

Spectroscopic investigations of molten salt systems. Theory and experiment

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Abstract - The properties of coordination compounds in melts - species of quasi-binuclear (cluster) heteronuclear structure - are considered in terms of a proposed complex-cluster structural model for molten salt systems with complex formation. Their electronic structure and IR, Raman, ESR and NMR spectra are discussed as a cluster approximation, which allows not only for the near ligand-environment of the central complexing ion but also for the far outer-sphere-ion environment. Such an approach is of great importance for the theoretical and experimental chemistry (and physics) of complexes in a condensed phase in general and in molten salts in particular since it is with systems in the phase states such as crystals, melts and solutions that coordination chemistry operates in most real cases. Experimental examples of electronic, vibrational and radiospectral characteristics of molten salts are given, which confirm the fruitfulness of such a theoretical approach.

INTRODUCTION

Molten salt systems, whether they be binary systems with common anion (MX-AX) or with common cation (MX-MY), or more complex ternary reciprocal systems of the type MX-AY a.o. (Note a), exhibit, owing to the nonequivalence of their components (of their ionic moments=charge/radius in the explicit form and of their electronic structure and other parameters in the implicit form), a tendency to a strong interparticle interaction, which transforms into complex formation at the very different parameters of the partners, e.g., in alkali halide systems (AX, AY) and d- or f-metal halide systems (MX).

Unlike complex formation processes in aqueous and nonaqueous media, complex formation in molten salts has a distinctive feature (Fig. 1) which consists in there being no conventional solvents, due to which the "background" ions of a molten medium (generally A^+ cations) are outer-sphere ions and are not separated from complexes (generally anions of the type MX_m^{z-} , m = coordination number) by the solvation shells of solvents (ref. 1). Due to this they can, while in the second coordination sphere, come into considerable, partly covalent interaction. This leads to the formation of both heteronuclear ($A_n [MX_m]$) and homonuclear ($M_n [MX_m]$) quasi-cluster groups: the former in binary, ternary and the like molten salt systems and the latter in a molten salt proper of the complexing metal or in the system concentration region rich in it.

Such a quasi-cluster approach to the chemistry of coordination compounds in molten salts (ref. 2) allows one to discuss problems of the structure of both the complexes in them and melts in general (and their crystals), the thermodynamics and kinetics of interaction and to propose a number of theoretical approaches and models.

Note a: The formal oxidation states and corresponding stoichiometric coefficients have been omitted for simplicity.

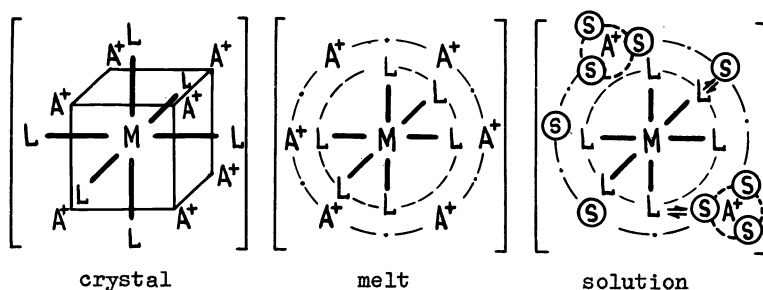


Fig. 1. Model representations of complexes as clusters with an outer-sphere environment in various media (M = metal, L = ligand, A⁺ = outer-sphere cation, S = solvent)

It should be noted that melts with complex formation were chosen to illustrate the structure of molten salt systems only due to their relations manifesting themselves more distinctly, which are, generally speaking, observed (though in more veiled form) in all molten salt systems, including those with components that are less widely different in ionic parameters of the components.

We shall not discuss here more ordinary cases of complex MX_m^{n-} ion formation in a molten solvent (Solv.), e.g., alkali nitrate, since in this case complex formation in a melt is similar to the same process in any solvent, which involves displacement of solvent molecules (Solv. = NO_3^- a.o.) from the coordination sphere of the solvato-complex $M(\text{Solv.})_m^n$ by a stronger ligand ($X^- = Cl^-, Br^-, I^-$ a.o.).

