (MC) and supramolecular polymers (SMP) have been accumulated, the definition of SMCh was modified. For example, it was stated [5] that, whereas non-covalent interactions play a key role in the formation of secondary and tertiary structures in natural macromolecules, in the case of linear supramolecular polymers, strong, highly directed interactions are more desirable in order to create materials with bonds able to make an alternative to covalent bonds. Currently, there is no consensus of opinions about this issue. It has been even doubted [6] whether it is possible to distinguish between the chemistry of polynuclear metal complexes and SMCh. Generalisation of the proposed mechanisms of SMA formation [1–8] shows that they include all types of interactions between structural units ranging from weak intermolecular [1–4] to strong coordination bonds.[5,7,8] No new, previously unknown types of interaction have been found in the SMCh.

The concepts and notions borrowed from biology have played a significant role in the formation of supramolecular chemistry as a separate field of science. The most important of such concepts are the molecular recognition and cooperativity. The formation of SMA is considered [1–20] to be a cooperative process based on the molecular recognition of the interacting 'building blocks' related to the complementarity principle.

The structural blocks in SMCh include nitrogen- and sulfur-containing heteroaromatic compounds, polypyridine ligands, cyano-substituted aromatic ligands, hydroxamates, *o*-catecholamides, calixarenes, *etc*.[6–25] Recent reviews are devoted to the synthesis and properties of crown-substituted porphyrinates and phthalocyaninates;[7] stereochemical aspects of chiral self-assembly,[6] development of the assembly principle of SMC,[8,9] dendrimers,[10,11] tetrathiafulvalenes,[12] rotaxanes,[13] molecular 'containers',[14] crown ethers,[15] the photochromism of SMA,[16] molecular wires,[17,18] helical polycyanides and SMP [19] and supramolecular fullerene aggregates.[20] Some studies discuss the synthesis of new SMA (including SMC) and their practical application as sensors;[21] nanopores and mesopores; the properties of individual nanoparticles and metallic nanoclusters;[23] and plastic cylinders.[24] Although s-, p- and d-metal complexes are used as building blocks,[25] preference is given to soft (according to Pearson's classification [26]) metal cations: Cu^+, Ag^+, Au^+, Pd^{2+}, Pt^{2+}, Cd^{2+}, Pd^{4+}, Pt^{4+}, and cations having intermediate properties: Fe^{2+}, Co^{2+}, Ni^{2+}, Ru^{2+}, Os^{2+}, Rh^{3+} and Ir^{3+}. A number of publications deal with the SMCh of lanthanides [7,27] and actinides.[28] The preparation of polymetallic SMA for Ln^{3+} and An^{3+} may provide a new solution to an important processing problem, namely, the separation of these elements by extraction.

According to Pearson,[26] all Ln and An cations are classified as hard acids, irrespective of the oxidation state. The

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hardness of Ln and An was characterised quantitatively depending on the oxidation state.[29,30] It was shown [31,32] that An^{3+} ions are softer acids than Ln^{3+} and they should be better coordinated to soft bases.

Supramolecular assemblies can contain three and more metal ions. For example, a metallodendrimer containing 64 ferrocenyl ions and a polycobaltocene dendrimer with 32 cobalt ions have been obtained in solutions.[10] The strategy of self-assembly allows one to prepare SMA with pre-specified properties.[9] In these SMA, metal ions can exhibit new and unexpected redox and magnetic properties. The unique features of SMA include the selective inclusion of guest ions and molecules into the cavities to give new SMA of the guest–host type.[1,2,8,9]

This review is concerned with SMA constructed from s-, p-, d- and f-metal ion complexes. In these SMA, discrete structures formed through coordination bonding and incorporating metal ions are combined into large stable assemblies. As the experimental data have been accumulated, it became necessary to perform quantitative analysis of the interaction energies between the building blocks, which contribute to the formation enthalpy of SMA. In this review, we attempted to compare quantitatively different mechanisms for SMA formation, in particular, the formation through weak intermolecular interactions,[1–4,18] strong coordination and ionic interactions [5–17,19] and mixed type interactions.[1,2,6,18,22]

Comparison of the energetic characteristics of metal-containing building blocks and the structural fragments linking them to form SMA is an important stage in the study of the thermodynamics of SMA formation. In SMC, the metal–metal interaction even at large distances, as well as interaction through bridging ligands may play a significant role in the formation of stable SMA. All available estimates of the D_0(AB) bond energy are based on the structural thermodynamic model (STM).[32–34] The basis equations include the following parameters: the radius of the maximum electron density R_0, which can be found by solving the Schrödinger equation with allowance for relativistic corrections for free atoms in the ground state; the experimental R_e(AB) value, *i.e.*, the equilibrium internuclear distance for the A–B bond in the given compound; R_e^{di} is the experimental internuclear distance in the diatomic AB(g) molecule; χ(A) and χ(B) are the chemical potentials of atoms A and B, respectively; χ(AB) is the relative chemical potential, which is close to the Pauling electronegativity; χ^{di}(AB) corresponds to a diatomic AB(g) molecule.

$$\ln[D_0(AB)] = \chi(AB) + \gamma(AB) = \lambda(AB);$$

$$D_0(AB) = k e^{\lambda(AB)}, k \approx 1 \text{ eV};$$

$$\chi(AB) = \chi(A) + \chi(B) = \chi^{di}(AB) e^{y};$$

$$y = (R_e - R_e^{di})(R_e + R_e^{di})^{-1};$$

$$\gamma(AB) = \gamma(A) + \gamma(B);$$

$$\gamma(A) = [R_0(A)][R_e(AB)]^{-1} - [R_e(AB)][R_0(A)]^{-1}.$$

In a number of studies,[30,32,33,35–38] the STM has been used to calculate the thermodynamic properties of d- and f-element complexes with various ligands (H_2O, NO_3, O-, S- and N-donor ligands, F, Cl, Br). The D_0(AB) bond energies determine the thermodynamic properties of compounds, in particular, the standard enthalpies of their formation in solution ΔH_f°(aq), in the crystalline state ΔH_f°(s) and in the gaseous state ΔH_f°(g). If ΔH_f° have not been measured, they can be calculated from known D_0(AB) values; conversely, if ΔH_f° have been measured, they can be used to evaluate the accuracy of D_0(AB) by solving the inverse problem.

The following properties were calculated [35,36] for compounds of d elements: $\Delta H_f^\circ(ML_4, g)$ and $\Delta H_f^\circ(ML_4, s)$, L = Cl, Br; $\Delta H_f^\circ(MCl_6^{2-}, g)$, $\Delta H_f^\circ(MCl_6^{2-}, aq)$ and $DH_f^\circ(A_2MCl_6, s)$, where M are 4d, 5d, 6d and 5f elements (Zr, Hf, Th, Rf; Nb, Ta, Pa, Db; Mo, W, U, Sg; Tc, Re, Np, Bh; Ru, Os, Pu, Hs; Rh, Ir, Am, Mt; Pd, Pt, Cm, ^{110}TAn; TAn are transactinides). The ΔH_f° values for many compounds of 3d, 4d, 5d and 5f elements have been measured. The calculations [30,32,33,35–38] of ΔH_f° and D_0(AB) reproduce the experimental values to within $\pm$15 kJ mol^{-1}; this has stimulated the use of the STM for predicting the properties of transactinides [D_0(TAn–Hal) and ΔH_f°(TAnHal$_4$)] [35,36] and the properties of SMA. The structural thermodynamic model has also been used to estimate the thermodynamic parameters for the extraction of Ln^{3+} and An^{3+} ions with amides,[32] acids R_2PSSH and O-containing co-extractants such as phosphates, amides and phosphine oxides.[30,37]

In supramolecular chemistry, polypyridine ligands, for example, 2,2′:6′,2″-terpyridine, are widely used as building blocks. Data on the thermodynamic properties of the complexes of f elements with this class of ligands are scarce.[27] The stability constants $K(LnL^{3+})$ for 70 complexes with these ligands were calculated, while for 15 complexes they were measured.[38] The accuracy of calculation was $\pm$10% of the experimental $\log K(LnL^{3+})$ values.

II. Molecular recognition in biology and coordination chemistry

The progress in the development of nanochemistry and nanotechnology is largely due to the use of biological concepts.[8,39–42] The idea of designing machines at the molecular level has also come to chemistry from biology: numerous biological 'machines', for example, cell proton pumps, transmembrane ion channels, *etc.*, are known.[42] A classical example of molecular recognition in biology is the complementary binding of nucleotides into the DNA double helix.[1,43] A classification of different types of molecular recognition has been proposed.[2,44] Weak specific interactions between the receptor and the substrate play an important role in the formation of complex biological structures at the cellular level, hydrogen bonds being especially significant.[43,45]

The supramolecular chemistry usually considers two limiting mechanisms for SMA formation: non-covalent [1,2,45] and covalent interactions.[42] However, this differentiation is rather conventional.[5,6] The formation of SMA through hydrogen bonds has been discussed in the literature.[18,41,43,45] Coordination bonds can also act as strong interactions.

The coordination mechanism of SMA formation, which is also called metal-directed self-assembly,[8,9,42] is an alternative to the mechanism based on weak intermolecular interactions (this is called in some cases the biological mechanism). The key features of the coordination mechanism include [8,39,42] the directional character of the metal–ligand bonds; the diversity of SMA caused by the diversity of building blocks (polydentate ligands and metals), a combination of strong and weak bonds,[22] the possibility of a control over the reaction mechanism, *i.e.*, of carrying out the reaction under thermodynamic or kinetic control.[8,9,39]

The molecular recognition principle in the coordination mechanism is based on the stereochemical model developed in a number of papers.[8,9,39] It is noteworthy that the decrease in the free energy upon the formation of SMA according to this mechanism is due to the appearance of weak coordination bonds between the metal atoms either directly (M···M) or through bridging ligands (M···L···M).[15] The properties of cations (the electronic configuration and the size determining the geometry of the polyhedra in the local environment), the softness or hardness of cations and ligands and the chelation effects are to be taken into account in the coordination mechanism of SMA formation. Chelating polypyridine ligands have found extensive use in SMCh.[1,2,6,8,9,14,18,39,42] It was

shown [46] that in the formation of the ML_n^{3+} complexes, where $M = Ln^{3+}$ (Ln = La, Ce, ..., Lu) and An^{3+} (An = Pu, Am, Cm), with such ligands, the chelation effect can stabilise complexes both by increasing the entropy and by decreasing the enthalpy, depending on the cation and the number of ligands n ($n = 1-3$). The effect of chelation on the thermodynamics of self-assembly of molecules to SMA has not yet been considered.

III. Transition d and f elements as structural components of polymers

The self-assembly giving rise to supramolecular systems is a new line of research in the polymer science.[5] This research is at the boundary of organic, bioorganic and inorganic chemistry. Polymers of new generation are synthesised based on a preset (*i.e.*, inherent in the synthetic strategy) [47] combination of intramolecular and/or intermolecular interactions.[6] A prominent achievement in this field is the synthesis of polymers with one-dimensional structure. The search for and the targeted synthesis of quasi-one-dimensional systems is an important problem in the solid-state physics and chemistry. This Section deals with the properties of the new-generation polymers.

1. Self-assembly in the formation of inorganic polymers: the effect of the electronic structures of metals and ligands

In recent years, dinuclear metal complexes have been actively used to design molecular assemblies. The synthesis of one-dimensional tetracarboxylate SMP where the blocks containing Rh_2^{4+} or Re_2^{6+} are combined by hydrogen bonds has been reported.[47] Many polymers of this type in which dinuclear blocks are connected by bridging ligands have been studied previously. The structure of the first inorganic formate-containing polymer $Rh_2(HCOO)_4 \cdot H_2O$ (**1**) with the Rh^{2+} ions linked by bridging oxygen atoms $Rh^{2+} \cdots O \cdots Rh^{2+}$ has been reported in a review;[48] the references cited therein have initiated the study of SMP based on dinuclear d-element cations. Although dimeric Cr, Rh, Cu and Mo carboxylates were the first to be prepared, their structural studies were performed somewhat later. Using the results of early synthetic and structural works [48,49] and later publications,[47,50–52] we compared the bond energies in the polymers constructed from the same dinuclear blocks connected by either bridging ligands [48,49] or hydrogen bonds.[5,47,50–52]

Inorganic metal-containing SMP can exist in different conformations: helical, zigzag and so on. A theoretical model interpreting the reasons and the mechanism for the formation of a particular conformation in inorganic SMP should take into account the electronic structure of the metal cation.

As an example, consider compounds of monovalent elements of the copper group: Cu^+, Ag^+ and Au^+. In the crystals of $KCu(CN)_2$ (**2**), the Cu atoms have a coordination number (C.N.) of 3. The C and N atoms and the Cu atoms to which they are bonded are nearly coplanar.[53] One CN group is terminal and the other two groups are bridging. This gives rise to helical polymeric chains $\cdots CN \cdots Cu \cdots CN \cdots$. In the $KCu_2(CN)_3 \cdot H_2O$ crystal, the polymeric layers $[Cu_2(CN)_3]_n^-$ are composed of helical $(CuCN)_n$ chains (as in compound **2**) and zigzag $(CuCN)_n$ chains; the Cu atoms in the polymeric chains with different conformations are linked through the third cyano group. It should be emphasised that the anions in $KAg(CN)_2$ (**3**) and $KAu(CN)_2$ (**4**) are discrete and form no polymeric structures.[53] A linear coordination and C.N. equal to 2 have also been found for the Ag atom in AgSCN and AgCN, which are zigzag polymers in the solid state.

A triangular coordination of the metal atom like that in compound **2** may arise in the case of ds^2, dp^2 or sp^2 hybridisation. The Cu, Ag and Au atoms have the same electronic configuration $nd^{10}(n+1)s^1$, $n = 3-5$; however, the formation of the $nd^9(n+1)s^2$ electronic configuration corresponding to these types of hybridisation requires different energy expenditures ΔE(ds). The ΔE(ds) value is abnormally high for Ag and is the lowest for Cu:[54]

Element	Cu	Ag	Au
ΔE(ds) /kJ mol^{-1}	34.4	91.8	40.2

As a result, among the three compounds with the same composition $KM(CN)_2$, compound **2** has a polymer structure (the C.N. of Cu is 3) and compounds **3** and **4** have a discrete structure (the C.Ns of Ag and Au are 2). Thus, the electronic structure determines the C.N. Note that the mechanism of formartion of these inorganic polymers is determined by strong (ionic and covalent) rather than weak interactions. Thus the thermal stability and low solubility of the acetylenide polymer $Cu_2C_2 \cdot H_2O$ are due to the formation of strong π-bonds.[53] Transitions between conformations of inorganic polymers require, most often, large energy expenditure.

Concluding this Section, consider an interesting example in which the metal complex serves as the polymerisation catalyst of aliphatic and aromatic isocyanides.[19]

$$\underset{\mathbf{A}}{Ni(acac)_2(RNC)_2} \overset{H^+}{\rightleftharpoons} \underset{\mathbf{B}}{Ni(acac)(RNC)_2^+} + acac$$

Complex **A** has a *trans*-configuration; however, for polymerisation to start, the complex must have two vacant *cis*-sites. Complex **B** formed under the action of an acid serves as an efficient polymerisation catalyst. The driving force of this reaction is the transformation of formally divalent carbon in the monomer into the tetravalent carbon in the polymer. The reaction readily proceeds at room temperature, the reaction heat being 81.4 kJ mol^{-1}. It cannot be ruled out that the heat of polymerisation is related to the electron excitation energy accompanying the transition of carbon into the tetravalent state.

The considered examples demonstrate the importance of electronic effects in the thermodynamics of the formation of polymers involving metals and non-metals.

