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Cation – cation interaction in crystalline actinide compounds

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Contents

I. Introduction 89
II. Crystal structures of Np(V) compounds with cation – cation bonds 90
III. Influence of the cation – cation interactions on the properties of Np(V) compounds 94
IV. Cation – cation interactions in compounds of other actinide ions 97
V. Comparison of cation – cation interactions in solutions and crystals of actinide compounds 98

Abstract. The published data on the structures and properties of crystalline actinide compounds having mutually coordinated AnO_2^+ or AnO_2^{2+} cations as structural elements are surveyed. This cation – cation interaction is an important structure-forming factor for many crystalline compounds of Np(V) and U(VI). It strongly affects their UV-Vis and IR spectra as well as other properties. Differences and similarities between the cation – cation interactions of actinide ions in solutions and crystals are discussed. The bibliography includes 114 references.

I. Introduction

The specific complexation of AnO_2^+ and AnO_2^{2+} ions with certain cations commonly referred to as cation – cation (CC) interaction has been observed for the first time [1] in a study of behaviour of Np(V) in solutions of uranyl perchlorate. Later, the CC interactions were also revealed in NpO_2^+ solutions containing such cations as Th(IV), Cr(III), Fe(III), Al(III), Ga(III), Sc(III), In(III), Bi(III), Pb(II), Hg(II), Hg(I) (see Ref. 2) and Rh(III).[3] As for sodium, magnesium and some lanthanide [*e.g.*, La(III), Ce(III) and Y(III)] cations, they are inactive with respect to NpO_2^+.[1,2] Apart from Np(V), CC interactions are characteristic of U(V),[4,5] Pu(V) [6] and Am(V) [7] ions.

Different aspects of the CC interaction in solutions of pentavalent actinides have been considered in numerous publications.[1–41] For its characterisation, traditional spectrophotometry in visible and nearest IR regions as well as other techniques, such as potentiometry,[1] IR,[28] Raman,[31,34,36] Mössbauer,[24] ESR,[26] NMR [33] spectroscopies, large-angle X-ray scattering (LAXS) [32,35] and laser-induced photoacoustic spectroscopy [41] have been used. Special attention has been paid to the elucidation of the nature of the CC interactions in solutions. The principal results of these studies are considered below (Section V).

The kinetics of formation [2,3,9,12,17] and stability [1,3,9,29,34,36,40,41] of CC complexes have been studied in numerous publications. In particular, it has been shown that the complexation rate is defined primarily by the nature of highly charged cations interacting with the AnO_2^+ ions. This process proceeds very fast (*viz.*, during mixing of the components) with cations that have labile coordination spheres. In contrast, such cations as Cr_{aq}^{3+} (see Refs 2, 9, 12 and 17) and Rh_{aq}^{3+} (see Ref. 3) behave differently. In those cases, the formation and dissociation of CC complexes proceed quite slowly which is typical of substitution of water molecules by other ligands in the inner coordination spheres of aforementioned hydrated ions. The kinetic stability of AnO_2^+ CC complexes with Cr(III) and Rh(III) ions makes possible the utilisation of strongly basic cation-exchange resins for their isolation and purification by means of consecutive sorption, washing and desorption avoiding a significant decomposition.[2,3,6,24]

The stability of actinide CC complexes is relatively low but it increases substantially with an increase in the ionic strength (μ) of solutions or with a change from aqueous to organic solutions.[14,39] Neptunoyl cation [NpO_2^+, also referred to as neptunyl (V)] forms most stable complexes with such 'active' cations as UO_2^{2+} (see Refs 40 and 41), Cr(III) [9] and Rh(III).[3] The respective stability constants at 25 °C and $\mu = 6-10$ lie in the range of 2 – 4 litre mol^{-1}. The stability of An(V) CC complexes with a specific 'active' cation decreases in the series $UO_2^+ > NpO_2^+ > PuO_2^+ > AmO_2^+$.[29,41] The activity of AnO_2^{2+} ions as coordinating centres in the CC interactions decreases in the same series:[29] $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+}$. These regularities correlate well with decreases in the effective positive and negative charges localised on the actinide atom and oxygen atoms of the corresponding dioxocations, respectively.[37,42] Therefore, it may be soundly assumed [3] that the electrostatic forces play a crucial role in the CC interactions though an involvement of other factors, such as the energy difference between donor and acceptor orbitals of the dioxocations, cannot also be ruled out.[37]

As has been established by numerous studies, the CC interactions strongly affect the rates of various redox reactions [6,8,11,16–19,23,26] and the isotope exchange [12] involving the AnO_2^+ ions. Typically, the reactivity of AnO_2^+ ions is reduced in the presence of 'active' cations. For instance, a complex of PuO_2^+ with a hydrated Cr(III) cation reacts with Cr(VI), Np(VI) and Ce(IV) more slowly by several orders of magnitude than hydrated PuO_2^+ under identical conditions.[6]

The CC interaction or CC bond in solid compounds was revealed for the first time in the $Rh(H_2O)_5NpO_2F_4$ complex.[3] However, this compound has not been isolated in the individual form and its structure has remained obscure. The existence of CC bonds in the crystal structures of several Np(V) compounds was first established by X-ray diffraction in the mid 1980s.[43–46]

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Subsequently CC bonds have been revealed in many (more than 20) actinide compounds, whose crystal structures have been determined. This made it possible to analyse some general features of the CC interactions in crystalline compounds of actinides and compare them with the known data for the corresponding solutions. This is the aim of the present review, which surveys the results of studies published prior to 2001 inclusive and, partly, in 2002. Some aspects of the CC interactions in An(V) compounds are discussed elsewhere.[47–49]

II. Crystal structures of Np(V) compounds with cation–cation bonds

To date, there are 23 compounds whose crystal structures involve CC bonds as confirmed by single-crystal X-ray diffraction studies (Table 1). It would be helpful to precede the discussion of the above compounds with a brief description of their structural features. More detailed information may be found elsewhere.[43–46,49–68]

The most striking structural peculiarity of double Np(V)-sodium mellitate $Na_4[(NpO_2)_2C_6(COO)_6]\cdot 8H_2O$ (**1**) is the presence of dimeric groups composed of two mutually coordinated NpO_2^+ ions (see Refs 43 and 44). Therein, both neptunoyl ions act as coordinating centres and ligands simultaneously (Fig. 1). Such a coordination type is not found in structures of other Np(V) compounds listed in Table 1. It is characterised by a relatively short distance between neighbouring Np atoms (*ca.* 3.48 Å). The neptunoyl ions within the dimers are additionally linked by two bridging bidentate carboxyls of different mellitate ions. Two other mellitate anions are bound to NpO_2^+ through adjacent monodentate carboxy groups.

The crystal structure of double Np(V)-ammonium pyromellitate $(NH_4)_3[(NpO_2)_5\{C_6H_2(COO)_4\}_2]\cdot 7H_2O$ (**2**) is quite complicated.[45] It includes five crystallographically nonequivalent NpO_2^+ ions forming the CC bonds (Fig. 2*a*). Two of them may be considered as bidentate ligands, which both act as coordination centres for an oxygen atom of an adjacent neptunoyl group. Therefore, they both form three CC bonds though they differ from each other in the origin of oxygen atoms in the equatorial planes and the Np–O bond lengths. Two other NpO_2^+ ions also form three CC bonds but they act as monodentate ligands and coordinate two adjacent neptunoyl groups. The fifth NpO_2^+ ion forms only two CC bonds. It acts as a monodentate ligand and a coordinating centre for one neighbouring neptunoyl ion.

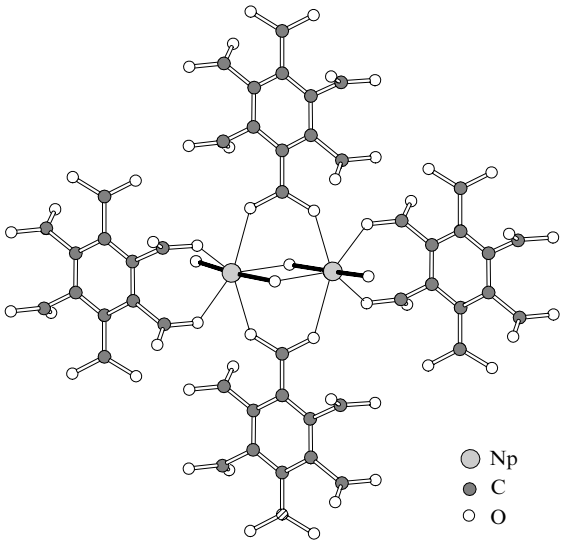


Figure 1. The CC interaction in the crystal structure of **1**.[44]

The crystal structure of $Cs_4[(NpO_2)_2Cl_4NpO_2Cl_2(NO_3)H_2O]$ (**3**) also contains nonequivalent NpO_2^+ ions, which however differ

Table 1. Np(V) compounds with known crystal structures containing CC bonds.