The instances of complex formation in binary systems of the type $MX-AX$, which resemble the formation of aqua (solvato) complexes, are much more interesting both basically (which was spoken of above) and topically (in terms of ISSSSI) since in this case part of the anions of the melt (X^-) acts as ligand and the other part of them as solvent.

As outlined above, the aims of the present paper are:

- I. elucidation of the question whether there are molten salts of true (in the classical sense) complex ions in such systems and detection of the region of their existence;
- II. elucidation of the question whether these complex ions in melts are similar to or different from conventional complexes in aqueous and nonaqueous media with a view to apply known theoretical and experimental relations of structure and properties to the former (if they are identical);
- III. development for them of theoretical concepts which would explain the available experimental material and have a predicting ability (if they are not identical due to the specific structure of molten salts).

I. COMPLEX-CLUSTER STRUCTURAL MODEL FOR MOLTEN SALT SYSTEMS WITH COMPLEX FORMATION

Let us consider the structure of molten salt systems with complex formation of the type $MX-AX$, which are essentially a particular case of solvato systems with coordinating solvent. To do this, let us discuss two typical composition regions of such systems.

1) With dilute solutions of M^+ ions in a large excess of the molten salt AX , whose anion X^- acts both as ligand and as solvent, the complex MX_m^{n-} formed may be undoubtedly characterized by two of the known three attributes of a coordination compound (ref. 1): coordination phenomenon, i.e. specific arrangement of ligands around the central ion, and definite complex-composition, which manifests itself by the noncoincidence of the formal oxidation state of the complexing metal with coordination number. It is difficult, however, to extend the third notion necessary for the complex - dissociation of heterolytic type - to such systems since dissociation (stability, instability) constants can be only measured in the case of systems

with unambiguously established stoichiometry of complex formation reaction and distinct discrimination between inner and outer coordination spheres, which is not evident in the present instance. The above peculiarity is common for all solvato systems with coordinating solvents (including molten salts), and the question of the possibility to introduce a notion of dissociation constant comes in the present case to be of principle. In such systems and under such concentration conditions we have only to do with exchange between identical ligands and realization, in all cases, of the highest coordination number of the central complexing ion in a condensed phase. It is understandable that the reasonable equivalents of the third typical attribute of a complex compound - dissociation constant of heterolytic type - must be also characterized (with invariable stoichiometry of the complex) by a constancy of these alternative parameters.

To confirm the validity of this statement for melts, one can cite numerous thermodynamic investigations of dilute solutions (under 10 M/o) of BeCl_2 , TiCl_2 , TiCl_3 , ZrCl_4 , HfCl_4 , VCl_3 , LaCl_3 , CeCl_3 , MoCl_3 a.o. in molten alkali chlorides, which demonstrated constant activity-coefficients of these compounds in the concentration range studied. The spectral parameters, i.e. the extinction coefficients and band half-widths of electronic absorption spectra (EAS) of the $\text{Co}(\text{NO}_3)_4^{2-}$ and $\text{Ni}(\text{NCS})_6^{4-}$ complexes, as well as the magnetic susceptibility values of the NiCl_4^{2-} complex in melts up to 20 M/o of MX_2 show the same constancy (Fig. 2).

The Raman spectral data for the molten salt systems $\text{ZnCl}_2\text{-KCl}$, $\text{CdCl}_2\text{-KCl}$, $\text{MnCl}_2\text{-KCl}$, $\text{MgCl}_2\text{-KCl}$ are very convincing; from them it is evident that the vibrational frequencies of M-Cl bonds are constant up to the composition $X_{\text{MX}_2} \leq 0.33$, i.e. a single complex anion, MCl_4^{2-} in the case in point, is detected in dilute melts, and its parameters are constant (Fig. 3). All these and numerous other instances in the literature indicate unambiguously that in the dilute melt region we have to do with a single discrete maximally coordinatively saturated complex compound, for which a notion of heterolytic-type dissociation can be in principle introduced (ref. 1). Such an alternative notion for solvato complex systems according to D. Bockris may be "the lifetime of an entity", defined as $1/\bar{k}_1$, where \bar{k}_1 is the dissociation rate constant of the complex (ref. 3), which is determined galvanostatically or spectroscopically (Raman).