2. Coordination mechanism of the formation of inorganic carboxylate polymers containing M_2^{4+} dimers of d elements

Quasi-one-dimensional systems have long been of only theoretical interest as hypothetical models in the solid-state physics and chemistry; they were used to start the solution of many problems. However, more recently, synthetic chemists have manufactured species that can be regarded, to a first approximation, as one-dimensional solids.[55] Among these, an important place is occupied by divalent 3d-element carboxylates. For example, the compound $Cu(PhCOO)_2 \cdot 3\,H_2O$ is a one-dimensional ferromagnet and is described by the Heisenberg model.[55] On the basis of M_2^{4+} carboxylate complexes (M = Cr, Mo, Cu, Rh), polymers with a quasi-one-dimensional chain structure have been prepared. The simplest compound, dirhodium tetraformate monohydrate $Rh_2(HCOO)_4 \cdot H_2O$ (**1**) consists of two types of complexes:[48] $Rh_2(HCOO)_4 \cdot (H_2O)_2$ (**1a**) and $Rh_2(HCOO)_4$ (**1b**). Complexes **1a** have a distorted octahedral geometry and consist of $Rh^{2+}-Rh^{2+}$ dimers connected by four bridging $HCOO^-$ groups, and two H_2O molecules occupy the *trans*-positions with respect to the $Rh^{2+}-Rh^{2+}$ bond. Complex **1b** contains no coordinated H_2O molecules; they are replaced by the O atoms of the $HCOO^-$ groups of the neighbouring complexes **1a**. The $Rh^{2+}-Rh^{2+}$ bonds are oriented either along the polymer axis or at an angle, which is favourable for binding Rh_2^{4+} dimers through the bridging O atoms: $Rh_2^{4+} \cdots O \cdots Rh_2^{4+}$. Compound **1** has one coordination vacancy. In the polymer, weak cooperative charge ordering is formed along the $(Rh_2^{4+\delta} \cdots Rh_2^{4-\delta})_x$ axis, resulting in polymer stabilisation. The coordinatively saturated compound

$Rh_2(OAc)_4(H_2O)_2$ (**5**) does not form a polymer, as the 'excess' water molecule (missing from compound **1**) saturates the coordination. Numerous non-polymeric compounds $M_2(RCOO)_4L_2$ (M = Cr, Mo, Cu, Rh, *etc.*, L is a neutral ligand) have been prepared; they do not undergo disproportionation to give two complementary complexes.[49]

The interactomic distances $R(Rh-Rh) = 2.38 \pm 0.02$ Å, $R[Rh-O(water)] = 2.20 \pm 0.06$ Å, average $R(Rh-O) = 2.03 \pm 0.05$ Å in polymer **1**[48] are much shorter than the $R(Rh-O) = 2.45 \pm 0.03$ Å distance to the inter-moiety bridging oxygen atom. Here and below, the bond energies in the structural blocks were calculated[22] based on the STM[32,33] with experimental $R(A-B)$ distances reported in the studies cited and with handbook[56] data for R_e^{di}: $D_0(Rh^{2+}-Rh^{2+}) = 233.5$, $D_0(Rh^{2+}-O) = 246.9$ and $D_0(Rh^{2+}-OH_2) = 178.8$ kJ mol^{-1}, while the energy of the bridging $Rh^{2+}-O$ bonds combining these blocks into a polymer, $D_0(Rh^{2+}-O)$ is equal to111.2 kJ mol^{-1}.

The driving force of polymerisation is disproportionation $2\,\mathbf{1} \rightarrow \mathbf{1a} + \mathbf{1b}$, resulting in alternation of the complementary complexes **1a** and **1b**. It follows from the bond energies that complexes **1a** and **1b** are constructed through strong coordination bonds and are connected to each other by weaker bridging bonds.

3. Mechanism of formation of supramolecular polymers containing M_2^{4+} dimers of d elements with participation of hydrogen bonds

In recent years, the trend of using combinations of strong valence bonds with weak intermolecular contacts ($\pi-\pi$-interactions, hydrogen bonds and so on) has started to develop in the SMP synthesis. In order to connect metal-containing blocks into the SMP through hydrogen bonds, pyridinecarboxylic acids and their amides are used most often.[57,58] Another synthetic strategy for the preparation of one-dimensional SMP using dinuclear M_2 fragments was developed in parallel.[51,52] The two possible limiting M_2 orientations with respect to the polymeric chain dictate the range of bridging ligands: parallel (axial bridges) and perpendicular (equatorial bridges) orientations. The complexes containing Rh_2^{4+} or Re_2^{6+} dimers were used to prepare one-dimensional SMP:[47] $Rh_2(OAc)_4(INA)_2 \cdot 2\,Me_2CO$ (**6**); $Rh_2(OAc)_4(NIA)_2 \cdot 2\,Me_2CO$ (**7**); *cis*-$Re_2(OAc)_2Cl_4(INA)_2$; *cis*-$Re_2(OAc)_2Cl_4 .(NIA)_2 \cdot 2$ (NIA), where INA is isonicotinamide and NIA is nicotinamide. The idea was to replace two water molecules in complex **5**, which cannot be self-assembled due to the coordination saturation, by the ligands NIA or INA, which form hydrogen bonds like other amides. Pyridinecarboxamides are used as donors in the axial positions, while hydrogen bonds are formed due to complementarity of the amide groups. The conformation of SMP depends on the geometry of the linkers (NIA and INA). As a result, compound **6** contains linear polymer chains and complex **7** contains zigzag chains.

Presumably, the stability of the dirhodium SMP is due to the presence of a stable diamagnetic structural block, $Rh^{2+}-Rh^{2+}$. Then one can expect that $R(Rh-Rh)$ in SMP **6**, **7** and in compound **5** would be different. Although these differences are slight: $R(Rh-Rh) = 2.4034(16)$ (for **6**), 2.3972(12) (for **7**), 2.3855(5) (for **5**), 2.38(2) Å (for **1**),[47–49] the secondary effect is still observed, namely, the $Rh^{2+}-Rh^{2+}$ bonds in complexes **6** and **7** are slightly weaker than those in non-polymeric compound **5**, and these bonds in complex **1** are slightly stronger than those in **5**. The $D_0(Rh-Rh)$ values were calculated in terms of the STM (to the accuracy of ± 2 kJ mol^{-1}): $D_0(Rh-Rh) = 224$ (for **6**) $\leqslant 226$ (for **7**) $<$ 231 (for **5**) $\leqslant 234$ kJ mol^{-1} (for **1**).

The average $R(Rh-O)$ distances to the carboxylate oxygen atoms in the three SMP are similar:[47,48] $R(Rh-O) = 2.03(5)$ (**1**); 2.036(6) (**6**) and 2.037(4) Å (**7**). The key difference between the SMP **1** and **6**, **7** is related to the energetic properties of linkers, *i.e.*, the $Rh_2^{4+}\cdots O\cdots Rh_2^{4+}$ bridging bonds in complex **1** and hydrogen bonds in complexes **6** and **7**. The interaction energy between the blocks upon the formation of hydrogen bonds is much lower than the bridging bond energies, which accounts for the higher stability of polymers of type **1**.

The difference between the energetic properties of linear and zigzag polymers **6** and **7** is due to the difference between the $R(Rh-N)$ distances to the pyridine N atoms: $R(Rh-N) = 2.205(7)$ (INA) and 2.224(5) Å (NIA). The calculated values, $D_0[Rh-N(INA)] = 240$ and $D_0[Rh-N(NIA)] = 232$ kJ mol^{-1}, differ by 8 kJ mol^{-1}. The stronger Rh–N bond in SMP **6** results in weakening of hydrogen bonds: $R(N-H\cdots O) = 2.922$ Å with respect to $R(N-H\cdots O) = 2.865$ Å in SMP **7**.

The thermodynamic and structural properties of compounds with hydrogen bonds have been studied in numerous works.[5,18,41,43,59–64] The first estimates of the energies of such bonds concern the peptide structure.[61] Then the energies of the $O-H\cdots O$, $O-H\cdots N$, $N-H\cdots O$, $N-H\cdots N$, $O-H\cdots Cl$, $N-H\cdots F$, $N-H\cdots Cl$, $F-H\cdots F$ and other hydrogen bonds were determined from thermodynamic properties of the corresponding compounds or from spectroscopic data[63–65] or calculated in terms of the STM.[66] In a review,[41] the reference values for hydrogen bond energies have been compared with the energies of conventional single bonds. The S–S, C–P, C–N, C–Cl, C–C, N–H, C–H, H–H and O–H bond energies vary in the range of 260–460 kJ mol^{-1}, while hydrogen bond energies lie in the 10–65 kJ mol^{-1} range; however, if the hydrogen bond is formed with an ion (for example, $HCOOH\cdots F^-$), the range is broadened to 40–190 kJ mol^{-1}.

It follows from the reported data[18,41,60,63,64,66] that the dependence of the hydrogen bond energy $D(AH\cdots B)$ (A = N: B = O, Cl; A = B = O, and so on) on the $R(A\cdots B)$ distance is described by the equation

$$D(AH\cdots B) = \alpha \exp[-\beta R(A\cdots B)],$$

where α and β are empirical constants.

Using this equation, $D(AH\cdots B)$ can be estimated from the measured $R(A\cdots B)$ values to the accuracy of $\pm 3\%$ relative to the values determined from spectroscopic and thermodynamic characteristics of the corresponding compounds.[63–65] The hydrogen bond energies were calculated in terms of the STM.[66]

The hydrogen bond energies for SMP **6** and **7** were found to be 6.5 and 7.6 kJ mol^{-1}, respectively. Since each complex is linked to two neighbouring complexes by four hydrogen bonds, the total energy difference for two conformations is equal to ~ 5 kJ mol^{-1}. Hydrogen bonds formed at so long distances (2.8–2.9 Å) cannot be strong. The energies of the bridging coordination bonds [$D_0(Rh^{2+}-O) = 111.2$ kJ mol^{-1}] in inorganic polymer **1** are much higher than the hydrogen bond energies in SMP **6** and **7** [$4\,D_0(N-H\cdots O) \approx 30$ kJ mol^{-1}]. Apart from hydrogen bonds, other non-valent contacts should also be taken into account in the structures of complexes **6** and **7**; however, they are also present in SMP **1**.

The $N-H\cdots O$ distances and the hydrogen bond energies in polymers **6** and **7** fall in the range typical of biological systems. Indeed, in the case of peptides,[63] the $R(NH\cdots O)$ distance ranges from 2.80 to 3.16 Å. However, a value of 2.90 Å equal to the sum of the van der Waals radii of the oxygen and nitrogen atoms $R^{VW}(NO)$ is encountered most often. Meanwhile, in the linear SMP **6**, $R(N\cdots O) = 2.922$ Å $> R^{VW}(NO)$, and in the zigzag SMP **7**, $R(N\cdots O) = 2.865$ Å $< R^{VW}(NO)$.

It has been noted above that the presence of axial ligands relative to the Rh–Rh bonds prevents the formation of SMP, because these complexes are coordinatively saturated. This is also valid for other metal compounds. Thus all non-solvated compounds $Cr_2(O_2CR)_4$ form polymeric chains in the crystalline state where $R(Cr-Cr)$ varies from 2.2 to 2.5 Å,[49] and the

bond energy $D_0(Cr^{2+}-Cr^{2+})$ that we calculated falls in the range of 154–232 kJ mol^{-1}. However, the lack of axial ligands is a necessary but not a sufficient condition for self-assembly to give SMP. If very short bonds, $R(Cr-Cr) <$ 1.9 Å, are formed in the complexes, their energy sharply increases and the complexes lose flexibility. These complexes contain no axial ligands but still they do not tend to self-assemble.

Thus, a comparison of the two mechanisms of SMP formation from identical dinuclear blocks (through bridging oxygen ligands or hydrogen bonds) indicates that the bridging coordination bond energy for inorganic polymer **1** is higher than the total energy of all hydrogen bonds in SMP **6** and **7** and that the stronger the coordination bonds in the initial building block, the weaker the hydrogen bonds between the blocks.

4. Self-assembly of trivalent lanthanide and actinide complexes

As mentioned above, the lanthanide ions Ln^{3+} are classified as hard acids; they form strong bonds with hard bases.[26, 67] However, in recent years, interest has arisen in Ln^{3+} compounds in which the coordination sphere contains both hard and soft donor atoms: (F, S, O),[68] (O, S, N).[30, 36–38, 69, 70] These compounds were found to exhibit unusual properties not inherent in Ln^{3+} compounds containing either only hard or only soft ligands. These properties have already found application in the separation of Ln^{3+} and An^{3+} ions by extraction.[30, 36–38] In sulfur-containing crystalline compounds, Sm and Eu are known to exhibit mixed valence.[67] The reactions of metallic Sm and Eu with mercury perfluorobenzenethiolate $Hg(SC_6F_5)_2$ in THF give dimer $[(THF)_2Sm(SC_6F_5)_2.(\mu\text{-}SC_6F_5)]_2$ (**8**) and one-dimensional polymer $[(THF)_2Eu.(SC_6F_5)_2(\mu\text{-}SC_6F_5)_2]_n$ (**9**), respectively.[68] In dimer **8**, two thiolate ligands form rings through the Sm–S and Sm–F bonds, while the bridging thiolate ligands are not coordinated by F atoms. The coordination sphere is completed by two THF ligands. In compound **9** (unlike dimer **8**), the bridging thiolates interact with Eu atoms through F atoms, thus forming an SMP. This is a rare example where a 'hard' F atom is coordinated as a neutral donor and, in combination with a 'soft' S atom, gives rise to an eight-coordinate Eu^{2+} (4 S + 2 F + 2 O).

The charge transfer energies from the higher occupied non-bonding molecular orbitals (MO) $\Delta E(L \rightarrow M^{3+})$ (L = S, F) in S- and F-containing lanthanide and actinide compounds (M = La, Ce, Pr, ..., Lu; Ac, Th, Pa, ...,Lr) have been discussed.[30, 37] On the basis of the $\Delta E(L \rightarrow M^{3+})$ values, one can find out what lanthanides (apart from Eu) and light actinides (from Ac to Am) could form SMP similar to polymer **9** according to the same mechanism. The $\Delta E(L \rightarrow M^{3+})$ values are known to correlate with the reduction potentials $E^{\circ}(3+/2+)$. It was found experimentally [30, 37] that the lowest $\Delta E(S \rightarrow Ln^{3+})$ values in the lanthanide series (in eV) are found for Eu (2.79), Yb (3.26) and Sm (3.77), while among light actinides, this is observed for Am (4.22). The corresponding $E^{\circ}(3+/2+)$ values are 0.35 (Eu), 1.05 (Yb), 1.55 (Sm) and 2.3 V (Am).[37] The measured distances, $R(Sm-S) = 2.822$ (**8**) and $R(Eu-S) = 3.034$ Å (**9**),[68] correspond to the ionic radii $R_{ion}(Sm^{3+})$ and $R_{ion}(Eu^{2+})$. Using the correlation between $E^{\circ}(3+/2+)$ for Eu, Yb, Sm, Am and the measured $R(Sm-S)$ and $R(Eu-S)$ values, one gets $R(Yb-S) = 2.954$ and $R(Am-S) = 2.850$ Å. These distances correspond to ionic radii $R_{ion}(Am^{3+}) = 1.106$ and $R_{ion}(Yb^{2+}) = 1.186$ Å. The qualitative estimates lead to the conclusion that Am, like Sm, would not be reduced within the thiolates under discussion, while Yb is expected to be reduced like Eu. In the former case, the reaction gives a dimer and in the latter case, an SMP is formed. It can be seen that the polymer is formed if the $E^{\circ}(3+/2+)$ and $\Delta E(L \rightarrow M^{3+})$ values obey the following conditions: $0.35 \leqslant E^{\circ}(3+/2+) < 1.55$ V and $2.79 \leqslant \Delta E(L \rightarrow M^{3+}) < 3.26$ eV.

An exceptionally high level of cooperative $\pi-\pi$-interaction of the thiolate rings has been noted [68] for the SMP.

IV. Complexes of d and f elements as the building blocks in macrocycles

The square planar ($M = Pd^{2+}$, Pt^{2+}), tetrahedral ($M = Cu^{+}$) and octahedral ($M = Fe^{2+}$, Co^{2+}, Ni^{2+}) complexes are used most often in self-assembly reactions. To date, supramacrocycles containing from 2 to 12 metal atoms have been prepared in the solid state and in solution. These can be classified into three types: (1) SMC in which the metal atoms are separated by bridging ligands; however, a weak M···M interaction exists and contributes to the thermodynamics of SMC formation; (2) SMC in which the metal atoms are shielded by bulky ligands, the distances M···M > 5 Å and M···M interaction is lacking; (3) SMC with short and strong M···M bonds making an appreciable contribution to the thermodynamics of SMC formation.

In the SMC chemistry, the principle of SMA formation is formulated [8, 9, 14, 39] as metal-directed self-assembly. The most typical features of the self-assembly of discrete metal-containing blocks into large cyclic aggregates have been summarised in a review:[8] (1) upon self-assembly, the blocks are selectively bound by coordination bonds based on the molecular recognition principle; (2) self-assembly is a cooperative process; (3) the SMA formed are discrete. The above-listed publications mention all types of interactions ranging from weak intermolecular to ionic and covalent ones. Therefore, we consider it important to compare the energetic properties of the strong coordination bonds M···M, M←L and hydrogen bonds (OH···O, NH···O, NH···Cl), which contribute to the formation energy of SMC.

Note that the properties of SMC are determined by not only the nature of intermolecular interactions but also the electronic structure of the metal ions, their Lewis acid properties (soft or hard),[26, 69] their redox potentials and their dependence on the number (q) of p^q, d^q and f^q electrons.[29, 70]

It is necessary to emphasise that the macrocyclic systems we discuss differ fundamentally from the previously studied polynuclear metal complexes by the fact that the large ring system exists not only in the solid state but is also formed and retained in solutions. This feature opens up broad prospects for the use of these systems in nanotechnology and molecular-level technology.

The experimental thermodynamic data concerning the free energy or enthalpy of formation of SMC are few. As a rule, they are used to draw qualitative conclusions concerning the driving force of the formation of various SMC: some studies assume the entropy mechanism and other studies, the enthalpy or mixed (enthalpy and entropy) mechanisms. We attempted to estimate quantitatively the contribution of weak and strong interactions to the formation of SMC.