Compound	Coordination polyhedron [a]	Np–O bond length /Å [b,c]			Ref.
		l_1	l_2	l_3	
$Na_4[(NpO_2)_2C_6(COO)_6]\cdot 8H_2O$ (**1**)	PBP	1.91	1.85	2.48	43, 44
$(NH_4)_3[(NpO_2)_5\{C_6H_2(COO)_4\}_2]\cdot 7H_2O$ (**2**)	PBP	1.832–1.876	1.806–1.843	2.373–2.481	45
$Cs_4[(NpO_2)_2Cl_4NpO_2Cl_2(NO_3)(H_2O)]$ (**3**)	PBP	1.85	1.80	2.37	46
$[(NpO_2)_2SO_4(H_2O)_2]$ (**4**)	PBP	1.829–1.854		2.426–2.443	50
$[(NpO_2)_2SO_4(H_2O)]$ (**5**)	PBP, SBP	1.848–1.874		2.354–2.466	51
$[NpO_2Cl(H_2O)]$ (**6**)	PBP	1.83–1.85		2.36–2.50	52
$K_4(H_5O_2)[(NpO_2)_3(MoO_4)_4]\cdot 4H_2O$ (**7**)	PBP, TBP	1.900	1.844–1.846	2.393–2.394	53
$Na_2[(NpO_2)_2(MoO_4)_2H_2O]\cdot H_2O$ (**8**)	PBP	1.88	1.81–1.83	2.54	54
$[NpO_2ClO_4(H_2O)_4]$ (**9**)	PBP	1.860	1.810	2.396	55
$[(NpO_2)_2(NO_3)_2(H_2O)_4]\cdot H_2O$ (**10**)	PBP, HBP	1.837–1.846	1.812	2.419–2.481	56
$[La(H_2O)_6][(NpO_2)_3(NO_3)_6]\cdot 4H_2O$ (**11**)	HBP	1.852		2.417	57
$[NpO_2HCOO(H_2O)]$ (**12**)	PBP	1.846–1.850		2.388–2.434	58
$[NpO_2HCOO]$ (**13**)	PBP	1.857–1.915		2.363–2.434	58
$[NpO_2CH_2(OH)COO(H_2O)]$ (**14**)	PBP	1.828	1.801	2.442	59
$[NpO_2C_6H_5COO(H_2O)]\cdot 0.75H_2O$ (**15**)	PBP	1.82–1.87		2.40–2.50	60
$[(NpO_2)_2(CH_3COO)_2(H_2O)]\cdot CH_3CN$ (**16**)	PBP, SBP	1.811–1.874		2.334–2.473	61
$NH_4[NpO_2C_2O_4]\cdot 2.67H_2O$ (**17**)	PBP	1.886	1.824	2.364	62
$[(NpO_2)_2C_2O_4(H_2O)_4]\cdot 2H_2O$ (**18**)	PBP	1.858	1.830	2.392	63
$[(NpO_2)_2CH_2(COO)_2(H_2O)_3]\cdot H_2O$ (**19**)	PBP	1.840–1.842	1.828	2.436–2.477	64
$[(NpO_2)_2CH_2(COO)_2(H_2O)_2]\cdot H_2O$ (**20**)	PBP	1.840–1.870		2.420–2.502	65
$[(NpO_2)_2(DMSO)_7(H_2O)_2](ClO_4)_2\cdot H_2O$ (**21**)	PBP	1.86	1.82	2.49	66
$[(NpO_2)_2\{o\text{-}C_6H_4(COO)_2\}(H_2O)_3]\cdot H_2O$ (**22**)	PBP	1.841–1.852		2.373–2.437	67
$[NpO_2NO_3(CH_3CONH_2)_2]$ (**23**)	PBP	1.859	1.821	2.379	68

[a] Notations: PBP, SBP, HBP and TBP stand for pentagonal, special (see text, Fig. 3*b*), hexagonal and tetragonal bipyramids, respectively; [b] $O\overset{l_2}{=}Np\overset{l_1}{=}O\overset{l_3}{\cdots}Np$; [c] estimated standard deviations of Np–O bond lengths lie in the range of 0.003–0.01 Å except for **3**, for which it amounts to 0.03 Å.

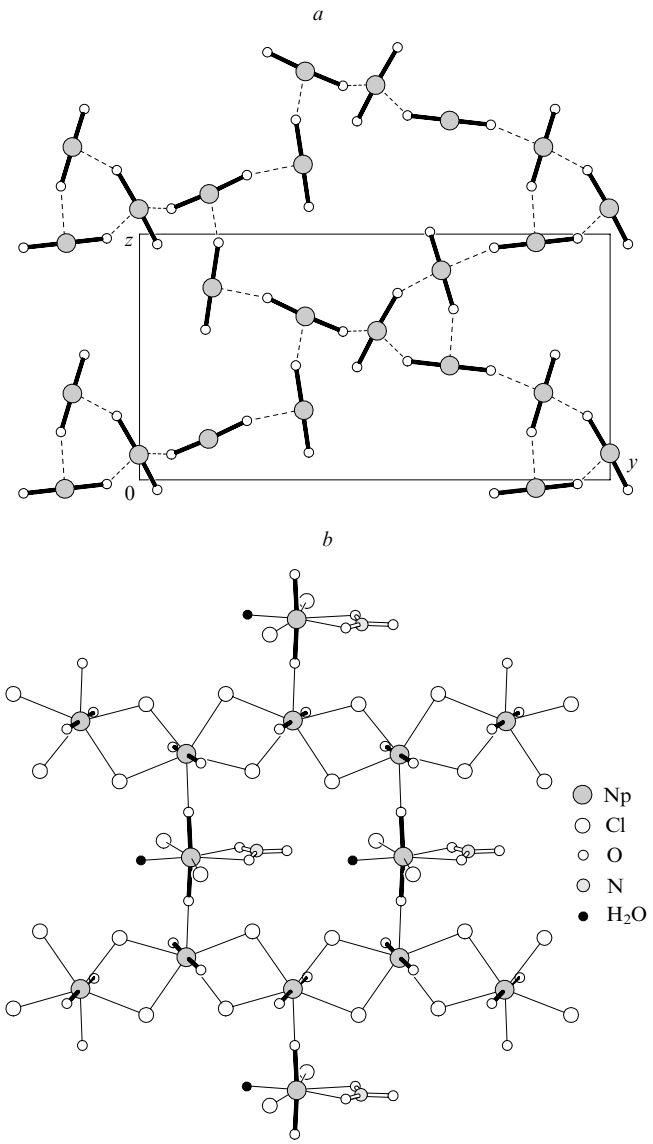


Figure 2. The CC interaction in the crystal structures of **2** (*a*)[45] and **3** (*b*).[46]

in the CC interactions from **2**.[46] One third of the NpO_2^+ ions is coordinated to adjacent Np atoms through both oxygen atoms and does not form other CC bonds (Fig. 2 *b*). In the equatorial plane, each ion of that type is coordinated by two Cl^- ions, two oxygen atoms of the NO_3^- ligand and a water molecule. The remaining neptunoyl groups form only single CC bonds acting as coordinating centres. Their equatorial coordination numbers are also equal to 5: an oxygen atom of an adjacent NpO_2^+ ion and four bridging Cl^- ions are located in their equatorial planes. The Np···Np interatomic distance corresponding to the CC interaction is 4.222 Å.

The pattern of CC bonds in $[(NpO_2)_2SO_4(H_2O)_2]$ (**4**)[50] is of particular interest since it is often found in the crystal structures of other Np(V) compounds. It may be represented as a distorted square net built up of two crystallographically nonequivalent NpO_2^+ ions (Fig. 3 *a*). All neptunoyl ions act as bidentate ligands and at the same time coordinate two adjacent neptunoyls. As a result, each Np atom is involved in four CC bonds. The square nets are linked through tetradentate bridging SO_4^{2-} anions, which are bound to four Np atoms. For both types of NpO_2 ion, the coordination polyhedra (CP) of the central atoms are pentagonal bipyramids though the Np – O bond lengths are slightly different. The equatorial planes of both coordination polyhedra include,

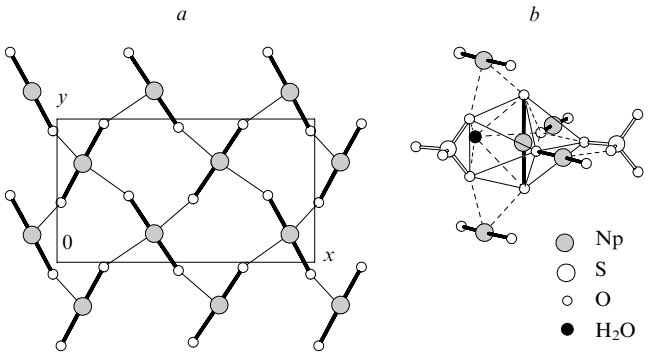


Figure 3. The CC interaction in the crystal structures of **4** (*a*)[50] and **5** (*b*).[51]

apart from oxygen atoms of the SO_4^{2-} anions and adjacent NpO_2^+ ions, one water molecule.

A similar type of CC interaction is also revealed in the crystal structures of $[NpO_2Cl(H_2O)]$ (**6**),[52] $[NpO_2HCOO(H_2O)]$ (**12**),[58] $[NpO_2C_6H_5COO(H_2O)]\cdot 0.75\,H_2O$ (**15**),[60] $[(NpO_2)_2CH_2.(COO)_2(H_2O)_2]\cdot H_2O$ (**20**)[65] and $[(NpO_2)_2\{o\text{-}C_6H_4(COO)_2\}.(H_2O)_3]\cdot H_2O$ (**22**).[67] Nevertheless, nets of cations in these compounds have some distinctions. For example, the crystal structure of **6** includes NpO_2^+ cations of two types differing from each other in numbers of bridging Cl^- ions (1 *vs.* 3) and H_2O molecules (2 *vs.* 0) in their coordination spheres. In contrast, all neptunoyl groups in the crystal structure of **12** are equivalent: in the equatorial plane, they contain two oxygen atoms of adjacent NpO_2^+ groups, two oxygen atoms of bridging carboxy groups and a water molecule. The net of cations in the crystal structure of **15** is formed by neptunoyl ions of four nonequivalent types though in all cases, the central atom CP is a pentagonal bipyramid. The equatorial planes of the coordination polyhedra revealed in **15** are similar to those in **12**. They differ only in the interatomic distances and the dispositions of oxygen atoms from various ligands. The crystal structures of **20** and **22** reveal two nonequivalent NpO_2^+ ions, which are characterised by the coordination number 5 and contain oxygen atoms of various origins in their equatorial planes. In compound **20**, the first type of neptunoyl ions bind two oxygen atoms of adjacent neptunoyls, one oxygen atom of a carboxy group and two water molecules. In the case of the second type of neptunoyl ions, the equatorial plane is built up of two oxygen atoms of adjacent NpO_2^+ ions and three oxygen atoms of two carboxy groups. In compound **22**, the CP of neptunoyl ions of the first type is analogous to that in **20**. Another type of NpO_2^+ ions in **22** coordinates one water molecule, two oxygen atoms of adjacent NpO_2^+ cations and two oxygen atoms of carboxy groups. The shortest Np···Np distances within the cation nets of **4**, **6**, **12**, **15**, **20** and **22** lie in the range of 3.776 – 4.238 Å.