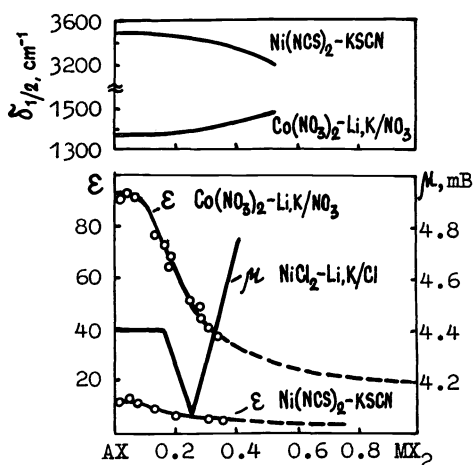


Fig. 2. Extinction coefficient (ϵ), EAS band half-width ($\delta_{1/2}$) and magnetic susceptibility (μ) of different complex ions in melts as a function of the composition of $\text{MX}_2\text{-AX}$ systems

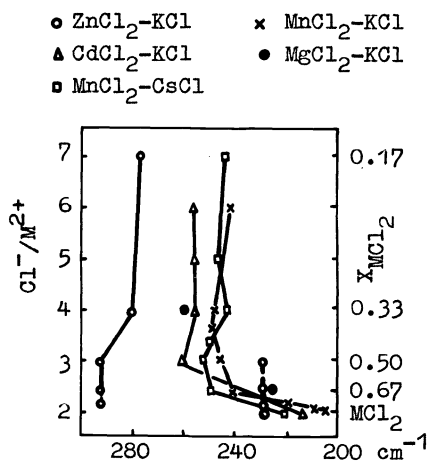
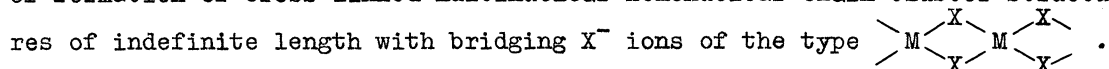


Fig. 3. M-Cl bond vibration Raman frequencies of complexes in melts as a function of the concentration of outer-sphere K^+ , Cs^+ cations

2) Let us now proceed to discussing the second typical region: concentrated solutions of M^+ ions in systems with X^- ligand deficiency. For the systems of the type $MX-AX$ under discussion it is logical to think that in this concentration region $MX \geq AX$ a gradual transition must be observed from the structure of the complex ion MX_m^{n-} just considered to the structure of the individual molten salt MX as a limiting case. To retain the coordinative saturation of the central complexing ion, one has to suggest a logical idea of formation of cross-linked multinuclear homonuclear chain cluster structures of indefinite length with bridging X^- ions of the type



This model is convincingly substantiated both by our EAS investigations of individual molten salts: $MnCl_2$, $CoCl_2$ a.o. (Fig. 4), from which it is seen that all the central complexing-metal ions, Mn^{2+} and Co^{2+} , are tetrahedrally surrounded by chlorines, and by neutron diffraction investigations of $ZnCl_2$ and $MgCl_2$, which have also a tetrahedral structure in the former case and a square-planar one in the latter case.