1. Mechanism of self-assembly of macrocycles

A number of mechanisms for the self-assembly of macrocycles have been considered in biology and coordination chemistry.[8, 39] A fast kinetic process and thermodynamic equilibrium between the reactants and products in every reaction stage are the key features of the self-assembly mechanism typical of coordination chemistry. This mechanism has been called [39] thermodynamic or strict. The ratio of the products in the final stage of self-assembly is determined by their thermodynamic stability. The thermodynamic self-assembly should result in one, most stable product to be of practical value.[2] Other self-assembly mechanisms characteristic of both biology and coordination chemistry also exist. They have been classi-

fied and analysed.[71] (1) An irreversible or kinetically controlled mechanism of self-assembly induces a cascade of irreversible reactions and the equilibrium is not reached. (2) An assisted mechanism involving an auxiliary reagent that does not participate in either self-assembly or the formation of the final product but prevents the formation of intermediate products. (3) The directed mechanism requires the presence of a recognition pattern reagent, which directs the self-assembly without being involved in the formation of the final product. Other mechanisms assuming various ways of modification of either reactants prior to self-assembly or final products after the self-assembly (post-modification) have also been considered.[71] Although many SMA have been prepared according to the thermodynamic mechanism of self-assembly, other self-assembly mechanisms (irreversible, directed, and self-assembly with post-modification) are also widely used, for example, in Sauvage's studies.[72–74] Molecular knots, most of catenanes and some kinetically stable helical SMA have been prepared by self-assembly with post-modification.[75,76]

The present review considers the SMA prepared according to the thermodynamic self-assembly mechanism. Note once again that the so-called biological (*i.e.*, caused by intermolecular interactions) and coordination self-assembly mechanisms are not always easily differentiated. For example, complexes of the type MA_2X_2, where M = Pd^{2+}, Pt^{2+}, A is a neutral ligand, X is an anion, are widely used in the SMC synthesis.[1,2,9,10,39] In the solid state, these compounds form islet structures MA_2X_2 in which the complexes are linked by weak intermolecular interactions. For example, in the *cis*-isomer of dichlorodiammineplatinum, a 'column motif' is repeated.[77] In the neighbouring columns, two Cl atoms of the same complex are linked to two NH_3 groups of another complex by hydrogen bonds with the distances R[Cl(1)–N(2)] = 3.34 and R[Cl(2)–N(1)] = 3.30 Å.[77] The R(Pt–Pt) distances are 3.372 and 3.409 Å. Each pair of complexes in the columns is linked by two hydrogen bonds the energies of which (our calculations) are as follows (in kJ mol^{-1}): D_0[NH_3···Cl(1)] = 49.7; D_0[NH_3···Cl(2)] = 45.6. The Pt–Pt bonds also contribute to stabilisation of the *cis*-isomer: D_0(Pt–Pt) = 28.7 kJ mol^{-1} for R(Pt–Pt) = 3.409 Å; D_0(Pt–Pt) = 29.9 kJ mol^{-1} for R(Pt–Pt) = 3.372 Å. For each pair of complexes in neighbouring columns, the intermolecular interaction energy is relatively high: $\Sigma D_0 \approx 125$ kJ mol^{-1}. This example demonstrates that weak intermolecular M–M contacts may be important both for the coordination chemistry and in SMC by determining the self-assembly process.

It is emphasised in a review[8] that self-assembly is a cooperative process. A monograph[55] devoted to the theory of cooperative processes and order–disorder type models presents the result of a quasichemical approximation in the solution of the Ising problem for the Bethe lattice, which represents a tree within the framework of the graph theory. Numerous dendrimers with this type of structural motif have been described in reviews.[10,11] Theoretical physicists have anticipated, to some extent, the existence of some structural motifs, which have been later considered in the SMCh. Similarly, theoretical physicists have predicted[55] some structural motifs and called them 'ladder cluster', 'ladder pseudo-assembly' and so on; more recently, the SMA called the 'ladder', 'rack' and 'grid' have been synthesised in solution and in the solid state.[1,39]

2. Structural factors in the formation of supramacrocycles

The structural principles of the design of SMC were developed at a qualitative level in the studies by Lehn,[78,79] Raymond,[80] Verkade,[81] Fujita[9,82] and Stang.[8] Lehn introduced into practice[78,79,83] the method of SMA formation with the use of branched chelating ligands, which are highly pre-organised and have a large binding energy to metals. As compared with monodendate ligands, the benefit in the free energy is due to the chelation effect. At an early stage of the development of SMCh, various SMA have been synthesised by mere screening diverse ligands and metals. Subsequently, rational approaches to the synthesis of these assemblies have been developed; these can be described systematically as two models.[8]

The first approach was called the symmetry interaction model.[8,79–83] This model considers free metal ions and ligands, most often, rather rigid bi- and tridentate chelating ligands as the starting fragments. The preferential coordination number and the preferential polyhedron for a given metal are taken into account. On the basis of analysis of the point group of symmetry of the target assembly with allowance for the mutual arrangement of the symmetry axes of various types, the synthesis is planned with particular metal ions and particular ligands. For more precise description of the geometric relations between the ligands and the metal ion, a number of special terms were defined (chelation vector, chelate plane, approach angle).[8,80]

The other ideology can be called a molecular library model.[1,2,8,9,39] In this case, coordinatively unsaturated metal-containing fragments with vacant sites oriented at a definite angle rather than free metal ions are considered as the starting blocks. These are supplemented by linking fragments with different numbers of donor atoms (di-, tri- and tetratopic) and different geometry (linear, angular, *etc.*). By combining a moderate number of such elementary blocks, one can construct a variety of cyclic and polyhedral SMA. It is assumed that the geometric parameters (first of all, the angles) of the free blocks do not change much upon association.

Thus, the use of only ditopic ligands resulted in diverse SMA (ranging from a triangle to a dodecahedron) with many d and f elements.[83–99]

3. Macrocycles based on d and f elements and their thermodynamic properties

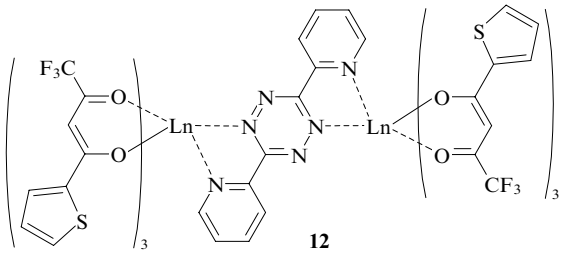
a. Dinuclear structures

Numerous dimers have been prepared in coordination chemistry and their physicochemical properties (spectral, thermodynamic, magnetic, and so on) were studied. The dimers $Cu_2(OAc)_4 \cdot 2H_2O$, which interact through hydrogen bonds in the solid state, have been reported;[53] the distance R(Cu–Cu) = 2.64 Å is somewhat larger than in the metal, while the exchange interaction between the Cu atoms is ~ 300 cm^{-1}. The water molecules can be replaced by dioxane, pyridine or aniline.

Many dinuclear assemblies with different metals have been obtained; these metals include Cu,[84,98] Ag,[85] Mo,[86] Cd,[87] Zn,[88] Fe, Ga,[89] Os,[90] and, most often, Pd and Pt,[91–97] which is not surprising, because Pd^{2+} and Pt^{2+} dimers have been studied for a very long period.[48,77] Let us compare the previously studied[77] dimer $[PdL_2Cl_2]_2$ (**10**) (L = $NH_2CHMeCHMeNH_2$) with the recently synthesised[96] SMC $[PdL_2Cl_2]_2$ (**11**) [L is 3,5-bis(dimethylaminomethyl)pyridine]. In SMC **11**, the Pd atoms are coordinated by two N atoms (the pyridine atom of one L and the aminomethyl N atom of the other L molecule) and two Cl atoms. The distance R(Pd–Pd) = 4.6 Å is rather long; therefore, the interaction between the metal ions does not contribute to dimer stabilisation. In dimer **10**, the Pd atoms also form two Pd–Cl bonds and two Pd–N bonds. Dimerisation is due to weak Pd–Pd intermolecular interactions and hydrogen bonds,[97] which, according to a definition,[1–4] are rather characteristic of SMCh: R(NH···Cl) = 3.29 and 3.35 Å, and the distance R(Pd–Pd) = 3.34 Å is shorter than that in SMC **11**. The following energy values correspond to these distances (in kJ mol^{-1}): D_0(Pd···Pd) = 12.8; D_0(NH···Cl) = 50.6 and 44.7. The overall contribution to dimerisation enthalpy is rather high: $\Sigma D_0 = 12.8 + 2(50.6 + 44.7) = 203.4$ kJ mol^{-1}.

Both SMC **11** and dimer **10** contain usual Pd−N and Pd−Cl coordination bonds present in compounds of the ML_2Cl_2 type (M = Pd, Pt). However, the structural difference is obvious: in the case of SMC **11**, the self-assembly stops after formation of the dimer (*i.e.*, a discrete ring) both in the solid state and in solution, while in compound **10**, dimers form an infinite structure in the solid state due to weak intermolecular contacts.

The experimental thermodynamic data on the formation of dinuclear SMC in solutions are still scarce. It has been shown [100] that the complexes $Ln(tta)_3(H_2O)_2$ [tta is 2-thenoyl-(trifluoro)acetone] react with bis-bidentate bridging ligand bptz [3,6-bis(2-pyridyl)tetrazine] in aqueous ethanol to form mononuclear complexes $[Ln(tta)_3(bptz)]$ (Ln = La, Nd) for the first half of the lanthanide series and dinuclear complexes $[\{Ln(tta)_3\}_2(\mu\text{-bptz})]$ (**12**) (Ln = Gd, Er, Yb) for the second half of the lanthanide series.



12

Ln = Gd, Er, Yb.

The stability constants (K_1 and K_2) of the complexes formed in the following reactions, respectively, were measured:

$$\text{bptz} + Ln(tta)_3(H_2O)_2 \overset{K_1}{\rightleftharpoons} [Ln(tta)_3(bptz)] + 2\,H_2O,$$

$$Ln(tta)_3(H_2O)_2 + [Ln(tta)_3(bptz)] \overset{K_2}{\rightleftharpoons} [\{Ln(tta)_3\}_2(\mu\text{-bptz})] + 2\,H_2O,$$

Ln	$\log K_1$	$\log K_2$
La	6.32	5.42
Yb	6.0	4.8

However, dinuclear complex **12** was isolated only with Yb but not with La. In dimer **12**, the C.N. of the Ln^{3+} ion is equal to 8 (2 N + 6 O), the coordination polyhedron has an approximate square antiprism geometry. This geometry is also characteristic of solvated cations of heavy lanthanides (Ln = Dy, Ho, ..., Lu),[101] whereas solvated cations of light lanthanides have a tricapped trigonal prismatic coordination and C.N. 9. Thus, light lanthanides do not form dimers, because the coordination geometry required for dimer formation is associated with considerable steric hindrance.

The change in the thermodynamic parameters (ΔH°, $T\Delta S^\circ$ and ΔG°) upon the formation of Ln^{3+} complexes with chelating ligands has been considered along the lanthanide series.[27, 102] It was shown that $\gamma = |\Delta H^\circ / T\Delta S^\circ| \approx 0.25 \pm 0.1$. With this γ for dimer **12** with the measured [100] value of $\Delta G^\circ = -62.1$ kJ mol^{-1}, one gets the approximate values $\Delta S^\circ \approx 165 \pm 20$ J mol^{-1} K^{-1}; $\Delta H^\circ \approx -13 \pm 6$ kJ mol^{-1}. The formation of dimer **12** is mainly an entropy-driven process, like all other processes of formation of Ln^{3+} complexes in aqueous solutions.[27]

The thermodynamics of the Eu^{3+} self-assembly in MeCN with the bis[1-methyl-2-(6-[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl)]pyridin-2-yl)benzimidazol-5-yl]methane ligand (L^d), composed of two tridentate bis(benzimidazolyl)pyridine fragments, has been studied.[103] The stepwise and overall stability constants were measured for the reactions:

$$Eu + L^d \rightleftharpoons EuL^d,\ \log K_1 = 4.6 \pm 0.3;$$

$$EuL^d + L^d \rightleftharpoons EuL_2^d,\ \log K_2 = 7.0 \pm 0.4;$$

$$EuL_2^d + Eu \rightleftharpoons Eu_2L_2^d,\ \log K_3 = 6.5 \pm 0.4;$$

$$Eu_2L_2^d + L^d \rightleftharpoons Eu_2L_3^d,\ \log K_4 = 6.2 \pm 0.5;$$

overall reaction

$$2\,Eu + 3\,L^d \rightleftharpoons Eu_2L_3^d,\ \log \beta_4 = 24.3 \pm 0.4.$$

From these data, it follows that

$$\log \beta_4 \approx \log K_1 + 3 \log K_3 = 4.6 + 3 \times 6.5 = 24.1,$$

which is similar to the experimental value equal to 24.3. The first step of the reaction depends on the energy expenditure for the change in the ligand conformation, while the subsequent steps, on the properties of ligands and their interactions with cations.

The relations between the stability constants of the Ln complexes with monotopic chelating ligands have been derived for the reactions below [31, 46]

$$Ln + L \overset{K_1}{\rightleftharpoons} LnL,$$

$$LnL + L \overset{K_2}{\rightleftharpoons} LnL_2,$$

$$LnL_2 + L \overset{K_3}{\rightleftharpoons} LnL_3,$$

$$Ln + 3\,L \overset{\beta_3}{\rightleftharpoons} LnL_3,$$

$$\log K_1 > \log K_2 > \log K_3,$$

$$\log K_1 - \log K_2 \approx \log K_2 - \log K_3,$$

$$\log \beta_3 \approx 3 \log K_2.$$

These relations hold with high accuracy for approximately 200 Ln complexes with monotopic ligands and for a Eu^{3+} complex with the ditopic ligand L^d. No other data on Ln complexes with ditopic ligands are available. The enthalpy changes upon the formation of dinuclear Eu^{3+} complexes have not been measured. Presumably, $\Delta S_j^\circ < 0$, because it is known that in MeCN, lanthanide complexes are formed by an enthalpy mechanism rather than by an entropy mechanism [27] as in aqueous solutions.

The thermodynamics of formation of the dinuclear Eu^{3+} complex with the ditopic ligand L^d implies an important role of ligand pre-organisation at the first stage of the reaction.[103] For the subsequent stages, the derived relations between $\log K_i$ (i = 2, 3, 4) and $\log \beta_3$ allow one to calculate the stability constants. Using lanthanide complexes (Ln = La, Nd, Gd, Er, Yb) with tta and μ-bptz as examples, the role of the cation size in the formation of dinuclear SMC in aqueous solutions has been demonstrated.[100]

b. Trinuclear structures

Triangular structures with weak M−M bonds. According to the molecular library model, the triangular SMC may be formed based on three building blocks arranged at 60° angles and linked by three linear fragments. The M_3 building blocks are widely known in the cluster chemistry. They can be combined to form tetrahedra, octahedra and other polyhedra.[104–110] The M_3 metal rings with the M−M or M−L−M bonds can behave as both Lewis acids and bases;[104] hence, they can be used for the synthesis of SMC with diverse ligands in solution and in the solid state. A number of reviews [105–110] have discussed the concept of the 'magic' number of valence electrons m = 48 for the M_3 clusters composed of d elements. Deviations from m = 48 exist, *i.e.*, this number is not universal [105–110] even for elements of the same group, for example, M = Cu, Ag, Au or M = Ni, Pd, Pt. Indeed, inclusion of

relativistic effects for Pt or Au metal rings would change the sequence and structure of the MO.

Two factors, *viz*., the electronic structure of the metal and the effect of bridging groups, determine the M—M interaction.[111–115] As was discussed in Section IV.3.a, many metals form dimeric complexes $M_2(OAc)_4L_2$ (M = Cu, Rh, Ru, Re, Cr, Mn, but not Pd or Pt). In the crystalline state, Pd^{2+} diacetate $Pd_3(OAc)_6 \cdot H_2O$ (**13**) contains trimeric ring complexes. The Pd atoms form a nearly regular triangle with the distances R(Pd—Pd) = 3.105–3.203 Å (on average, 3.154 Å) and R(Pd—O) = 1.973–2.014 Å (on average, 1.99 Å).[112] Although, according to STM calculations,[32,33] the Pd—Pd bond energy is markedly lower than the energy of one Pd—O coordination bond: D_0(Pd—Pd) = 19.5 kJ mol^{-1}, D_0(Pd—O) = 191.6 kJ mol^{-1}, the contribution of three Pd—Pd bonds equal to ~60 kJ mol^{-1} stabilises trimer **13**. The palladium acetatoacetoneoximate $Pd_3(OAc)_3 \cdot (ONCMe_2)_3 \cdot 0.5\,C_6H_6$ (**14**) has a similar structure;[77] however, the R(Pd—Pd) distances (3.009 Å) are shorter and the energy of three Pd—Pd bonds [$3\,D_0$(Pd—Pd) = 3×27.3 = 81.9 kJ mol^{-1}] is greater than those in the acetate.

A number of SMC have been prepared on the basis of palladium acetate. The reaction of $Pd(OAc)_2$ with 1,3-bis(1-R-benzimidazol-2-yl)benzene (RbzimPh) gives the compound $[Pd(RbzimPh)(OAc)]_3 \cdot 9\,MeCN$ (**15**), where R = Me, Et, CH_2D.[39,114,115] Supramacrocycles **15** are based on the structural motifs of compounds **13** and **14**. In the solid state, the cavity is occupied by the MeCN molecules. The triangular shape of these rings is due to the acetate structure in which the carboxy groups combine three Pd^{2+} cations (rather than two, as in Cr, Mn, Cu, Ru, Rh and Re dimers).