The pattern of the CC bonds in the crystal structure of $[(NpO_2)_2SO_4(H_2O)]$ (**5**) is substantially more complex than in **4** though NpO_2^+ ions in both cases act as bidentate ligands and coordinate two adjacent neptunoyl ions.[51] In the crystal structure of **5**, the CC interactions give rise to a spatial net involving two types of CP. The first one is a pentagonal bipyramid and the second one is a special polyhedron type, which has not hitherto been observed (Fig. 3 *b*). It can be represented as a pentagonal bipyramid with one of the equatorial vertices occupied by two oxygen atoms, which are situated above and below the equatorial plane. The two oxygen atoms belong to one SO_4^{2-} anion. Other oxygen atoms in the equatorial plane come from two NpO_2^+ ions, H_2O and SO_4^{2-}. The equatorial plane of the normal pentagonal bipyramid is composed of three oxygen atoms of different bridging sulfates and two O atoms of the NpO_2^+ ions. The distances between neighbouring Np atoms involved in the CC interaction lie in the range of 3.923 – 4.253 Å. The layered structure of **16** reveals CC interactions and coordination polyhedra of a similar charac-

ter.[61] Nevertheless, the pattern of CC bonds therein differs from that in **5**. The pattern may be described as a distorted square net resembling the structure of **4**.

In the crystal structure of $K_4(H_5O_2)[(NpO_2)_3(MoO_4)_4]\cdot H_2O$ (**7**), neptunium atoms have two types of coordination polyhedra, *viz*., pentagonal and tetragonal bipyramids, in the ratio 2 : 1, respectively.[53] The former polyhedra are linked by molybdate ions to form layers. In those layers, NpO_2^+ ions act as monodentate ligands for neptunoyl ions of the latter type, which have four oxygen atoms in their equatorial planes and are located between the layers (Fig. 4 *a*). Therefore, NpO_2^+ ions of the latter type (with equatorial coordination number 4) form two CC bonds without involvement of their own oxygen atoms. The Np···Np distance responsible for the CC interaction is 4.130 Å.

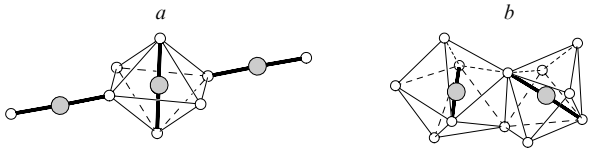


Figure 4. The CC interaction in the crystal structures of **7** (*a*)[53] and **8** (*b*).[54] Notations are the same as in Fig. 3.

The crystal structure of $Na_2[(NpO_2)_2(MoO_4)_2(H_2O)]\cdot H_2O$ (**8**)[54] includes two types of NpO_2^+ ions with coordination numbers 5. Ions of the two types are bound in pairs by virtue of the CC interaction and bridging ligands (Fig. 4 *b*). In the pairs, one of the NpO_2^+ ions acts as a monodentate ligand, while the second one acts only as a coordinating centre. The Np···Np distance within the dimers is 3.727 Å. Equatorial planes of both types of NpO_2^+ ions are occupied by oxygen atoms of bridging MoO_4^{2-} ions, which thus link the neptunoyl dimers into a three-dimensional framework. A similar type of CC interaction giving rise to formation of neptunoyl dimers was revealed in the crystal structure of $[(NpO_2)_2(DMSO)_7(H_2O)_2](ClO_4)_2\cdot H_2O$ (**21**) (see Ref. 66). In this compound, the dimers may be considered as complex cations occupying sites of an ionic crystal lattice. They are composed of two CP (pentagonal bipyramids) linked by an oxygen atom of one of the NpO_2^+ ions. For the latter NpO_2^+ ion, which acts as a ligand, the equatorial plane includes one water molecule and four DMSO molecules. The second neptunoyl ion of the dimer binds one water molecule, three DMSO molecules and one oxygen atom of the adjacent NpO_2^+ ion. The Np···Np distance within the dimer (4.252 Å) is noticeably longer than that in the structure of **8**. The reason for this difference relates to the different ways of assembling the Np coordination polyhedra in the CC interaction. In the crystal structure of **21**, the polyhedra have a shared vertex, which is apical for one of the CP and equatorial for another. In contrast, in the crystal structure of **8**, the Np atoms involved in the CC interaction are linked through one of the oxygen atoms of a molybdate ion so the polyhedra have a shared edge. In one of the polyhedra, this edge connects an apical and an equatorial vertex, while in the other one, it connects two equatorial vertices.

The crystal structure of $[NpO_2ClO_4(H_2O)_4]$ (**9**) (see Ref. 55) reveals particular zigzag chains formed by NpO_2^+ ions owing to the CC interaction (Fig. 5 *a*). Each neptunoyl group in the chains is involved in two CC bonds acting as a monodentate ligand and a coordinating centre simultaneously. The equatorial planes of the CP of Np atoms consist of an oxygen atom of an adjacent NpO_2^+ ion and four water molecules. Similar zigzag chains are also present in the crystal structures of $[NpO_2CH_2(OH)COO(H_2O)]$ (**14**) (see Ref. 59), $[(NpO_2)_2C_2O_4(H_2O)_4]\cdot 2H_2O$ (**18**) (see Ref. 63), and $[NpO_2NO_3(CH_3CONH_2)_2]$ (**23**) (see Ref. 68). In the crystal structure of **14**, the equatorial plane of NpO_2^+ ions consists of a water molecule, an oxygen atom of an adjacent NpO_2^+ ion, two oxygen atoms of a carboxy group and a hydroxy group. Meanwhile, in the crystal structure of **18**, the equatorial plane includes two H_2O molecules, two O atoms of a tetradentate bridging oxalate group and an oxygen atom of an adjacent neptunoyl. In the crystal structure of **23**, the equatorial plane is formed by an oxygen atom of an adjacent neptunoyl, two oxygen atoms of an NO_3^- ion and two oxygen atoms of two acetamide molecules. The shortest Np···Np interatomic distances within the neptunoyl chains revealed in the crystal structures of **9**, **14**, **18** and **23** lie in the range of 4.075 – 4.207 Å.

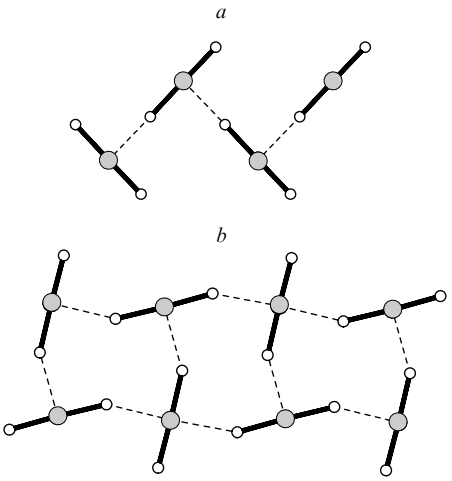


Figure 5. The CC interaction in the crystal structures of **9** (*a*)[55] and **10** (*b*).[56] Notations are the same as in Fig. 3.

In the crystal structure of $[(NpO_2)_2(NO_3)_2(H_2O)_4]\cdot H_2O$ (**10**) (see Ref. 56), the system of CC bonds may be described as ribbons formed by NpO_2^+ cations with two types of coordination polyhedra, *viz*., pentagonal and hexagonal bipyramids (Fig. 5 *b*). Neptunoyl cations of the former type act as bidentate ligands and coordinate four water molecules and one NpO_2^+ cation of the latter type. Neptunoyl cations of the latter type are involved in three CC bonds acting as monodentate ligands. Their equatorial planes contain two oxygen atoms of adjacent NpO_2^+ cations and four oxygen atoms of two NO_3^- ions. The Np···Np interatomic distances lie in the range of 4.130 – 4.200 Å.

The crystal structure of $[La(H_2O)_6][(NpO_2)_3(NO_3)_6]\cdot 4H_2O$ (**11**) (see Ref. 57) is characterised by the presence of a highly symmetrical net of mutually coordinated NpO_2^+ cations acting as bidentate ligands (Fig. 6 *a*). Equatorial planes of the neptunoyl ions contain four O atoms of two bidentate NO_3^- ligands and two oxygen atoms of adjacent NpO_2^+ cations, which occupy *trans*-positions with respect to each other. The shortest Np···Np distances are 4.058 Å and 4.159 Å.