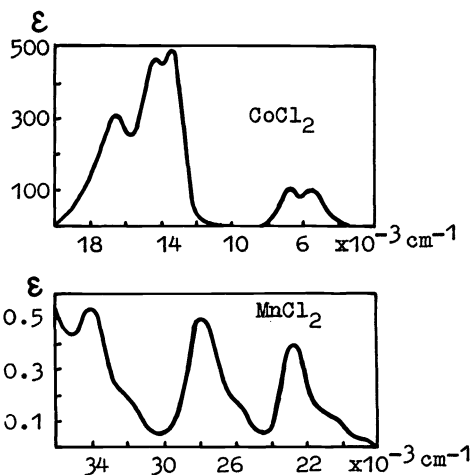


Fig. 4. Electronic absorption spectra of $CoCl_2$ and $MnCl_2$ melts at $700^\circ C$

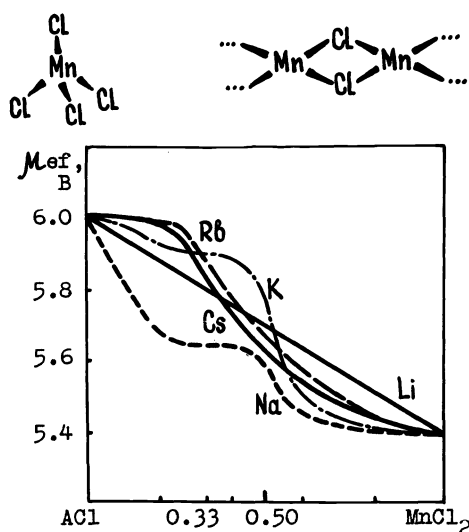
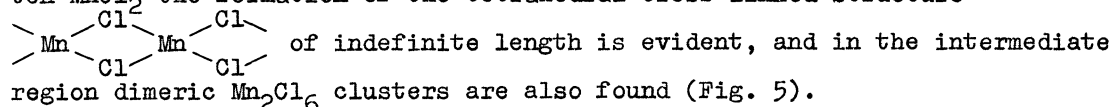


Fig. 5. Magnetic susceptibility of molten salt systems $MnCl_2-ACl$ ($A = Li, Na, K, Rb, Cs$)

This is also substantiated by the magnetic susceptibility studies of molten salt systems $MnCl_2-ACl$ ($A = Li, Na, K, Rb, Cs$): whereas in the dilute $MnCl_2$ solution region the complex ion $MnCl_4^{2-}$ is detected, in the individual molten $MnCl_2$ the formation of the tetrahedral cross-linked structure



Thus, even if these clusters show features of a complex compound such as coordination phenomenon and complex composition in these systems and concentration ranges, they cannot be treated as isolated complex ions of a definite composition. Hence it is difficult in principle to extend to them a parameter that is obligatory for a complex: dissociation constant or lifetime, or another equivalent but also constant parameter. As was seen from the figures, none of the parameters in this concentration region: magnetic susceptibility, extinction coefficient and EAS band half-width, Raman frequency, thermodynamic activity is constant, and the notion of thermodynamic and kinetic constants becomes meaningless for such multinuclear homonuclear cluster groups.

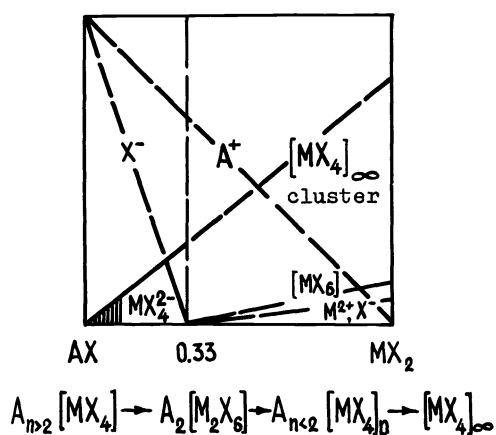


Fig. 6. Complex-cluster structural model of molten salt systems with complex formation