It is noteworthy that in SMC **15**, as in trimers **13** and **14**, the Pd atoms are separated by bridging ligands but the shortest Pd—Pd distances allow the metal–metal interaction, which is weak but still stabilises the triangular shape. The R(Pd—Pd) distances vary from 3.0 to 3.5 Å and the energy of one bond, D_0(Pd—Pd), ranges from 28 to 10 kJ mol^{-1}.

The bis(2-mercaptoethyl) sulfide anion is a promising ligand for the synthesis of triangular SMC. The crystal structure of $Pd_3(SCH_2CH_2SCH_2CH_2S)_3$ resembles that of palladium acetate trimers.[77] Each Pd atom is coordinated by four sulfur atoms (approximately square planar geometry); the Pd atoms form a triangle with R(Pd—Pd) = 3.41, 3.49 and 3.66 Å, the corresponding bond energies being $3\,D_0$(Pd—Pd) = 11.0 + 9.3 + 6.6 = 26.9 kJ mol^{-1}.

Platinum complexes of this type have been prepared. The acetate groups and the bis(2-mercaptoethyl)sulfide anion draw the metal atoms towards one another, shorten the M—M bonds and thus strengthen the M_3 core.

Triangular structures without stabilising M—M bonds. Bulky nitrogen-containing hetaryl ditopic bridging ligands shield the M—M interaction. Many SMC have been prepared with these ligands, in particular, $[Pd(dmpze)Cl_2]_3$ [dmpze is 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane];[116] $[Cu(tacn)(imd)]_3^{3+}$ (tacn is 1,4,7-triazacyclononane, imd is imidazolate);[117] $[Fe(ttpO)]_3$ (ttpOH is 2-hydroxytetrakis-4′-tolylporphyrin).[118]

The triangular SMC $[(en)M(pyrXpyr)_2]_3(NO_3)_6$ (**16**) (M = Pd, Pt; en = $H_2NCH_2CH_2NH_2$, pyr is 4-pyridyl; X = *p*-C_6H_4, C≡C, C≡C—C≡C) have been prepared in an aqueous solution using bis-hetaryl ligands and $Pd(en)(NO_3)_2$;[119] in solution, these complexes occur in equilibrium with square SMC. In our opinion, the presence of flexible linking pyrXpyr ligands and the absence of M—M contacts in SMC **16** reduce the stability of these supramacrocycles. The reaction of $Pt(en)(NO_3)_2$ in H_2O with 2,2′-bipyrazine (2,2′-bpz) yields only the triangular SMC $[Pt(2,2'\text{-bpz})]_3(NO_3)_6$, while in the case of Pd, only the mononuclear chelate complex is formed.[120]

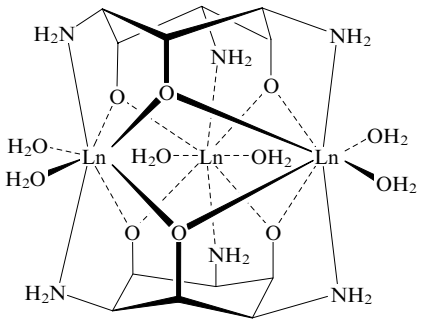
The above information leads to conclusions concerning the similarity of, and the differences between, the palladium and platinum SMA. Although Pd and Pt compounds, most often, have similar structures, thermodynamic characteristics of their SMC may be different. The difference between the cohesion energies[121] of metallic palladium and platinum is ~200 kJ mol^{-1}; the Pt—Pt bonds are stronger than the Pd—Pd bonds. In the absence of M—M bonds in SMC and in the formation of π-bonds with polydentate ligands, it is important that the 5d atomic orbitals of platinum are more diffuse than the 4d atomic orbitals of palladium and form stronger π-bonds with ligands. In addition, platinum atom has a higher electron affinity than palladium (2.1251 and 0.5621 eV, respectively). The electron affinity of platinum is nearly equal to that of sulfur and higher than that of oxygen (1.465 eV). Thus, the effective charges on the platinum atoms are much lower than those on palladium atoms and the bonds with ligands are stronger and more covalent.

Macrocycles with strong M—M bonds. Quite a few examples of triangular macrocycles formed by d elements and stabilised through the formation of M—M bonds can be cited. Thus the $Pt_3[\mu\text{-}C(OMe)C_6H_4Me\text{-}4]_3(CO)_3$ trimers have[122] short Pt—Pt distances (2.62 Å), the corresponding energy D_0(Pt—Pt) is equal to 73 kJ mol^{-1} (*i.e*., 219 kJ mol^{-1} for three bonds).

The first lanthanide-containing SMC were prepared not long ago.[123,124] The hexadentate 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol ligand (H_3L) and Ln^{3+} form the $[Ln_3L_2]^{3+}$ complex (**17**) in an aqueous solution according to the reactions

$$2\,H_3L \rightleftharpoons 2\,L_{aq}^{3-} + 6\,H_{aq}^{+}$$

$$3\,Ln_{aq}^{3+} + 2\,L_{aq}^{3-} \rightleftharpoons [Ln_3L_2]^{3+}$$



17

Ln = Gd, Lu.

Structural similarity of complexes **17** for Ln = Gd and Lu has been established: the Ln^{3+} cations are bound to two ligands through two N atoms and four O atoms; two water molecules complete the C.N. of the metal ion to 8. Three Ln^{3+} ions form a nearly regular triangle similarly to many other metal rings formed by d elements,[104] for example, $[M_3(\mu\text{-}H)_3(CO)_{12}]$ (M = Mn, Tc, Re); $[M_3(\mu\text{-}CO)_3(PR_3)_n]$ (n = 3, 4; M = Pd, Pt). Despite numerous studies of the triangular clusters and SMC of this type, the thermodynamics of self-assembly in solution has been reported only in two studies.[123,124] It was found that (a) the self-assembly is a purely entropic process: $\Delta S^\circ > 0$, $\Delta H^\circ > 0$; (b) the stability of SMC **17** increases from La to Lu in parallel with a decrease in the ionic radius R_{ion}; (c) $\Delta G^\circ[La_3L_2]^{3+}$ and $\Delta G^\circ[Lu_3L_2]^{3+}$ differ almost threefold. Such a pronounced change in the thermodynamic characteristics is unusual for the chemistry of Ln^{3+} complexes. This unexpected fact of the thermodynamics of SMC is attributable to the difference between the thermodynamic parameters of desolvation of the $[Ln_{aq}]^{3+}$ cations. The change in ΔG° during the reaction can be represented as follows:

Table 1. Change in the thermodynamic parameters of the formation of complexes **17** in the lanthanide series (at 298 K).

Parameter /kJ mol^{-1}	Pr	Sm	Gd	Dy	Er	Lu
$\delta\Delta G^\circ$	−48	−83	−95	−104	−111	−122
$\delta\Delta G_f^\circ[Ln_3L_2]^{3+}$	−27	−50	−11	−32	−66	−89
$-3\,\delta\Delta G_f^\circ(Ln_{aq}^{3+})$	−21	−33	−84	−72	−45	−33
$\delta\Delta H^\circ$	−24	−58	−72	−80	−76	−88
$\delta\Delta H_f^\circ[Ln_3L_2]^{3+}$	−14.4	−3.1	−4.8	−38.6	−72.1	−67.6
$-3\,\delta\Delta H_f^\circ(Ln_{aq}^{3+})$	−9.6	−54.9	−67.2	−41.4	−3.9	−20.4
$-\delta T\Delta S^\circ$	−24	−25	−22.6	−24.4	−34.6	−33.6
$-\delta T\Delta S_f^\circ[Ln_3L_2]^{3+}$	−12.6	−46.9	−6.2	6.6	6.1	−21.4
$3\,\delta T\Delta S_f^\circ(Ln_{aq}^{3+})$	−11.4	21.9	−16.8	−30.6	−41.1	−12.6

$$\Delta G^\circ = \Delta G_f^\circ[Ln_3L_2]^{3+} - 3\,\Delta G_f^\circ(Ln_{aq}^{3+}) - 2\,\Delta G_f^\circ(L_{aq}^{3-}) + 6\,\Delta G_f^\circ(H_{aq}^{+}),$$

where $\Delta G_f^\circ[Ln_3L_2]^{3+}$, $\Delta G_f^\circ(Ln_{aq}^{3+})$, $\Delta G_f^\circ(L_{aq}^{3-})$ and $\Delta G_f^\circ(H_{aq}^{+})$ are the standard free energies for the formation of the complex, the Ln^{3+} aqua ions, hydrated ligands and protons, respectively.

Then the difference between the ΔG° values of the reaction ($\delta\Delta G^\circ$) for different Ln^{3+} ions (with respect to Ln = La) is given by

$$\delta\Delta G^\circ = \delta\Delta G_f^\circ[Ln_3L_2]^{3+} - 3\,\delta\Delta G_f^\circ(Ln_{aq}^{3+}),$$

where

$$\delta\Delta G_f^\circ[Ln_3L_2]^{3+} = \Delta G_f^\circ[Ln_3L_2]^{3+} - \Delta G_f^\circ[La_3L_2]^{3+},$$

$$\delta\Delta G\circ_f(Ln_{aq}^{3+}) = \Delta G_f^\circ(Ln_{aq}^{3+}) - \Delta G_f^\circ(La_{aq}^{3+}).$$

The corresponding values are presented in Table 1; the $\Delta G_f^\circ[Ln_3L_2]^{3+}$ values were taken from the work by Chapon *et al.*,[124] and the $\Delta G_f^\circ(Ln_{aq}^{3+})$ values were reported by Morss.[125]

The reaction thermodynamics is determined by the contributions of two opposite effects: the energy gain due to the formation of two $Ln^{3+}-N$ bonds and four $Ln^{3+}-O(L)$ bonds and energy loss for the cleavage of six $Ln^{3+}-O(OH_2)$ bonds. The $\Delta G_f^\circ(Ln_{aq}^{3+})$ values (in kJ mol^{-1}) increase on passing from La to Gd and decrease from Gd to Lu:[125] $\Delta G_f^\circ(Ln_{aq}^{3+}) = -688$ (La), −660 (Gd); −677 (Lu). The contribution of the desolvation effect $3\,\delta\Delta G_f^\circ(Ln_{aq}^{3+})$ to $\delta\Delta G^\circ$ is from 30% to 70%. Two effects, *i.e.*, the decrease in the energy consumption for desolvation for heavy elements and the increase in the $Ln^{3+}-N$ and $Ln^{3+}-O(L)$ bond energies in the SMC of these elements, caused by the lanthanide contraction partially counterbalance each other. The enthalpy contribution of desolvation, $3\,\delta\Delta H_f^\circ(Ln_{aq}^{3+})$ (see Table 1), determines almost completely the $\delta\Delta H^\circ$ values for Sm and Gd, whereas the gain in energy caused by the formation of two $Ln^{3+}-N$ bonds and four $Ln^{3+}-O(L)$ bonds (Ln = Er, Lu) makes the major contribution to $\delta\Delta H^\circ$ of these elements. The balance of the two contributions to the reaction enthalpy results in a monotonic variation of $\delta\Delta H^\circ$ *versus* the ionic radius R_{ion} of the cations (C.N. 8) and allows one to estimate the ΔH° values for the SMC of Ce, Nd, Eu, Tb, Ho, Tm, Yb, which have not been measured. The entropy contribution $T\Delta S^\circ$ to the self-assembly reaction is documented[124] with the accuracy of ±7.5 kJ mol^{-1}. The $\delta T\Delta S^\circ$ values for Gd, Dy and Er are determined almost completely by the difference in the desolvation entropies $\delta T\Delta S_f^\circ(Ln_{aq}^{3+})$ (see Table 1, Fig. 1). The qualitative aspects of the variation of thermodynamic parameters upon the formation of SMC have been considered.[50, 126–128]

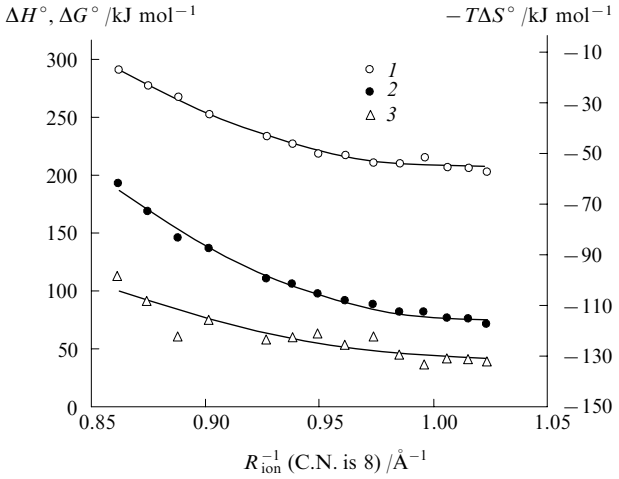


Figure 1. Variation of the thermodynamic parameters of the formation of Ln^{3+} complexes with 1,3,5-tramino-1,3,5-trideoxy-*cis*-inositol depending on the Ln nature.
(*1*) ΔH, (*2*) ΔG, (*3*) $T\Delta S$.

c. Supramacrocycles with square or rectangular geometry

Many metal complexes with square planar, trigonal bipyramidal, tetrahedral and octahedral coordination can be used as angular structural fragments in the construction of homonuclear square assemblies. The tetragonal SMC were prepared for the following metals: Ti;[8, 129] V, Cr;[14, 81] Mn;[14, 130, 131] Fe;[8, 14, 39, 130, 132] Co;[8, 14, 39, 130, 131, 133, 134] Ni;[130, 131] Cu,[8, 14, 39, 130, 135] Zn,[8, 14, 39, 130] Zr, Nb, Mo;[8, 14, 81, 136, 137] Tc, Ru;[39, 138, 139] Rh;[8, 140] Pd, Pt,[8, 9, 14, 39] Ag;[8, 39, 141] Cd;[39, 130, 131] Hf, Ta, W;[14, 81] Re;[8, 142, 143] Os, Ir, Au, Hg;[39] Na, Cs;[8] Ga [137] and Mg;[131] heteronuclear SMC have also been prepared: Pt−Pd, Ti−Pt, Re−Pd.[8] The supramacrocycles with a square geometry refer to the simplest representatives of the family of nanoassemblies. The steric strain in a square SMC depends on the ligands that form the square sides; therefore, their self-assembly is not always thermodynamically favourable; in these cases, kinetically labile oligomers are formed. In the self-assembly of square SMC, flexible or semiflexible linkers are used, for example, 4,4′-bipy; 1-(2-thiouracil-4-methylene)-3,6-diazahexane; bis(4-pyridyl)methane and -ethane; bis[4-(2-diphenylphosphinoethyl)phenyl] ether; 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene, amines and substituted bis-phosphonates; tetrakis(2-pyridyl)thiocarbazide and so on.

In the future, square supramacrocycles could find extensive practical use:[1, 2, 8, 9, 14, 18, 39] they participate in the hydrophobic/hydrophilic molecular recognition; form host–guest complexes by inclusion of various molecules into the cavity where they demonstrate high selectivity; they are used to transport salts into the organic phase and as artificial receptors. A promising trend in electrochemistry is the use of square SMC which change the oxidation state depending on the M−M interaction, *e.g.*, the metallacyclophane 'host' with four

reduced metal centres can transfer four electrons to a guest molecule. The redox reactions in a 'host–guest' system result in the change in properties (reactivity, magnetism, optical properties). Square SMC based on imine or azine Re complexes possess luminescent properties and are of interest as new promising sensors. The influence of the guest molecules on the excited states of the host molecule is considered as a new line of research in optics. The use of paramagnetic metal ions in square SMC allows one to study intermolecular interactions inside molecular layers; porphyrin-containing SMC are used to study the photochemical properties of the bound porphyrin layers, in particular, the processes occurring in the active sites of photosynthesis and in light-accumulating bacteria are modelled in this way; finally, square assemblies are used in catalysis.

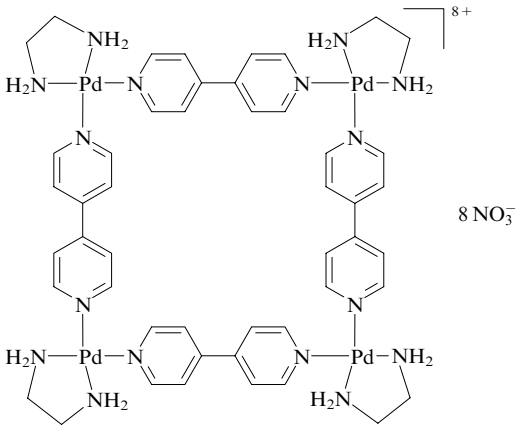
In square rings, the M–M interactions are shielded by bulky ligands, however the design of SMC as a rectangle from two dimers with relatively short M–M bonds connected by substituted aryl ligands gives SMC of a new type. This approach makes use of rhenium complexes with alkoxy [142] or thiolate [143] ligands. The reaction of the dimer $[(OC)_4Re.(\mu\text{-}SPr)]_2$ with 4,4′-bipyridyl (L) in chloroform gives SMC having a rectangular structure with two shorter sides $(OC)_3Re(\mu\text{-}SPr)_2Re(CO)_3$ and two longer sides, Re–L–Re [R(Re–Re) = 3.81 and 11.57 Å].[143] The shorter side of the rectangle, *i.e.*, the dimeric fragment, is stabilised by the Re–Re interaction, while the longer side, by Re–N coordination bonds [D_0(Re–Re) = $2 \times 18.3 = 36.6$ kJ mol^{-1}].