In the crystal structure of $[NpO_2HCOO]$ (**13**) (see Ref. 58), each NpO_2^+ is involved in four CC bonds, similarly to many other Np(V) compounds. Nevertheless, the pattern of CC bonds in **13** is peculiar. Indeed, it combines neptunoyl ions to form a diamond-like framework (Fig. 6 *b*). The coordination polyhedra of the Np atoms are pentagonal bipyramids containing two O atoms of adjacent NpO_2^+ ions and three carboxylic oxygen atoms of two bidentate chelate bridging $HCOO^-$ anions. The distances between neighbouring Np atoms within the framework of cations are 3.783 Å and 4.003 Å.

The crystal structure of $NH_4[NpO_2C_2O_4]\cdot 2.67H_2O$ (**17**) (see Ref. 62) reveals trimers of neptunoyl ions that are coordinated to each other as monodentate ligands (Fig. 7 *a*). As a consequence, each NpO_2^+ ion is involved in two CC bonds. The coordination polyhedra of the Np atoms are pentagonal bipyramids, whose equatorial planes contain one O atom of an adjacent NpO_2^+ ion and four carboxylic oxygen atoms of two tetradentate bridging oxalate ions. The Np···Np distance within such a cyclic trimer is 4.093 Å.

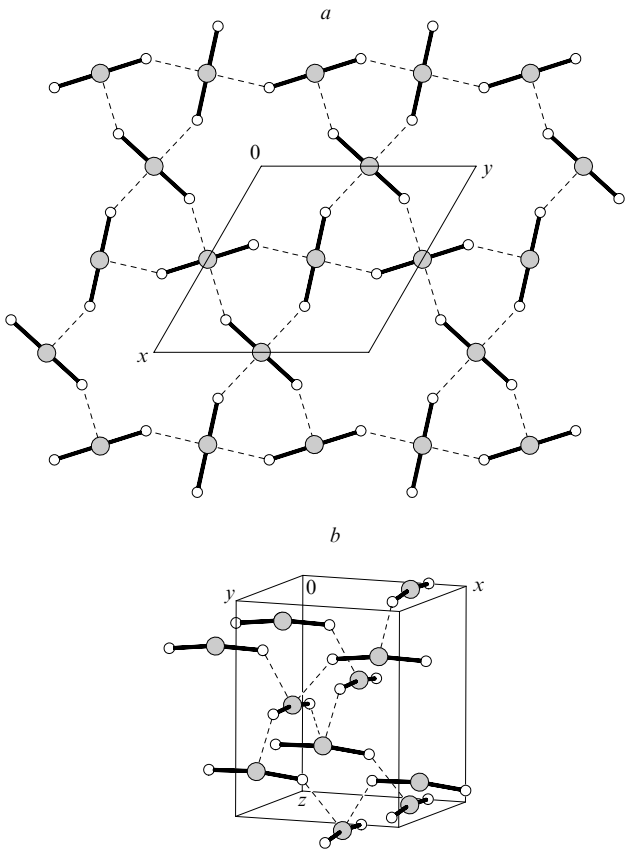


Figure 6. The CC interaction in the crystal structures of **11** (*a*)[57] and **13** (*b*).[58] Notations are the same as in Fig. 3.

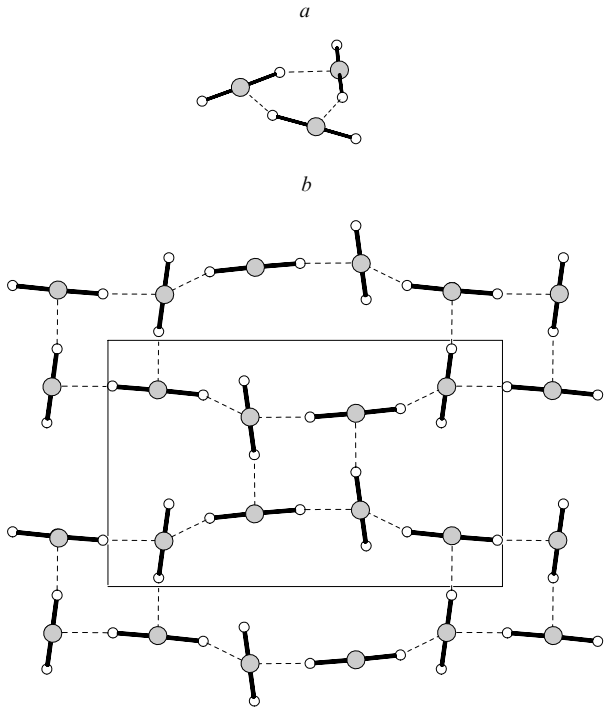


Figure 7. The CC interaction in the crystal structures of **17** (*a*)[62] and **19** (*b*).[64] Notations are the same as in Fig. 3.

Finally, in the crystal structure of $[(NpO_2)_2CH_2(COO)_2.(H_2O)_3]\cdot H_2O$ (**19**) (see Ref. 64), there is a planar net of cations composed of four- and eight-membered rings due to the CC interaction (Fig. 7 *b*). One half of the NpO_2^+ ions within the net acts as monodentate ligands coordinating at the same time two adjacent neptunoyl ions, a water molecule, and two oxygen atoms of two malonate ions. The remaining NpO_2^+ ions act as bidentate ligands and contain one O atom of NpO_2^+, two carboxylic O atoms of one $CH_2(COO)_2^{2-}$ anion and two water molecules in the equatorial planes of their CP. The shortest Np···Np distances within the net of cations lie in the range of 4.182 – 4.234 Å.

The data outlined above clearly demonstrate that the CC interaction is a widespread phenomenon in crystalline compounds of Np(V), which often governs their crystal structures. Below, we summarise some general regularities which characterise the CC interaction.

1. In the crystal structures of all Np(V) compounds studied, the CC bonds are always formed through the bridging oxygen atom, which belongs to one of the interacting neptunoyl groups. However, the identity of NpO_2^+ ions forming a CC bond is not lost since the corresponding Np – O bond lengths are significantly different ($l_1 \ll l_3$, for notations, see Note [b] to Table 1). This conclusion is supported by the fact that the geometry of the coordination environment of NpO_2^+ ions as regards their equatorial planes is only slightly modified by the formation of the CC bond.

2. The formation of the CC bond is accompanied by a significant change in the Np – O bond lengths within the NpO_2^+ ions. It is due to the electrostatic forces: the effective negative charge localised on the oxygen atom causes its attraction to the coordinating centre, which possesses a high positive charge. This positive charge, in turn, determines the repulsion of the Np atoms involved in the CC bond. As a result, the l_1 distance within the NpO_2^+ ion becomes noticeably longer than l_2. According to Table 1, the mean $l_1 - l_2$ difference is 0.04 Å. The fluctuation of this difference may be explained by effects of composition and structures of specific compounds on the distribution of the effective charges within NpO_2^+.

3. The bond length between the oxygen atom of the NpO_2^+ cation and the coordinating centre (denoted l_3 in Table 1) lies in the range of 2.33 – 2.54 Å. The respective mean value of 2.45 Å is close to typical bond lengths between an Np atom and O atoms of various ligands coordinated in the equatorial plane.

4. Neptunium atoms involved in a CC bond may have different coordination polyhedra though pentagonal bipyramids occur most frequently (see Table 1).

5. Neptunoyl ions may be involved in one or more (up to four) CC bonds. According to this criterion, they can be classified into eight types shown schematically in Fig. 8. Those types occur in Np(V) compounds in various combinations. For instance, the types *a* and *b* NpO_2^+ ions are present as dimers in the crystal structures of **8** and **21**. The type *c* mutual coordination of ions ensures the formation of dimers in **1**, cyclic trimers in **17** and

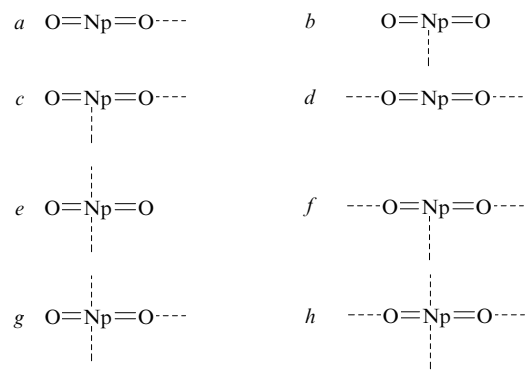


Figure 8. Types of NpO_2^+ ions depending on the number and character of the CC bonds formed.

zigzag chains in **9**, **14**, **18** and **23**. A mutual combination of the type *h* NpO_2^+ ions produces planar (**4**, **11**, **12**, **15**, **16**, **20** and **22**) or three-dimensional (**5** and **13**) cationic nets. The types *d* and *e* neptunoyl ions were found only in the crystal structures of **3** and **7**, respectively. Combinations of the types *f* and *g* NpO_2^+ ions were revealed in the crystal structures of **2** and **10**.

The formation of a specific pattern of CC bonds in the crystal structures of Np(V) compounds depends upon a number of factors, among which the following are of major importance:

— the nature of anionic or molecular ligands in the equatorial planes of NpO_2^+ ligands involved in the formation of the CC bonds;

— the number and the nature of outer-sphere cations in the case of double salts of Np(V);

— the number of water molecules in the crystal structure;

— preparation conditions.

The influence of the nature of ligands in the equatorial plane of NpO_2^+ ions on the CC pattern can be clearly illustrated with the crystal structures of Np(V)-sodium double mellitate [43, 44] and pyromellitate.[69] Despite the similar character of the ligand coordination in the two structures, CC bonds are present in the former compound and are absent in the latter. This can be due to different charges localised on the respective ions. A typical effect of the ligand nature on the CC interaction between neptunoyl ions is also observed in the crystal structures of **16** and **14**. Both compounds, *viz*., Np(V) acetate and glycolate, are characterised by similar compositions whereas planar nets composed of the *h* type of the NpO_2^+ ions as opposed to zigzag chains of the *c* type of the neptunoyl ions are revealed in the crystal structures of the former and the latter, respectively.