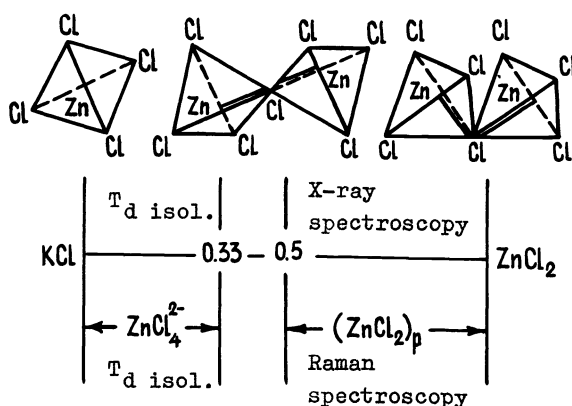


Fig. 7. X-ray diffraction and Raman spectral studies of $ZnCl_2$ -KCl melts

It was on the basis of spectroscopic, magnetic, diffraction and thermodynamic (ref. 4) investigations of molten salt systems with complex formation that we proposed in 1974 a complex-cluster structural model for such melts (Fig. 6). This model is based on the analysis of equilibrium properties and stems from the concepts of preferential dominant structural groups for each specific composition region.

The region $0 < X_{MX} \leq 0.1$ is regarded as containing, in addition to uncoordinated X^- anions and A^+ cations, discrete, in a first approximation, maximally coordinatively saturated complex anions MX_m^{n-} which are not distorted by the spherical fields of outer-sphere A^+ cations.

In the region $0.1 \leq X_{MX} \leq 0.33$ (with MX_4^{2-} complexes) the conditions of complete isolation of complexes one from another by the sufficiently spherical field of outer-sphere A^+ cations are no longer met as complex concentration increases, and already distorted, essentially discrete (again in a first approximation) complex anions are observed.

The structural model for melts in the region $0.33 \leq X_{MX} < 1$ stems from the concepts of formation of clusters preferential for these conditions, which become gradually homonuclear with the same maximal coordinative saturation of the cell $[MX_m]$ due to bridging Xs.

Later studies, e.g., of Øye and coworkers, on IR and Raman spectroscopy and of Blander on the molecular dynamics of the molten salt system $AlCl_3$ - $AlCl$ (1983) substantiated the complex-cluster structural model and showed that only a single complex, $AlCl_4^-$, is detected in this system up to the component ratio 1:1, and at $X_{AlCl_3} > 0.5$ $Al_2Cl_7^-$, $Al_3Cl_{10}^-$ a.o. are such clusters.

Nakamura and coworkers (1983) also confirmed by X-ray examination and Raman methods that in the system $ZnCl_2$ -KCl only the isolated tetrahedral $ZnCl_4^{2-}$ anion is detected up to $X_{ZnCl_2} = 0.33$, and at higher concentrations the $Zn_2Cl_7^{3-}$ dimer with linear-bridge chlorine is detected, which regenerates into the polymeric structure of individual zinc chloride with the same fragment $Zn_2Cl_7^{3-}$ but with an angular position of the Zn-Cl-Zn bond (Fig.7). Thus, the complex-cluster structural model for molten salt systems is unambiguously substantiated experimentally.

However, the main conclusion of this part of the paper is, in addition to it, the fact that along with the cluster formation region in the molten salt systems under discussion there is a discrete complex formation region, which has thermodynamic and kinetic constants.

II. DISCRETE COMPLEX ION IN MELTS AS BINUCLEAR HETERONUCLEAR SYSTEM

It would seem that having established the conditions and boundaries of existence of discrete complex ions, we can now apply to them the whole arsenal of current theoretical and experimental relations. Unfortunately, it is not quite so or rather not so at all.

It is sufficient to simply compare, e.g., the instability constants of complex ions in melts and in aqueous solutions (Table 1), to make sure that their thermodynamic stability characteristics are different. Although these data are not absolute and bear a relative information on overall competitive recomplexation or so-called primary resolution processes: about nitrate (chloride[⊗]) complexes in melts and about aqua complexes in water, some conclusions can be drawn from Table 1. The first conclusion is obvious. The stability of bromide, iodide, cyanide and ammonia complexes is, in most cases, higher than that of analogous complexes in nitrate melts (some chloride complexes are an exception?). From this it becomes understandable that the aqua complexes of the metals listed in Table 1 would seem to be less stable than their nitrate complexes, and the absence of the latter from aqueous solutions may be due to the mass action law.