The longer side of this SMC can be shortened by replacing bipyridyl by pyrazine; the Re–Re contact would also contribute to stabilisation of the ring. Generally, the development of this strategy appears to hold promise. When designing rectangular SMC, one can choose various dimers of transition d elements with strong or weak M–M bonds.[49] The length of the other two bonds in the rectangular SMC can be varied by 'elongating' the 4,4′-bipy ligand, *i.e.*, by using pyrXpyr ligands of different length, for example, X = *p*-C_6H_4, C≡C, C≡C–C≡C. Rectangular supramacrocycles are able to accommodate neutral aromatic guest molecules.

Among the factors that stabilise SMC, a new type of ligand–ligand interaction, the so-called π–π-stacking interaction, is often mentioned. However, it is difficult to confirm this effect experimentally. It was hypothesised [8] that the ring structure of the tetranuclear assembly $[Cu_4(dppn)_4](OTf)_4$ [dppn is 3,6-bis(2-pyridyl)pyradazine, OTf = CF_3SO_3] with a distorted tetrahedral coordination of Cu(I) is stabilised by the π–π-stacking interaction of two pairs of ligands. This could be accepted if Cu^+ compounds with C.N. 4 devoid of the stabilising π–π-stacking interactions were unstable. However, in all compounds (both with σ and with π Cu^+–L interactions, in polymers, and in isolated molecules, and now in SMC), Cu^+ has a tetrahedral coordination and all these compounds are stable. Now the role of π–π-stacking interactions between the aryl ligands in the SMC remains an interesting hypothesis. The variation of the stability of $[LnL_3]^{3-}$ complexes (L is pyridine-2,6-dicarboxylate) along the lanthanide series was attributed [128] to the π–π-stacking interaction between the ligands. It turned out, however, that in the complexes of heavy Ln, the conformation of the ligands changes. Probably, the π–π-stacking interaction is important for biological systems, but in the case of SMC containing metals that form strong dπ(M)–pπ(L) bonds, multicentre L(π–π)–M–(π–π)L interactions arise. The problem of π–π-stacking interactions is related to the important theoretical problem of the degree of electron delocalisation in SMC.

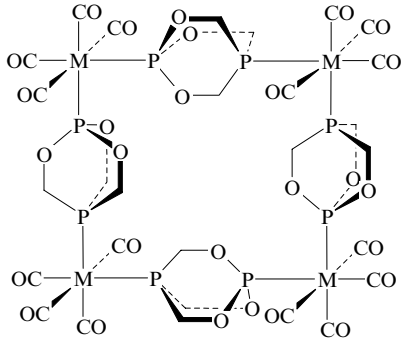
Although many metals form square assemblies, Pd^{2+} and Pt^{2+} complexes possess a number of specific properties. A square coordination geometry is typical of the electronic configuration d^8. Square Pd^{2+} and Pt^{2+} complexes are self-assembled to form a square SMC in the case where the *cis*-positions of the complex are 'protected', *i.e.*, they do not interact with other ligands.

A square supramacrocycle, $[Pd(en)(4,4'\text{-bipy})]_4^{8+}$ (**18**), has been synthesised [82] by the reaction between a ditopic non-chelating ligand, 4,4′-bipyridyl, and the kinetically labile $Pd(en)(NO_3)_2$ complex. The 4,4′-bipy ligand replaces the nitrate anions in the *trans*-positions with respect to N atoms of ethylenediamine and forms bonds with two cations.



18

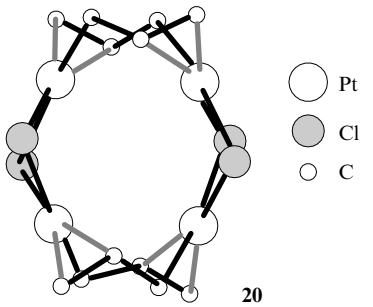
This method of synthesis, *i.e.*, self-assembly of *cis*-protected Pd^{2+}, Pt^{2+} and other metal complexes has been analysed in many publications,[6, 8, 12, 14, 18, 39] as it allows one to prepare SMC with different types of bonds, ranging from strong coordination M–N, M–O, M–C, M–P and M–Cl bonds to weak intermolecular M···M and hydrogen bonds. However, in the Jones opinion,[14] the studies [9, 82] are not pioneering, because the first square-shaped SMC **19** were prepared, based on the same idea (the use of *cis*-protecting ligands), ten years earlier, in particular, by reactions of $M(CO)_6$ (M = Cr, Mo, W) with ditopic donor $P(OCH_2)_3P$ ligands.[81]



19

M = Cr, Mo, W.

Even earlier, an extensive class of Pd and Pt metallacycles, for example, allylplatinum chloride $[(\pi\text{-}C_3H_5)PtCl]_4$ (**20**), have been studied in the solid state.[144] In the solid tetramer **20**, each

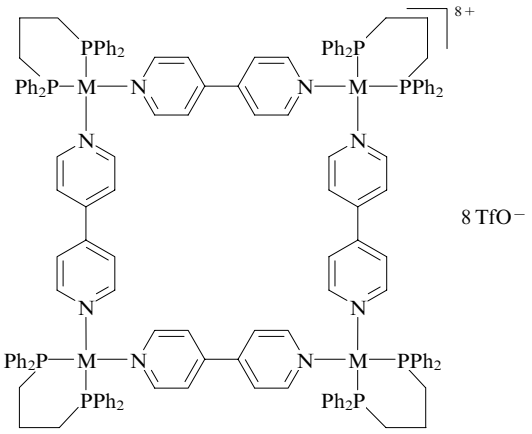


20

Pt atom is coordinated in the π-mode by the C=C bond of the allyl group, in the σ-mode by the CH_2 fragment of another allyl group and also by chlorine atoms. The bridging allyl ligands in complex **20** protect the *cis*-positions, similarly to the en and CO ligands in compounds **18** and **19**, respectively. It seems likely that the proper idea of *cis*-protection has long been used for the synthesis of tetramers with a rectangular or square coordination.[77] The Pt atoms in tetramer **20** are arranged at the corners of a square, the Pt – Pt distances being 3.270 and 3.235 Å, and the contribution of Pt – Pt bonds into the tetramer formation is essential [D_0(Pt – Pt) = 2 × 33.3 + 2 × 34.6 = 135.8 kJ mol^{-1}].

One can compare the properties of tetramers **18** and **20**. According to NMR spectroscopy and mass spectrometry, the structure of the ring in **18** is the same in solution as in the crystalline state (determined by X-ray diffraction). No experimental data on the structure of tetramer **20** in solution are available. The sides of rings **18** and **20** are ~8 and < 3 Å long, respectively; note that the size of the former can be varied. The supramacrocycle **18** is capable of molecular recognition, as it can host some guest molecules such as benzene, naphthalene, and so on; the ring size in tetramer **20** is too small for the insertion of guest molecules. The difference between Pt and Pd is noteworthy.[8] Thus Pt(en)$(NO_3)_2$ and 4,4′-bipy react to give a mixture of oligomers from which a thermodynamically stable square-shaped SMC can be isolated on heating. This effect was attributed to the fact that the Pd – N(bipy) bond is weaker than Pt – N. For the statistically average distances, R(Pd – N) = 2.04 and R(Pt – N) = 2.06 Å,[77] the bond energies we calculated are as follows: D_0(Pt – N) = 274, D_0(Pd – N) = 238 kJ mol^{-1}.

Square-shaped SMC have also been synthesised from bisphosphine derivatives [M(dppp)$(OTf)_2$] [M = Pt, Pd; dppp = $Ph_2P(CH_2)_3PPh_2$] and 4,4′-bipy in a non-aqueous solvent (CH_2Cl_2).[145, 146] The existence of the square SMC [M(dppp)(4,4′-bipy)]$_4$$(OTf)_8$ (**21**) was proved by NMR spectroscopy. The researchers cited noted a remarkable fact: even with a 100-fold excess of the 4,4′-bipy ligand, only square SMC **21** are formed in solution, *i.e.*, a fragment corresponding to a side or a corner of the SMC cannot be isolated.



21

M = Pd, Pt.

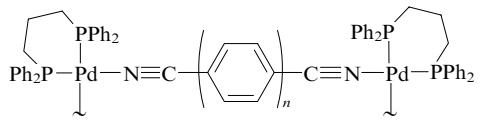
For solid compound **21** with M = Pt, it was shown that a square side is equal to 11.2 and the diagonal is 14.3 Å. The Pt^{2+} ions have C.N. 4: each Pt^{2+} ion is connected to two P atoms of the dppp ligand and two N atoms of the two 4,4′-bipy ligands. The N – Pt – N bond angles are equal to 84° and the P – Pt – P angles are about 90°, so that the whole ring is essentially non-planar. It was assumed [145] that the stability of this SMC is related to the strong π – π-stacking interaction between the ligands, in particular, between the π-electrons of the benzene rings of the chelating bis-phosphine ligands and π-electrons of one of bipyridyl rings. If this interaction was responsible for the stability of SMC **21**, the effect would be manifested in the interatomic distances in square SMC compared to those in the Pt^{2+} and Pd^{2+} complexes studied previously.[77] Our analysis of the reported structural data [8, 9, 14, 77, 145] has shown that the M^{2+} – N and M^{2+} – P distances (M = Pt, Pd) in the phosphine and pyridine complexes and in square SMC **21** are equal to within the accuracy of measurements. Indeed, in Pd[$Ph_2P(CH_2)_2PPh_2$]$(SCN)_2$, the measured [77] distances are R(Pd – P) = 2.245 – 2.260 Å, while in SMC **21**, R(Pt – P) = 2.23 – 2.25 Å.[145] An early publication [77] reports the average R(Pt – N) and R(Pd – N) values in the Pt^{2+} and Pd^{2+} pyridine compounds to be 2.02 – 2.06 Å, and the R(Pt – N) distances in SMC are 2.03 – 2.07 Å.[8, 9, 14, 145] Thus, the assumption of stabilisation of the SMC by π – π-stacking interactions between the ligands is not confirmed.

Analogous square SMC based on *cis*-phosphine derivatives have been obtained:[145] [M$(PEt_3)_2X]_4(OTf)_8$ (M = Pd^{2+}, Pt^{2+}; X is 4,4′-bipy, 2,7-diazapyrene, and so on). For all square SMC considered above, the *cis*-positions in the starting complexes (*i.e.*, the square corners) are protected by bidentate (en, dppp) or monodentate (PEt_3) ligands, which form strong M – P bonds. Neutral phosphines are strong electron donors, therefore, their interaction with metals is accompanied by a substantial charge transfer.[37] In the initial MA_2X_2 complexes (M = Pd, Pt; A = PEt_3; X is anion), the R(Pt – P) and R(Pd – P) distances vary in the 2.22 – 2.34 Å range.[77] According to our estimates, the M – P bond energy is fairly high [D(M – P) = 415 – 358 kJ mol^{-1}]; phosphine ligands protect the *cis*-positions of the structural blocks by a thermodynamic mechanism, *i.e.*, they stabilise the SMC by a great contribution of the M – PEt_3 and M – PPh_2 interaction energy. In addition, the PPh_2 ligands provide a steric protection of the *cis*-positions, which opens up broad opportunities for the synthesis of SMC using these ligands.[8, 14, 39]

In the absence of groups shielding the *cis*-positions, square-coordinated SMP may form. For example, this is the case in the reaction of Co$(NCS)_2$ with 4,4′-bipy.[147]

Although the properties of many palladium and platinum SMC are largely similar, note once again the difference in the self-assembly mechanisms: under the same conditions, square SMC are formed for palladium but oligomer mixtures are formed for platinum, because the Pd – N bonds are weaker than Pt – N bonds and more labile in the self-assembly processes giving SMC.[8]

The reaction of [Pd(dppp)$(OTf)_2$] with p-NC$(C_6H_4)_n$CN-p (n = 1, dcp; n = 2, dcdp) in CH_2Cl_2 produces square SMC [Pd(dppp)(dcp)]$_4$$(OTf)_8$ (**21a**) and [Pd(dppp)(dcdp)]$_4$$(OTf)_8$ (**21b**), the sides of which can be represented as follows:



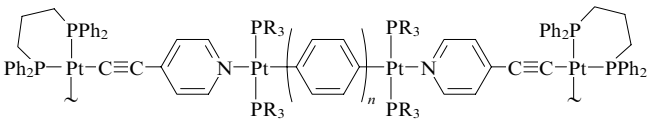
n = 1, 2.

Thus, although a large number of homonuclear and heteronuclear SMC based on complexes of almost all of d elements have been prepared in recent years, nitrogen-containing SMC with Pt^{2+} and Pd^{2+} are most numerous. This can be attributed to several reasons. The Pt^{2+} and Pd^{2+} ions are soft acids and the nitrogen atom, being a softer ligand than oxygen, forms numerous complexes with these ions, which is not so typical of other d elements. The Pd – N and Pt – N bond energies are higher than the Pd – O and Pt – O bond energies. This is an important thermodynamic factor affecting the self-assembly. As an illustration, one can compare the energies of

the Pd–N and Pd–O bonds having standard interatomic distances, R(Pd–O) = 2.0 and R(Pd–N) = 2.05 Å.[77] The calculated energies are as follows: D_0(Pd–N) = 243.4, D_0(Pd–O) = 191.6 kJ mol^{-1}, so that the energy gain due to the formation of two Pd–N bonds instead of two Pd–O bonds is significant: $\delta D_0 = 2[D_0(\text{Pd–N}) - D_0(\text{Pd–O})] = 2 \times (243.4 - 191.6) = 85.6$ kJ mol^{-1}.

The thermodynamics of the self-assembly process is substantially affected by the solvent. The formation of complexes of d elements and lanthanides in aqueous solutions is entropy controlled, while in non-aqueous solutions, it is enthalpy controlled.[26, 121] Without experimental data, it is unknown whether this would be valid for the self-assembly of SMC from complexes. Various hypotheses on the thermodynamics of the self-assembly of SMC have been put forward; it was noted[39] that the formation of ring structures is preferred over the formation of linear structures from the enthalpy standpoint, while the formation of small rings is preferred over the formation of large rings (at low concentrations) from the entropy standpoint.[126, 127]

Nanosized square SMC have now been prepared.[8, 111] For example, the addition of a solution of *cis*-[(dppp)Pt{C≡C(C$_5$H$_4$N-4)}$_2$] in CD_2Cl_2 to the solid bis-triflates TfOPt(PR$_3$)$_2$(*p*-C$_6$H$_4$)$_n$Pt(PR$_3$)$_2$OTf gave square SMC of different size the side of which can be represented as



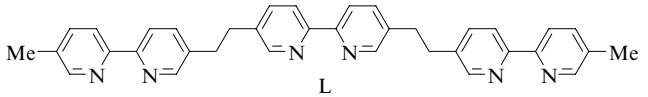
R = Et: n = 1, 2; R = Ph: n = 2, 3.

This nanosquare contains 12 platinum ions; each side has four ions, two of these being common to two sides. Generally, the synthetic strategy is the same as for the smaller SMC described previously (**18**, **21** and so on), namely, *cis*-protection of the metal ion. The calculated square diagonal is ~36 Å long.[8]

Nanosquares of this type are promising for the design of molecular switches and molecular machines. Another possibility is to use the magnetic properties of these SMC. These macrocycles are classified as ultrathin particles with a diagonal dimension of 3.4–4.8 nm. Nanoparticles applied onto a substrate are known to form ordered one-, two- and three-dimensional structures,[23] which find application due to the possibility of magnetic transitions (paramagnet–ferromagnet–antiferromagnet) or metal–dielectric phase transition.[76]

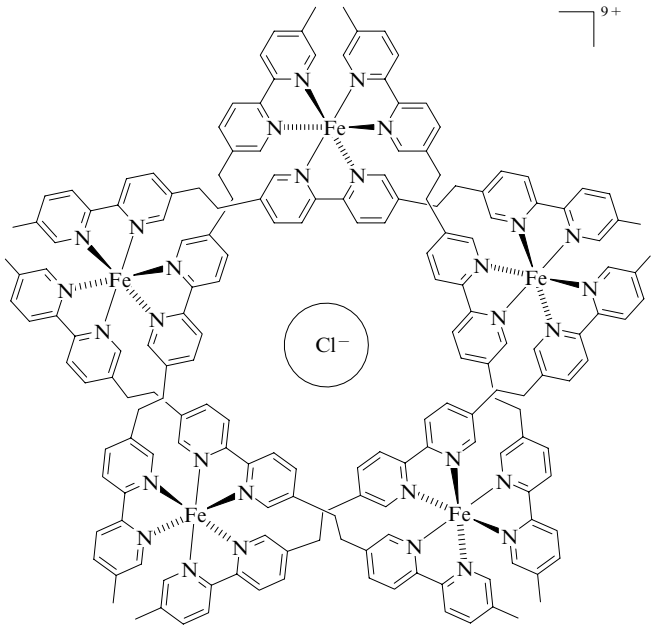
d. Polygonal supramacrocycles and three-dimensional structural motifs

Pentagonal and hexagonal supramacrocycles. The first SMC with pentagonal or hexagonal geometry were obtained by Lehn[148, 149] in ethylene glycol using $FeCl_2$ or $FeSO_4$, respectively, in the presence of NH_4PF_6 and ligand L.