In double salts of Np(V), the CC interaction between NpO_2^+ cations is generally weaker than in monocationic derivatives. Probably, this is caused by the electrostatic interactions of NpO_2^+ ions with outer-sphere cations, which impedes a mutual coordination of neptunoyls. The effect of monovalent cations (M^+) on the CC interaction of the NpO_2^+ ions decreases in the series $Na^+ > NH_4^+ \approx K^+ > Cs^+$, in agreement with expectations. For instance, CC bonds are absent in the crystal structure of the $Na[NpO_2C_2O_4(H_2O)]\cdot 2H_2O$ double salt [70] although cyclic trimers of NpO_2^+ ions are revealed in the structure of a closely related compound $NH_4[NpO_2C_2O_4(H_2O)]\cdot 2.67H_2O$ (**17**).

The CC interaction in double salts of Np(V) strongly depends not only on the nature of the cations M^+ but on their number, *i.e*., on the $M^+ : NpO_2$ ratio as well. An increase in this ratio increases saturation of the coordination sphere of NpO_2^+ ions with anionic ligands, which evidently hampers the formation of the CC bonds. This effect can be illustrated with the crystal structure of $Cs_3[NpO_2(SO_4)_2]\cdot 2H_2O$ (see Ref. 71), which contains no CC bonds.

An increase in the number of water molecules in an Np(V) compound generally results in a substantial weakening of the CC interaction. For example, in the crystal structure of **20**, every NpO_2^+ ion is involved in four CC bonds whereas only two CC bonds are formed by neptunoyl ions in the crystal structure of **18**. This effect may be explained by the formation of H-bonds between oxygen atoms of NpO_2^+ ions and water molecules, which interfere with the CC interaction.

Synthetic conditions often have a definitive influence on the composition of Np(V) compounds and thus on the occurrence and the character of the CC bonds in their crystal structures. For instance, compounds **12** and **13** are crystallised from formate solutions under hydrothermal conditions at 120 °C and 160 °C, respectively. As has been mentioned above, these compounds have totally different patterns of the CC bonds.

Unfortunately, the regularities formulated above are only qualitative and do not allow an unambiguous prediction of patterns of the CC interaction in the crystal structures of novel Np(V) compounds. Meanwhile, they provide valuable assistance in suggesting occurrence and the type of the CC bonds in compounds of a known composition but unknown crystal structure.

III. Influence of the cation – cation interactions on the properties of Np(V) compounds

1. Crystallisation and dissolution

The cation – cation interactions in crystalline compounds of Np(V) have a strong influence on their properties. In particular, many compounds possessing CC bonds behave abnormally on dissolution and crystallisation. Probably, it is due to the involvement of the CC bonds in the formation of infinite fragments of the crystal structure. This conclusion can be illustrated with several examples. The solubility of Np(V) double oxalates with the common stoichiometry $MNpO_2C_2O_4\cdot nH_2O$, where M^+ is ammonium or alkali metal ion, decreases noticeably upon their storage for several days.[72] As has been shown,[73] this decrease is explained by slow conversion of the above compounds into simple oxalate $(NpO_2)_2C_2O_4\cdot 6H_2O$. The low solubility and slow formation of the latter compound relate evidently to the infinite chain-like system of the CC bonds revealed therein.[63]

A typical trend in the solubility change due to formation of an infinite system of the CC bonds is also observed in the precipitation of simple Np(V) formates.[58, 74] Solutions of NpO_2OH with the concentration $[NpO_2^+] = 0.1 - 0.3$ mol litre^{-1} in an excess of HCOOH remain transparent for several hours. Then, slow crystallisation of $NpO_2HCOO\cdot 2H_2O$ begins. The latter is characterised by a solubility of 5.32×10^{-2} mol litre^{-1} at 23 °C and [HCOOH] = 0.2 mol litre^{-1}. With an increase in temperature up to 65 °C, the solubility does not change significantly. Nevertheless, upon heating of the saturated solution in a boiling water bath, crystals of **12** precipitate. This compound is characterised by a solubility of 2.42×10^{-2} mol litre^{-1} at 100 °C and [HCOOH] = 0.3 mol litre^{-1}. At temperatures above 140 °C, the monohydrate **12** converts into anhydrous salt **13**, which leads to a further decrease in the concentration of Np(V) in the liquid phase.

Similar trends in the crystallisation of various hydrates are observed in the preparation of Np(V) simple salts with sulfate,[50, 51, 75] acetate,[76] benzoate [60, 77] and other carboxylate [59, 78, 79] anions. In general, slow formation and dissolution of precipitates as well as relatively low solubility in water and organic solvents are characteristic of Np(V) compounds with infinite nets of CC bonds. Such compounds are typically nonhygroscopic.

2. UV-Vis absorption spectra

The cation – cation interaction specifically affects optical properties of Np(V) compounds. This is confirmed by an analysis of the UV-Vis absorption spectra of more than 30 simple and complex neptunoyl salts with known crystal structures.[55, 56, 77 – 87] A comparison of UV-Vis spectra of crystalline compounds with CC bonds and those without CC bonds, on the one hand, and of the respective solutions, on the other hand, revealed several important regularities.[81, 88, 89] One of them concerns correlations between the symmetry of the CP of Np atoms in a compound and the general shape of its UV-Vis spectrum. As has been noted above, pentagonal bipyramid and, less frequently, hexagonal bipyramid are the major types of coordination polyhedra occurring in neptunoyl compounds. According to extensive experimental studies, UV-Vis spectra of all crystalline salts of Np(V) characterised by the pentagonal-bipyramidal coordination of the central atom (D_{5h} symmetry) manifest narrow and intense absorption bands in the region of 970 – 1050 nm similar to the dominant band in the spectra of hydrated NpO_2^+ ions (Fig. 9 *a*). In contrast, such narrow absorption bands are absent in the case of compounds with hexagonal bipyramids (D_{6h} symmetry) as the coordination polyhedra of the Np atoms (Fig. 9 *b*). This can easily be rationalised.[90] According to the Laporte selection rules, *f*–*f* transitions are forbidden in a centrosymmetric ligand field (including the case of D_{6h} symmetry). For CP without an inversion centre (such as the pentagonal bipyramid), the probability of such transitions

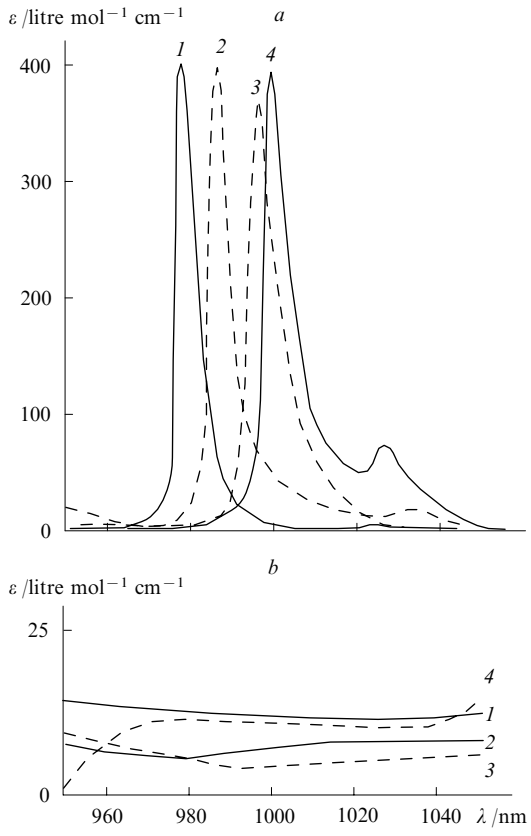


Figure 9. The UV-Vis absorption spectra of hydrated Np(V) ions and different neptunoyl compounds: (*a*) NpO_2^+ (aq) (*1*), **24** (*2*), **28** (*3*),[84] **12** (*4*);[82] (*b*) $NH_4[NpO_2(HCOO)_2]$ (*1*),[74] $K[NpO_2CO_3]$ (*2*),[81] $Cs_2[NpO_2.(CH_3COO)_3]$ (*3*),[82] **11** (*4*).[57]

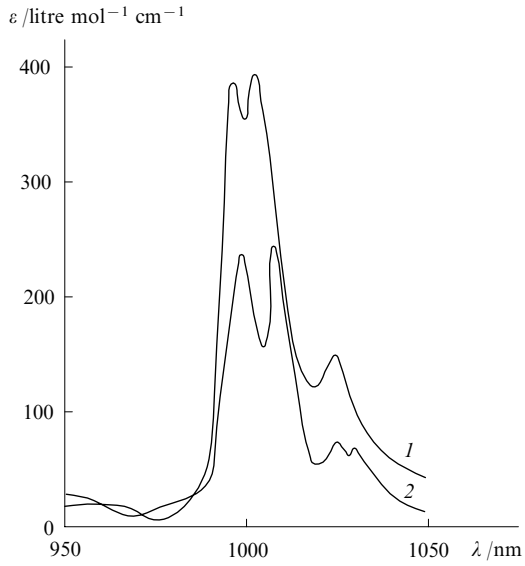


Figure 10. The UV-Vis absorption spectra of **4** (*1*) and **6** (*2*).[62]

becomes appreciable giving rise to narrow and fairly intense absorption bands in the UV-Vis spectra.