This conclusion would be faultless if the data of Table 1 were reduced to a unique ionic strength value of the solution. It is in this, however, that the main reason of their disagreement lies: the instability constants of complex ions in aqueous solutions were obtained at ionic strength values of 0.5-5 (maximum), whereas in melts they were obtained at ~ 20 and up. But an increase even of unity (unities) in the ionic strength of a solution can decrease the stability constant of a complex by an order(s) of magnitude. It is in this fact that the second conclusion consists: the main reason of such a disagreement of complex ion instability constants in these different media lies in the competitive action of the "bare" background ions of the molten medium on the characteristics of the complex ion as compared with the milder action of solvated background ions in aqueous and nonaqueous solutions.

For the same reason, in the chemistry of molten salts (and crystals) the specific action of each background cation form should be taken into account unlike the chemistry of complex compounds in solutions, which operates with the overall macroproperty of many ions - ionic strength. To visualize this statement, Fig. 8 shows the vibrational Raman $\nu_1(A_1)$ frequency values of

TABLE 1. Some instability constants of complex ions in nitrate, chloride[⊗] melts and aqueous solutions (ref. 1 & 4)

Complex ion	in melt	in water	Complex ion	in melt	in water
CeF^{2+}	$4-7.75 \times 10^{-3}$	6.3×10^{-4}	AgBr_2^-	$3.2-7.2 \times 10^{-3}$	7.8×10^{-8}
LaF^{2+}	$2.7-4.2 \times 10^{-3}$	1.7×10^{-3}	AgBr_3^{2-}	1.7×10^{-5}	1.3×10^{-9}
$\text{VO}_2\text{F}_4^{2-}$	3.23×10^{-9}	1.4×10^{-12}	CdBr_4^{2-}	1×10^{-2}	2×10^{-4}
AgCl_2^-	$2.1 \times 10^{-3}-6 \times 10^{-4}$	1.7×10^{-5}	PbBr_2	$2.8-4 \times 10^{-2}$	1.2×10^{-2}
PbCl^+	$1.6-4 \times 10^{-3}$	2.3×10^{-2}	ZnBr^+	0.04	4
PbCl_3^-	$1.4-5.5 \times 10^{-2}$	1.4×10^{-2}	AgI_3^{2-}	4.3×10^{-8}	1.4×10^{-14}
ZnCl^+	$2.8-7.3 \times 10^{-4}$	0.19	CdI_4^{2-}	8×10^{-9}	8.3×10^{-7}
CdCl_3^-	$4-6 \times 10^{-5}$	3.4×10^{-3}	AgNH_3^+	$1 \times 10^{-3}-6 \times 10^{-4}$	6.3×10^{-4}
CdCl_4^{2-}	1.5×10^{-6}	9.3×10^{-3}	$\text{Ag}(\text{NH}_3)_2^+$	2.17×10^{-7}	9.3×10^{-8}
CuSO_4	0.37	0.112-0.42	$\text{Ag}(\text{CN})_2^-$	1.34×10^{-11}	8×10^{-22}

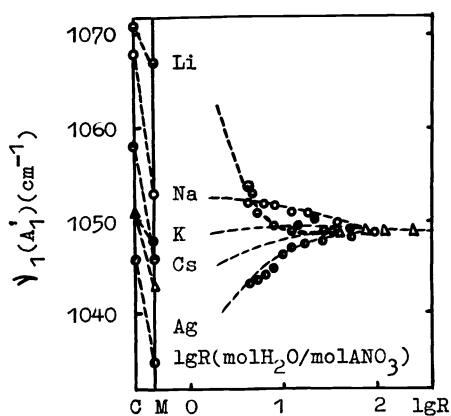


Fig. 8. NO_3^- Raman frequency $\nu_1(A_1')$ in crystals, melts and aqueous ANO_3 solution (A = Li, Na, K, Rb, Cs) as a function of cation