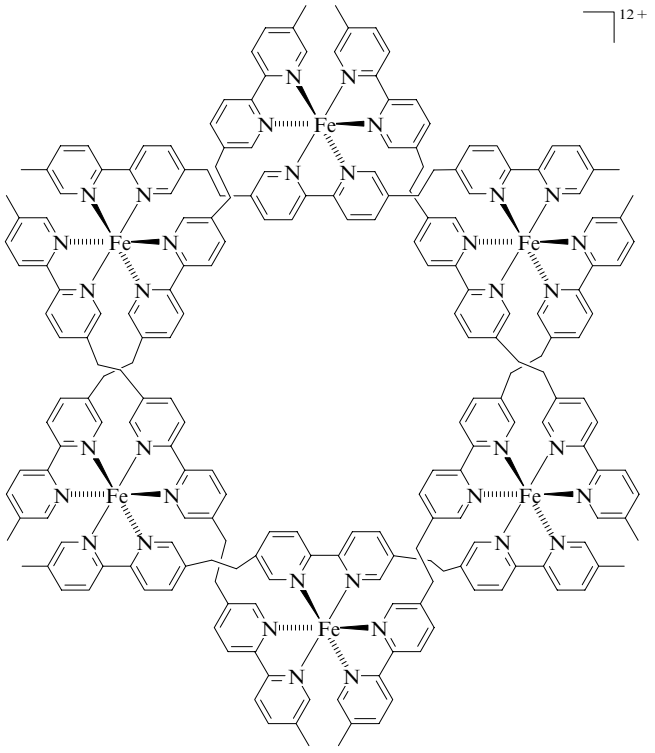


L

These are helical SMC {[FeL]$_5$Cl}(PF$_6$)$_9$ (**22**) and [FeL]$_6$(PF$_6$)$_{12}$ (**23**). In compound **22**, the Cl^- ion resides in the SMC cavity. By analogy with SMC **22**, the compound {[NiL]$_5$Cl}(PF$_6$)$_9$ (**24**) was prepared.[39]



22

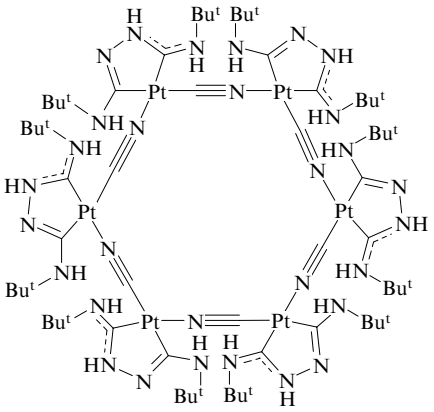


23

The authors[148] noted that the inner cavity of SMA **22** has a radius of 1.75 Å The size of the Cl^- ion (the ionic radius is 1.7 Å) fits the cavity and strong binding is due to the high positive charge of the SMA. However, when $FeSO_4$ is used, a large six-membered SMA containing no anion is formed. Analogous SMA were synthesised with Fe(BF$_4$)$_2$ and $FeSiF_6$. The use of $FeBr_2$ resulted in an approximately equimolar mixture of five- and six-membered SMA. Thus, it was concluded that the structure of SMA is influenced by the size rather than the charge of the counter-ion. However, the mechanism of this influence remains an open question, *i.e.*, whether the anion serves as the template in the SMA formation

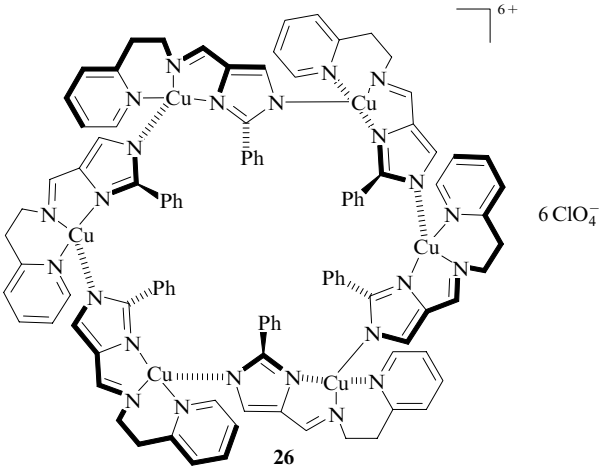
or the assemblies capable of strong binding of the anion (substrate) as receptors are formed owing to the reversibility of self-assembly.

Using K_2PtCl_4, H_2NNH_2 and Bu^tNC, SMC **25** has been synthesised in an aqueous solution.[112] This compound possesses luminescent properties being responsible for a strong band in the visible region at 356 nm. This band was assigned to a $Pt \rightarrow \pi$(carbene) charge transfer transition. An X-ray diffraction study showed that the SMC is non-planar, its conformation resembling the 'chair' conformation. The $CN-Pt-CN$ angles are equal to 92.4° and the $Pt-N\equiv C$ and $Pt-C\equiv N$ fragments are nearly linear (angle 174°).



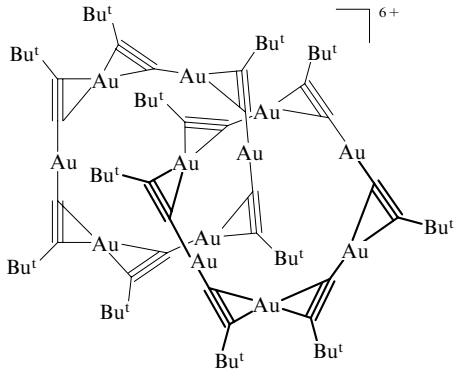
25

Six-membered SMC have also been prepared for other metals. The compound $[CuL]_6(ClO_4)_6$ (**26**) was synthesised[135] by triethylamine-induced deprotonation of the complex $Cu(HL)(ClO_4)_2$, where HL is *N*-(2-phenylimidazol-4-ylmethylidene)-2-aminoethylpyridine.



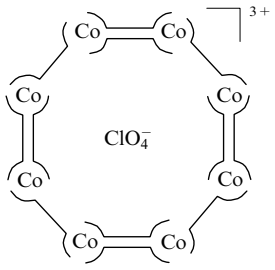
26

The complex $[\{Au(C\equiv CBu^t)\}_6]_2$ (**27**) was isolated upon the reaction of $[Au(NH_3)_2]BF_4$ with $Bu^tC\equiv CH$ in acetonitrile.[150] It was found that this compound is a catenane consisting of two interlinked six-membered SMC; each SMC contains six Au^+ ions and six acetylene groups. Within each ring, metal ions form a planar hexagon in which the R(Au—Au) distances are 3.30–3.36 Å. Although these distances are longer than those in metallic gold (2.88 Å), the Au—Au contacts determine the stability of this SMC. The energy of six Au—Au bonds D_0(Au—Au) [for average R(Au—Au) = 3.33 Å] equals $6 \times 26 = 156$ kJ mol^{-1}.



27

Octagonal supramacrocycles. The reaction of $[Co(OAc)_2(H_2O)_4]$ with the salt KL {L is bis[3-(2-pyridyl)pyrazol-1-yl]dihydroboronate} in MeOH with the addition of KPF_6 or $NaClO_4$ for precipitation gave[151] SMC containing eight Co^{2+} cations, twelve L^- bridging ligands and the PF_6^- or ClO_4^- anion: $[M_8L_{12}A]^{3+}(A^-)_3$, M = Co, Ni; A = ClO_4, PF_6. The ligand L = $C_5H_4N-C_3H_2N_2-BH_2-N_2C_3H_2-C_5H_4N$ forms a bridge between the neighbouring Co^{2+} ions.



28

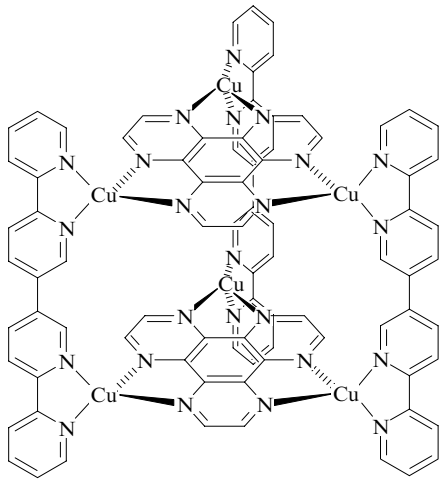
⌒ = L^-.

According to electrospray mass spectrometry and X-ray diffraction analysis, one anion resides in the SMC cavity of $[Co_8L_{12}(ClO_4)]^{3+}(ClO_4^-)_3$ (**28**). No $[M_8L_{12}]^{4+}$ cation without an anion in the cavity was detected; thus, the anion stabilises the eight-membered ring and, apparently, controls its size. We present our interpretation of this effect based on the thermodynamics of anion formation in solution. Note first of all that in the hexagonal SMC **26** of a smaller size, the ClO_4^- anion is not inserted in the cavity, *i.e.*, the size effect is significant for SMC **26** and **28**.

It is known that thermodynamics of formation of anions affects their outer- or inner-sphere coordination. Thus the standard free energies of formation[121] $\Delta G_f^\circ(ClO_4^-)_{aq} = 7163.5$ and $\Delta G_f^\circ(Cl^-)_{aq} = -164.5$ kJ mol^{-1} are similar but the coordination of the ClO_4^- anion is usually outer-sphere, while the Cl^- ion can be coordinated as both an outer- and an inner-sphere ligand. The standard entropy of formation of the ClO_4^- anion in an aqueous or ethanolic solution is positive and high, while that of the Cl^- ion is negative [$\Delta S_f^\circ(ClO_4^-)_{aq} = +118.7$, $\Delta S_f^\circ(Cl^-)_{aq} = -8.7$ J mol^{-1} K^{-1}]. Thus, the entropy factor mainly determines the outer-sphere coordination of the ClO_4^- anion, because the inner-sphere coordination is entropically unfavourable. For insertion into an SMC, the ClO_4^- anion should be stabilised by a gain in enthalpy, *i.e.*, by the formation of strong bonds with the atoms of SMC, in order to counterbalance both the entropy and enthalpy loss. Apparently, this is the case for SMC **28** in which the ClO_4^- anion is strongly bound to atoms of the eight-membered ring[8] and the size effect allows the anion to be inserted into the cavity. The possibility of insertion of the SO_4^{2-}, Cl^- and ClO_4^- anions has been studied from the standpoint of the size effect.[148,151]

However, it should be borne in mind that thermodynamics of their insertion into SMC are fundamentally different due to different thermodynamics of their formation in solutions. Thus the values $\Delta S_f^\circ(SO_4^{2-})_{aq} = -112.2$ and $\Delta S_f^\circ(ClO_4^-)_{aq} = +118.7$ J mol^{-1} K^{-1} are close in magnitude but have opposite signs. The insertion of $(SO_4^{2-})_{aq}$ into SMC is entropically favourable but the enthalpy loss is high because $\Delta H_f^\circ(SO_4^{2-})_{aq} = -875.9$ kJ mol^{-1}. The $(ClO_4^-)_{aq}$ anion has the maximum entropy of formation and the $(SO_4^{2-})_{aq}$ ion has the minimum enthalpy of formation. Hence, in order to surpass the enthalpy loss upon the insertion of SO_4^{2-}, it is necessary to select an appropriate SMC with very strong bonds between its atoms and the inserted SO_4^{2-} anion.

Apart from two-dimensional SMC, three-dimensional SMA with a tetrahedral,[152] prismatic[91] or cylindrical[28,98] geometry have also been prepared. For example, SMA **29** was synthesised by the reaction of $[Cu(MeCN)_4]BF_4$ with hexaphenylhexaazatriphenylene and quaterpyridine in chloroform.[98] The structure of this SMA was determined by X-ray diffraction analysis. By introduction of various fragments (acetylene, benzene and so on) into quaterpyridine, the height of SMA **29** can be increased to 33 Å.[78]



29 (the phenyl groups are omitted for clarity)

As the conclusion of this Section, we would like to note that Pt^{4+} and Pd^{4+} compounds could also be used in the SMCh. However, this would require an absolutely different strategy of the preparation of SMA. The stereochemistry of these compounds, for example, R_3PtX (R = Me, Et; X = OH, Cl, I), shows[144] that the PtR_3^+ groups tend to acquire a pyramidal structure and Pt^{4+} tends to an octahedral geometry. This gives compounds with a cubane structure, which is based on a cube with vertices occupied by alternating Pt^{4+} and X^- ions. In these systems, the R(Pt–Pt) distances vary from 3.41 (Me_3PtOH) to 3.90 Å (Me_3PtI, Et_3PtCl), so that the contribution to the enthalpy stabilisation ranges from D_0(Pt–Pt) = 4 × 28.7 = 114.8 to D_0(Pt–Pt) = 4 × 17.8 = 71.2 kJ mol^{-1}. As a result of competition between the tendency of PtR_3^+ to form a pyramidal coordination and the tendency of Pt^{4+} to an octahedral coordination, depending on the number and the coordination capacity of the anions and polar molecules, either oligomers or SMC are formed.

4. Thermodynamic factors in the formation of supramacrocycles

The role of thermodynamic factors in the formation of SMC has been considered in a number of studies.[8,39,50,71,126,128] As noted above, several mechanisms have been proposed[8,39,71] for the formation of supramolecular systems, which reflect to one or another extent the thermodynamics of self-assembly, namely, these are thermodynamic, kinetically controlled and irreversible, assisted, directed mehanism, *etc*. According to the thermodynamic mechanism of the self-assembly in solution, a thermodynamic equilibrium between the starting reactants and one, thermodynamically the most stable product is attained. Thermodynamically unstable products either dissociate or are formed in minor amounts with respect to the major product. The self-assembly of the structural blocks to give SMC or a linear oligomer decreases the disorder in the system and, hence, results in a negative change in entropy, which can be counterbalanced by the enthalpy effect. In a review,[8] it has been suggested that both the enthalpy and entropy changes are favourable for the self-assembly of SMC. It has been shown above, using numerous examples, that the metal–metal bonds present in SMC contribute considerably to the enthalpy of formation of SMC.

The thermodynamic parameters of the self-assembly process largely depend on the properties of the solvent.[124] It was found experimentally that the formation of Ln^{3+} and An^{3+} complexes in acetonitrile is characterised by the following relationship between the enthalpy and entropy contributions to the free energy:[153–155]

$$\Delta S^\circ < 0, \Delta H^\circ < 0, |T\Delta S^\circ| < |\Delta H^\circ|.$$

However, in water, the formation of Ln^{3+} and An^{3+} complexes with various N- and O-donor ligands obeys other relations:[125,156]

$$\Delta S^\circ > 0, \Delta H^\circ < 0, T\Delta S^\circ > |\Delta H^\circ|.$$

In water, the 3 Ln^{3+} + 2 L self-assembly to give triangular SMC **17** is entropy-driven, *i.e*., similar to the formation of Ln^{3+} and An^{3+} complexes.[156] However, it is not clear whether this conclusion can be extended to the formation of SMC with other metals, a different geometry (for example, squares), and in other solvents.

The self-assembly processes often use chelating *n*-dentate ligands. In SMC **17**, the ligand is hexadentate ($n = 6$); two ligands form a common electronic system; therefore, for two chelating ligands, we get $n = 12$. Let us assume that the change in entropy upon self-assembly is due to the chelation effect. The entropy change caused by the chelation effect is determined[156] by the equation

$$\Delta S^\circ = R(n-1)\ln M = 367 \text{ J mol}^{-1} \text{ K}^{-1},$$

where R is the universal gas constant, M is the molality of water. The change ΔS° upon the formation of SMC **17** ranges[124] from 329 (La) to 442 J mol^{-1} K^{-1} (Lu). With allowance for the inaccuracy of ΔS° equal to ±25 J mol^{-1} K^{-1}, the average entropy of self-assembly for SMC **17** is $\Delta S^\circ = 408$ J mol^{-1} K^{-1} (Ref. 124); this value is consistent with the estimate $\Delta S^\circ = 367 \pm 50$ J mol^{-1} K^{-1} made using the chelation model.

The role of the solvent is highly important in both complexation and the self-assembly: the free energy of formation of SMC **17** ΔG_f° correlates with the free energy of formation of the aqua ions 3 $\Delta G_f^\circ(Ln_{aq}^{3+})$; therefore, from the known $\Delta G_f^\circ(Ln_{aq}^{3+})$ and $\Delta G_f^\circ(An_{aq}^{3+})$ values and the measured ΔG_f°(**17**) values, one can estimate the standard free energy of formation of similar SMC with other metals and, hence, the changes in the free energy ΔG° for the corresponding self-assembly reactions:

Ln	Eu	Pu	Am	Cm
ΔG° /kJ mol^{-1}	104	83.6	93.3	90.0

An important problem in the processing of radioactive elements is the separation of Eu^{3+}, Am^{3+} and Cm^{3+}. The obtained values $\delta\Delta G^\circ$(Eu–Am) = 10.7 and $\delta\Delta G^\circ$(Eu–Cm) = 14.0 kJ mol^{-1} show that using SMC, one

can achieve high selectivity in the separation of Ln^{3+} and An^{3+} ions.