UV-Vis spectra of crystalline compounds and respective solutions are normally characterised by similar values of the molar extinction (ε_m) at the absorption maxima. Somewhat reduced ε_m values are observed only for amorphous, such as Np(V) hydroxide, or poorly crystalline substances.[89]

Based on the resemblance of the UV-Vis spectra of neptunoyl derivatives in aqueous solutions to those of crystalline compounds characterised by the D_{5h} symmetry of the coordination polyhedron of the neptunium atoms, one may assume that the hydration number (h) of NpO_2^+ ions in dilute aqueous solutions is 5. Suggestions that $h = 6$ or 4 adopted by several authors[33,77,91] are most probably erroneous.[92] A similar conclusion is also valid for AmO_2^+ ions, since the UV-Vis spectra of the respective aqueous solutions manifest narrow and fairly intense bands assigned to f–f transitions. Furthermore, the effects of the CP symmetry on the UV-Vis spectra established for neptunoyl ions are also applicable to PuO_2^{2+} ions as confirmed by the UV-Vis spectra of a series of Pu(VI) double oxalates (see Ref. 93). Thus, plutonoyl like other actinoyl ions are characterised by the hydration number 5 in aqueous solutions.

In the UV-Vis spectra of some crystalline compounds with D_{5h} symmetry of the Np coordination polyhedra, the main absorption band is split (Fig. 10).[66,78,80,85] This suggests the presence of several nonequivalent neptunoyl groups in the crystal structure. However, an unsplit UV-Vis band does not necessarily imply the crystallographic equivalency of all NpO_2^+ ions. For example, in the crystal structure of **15**, there are four types of neptunoyl ions despite the major absorption band in the UV-Vis spectrum of this compound being only slightly broadened rather than split.[77]

The position of the major absorption maximum in the UV-Vis spectrum of a crystal is normally red-shifted with respect to the corresponding solution provided that the CP of the Np(V) atoms in the crystal structure of this compound have no inversion centres. The magnitude of this shift ($\Delta\lambda_m$) depends on the nature of ligands in the equatorial plane of the NpO_2^+ ions and the occurrence of the CC bonds. For compounds without CC bonds, the positions of absorption maxima in the UV-Vis spectra of crystalline samples are quite close to those of the respective solutions with the shift not exceeding $\pm$ 5 nm (Table 2).

Table 2. UV-Vis spectral parameters of crystalline Np(V) compounds with known crystal structures without CC bonds.

Compound	λ_m /nm	$\Delta\lambda_m$ /nm	Ref.
$Na[NpO_2C_2O_4(H_2O)]\cdot 2H_2O$ (**24**)	989	2	70, 84
$Cs_3[NpO_2(SO_4)_2]\cdot 2H_2O$ (**25**)	986	1	71, 80
$[Co(NH_3)_6][NpO_2(SO_4)]\cdot 2H_2O$ (**26**)	989	4	80, 94
$[Co(NH_3)_6][NpO_2(C_2O_4)_2]\cdot 4H_2O$ (**27**)	1000	4	84, 95
$[Co(NH_3)_6][NpO_2(C_2O_4)_2]\cdot 3H_2O$ (**28**)	992	−4	84, 95
$[Co(NH_3)_6][NpO_2\{o\text{-}C_6H_4(COO)_2\}_2]\cdot 2H_2O$ (**29**)	996	4	86

The situation changes dramatically if the crystal structure of an Np(V) compound involves CC bonds. In those cases, the absorption band in the UV-Vis spectrum of the crystal is quite strongly shifted towards longer wavelengths with respect to the spectra of the corresponding complex in a solution. The magnitude of this shift depends on the character of the CC bonds. For compounds that contain neptunoyl ions acting as monodentate ligands, $\Delta\lambda_m$ lies in the range of 8 – 17 nm (Table 3). In the case of a bidentate coordination of NpO_2^+ ions, the shift amounts to 15 – 39 nm (Table 4). Crystal structures of some compounds contain both mono- and bidentate neptunoyl ions simultaneously. The major absorption bands in the UV-Vis spectra of such compounds are split into two components with distinctly different red shifts. The UV-Vis spectrum of **19** may be taken as a striking example of such a situation.

In the course of systematic UV-Vis studies of NpO_2^+ crystalline compounds, several unusual facts have been revealed. In particular, the spectra of Np(V) chromates[83,96–98] manifest intense broad bands strongly (> 40 nm) shifted towards longer wavelengths. According to X-ray crystallographic data,[96–98] this

Table 3. UV-Vis spectral parameters of crystalline compounds with the monodentate coordination of NpO_2^+.

Compound	λ_m /nm	$\Delta\lambda_m$ /nm	Ref.
$[NpO_2ClO_4(H_2O)_2]$ (**9**)	991	10	55
$[NpO_2CH_2(OH)COO(H_2O)]$ (**14**)	1004	16	59, 79
$NH_4[NpO_2C_2O_4]\cdot 2.67\,H_2O$ (**17**)	997	8	62, 84
$[(NpO_2)_2C_2O_4(H_2O)_4]\cdot 2\,H_2O$ (**18**)	1002	17	63
$[(NpO_2)_2CH_2(COO)_2(H_2O)_3]\cdot H_2O$ (**19**)	999	14	64
$[(NpO_2)_2(DMSO)_7(H_2O)_2](ClO_4)_2\cdot H_2O$ (**21**)	995	11	66
$[NpO_2NO_3(CH_3CONH_2)_2]$ (**23**)	1002	—	68

Table 4. UV-Vis spectral parameters of crystalline compounds with the bidentate coordination of NpO_2^+.

Compound	λ_m /nm	$\Delta\lambda_m$ /nm	Ref.
$[(NpO_2)_2SO_4(H_2O)_2]$ (**4**)	999; 1005	17; 23	50, 80
$[(NpO_2)_2SO_4(H_2O)]$ (**5**)	1007; 1021	25; 39	51, 80
$[NpO_2Cl(H_2O)]$ (**6**)	1000; 1009	19; 28	52, 85
$[(NpO_2)_2(NO_3)_2(H_2O)_4]\cdot H_2O$ (**10**)	996	15	56
$[NpO_2HCOO(H_2O)_2]$ (**12**)	1003	21	58, 82
$[NpO_2HCOO]$ (**13**)	1008	26	58, 82
$[NpO_2C_6H_5COO(H_2O)]\cdot 0.75\,H_2O$ (**15**)	1009	27	60, 77
$[(NpO_2)_2CH_2(COO)_2(H_2O)_3]\cdot H_2O$ (**19**)	1007	22	64, 78
$[(NpO_2)_2CH_2(COO)_2(H_2O)_2]\cdot H_2O$ (**20**)	1006; 1015	25; 37	65, 78
$[(NpO_2)_2\{o\text{-}C_6H_4(COO)_2\}(H_2O)_3]\cdot H_2O$ (**22**)	1007	23	67, 87

shift is not induced by the CC interaction. Probably, a partial charge transfer from the Np atoms to the CrO_4^{2-} due to a strong oxidising ability of the latter is responsible for the phenomenon.

Yet another anomaly, *viz*., a broad irregularly shaped band characterised by a strong red shift, was observed in the spectrum of crystalline Np_2O_5[99] (Fig. 11). Apparently, the neptunoyl moiety is substantially weakened or totally absent in the crystal structure of Np_2O_5.

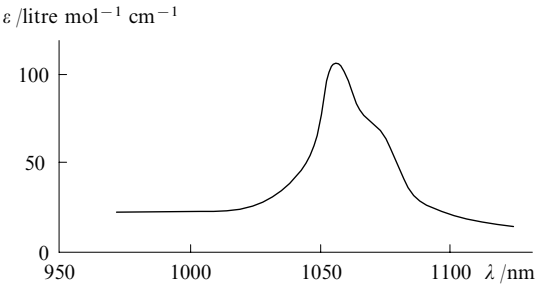


Figure 11. The UV-Vis absorption spectra of crystalline Np_2O_5.[99]

Finally, we note that the aforementioned regularities often allow reliable predictions of the occurrence and the character of the CC bonds in the crystal structures of novel Np(V) compounds on the basis of their UV-Vis spectra. Such predictions were made for a number of compounds including neptunoyl chloride,[87] oxalates,[84] malonates,[78] benzoates[77] and phthalates.[87] Afterwards, all of these predictions proved correct through direct determinations of the crystal structures of the respective compounds by means of single-crystal X-ray diffraction.[52, 60, 62–65, 67] Definitely, these predictions are only of qualitative character. The UV-Vis absorption spectroscopy of crystalline Np(V) compounds and conclusions based on the spectral results should not be taken as a substitute for other techniques. It should rather be considered as the first step in the structural study of newly prepared Np(V) compounds.

3. Infrared and other spectra

It has been demonstrated[100,101] that IR spectra of a number of simple Np(V) salts are characterised by intense broad bands of antisymmetric (ν_{as}) vibrations of the neptunoyl moiety. This observation was first explained by formation of H-bonds between water molecules and oxygen atoms of the neptunoyl ions. However, systematic structural studies have recently established that simple Np(V) salts usually contain CC bonds. Therefore, one may suggest that it is the CC interaction that is responsible for the intense broad vibrational bands of NpO_2^+ observed in these compounds. This suggestion is supported by IR spectroscopic studies of many Np(V) compounds with known crystal structures.[58, 66, 68, 75–79, 87] The distinct difference in the ν_{as} band between IR spectra of neptunoyl salts with (*a*) and without (*b*) the CC bonds is illustrated in Fig. 12 for a few typical cases.