The properties of solvents (dielectric constant, polarisability, the ability to form hydrogen bonds, viscosity) determine the soft or hard behaviour of the solvent.[44, 156] Using the set of these properties, it is possible to predict that the self-assembly involving hard Ln^{3+} cations in water is an entropy-driven process, that in acetonitrile or pyridine is enthalpy-driven, the process in octanol is rather enthalpy-driven, *etc*. In addition, it was shown [124] that ΔG° and the $\Delta S^\circ/\Delta H^\circ$ ratio for the self-assembly depend on the properties of cations. It is beyond doubt that the effects of solvents on the self-assembly thermodynamics should be different for compounds of soft M^+ (M = Cu, Ag, Au, Tl, Hg), M^{2+} (M = Pd, Pt, Cd, Hg) and hard (Ln^{3+}, An^{3+}) cations. Even among the same family (soft or hard cations), the $\Delta S^\circ/\Delta H^\circ$ ratio would substantially depend on the desolvation of this cation. Ten years ago the ΔG° values for self-assembly were still calculated using two-parameter models,[157] which define the electron-donor (C_D) and -acceptor (C_A) properties of the interacting Lewis acids and bases

$$\Delta G^\circ = \text{const}\, C_D\, C_A.$$

As new data have been accumulated, it became clear that these simplified models do not reflect either quantitative or qualitative features of thermodynamics of the SMA formation.

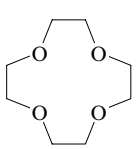
V. Thermodynamic properties of macrocyclic complexes in solution

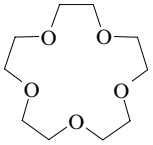
Among the macrocyclic ligands, crown ethers, cryptands, spherands, calixarenes and their derivatives have been most studied.[1, 2, 7, 128, 158–161] The advances in the synthesis of the alkali and alkaline earth metal complexes [1, 2, 7, 159–162] have stimulated the development of analogous studies dealing with lanthanides.[27, 128, 161, 162] The particular interest in this field is related to the extensive use of lanthanides in catalysis, in the manufacture of glass, ceramics, optical and electronic devices, in nuclear power engineering (separation processes), in biology and medicine.

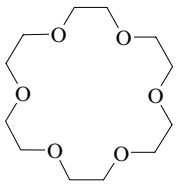
As regards the stability of Ln complexes with crown ethers containing 4, 5, 6 and 10 oxygen atoms, it has been noted [162] that the plots log β *vs*. R_{ion}^{-1}(Ln) do not show any general trend, some passing through an extremum and some other monotonically descending or ascending. This reflects the relationship between parameters such as the ion diameter and the size of the ligand cavity. Although the idea of size fitting has not lost its importance in analysis of the selectivity of complexation of macrocyclic ligands with alkali and alkaline earth metals, the experimental data indicate that other properties of cations such as desolvation parameters and the ability to accept electron density have a substantial influence on the thermodynamic properties of MC.

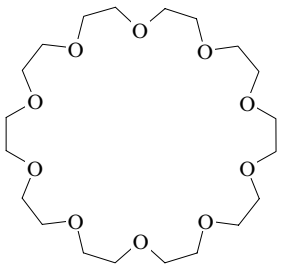
1. Size selectivity of macrocyclic ligands with respect to cations

It was found that the ratio of the cation to cavity dimensions ($R_{ion}/R_c = r$) is an important factor determining the selectivity of complexation with the crown ethers, 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6), 21-crown-7 (21C7) and 30-crown-10 (30C10) in solution.


12C4


15C5


18C6


30C10

The stability constants log β_1 of lanthanide(III) complexes with a number of crown ethers in propylene carbonate (PC) were measured and the log β_1 values were statistically processed depending on r:[162]

Crown ether	21C7	18C6	15C5	12C4
log β_1(La – Lu)	5.0 – 7.5	7.0 – 9.0	6.0 – 7.5	5.0 – 5.5
r	0.6 – 0.75	0.75 – 0.95	1.20 – 1.40	1.70 – 2.0

The log β_1 values are maximum for the complexes with 18C6. For $r \ll 1$ or $r \gg 1$, the stability of the complexes decreases. For the complexes of light lanthanides with 18C6, $r \approx 1$, which accounted for their higher stability compared to heavy lanthanide complexes. The decrease in log β_1 of the complexes with this crown ether in methanol [160] following an increase in Z(Ln) from La to Eu could also be attributed to the better fit between R_{ion} and R_c. It may seem that the trends in variation of log β_1 upon complexation of alkali metals with crown ethers can also be interpreted in this way; however, on going from Na^+ to Cs^+ the ionic radius increases 1.6-fold and on going from La^{3+} to Lu^{3+}, only 1.2-fold. This implies the need for essential preorganisation of macrocyclic ligands for the reaction with M^+: in the complexes with 18C6, the K^+ cation fits in the plane of the ligand molecule with D_{3d} symmetry, while the large Cs^+ ion deviates from this plane. However, the Na^+ ion is too small for the large ring; therefore, its symmetry is highly distorted compared to D_{3d}.

The enthalpy of desolvation (ΔH_h) and electronegativity of cations play an important role in the complexation. Compare two ion pairs, Sr^{2+}/Pb^{2+} and Rb^+/Tl^+, having similar ΔH_h, R_{ion} and similar enthalpies of complexation with 18C6 [ΔH(18C6)]:

Sr^{2+} and Pb^{2+}:

$\Delta H_h = -1521$ and -1556 kJ mol^{-1};

$R_{ion} = 1.18$ and 1.19 Å,

$\Delta H(18C6) = -15.1$ and -21.8 kJ mol^{-1};

Rb^+ and Tl^+:

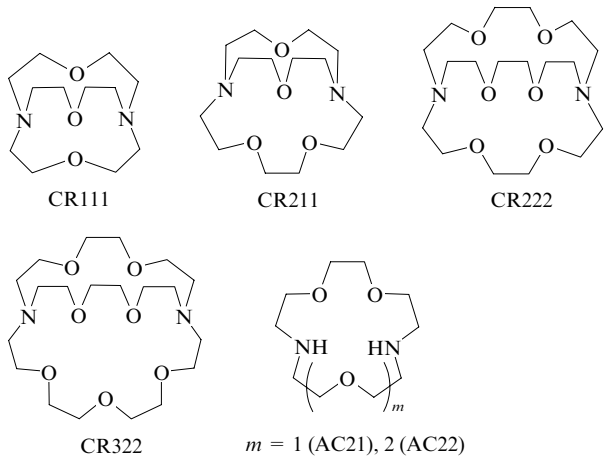
$\Delta H_h = -339$ and -364 kJ mol^{-1};

$R_{ion} = 1.52$ and 1.50 Å,

$\Delta H(18C6) = -15.9$ and -18.4 kJ mol^{-1}.

The negative ΔH(18C6) values larger in magnitude found for Pb^{2+} and Tl^+ were attributed [156] to higher electronegativity of Pb (1.8) and Tl (1.8) compared to Sr (1.0) and Rb (0.8); apparently, the 5d-AO of lead and thallium participate in the formation of bonds with macrocyclic ligand atoms, resulting in more exothermic complexation.

In the case of cryptands, the size fitting principle is believed [156] to be more significant than for crown ethers or tetraazamacrocycles, which is reflected in the stability constants log K_{211}, log K_{222}, log K_{322}.



The highest stability is attained for smaller cations, which fit in small cavities:

Li^+: R_{ion} = 0.675 Å,

$\log K_{211} > \log K_{221}$;

Na^+: R_{ion} = 1.0 Å,

$\log K_{211} < \log K_{221} > \log K_{222} < \log K_{322}$;

K^+: R_{ion} = 1.376 Å,

$\log K_{221} < \log K_{222} > \log K_{322}$;

Ca^{2+}: R_{ion} = 0.72 Å,

$\log K_{211} < \log K_{221} > \log K_{222} < \log K_{322}$;

Ba^{2+}: R_{ion} = 1.389 Å,

$\log K_{221} < \log K_{222} > \log K_{322} < \log K_{332}$.

The reason is in the greater hardness of cryptands CR111–CR322 and higher preorganisation compared to crown ethers.

2. Effect of the charge transfer energy from the ligand to the cation on the stability of macrocyclic complexes

Presumably, the interaction of macrocyclic ligands (cryptands and azacrown ethers, AC) with Ln^{3+} ions occurs through electron density transfer from the O and N atoms of the ligand to the cations. The higher the electron-acceptor capacity of the cation and the lower the electron transfer energy from the occupied MO of the ligands to vacant or partially occupied 4f-AO of the cation, the more stable the complex. If this hypothesis is valid, the charge transfer energy $\Delta E[2p(O) \rightarrow 4f(Ln^{3+})]$ and $\Delta E[2p(N) \rightarrow 4f(Ln^{3+})]$ should correlate with $\log\beta[Ln(CR221)]^{3+}$ and $\log\beta[Ln(AC21)]^{3+}$. The $\Delta E[2p(O) \rightarrow 4f(Ln^{3+})]$ have been measured for many complexes and systematised,[29,35] whereas no data on $\Delta E[2p(N) \rightarrow 4f(Ln^{3+})]$ are available. Figure 2 compares the trends of variation of $\Delta E[2p(O) \rightarrow 4f(Ln^{3+})]$ (Ref. 35) and $\log\beta[Ln(CR221)]^{3+}$ or $\log\beta[Ln(AC21)]^{3+}$ (Ref. 161). It can be seen that in the first half of the series, on going from Pr to Eu, the stability of complexes $[Ln(CR221)]^{3+}$ increases in line with a decrease in $\Delta E[2p(O) \rightarrow 4f(Ln^{3+})]$, *i.e.*, with an increase in the electron-acceptor ability of the cation. The extreme points of $\log\beta[Eu(CR221)]^{3+}$ and $\log\beta[Eu(AC21)]^{3+}$ correspond to the minimum of $\Delta E[2p(O) \rightarrow 4f(Eu^{3+})]$. The antiparallel variation of $\log\beta[Ln(CR221)]^{3+}$ and $\Delta E[2p(O) \rightarrow 4f(Eu^{3+})]$ in the second half of the lanthanide series from Gd to Yb is beyond doubt. The $\log\beta[Lu(CR221)]^{3+}$ has not been measured: in the model considered, one can expect that $\log\beta[Lu(CR221)]^{3+} < \log\beta[Yb(CR221)]^{3+}$. As a conclusion of this Section, note that the charge transfer energy in the MC of transition d elements has not been studied experimentally, although this could provide direct information on the electron density transfer from the ligands to the cations inserted in the cavity.

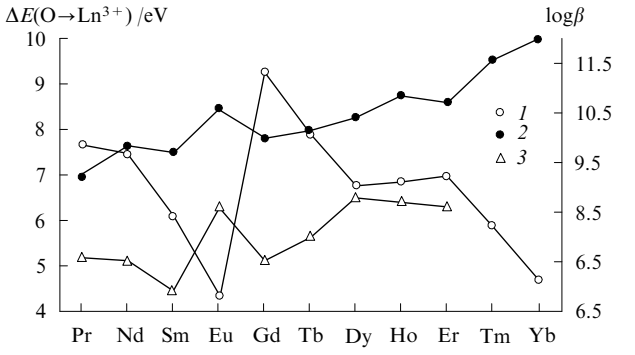


Figure 2. Energies of charge transfer from the oxygen atoms to the Ln^{3+} 4f-AO in the Ln^{3+} complexes (*1*), stability constants of the complexes with cryptand CR221 (*2*) and azacrown ether AC21 (*3*) in MeOH.

3. Effect of desolvation of cations on the stability of macrocyclic complexes

The stability of lanthanide cryptates depends on the solvent and increases in the sequence[161] DMF < DMSO < H_2O < MeOH < MeCN ≪ PC. In highly solvating solvents (DMF, DMSO, H_2O, MeOH), the lower the expenditure for desolvation, the higher the stability of complexes ($\log\beta$) (or the greater the magnitude of the negative ΔG° upon complexation). The free desolvation energy is determined by the free energy of formation of solvated ions; in the aqueous solution, the $-\Delta G_f^\circ(Ln_{aq}^{3+})$ values vary in the range from 576 (Eu) to 688 kJ mol^{-1} (La).[125,153–155]

Ln	$-\Delta G_f^\circ(Ln_{aq}^{3+})$ /kJ mol^{-1}	Ln	$-\Delta G_f^\circ(Ln_{aq}^{3+})$ /kJ mol^{-1}
La	688	Tb	668
Ce	676	Dy	664
Pr	681	Ho	675
Nd	672	Er	673
Sm	677	Tm	671
Eu	576	Yb	639
Gd	660	Lu	677

It was noted[161] that the dependences of $\log\beta[Ln(CR221)]^{3+}$ and $\log\beta[Ln(AC21)]^{3+}$ on $Z(Ln)$ are essentially non-monotonic. It should be emphasised that in the first half of the series, the extremal point is found for Eu in both cases. Evidently, neither the size of the cavity nor the ionic radius, which is a monotonic function $Z(Ln)$, can be responsible for the non-monotonic variation of the stability of the complexes and the presence of extremal points for Eu. Probably, the variation of $\log\beta[Ln(CR221)]^{3+}$ and $\log\beta[Ln(AC21)]^{3+}$ is determined by the desolvation parameters of the cations. Since there are no experimental data on the free energy of formation of Ln^{3+} in MeOH, we use the reported[125] experimental values of $\Delta G_f^\circ(Ln_{aq}^{3+})$. A comparison of $|\Delta G_f^\circ(Ln_{aq}^{3+})|$ for Sm, Eu and Gd shows that the extremal points in the $\log\beta[Ln(CR221)]^{3+}$ and $\log\beta[Ln(AC21)]^{3+}$ plots corresponding to an increase in the stability of Eu complexes with respect to Sm and Gd complexes are related to the desolvation of cations. The antiparallel variations of $|\Delta G_f^\circ(Ln_{aq}^{3+})|$ and $\log\beta[Ln(CR221)]^{3+}$ or $\log\beta[Ln(AC21)]^{3+}$ can be clearly seen (see Fig. 2).

If the correlation between $\log\beta[Ln(CR221)]^{3+}$ and $|\Delta G_f^\circ(Ln_{aq}^{3+})|$ is applied only to two elements, La and Yb, one

can determine $\log\beta[Ln(CR221)]^{3+}$ for Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy. The difference between these estimates and the experimental values equal to ± 0.4 for $\log\beta$ (or ~ 2.4 kJ mol^{-1} for ΔG°) signifies not only a qualitative but also a quantitative relationship between the MC stability and the desolvation energy of the cations inserted in the cavity. However, the $|\Delta G_f^\circ(Ln_{aq}^{3+})|$ values for Ln = Ho (675), Er (673) and Tm (671) differ by only 2 kJ mol^{-1} (Ref. 125). This is apparently lower than the experimental error in the determination of $\log\beta$; for these three elements, the variations of $\log\beta$ can be determined by other factors.

4. Effect of the solvent on the stabilisation of the unusual oxidation states of lanthanides and actinides

The charge transfer energies $\Delta E[2p(O)\rightarrow 4f(Ln^{3+})]$ can serve as a quantitative characteristics of the redox potentials $E^\circ(3+/2+)$.[153–155] The lowest $\Delta E[2p(O)\rightarrow 4f(Ln^{3+})]$ values for europium, samarium and ytterbium correspond to their most stable, divalent states in the series of lanthanides. The divalent state of europium, samarium and ytterbium can be stabilised upon complexation with cryptands or even coronands[161] in H_2O, MeOH and DMF. In these solvents, the cryptates and coronates of trivalent lanthanides are reduced at higher potentials than free (solvated) cations, which attests to stabilisation of the lanthanide(II) complexes. In MeCN or PC, no systematic stabilisation of the divalent state is observed.

Therefore, it may be promising to use cryptands and coronands for the separation of Ln^{2+}/Ln^{3+} and An^{2+}/An^{3+} pairs by extraction based on the difference between the redox potentials $E^\circ(3+/2+)$. It has been noted above that the separation of Eu^{3+}, Am^{3+} and Cm^{3+}, which are deservedly called the 'Bermuda Triangle' in the extraction chemistry is a challenge. The problem is that complexes of these cations in solutions have very similar thermodynamic characteristics due to the small difference between the free energies of formation of solvated cations ΔG_f°, in particular, in aqueous solutions, $\Delta G_f^\circ = -576$ (Eu^{3+}), -603 (Am^{3+}) and -594 kJ mol^{-1} (Cm^{3+}).[125] Upon complex formation with cryptands and coronands in aqueous solutions, Am^{3+} and Cm^{3+} are not reduced, unlike Eu^{3+}. However, the heavy actinide ions (Cf^{3+}, Es^{3+}, Fm^{3+} like Sm^{3+}, and Md^{3+} like Eu^{3+}) should be reduced to the divalent state. The good prospects of using cryptands and coronands for the separation of these elements are due to the use of readily available solvents and environmentally safe extractants, which do not give rise to the third phase, unlike the classical phosphorus-containing extractants.

5. Complexation with preorganised ligands

The thermodynamic characteristics, *i.e.*, the free energy and enthalpy changes upon the formation of $[Ln(CR221)]^{3+}$ complexes in MeCN and PC, were measured[161] for Ln = La, Pr, Nd, Er and for Ln = La, Pr, Nd, respectively. The ligand is hard and highly preorganised and both solvents are non-solvating. Presumably, the $\Delta G^\circ[Ln(CR221)]^{3+}$, $\Delta H^\circ[Ln(CR221)]^{3+}$ and $\Delta S^\circ[Ln(CR221)]^{3+}$ values are controlled by the size effect. The experimental values of ΔG° and ΔH° for seven lanthanides depend linearly on the ionic radii of the cations (C.N. 9) with a correlation factor of 0.99. This allows one to estimate $\Delta G^\circ[Ln(CR221)]^{3+}$, $\Delta H^\circ[Ln(CR221)]^{3+}$ and $T\Delta S^\circ[Ln(CR221)]^{3+}$ for Ce, Sm, Eu, Gd, Tb, Tm, Yb, Lu in MeCN and PC. Thus, in the case of MC $[Ln(CR221)]^{3+}$ we have at hand the $\Delta G^\circ[Ln(CR221)]^{3+}$ values for all lanthanides in MeOH, MeCN and PC and the $\Delta H^\circ[Ln(CR221)]^{3+}$ and $T\Delta S^\circ[Ln(CR221)]^{3+}$ values in MeCN and PC.

In the complexation of Ln^{3+} with O- and N-donor ligands in MeCN, both the entropy and enthalpy changes are negative;[128, 156] therefore, it is not unexpected that $\Delta S^\circ[Ln(CR221)]^{3+} < 0$ and $\Delta H^\circ[Ln(CR221)]^{3+} < 0$ in the case of formation of $[Ln(CR221)]^{3+}$ in MeCN (Fig. 3). However, it is difficult to explain why ΔS° for complexation in PC changes the sign: for light lanthanides, $\Delta S^\circ > 0$ (La – Nd), in the middle of the series, $\Delta S^\circ \approx 0$ (Eu, Gd) and in the second half of the series, $\Delta S^\circ < 0$ (Tb – Lu). The change in the entropy sign is rarely encountered in the chemistry of complex compounds; it is attributed to a change in the composition of complexes or the conformation of the ligands.[156] As regards the complexation of Ln^{3+} with CR221 in other solvents (H_2O or MeOH), the $\Delta S^\circ[Ln(CR221)]^{3+}$ values may be expected to be positive and the entropy contribution to the change in the free energy of complexation would predominate over the enthalpy contribution.

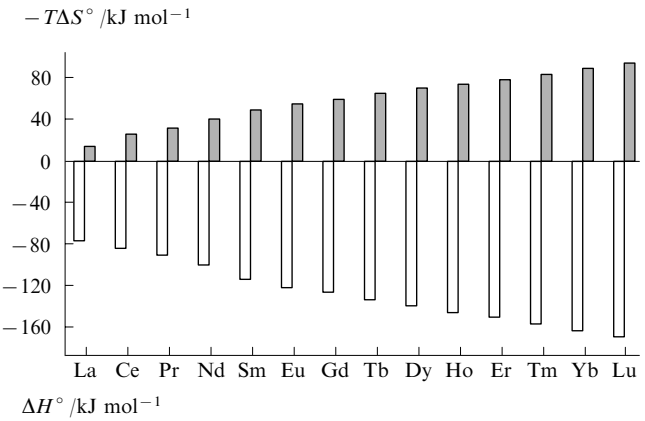


Figure 3. Enthalpy and entropy changes upon the formation of cryptates $[Ln(CR221)]^{3+}$ in MeCN.

6. Macrocyclic effect

When studying MC, it is general practice to estimate the macrocyclic effect by comparing the thermodynamic properties of the MC and its acyclic analogue; however, such an analogue cannot be easily selected.[156] We chose the lanthanide complexes with highly preorganised macrocyclic ligand CR221 synthesised in MeCN and MeOH and with a non-preorganised edta ligand in H_2O. Each ligand has six coordinating atoms (2 N + 4 O). The presence of the same donor atoms results in some linear relationships for the free energy of complexation ΔG°_{CR221}(MeCN), ΔG°_{CR221}(MeOH)[101] and $\Delta G^\circ_{edta}(H_2O)$[156] (all values are expressed in kJ mol^{-1}):

$$\Delta G^\circ_{edta}(H_2O) = \Delta G^\circ_{CR221}(MeCN) - 23.5, \quad (1)$$

$$\Delta G^\circ_{edta}(H_2O) = 0.985\,\Delta G^\circ_{CR221}(MeOH) - 36.5. \quad (2)$$

However, the trends in the variation of ΔH°_{CR221}(MeCN) and $\Delta H^\circ_{edta}(H_2O)$ as well as $T\Delta S^\circ_{CR221}$(MeCN) and $T\Delta S^\circ_{edta}(H_2O)$ are different. The change in the C.N. in lanthanide complexes with edta (C.N. is 10 for La – Nd, 9.5 for Sm and Gd, 9 for Tb – Lu)[102] is responsible for the non-monotonic variation of the entropy along the series and, as a consequence, a non-monotonic variation of the enthalpy (Fig. 4). Both ΔH°_{CR221}(MeCN) and $T\Delta S^\circ_{CR221}$(MeCN) vary monotonically along the lanthanide series. This is a consequence of high preorganisation of the ligand and the effect of the non-solvating solvent. As long as experimental ΔH°_{CR221}(MeOH) and $\Delta H^\circ_{CR221}(H_2O)$ values are missing, it is difficult to draw conclusions about the nature (either enthalpy or entropy) of the macrocyclic effect. It is clear that the degree of ligand preorganisation depends on the solvent. At a qualitative level, it can be noted that if a thermodynamic effect of ligand preorganisation in solvating solvents is pronounced, this can

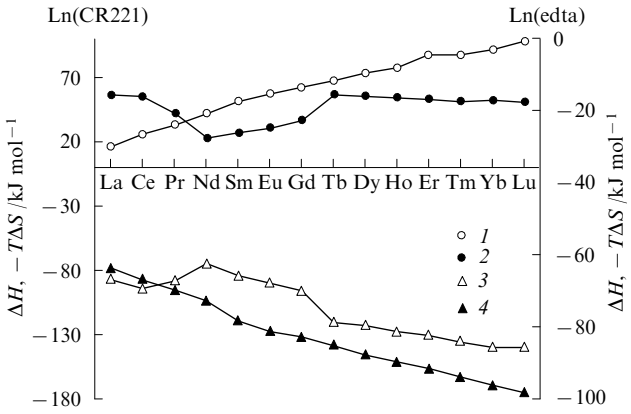


Figure 4. Changes in entropy (*1*, *3*) and enthalpy (*2*, *4*) upon the formation of complexes Ln(edta) in H_2O (*2*, *3*) and Ln(CR221) in MeCN (*1*, *4*).

mask the non-monotonic entropy and enthalpy changes along the lanthanide series.

For predicting the macrocyclic effect, it is important that in Eqns (1) and (2), the coefficient at ΔG°_{CR221} is ~ 1. Hence, the macrocyclic effect along the lanthanide series can be estimated using known ΔG° for the appropriate ligands with the same number and nature of the donor atoms as in the macrocycle, for example, nitrilotriacetate (1 N + 3 O), ethylenediaminetetraacetate (2 N + 4 O), ethylenetriaminepentaacetate (3 N + 5 O), *etc*.

7. Calixarenes and crown ethers

a. Interaction of calixarenes with lanthanide aqua ions

Water-soluble calixarenes are considered as promising ligands for the synthesis of MC.[163] *p*-Sulfocalix[4]arenes (*p*-SC[4]A) form SMA with a variety of guest molecules in both solution and the solid state. Two-dimensional hydrogen-bonded SMP with Ln^{3+}_{aq}: $[Ln(H_2O)^{3+}_8][p\text{-SC[4]A}]$ (Ln = Gd, Tb, Tm) have been synthesised. In the two-dimensional SMP, each aqua ion is connected by hydrogen bonds to four neighbouring sulfonate groups of *p*-SC[4]A, thus forming an infinite structure. For example, in the Tb complex, each $[Tb(H_2O)_8]^{3+}$ ion forms eight hydrogen bonds with the distances $R(O-H\cdots O) = 2.741$ Å and the energy $\Sigma D_0(O-H\cdots O) = 8 \times 12.98 = 103.8$ kJ mol^{-1}.

The enthalpy and entropy changes upon the formation of O−H···O bonds have been reported [43, 60] to be approximately equal, *i.e.*, $\Delta H^\circ/T\Delta S^\circ \approx 1.0$. In view of the reported $\Sigma D_0(O-H\cdots O)$, the change ΔS° upon the formation of hydrogen bonds of each aqua ion with four sulfonate groups equals $\Delta S^\circ(O-H\cdots O) = 174 \pm 40$ J mol^{-1} K^{-1}. The standard entropy of formation of the aqua ions is negative:[111] $\Delta S^\circ_f(Ln^{3+}_{aq}) = -219$, -224 and -236 J mol^{-1} K^{-1} for Ln = Gd, Tb and Tm, respectively;[125] hence, upon binding of Ln^{3+}_{aq} with *p*-SC[4]A, $\Delta S^\circ_f(Ln^{3+}_{aq})$ is largely counterbalanced by $\Delta S^\circ(O-H\cdots O)$.

A fundamental issue is the relationship between the coordination and hydrogen bond energies in the [Ln^{3+}_{aq} – calixarene] SMA and their variation along the lanthanide series. Structural data for solving this problem appeared only recently:[164] for the $[LnL(NO_3)_2(H_2O)_2]NO_3$ complexes [Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; L is 2,6-bis(2-pyridyl)-4-amino-1,3,5-triazine], the lengths of the coordination bonds $R(Ln-O)$ and the hydrogen bonds $R(O-H\cdots O)$ were measured. Using about 200 measured [164] $R(Ln-O)$ and $R(O-H\cdots O)$ values, it was established [30, 31] that the greater $R(Ln-O)$, the smaller $R(O-H\cdots O)$. Thus, the interaction of Ln^{3+}_{aq} with *p*-SC[4]A is accompanied by a decrease in $R(Ln-O)$ and an increase in $R(O-H\cdots O)$ on passing from light lanthanides to heavy ones. The energy of intermolecular hydrogen bonds Ln^{3+}_{aq} – calixarene decreases to the end of the series, whereas the energy of the coordination bonds increases.

b. Crown ethers and cryptands as guest molecules in calixarenes: encapsulation according to the 'matreshka doll' pattern

On the basis of a structural conformation analysis, structural reorganisation of crown ethers taking place upon the reaction of 18C6 with *p*-SC[4]A and Ln^{3+}_{aq} was studied. The SMA of a complicated structure formed in the case of Ce can be represented [163] by the following formula (the sign $\subset$ designates inclusion and the sign $\cap$ attests to the arrangement of the crown ether molecule above the calixarene bowl):

$$[(Ce(H_2O)_3\subset 18C6\cap p\text{-SC[4]A})Ce(H_2O)_6(Ce(H_2O)\subset 18C6\subset\{p\text{-SC[4]A}\}_2)].\,.Ce(H_2O)_9\cdot 23.5\,H_2O$$

The partially hydrated Ce(1) ion is incorporated in the 18C6 ring forming six Ce−O(18C6) bonds, three Ce−O(H_2O) bonds and one Ce−O−S(*p*-SC[4]A) bond. The Ce(2) ion is also incorporated into the 18C6 ring; remarkably, [Ce(2) + 18C6] are encapsulated by two *p*-SC[4]A ligands. Atwood [163] has called such encapsulation the 'matreshka doll'. One 18C6 molecule serves at the host for the Ce(1) guest ion but [Ce(2) + other 18C6] serve themselves as a guest for two *p*-SC[4]A molecules. The Ce(3) ion is bound to two sulfonate groups from two *p*-SC[4]A ligands, whereas the Ce(4) ion is completely hydrated, forms no coordination bonds with macrocyclic ligands and is involved only in the formation of hydrogen bonds. The energy spectrum of this SMA is fairly complicated (Fig. 5): the Ce(1)−O(18C6) bonds are weaker than Ce(1)−O(H_2O); the encapsulation of [Ce(2) + 18C6] in two *p*-SC[4]A strengthens all bonds in the inner 'doll', which is compressed by the outer one. The modification of all bonds is rather significant; for example, the hydrated Ce(4)$(H_2O)^{3+}_9$ ion in SMA is distorted due to the formation of hydrogen bonds to such an extent that $R(Ce-OH_2)$ varies from 2.352 to 2.674 Å. This cation does not resemble the hydrated cation with a nearly regular tricapped trigonal prismatic coordination considered in the traditional lanthanide chemistry.

As a conclusion of this Section, note that the chemistry of host–guest systems based on calixarenes, crown ethers and

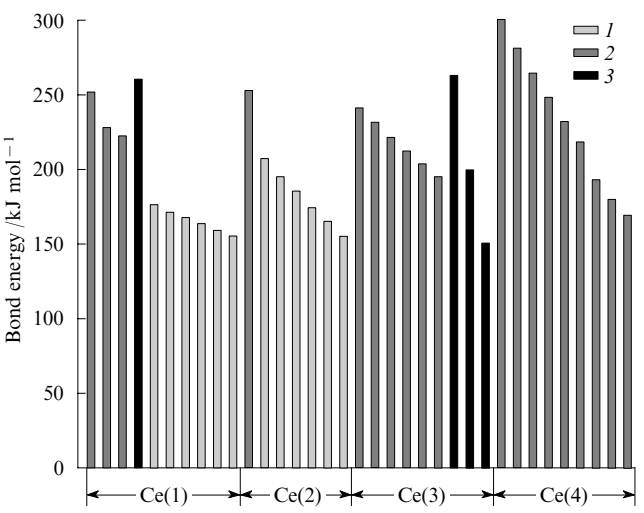


Figure 5. Energies of the $Ce^{3+}-O$ bonds with crown ether (*1*), water (*2*) and *p*-sulfonatocalix[4]arene (*3*).

cryptands represents a new field of SMC; which is most amazing, this is a new type of 'matreshka doll' encapsulation.

VI. Conclusion

The synthesis and structure of supramolecular assemblies containing ions of d and f transition elements is a relatively new and rapidly developing field of SMC. These SMA attract particular attention of researchers owing to a set of unique properties, which may enable their extensive practical use in the future.

The synthesis of quasi-one-dimensional polymeric structures, which had been previously considered to be only theoretical models, was an achievement in the supramolecular chemistry. A number of such SMP in which separate dinuclear metal-containing blocks are linked by coordination or hydrogen bonds have now been prepared. A necessary (but not sufficient) condition for the formation of SMP is the absence of axial ligands in the initial complex. The formation of SMP or discrete aggregates (for example, dimers) is determined by the electronic structure of the metal and the ligands. Depending on the geometry of the binding ligands, one can obtain SMP in various conformations (linear, zigzag and so on).

Supramolecular rings are apparently the most numerous class of SMA. The variation of metal-containing fragments and ditopic ligands connecting them gives SMC of various sizes and geometries. Currently, systematic approaches to their synthesis have been developed, which allows targeted design of the structure with a definite parameters.

Several mechanisms of the self-assembly of the structural blocks in SMC are known. Of these, thermodynamic mechanism is studied in most detail and used most often; according to this mechanism, equilibrium between the reactants and products is established in each step and, finally, the thermodynamically most stable product is formed. In the SMC synthesis, Pd^{2+} and Pt^{2+} complexes are used most widely; however, many SMC with other metals are also known (Cr, Mo, Cu, Au, *etc*.).

The stability of SMC depends on a number of factors among which the metal–metal interaction is the most important. In some cases, a contribution of $\pi-\pi$-stacking is probable. The self-assembly process depends considerably on the solvent properties.

A distinctive feature of SMC is that their structure is retained in solutions. As a result, the ring may function as the host molecule for small ions or molecules exhibiting high selectivity. This feature is of particular interest for researchers, the more so, because the SMC can be varied by selecting appropriate ligands.

Three- and four-membered SMC are best studied; however, examples of five-, six- and eight-membered and even larger rings are also known.

The advances in the synthesis and practical use of alkali and alkaline earth metal macrocyclic complexes stimulated the development of analogous research for lanthanides and actinides. Crown and azacrown ethers, cryptands, calixarenes and so on are used as macrocyclic ligands. Of particular interest is the study of the variation of MC stability along the lanthanide and actinide series. The elucidation of these trends with allowance for the electronic characteristics of metal ions and the solvent effect would open up the way to the development of an efficient method for the separation of poorly separable Ln^{3+} and An^{3+} ions. The differences between the reduction potentials $E^{\circ}(3+/2+)$, which correlate with the charge transfer energy $\Delta E[2p(O) \rightarrow 4f(Ln^{3+})]$ can be used for the same purpose.

Thus, a large body of experimental data on the synthesis of diverse SMA has now been accumulated. In the next stage, it is necessary to carry out in-depth studies of the mechanisms of their formation based on the methods and concepts of chemical thermodynamics, kinetics, and theoretical and quantum chemistry.[22, 165]

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