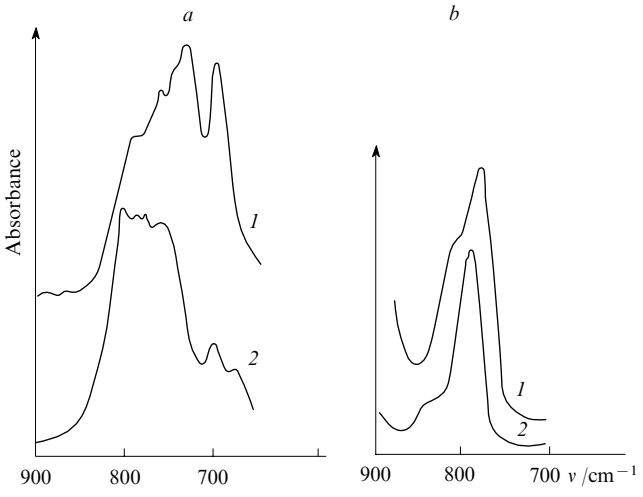


Figure 12. The IR spectra of some Np(V) compounds (see Ref. 78): (*a*) **20** (*1*) and **19** (*2*), which involve CC bonds; (*b*) $NH_4[NpO_2CH_2(COO)_2]$ (*1*) and $Cs[NpO_2CH_2(COO)_2]$ (*2*) without CC bonds.

Yet another distinctive feature of the IR spectra of Np(V) compounds possessing CC bonds in their crystal structures is a pronounced shift of the ν_{as} bands towards lower frequencies. The magnitude of this shift depends upon the number and the character of the CC bonds. In particular, it correlates to a certain extent with the changes in the Np–O bond lengths resulting from the CC interaction as well as with the red shift of bands in the UV-Vis spectra (Table 5). Unfortunately, this correlation bears only a qualitative character, partially due to ambiguities in the determination of precise positions of maxima for broad irregularly shaped ν_{as} vibrational bands in the IR spectra of compounds with the CC bonds. On the other hand, Np–O bond lengths change within a relatively narrow range and the precision of their determination is not sufficiently high.

Several publications[24, 43, 49, 58, 87, 93, 102] have reported on the Mössbauer spectra of Np(V) compounds, crystal structures of which reveal the CC interaction. However, no suggestions of spectral effects attributable exclusively to the CC interaction have been made.

An interesting result has been obtained in a study of magnetic properties of compound **14**.[103] According to the low-temperature magnetic susceptibility measurements, this salt (note that its crystal structure reveals a distorted planar square net of CC bonds[58]) undergoes a ferromagnetic transition at 12 K. It is the first observation of ferromagnetism for Np(V) compounds. We

Table 5. Correlations between the UV-Vis band position, Np – O bond length and ν_{as} vibrational frequencies in the IR spectra of Np(V) compounds with CC bonds.

Compound	λ_m /nm	$\Delta\lambda_m$ /nm	Np – O /Å	ν_{as} /cm^{-1}	Ref.
$[(NpO_2)_2SO_4(H_2O)_2]$ (**4**)	999; 1005	17; 23	1.830; 1.851 [a]	768; 760	50, 75
$[NpO_2Cl(H_2O)]$ (**6**)	1000; 1009	19; 28	1.835; 1.840 [a]	768	52
$[NpO_2ClO_4(H_2O)_4]$ (**9**)	991	10	1.810; 1.860	808; 776	55
$[NpO_2HCOO(H_2O)]$ (**12**)	1003	21	1.846; 1.850	764	58
$[NpO_2HCOO]$ (**13**)	1008	26	1.857; 1.915	740	58
$[NpO_2CH_2(OH)COO(H_2O)]$ (**14**)	1004	16	1.828; 1.801	802	59, 79
$[NpO_2C_6H_5COO(H_2O)]\cdot 0.75\,H_2O$ (**15**)	1009	27	1.82 – 1.87 [a]	745	60, 67
$NH_4[NpO_2C_2O_4]\cdot 2.67\,H_2O$ (**17**)	997	8	1.825; 1.887	794	62, 84
$[(NpO_2)_2CH_2(COO)_2(H_2O)_3]\cdot H_2O$ (**19**)	1007	22	1.840; 1.828 [a]	805; 765	64, 78
$[(NpO_2)_2CH_2(COO)_2(H_2O)_2]\cdot H_2O$ (**20**)	1006; 1015	25; 37	1.840; 1.870 [a]	760; 725	65, 78
$[(NpO_2)_2(DMSO)_7(H_2O)_2](ClO_4)_2\cdot H_2O$ (**21**)	995	11	1.86	800	66
$[(NpO_2)_2\{o\text{-}C_6H_4(COO)_2\}(H_2O)_3]\cdot H_2O$ (**22**)	1007	23	1.850; 1.843 [a]	755	67, 87
$[NpO_2NO_3(CH_3CONH_2)_2]$ (**23**)	1002	–	1.859	790; 778	68

[a] Np – O bond lengths are averaged for different types of NpO_2^+ ions.

believe that further investigations into the magnetic properties of Np(V) compounds will lead to new important findings.

IV. Cation – cation interactions in compounds of other actinide ions

The mutual coordination of UO_2^{2+} ions has been observed for the first time in a crystallographic study of UO_2Cl_2 (**30**) by means of neutron diffraction.[104] In the orthorhombic crystal lattice of this compound, the uranyl ions form infinite zigzag chains through the CC bonds, which is similar to the pattern of NpO_2^+ ions in the crystal structures of compounds **9**, **14**, **18** and **23**. Each UO_2^{2+} ion is involved in two CC bonds acting as a monodentate ligand with respect to the adjacent ion.

Similar infinite zigzag chains were revealed in the crystal structure of UO_2MoO_4 (**31**).[105] Furthermore, it has to be taken into account that all anhydrous salts with the common stoichiometry UO_2EO_4, where E = S, Se, Cr, Mo or W, are isostructural according to powder X-ray diffraction data.[106–108] Thus, their crystal structures contain identical chain-like patterns of the CC bonds.

Quite another pattern of the CC bonds was revealed in uranyl hexafluoroacetylacetonate $UO_2(C_5HF_6O_2)_2$ (**32**).[109] Its crystal structure, like that of compound **17**, contains trimers of uranyl ions. Nevertheless, in this compound all UO_2^{2+} ions in the trimers are crystallographically nonequivalent. According to some indirect evidence,[110, 111] CC bonds may also be formed in other uranyl β-diketonates though the corresponding crystal structures have not been determined so far.

The formation of CC bonds has been confirmed for a rather complicated and structurally uncommon oxothiolate uranyl complex $(HNEt_3)_2[(UO_2)_4(\mu_3\text{-}O)_2(SC_5NH_4)_6]\cdot Me_2CO$ (**33**). The crystal structure of this compound reveals tetranuclear anions composed of two identical fragments $(UO_2)_2(SC_5NH_4)_3^-$, in which uranyl ions form CC bonds of the O=U=O···U type. These fragments are bound to each other through two bridging O atoms. Therefore, as regards the pattern of the CC bonds within the complex anion, the two UO_2^{2+} ions act as monodentate ligands whilst two other ions act exclusively as coordinating centres.

No other uranyl derivatives possessing CC bonds have been reported so far. Nevertheless, we assume that CC bonds may well be revealed in further structural studies of a number of anhydrous uranyl salts containing anions of low coordination capacity as ligands.

The character of the CC bonds and their influence on the properties of uranyl compounds are similar to those discussed above for neptunoyl compounds. In both cases, the CC bonds are formed through bridging oxygen atoms, which are characterised by different An – O bond lengths ($l_1 \ll l_3$, Table 6). The formation of the CC bonds is also accompanied by a significant increase in the U – O bond length within the uranyl ions. The mean value of the $l_1 - l_2$ difference is 0.06 Å. The U – O distance to the oxygen atom of an adjacent uranyl ion coordinated in the equatorial plane is 2.51 Å on average, which is slightly longer than values typical of uranyl complexes with various oxygen ligands. Thus, UO_2^{2+} ions behave as relatively weak ligands in the formation of the CC bonds.

Table 6. U – O bond lengths (Å) in the crystal structures of uranyl compounds with CC bonds.[a]

Compound	l_1	l_2	l_3	Ref.
UO_2Cl_2 (**30**)	1.78	1.73	2.52	104
UO_2MoO_4 (**31**)	1.808	1.758	2.508	105
$UO_2(C_5HF_6O_2)_2$ (**32**)	1.79	1.72	2.47	109
	1.72	1.68	2.54	
	1.81	1.71	2.48	
$(HNEt_3)_2[(UO_2)_4(\mu_3\text{-}O)_2(SC_5NH_4)_6]\cdot$ $\cdot Me_2CO$ (**33**)	1.838	1.771	2.488	112

[a] $O\overset{l_2}{=}U\overset{l_1}{=}O\overset{l_3}{\cdots}U$.

Apart from the aforementioned Np(V) and U(VI) derivatives, no other An(V) or An(VI) compounds exhibiting CC bonds have been reported. Attempts to synthesise NpO_2MoO_4 and NpO_2EO_4, where E = S, Cr or W, which are presumably isostructural to UO_2MoO_4, failed due to reduction of Np(VI) to the pentavalent state. Nevertheless, the possibility of an occurrence of CC bonds in some anhydrous neptunyl compounds cannot be totally ruled out.

Several attempts to prepare Am(V) compounds analogous to Np(V) salts with known crystal structures have been undertaken. It was established that the isolation conditions and the crystal structures of $[Co(NH_3)_6][AmO_2(SO_4)_2]\cdot 2H_2O$ and $[Co(NH_3)_6]\cdot[NpO_2(SO_4)_2]\cdot 2H_2O$ devoid of CC bonds are virtually identical.[113] Meanwhile, it turned out that $(AmO_2)_2SO_4\cdot nH_2O$ is not isostructural to any of the known simple Np(V) sulfates with CC bonds. Moreover, Am(V), in contrast to Np(V), is not precipitated from concentrated formate solutions as $AmO_2HCOO\cdot nH_2O$ but rather is slowly converted into poorly soluble $Am(HCOO)_3$.[114] With a high level of confidence, we may assume that these results suggest a significant weakening of the CC bonds upon transition from NpO_2^+ to AmO_2^+. However, preparation of Am(V) com-

pounds with CC bonds should not be judged as completely impossible. Indeed, AmO_2^+ ions in solutions can serve as weak ligands in the CC interactions with highly charged cations, although uranyl ions do not manifest this ability. At the same time, as has been noted above, some crystalline compounds of U(VI) reveal CC bonds.

Since Pu(V) and, in particular, U(V) are prone to the CC interaction in solutions, one should expect the occurrence of CC bonds in crystal structures of some of their compounds. Most probable candidates in the search for such compounds are salts of suitable anions with kinetically stable cationic complexes of PuO_2^+ or UO_2^+ with Cr^{3+} or Rh^{3+} like $Rh(H_2O)_5NpO_2F_4$ (see Ref. 5). Preparation of compounds with a mutual coordination of PuO_2^+ or UO_2^+ ions is hardly possible taking into account their easy disproportionation.

V. Comparison of cation – cation interactions in solutions and crystals of actinide compounds

As has been noted in the Introduction, different aspects of the CC interaction have been considered in numerous publications. Special attention has been paid to the elucidation of the nature of this phenomenon. Several authors suggested that the CC interaction can be reduced to a special type of incomplete redox reaction between the AnO_2^+ cation and an 'active' cation.[7, 13, 14, 19, 20, 22, 23, 25] A series of arguments have been adduced in support. In particular, according to several reports, kinetics of formation of complexes owing to the CC interaction of NpO_2^+ with U(VI), Fe(III), Th(IV) or In(III) and of AmO_2^+ with U(VI) does not obey the law of mass action. Moreover, the UV-Vis spectra of NpO_2^+ (see Refs 14 and 20) and AmO_2^+ (see Ref. 7) in the presence of some 'active' cations manifest broad bands in the region of 600 – 900 nm attributed to the exciton absorption. The experimentally established weakening of the CC interaction in the series $UO_2^+ > NpO_2^+ > AmO_2^+$ was explained [7, 25] by an increase in the redox potentials of the corresponding An(VI)/An(V) pairs. These and some other arguments [14, 15] have been consistently rebutted in a series of studies,[26, 29 – 35] which at the same time substantiated an alternative suggestion stating that the CC interaction in a solution originates from complexation between the AnO_2^+ ions and the 'active' cations. However, the character of this complexation remains disputable. Two alternative concepts of the nature of the CC interaction in solutions have been formulated based on numerous experimental results.[2, 29, 32 – 35] The first concept states that the CC interaction may be considered as a process of substitution of water molecules within the coordination sphere of the 'active' cation by oxygen atoms of the actinoyl ion. The second concept suggests an outer-sphere interaction mediated by such ligands as H_2O or ClO_4^-. The following arguments may be adduced in favour of the first concept:

1. The formation of CC complexes of AnO_2^+ with Cr_{aq}^{3+} (see Refs 2 and 9) and Rh_{aq}^{3+} proceeds slowly, which is typical of inner-sphere substitution of water molecules by various ligands in 'active' cations mentioned.

2. The NMR data [33] on the CC interaction between NpO_2^+ and UO_2^{2+} support the hypothesis of the formation of a T-shaped inner-sphere complex (two linear AnO_2^{n+} groups arranged perpendicularly to each other).

3. The major band in the UV-Vis absorption spectra of hydrated NpO_2^+ ions at 980 nm is shifted in the presence of 'active' cations by 9 – 17 nm towards longer wavelengths.[1 – 3, 8] Such a large shift may be induced by either direct involvement of oxygen atoms of the neptunoyl groups into chemical bonds or incorporation of sufficiently strong ligands into the equatorial plane of the NpO_2^+ ions. Note that H_2O molecules and ClO_4^- anions are generally considered as weak ligands.

4. According to IR [28, 100, 101] and Raman [31, 34] spectra, vibrational frequencies of NpO_2^+ change substantially due to the CC interaction. The character of these changes is similar to that in the UV-Vis spectra.

5. The An···An interatomic distance in CC complexes of NpO_2^+ with UO_2^{2+} is 4.2 Å,[32, 35] which is surprisingly close to the sum of the Np – O bond length within neptunoyl (*ca.* 1.8 Å) and a typical distance between the U atom of uranyl and oxygen atoms of ligands coordinated in the equatorial plane (*ca.* 2.4 Å).

The above arguments strongly assume that the outer-sphere model of the CC interaction is hardly probable although these are not sufficient to rule it out decisively. In this respect, we note rather unexpected negative values of enthalpy and entropy of the CC interaction determined for NpO_2^+ complexes with Rh(III) (see Ref. 3), Cr(III) (see Ref. 9) and U(VI) (see Ref. 40). Though the negative values are normally typical of the outer-sphere complexation of actinides, these results can be rationalised taking into account higher hydration energy of the CC complex with respect to the starting species due to formation of a binuclear complex, which is characterised by a high specifically distributed charge.

Convincing evidence in favour of the inner-sphere nature of the CC interaction involving AnO_2^+ ions comes from results of the characterisation of the CC complexes in crystalline compounds of Np(V) summarised above. Indeed, in all crystalline structures discussed, the CC bonds are formed by direct incorporation of an oxygen atom of a neptunoyl ion into the coordination sphere of the adjacent NpO_2^+ ion. On the other hand, there is a close analogy between the CC interaction formed by AnO_2^+ ions in solutions and in crystals. This analogy becomes apparent if the UV-Vis spectra of NpO_2^+ CC complexes in solutions are compared with the spectra of the respective compounds in the crystalline state. As has already been mentioned, upon formation of CC complexes in solutions, the UV-Vis absorption band of Np(V) ions shifts by 9 – 17 nm. Crystalline compounds with a monodentate mutual coordination of NpO_2^+ ions (see Table 3) are characterised by virtually the same shift. Besides, the Np···Np interatomic distances between CC-interacting neptunoyl ions in perchloric acid solutions [32, 35] and in crystalline $[NpO_2ClO_4(H_2O)_4]$ (see Ref. 55) are close to each other being both equal to ~ 4.2 Å. Therefore, there is sufficient evidence that the CC interactions of actinoyl ions in solutions and in crystals are realised in similar ways. Notwithstanding, the two cases have distinctive features due to the following factors:

1. In solutions, the CC interaction is usually limited to formation of binuclear complexes. Trimeric and larger (*i.e.*, higher-nuclearity) species have been detected only in very concentrated ($c > 0.5$ mol litre^{-1}) solutions of Np(V) perchlorate.[31, 34] In contrast, formation of infinite systems of CC bonds (*viz.*, chains, ribbons, planar nets or three-dimensional frameworks) is typical of crystalline neptunoyl compounds. Dimeric ions have been revealed in the crystal structures of only two out of twenty-three compounds listed in Table 1, namely, in **1** and **21**.

2. Neither mutual coordination of AnO_2^+ ions nor their CC interaction with other 'active' ions (apart from AnO_2^+) in solutions has been observed. Meanwhile, the crystal structures of a number of uranyl compounds (see Table 6) contain CC bonds. This may be explained by a rather small effective charge localised on oxygen atoms within the AnO_2^+ ions. As a result, they cannot substitute water molecules in the coordination spheres of 'active' cations in aqueous media. Nevertheless, some U(VI) compounds with CC bonds can be crystallised from organic solutions or prepared by solid state methods.

3. Systematic structural studies of crystalline compounds of Np(V) have shown that the incorporation of a large number of water molecules in the crystal structure results in a weakening of the CC bonds and a prevalence of the monodentate coordination of NpO_2^+ ions. Upon transition from crystals to aqueous solution, this tendency becomes more pronounced. This may be explained by the formation of hydrogen bonds between oxygen atoms of the neptunoyl ions and H_2O molecules. This suggestion is supported by the fact that the CC interaction is intensified provided that a weaker proton donor is taken as a solvent instead of water.[14, 39]

The absence of infinite systems of CC bonds and their weakening in aqueous solutions result in a relatively low influence

of the CC interaction on the UV-Vis spectra of Np(V) compounds in concentrated aqueous solutions.[32, 35] Probably, the same factors along with the larger $l_3 - l_1$ difference are responsible for some peculiarities of the Raman spectra of Np(V) compounds in solutions.[31, 34, 36]

Therefore, one may conclude that the CC interaction of actinoyl ions both in solutions and in crystals is realised through the inner-sphere coordination of AnO_2^+ by the 'active' ions. The only difference for the two cases consists of the intensity of the processes.

* * *

According to the experimental data summarised above, the CC interaction of NpO_2^+ ions is a common phenomenon occurring in many Np(V) compounds with known crystal structures. It strongly affects physicochemical properties of compounds under consideration, such as precipitation and dissolution kinetics, UV-Vis and IR spectra, *etc*. The number of Np(V) compounds in which the presence of the CC bond has been confirmed constantly increases. Meanwhile, structural data for other pentavalent actinides, in particular, PuO_2^+ are lacking. Therefore, the development of preparative chemistry of Pu(V), which is immature as yet, is an urgent task. Undoubtedly, the accomplishment of this task will make a significant contribution to coordination chemistry of actinides.

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