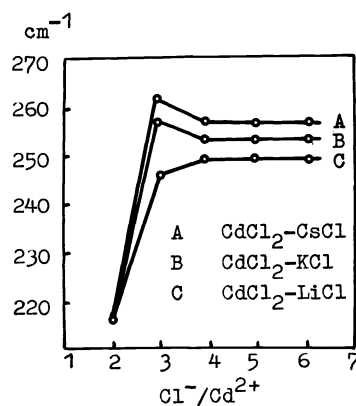


Fig. 9. Dependence of Cd-Cl stretching frequency on $\text{Cl}^-/\text{Cd}^{2+}$ ratio for a number of molten mixtures

the N-O bond in nitrate ion in crystals, melts and aqueous solutions of alkali nitrates (as a function of dilution). The hydrated NO_3^- in water exhibits, independent of salt, an N-O bond vibrational frequency (A_1') of 1048 cm^{-1} which is common for all solutions, whereas in solutions these frequencies are different and are 1067 cm^{-1} for LiNO_3 , 1053 cm^{-1} for NaNO_3 , 1048 cm^{-1} for KNO_3 , 1045 cm^{-1} for RbNO_3 and 1043 cm^{-1} for CsNO_3 .

A similar relation is also observed when analysing literature data: vibrational Raman frequencies (A_1) of the $\text{Cd}^{2+}-\text{Cl}^-$ bond in the CdCl_4^{2-} complex (Fig. 9). At high $\text{Cl}^-/\text{Cd}^{2+}$ ratios (≥ 4) the complex ion CdCl_4^{2-} always remains, as was pointed out previously, individual and stoichiometric, and its characteristics remain constant in each individual molten system. At the same time, when passing from the system $\text{CdCl}_2-\text{CsCl}$ to the systems CdCl_2-KCl and $\text{CdCl}_2-\text{LiCl}$, a change in the frequency characteristics of the $\text{Cd}^{2+}-\text{Cl}^-$ bond is clearly observed.

Thus, the experimental data presented show a direct interaction between complex anions and outer-sphere cations as compared with aqueous and non-aqueous solutions.

Let us now try to clearly demonstrate that such an interaction is determined by the variation of the degree of metal-ligand bond covalence under the influence of the outer-sphere cations of the melt. To do this, let us discuss the electronic absorption spectrum of the CoCl_4^{2-} complex in various media: $\text{HCl}-\text{H}_2\text{O}$ solution, ANO_3-ACl and ACl melts (A = Li, Na, K, Rb, Cs) (Fig. 10). If the Ballhausen and Liehr theory, which relates transition os-

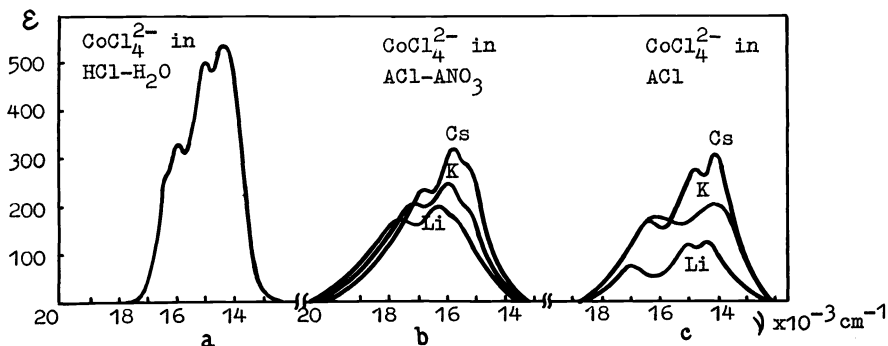


Fig. 10. Electronic absorption spectra of the CoCl_4^{2-} complex in $\text{HCl}-\text{H}_2\text{O}$ (a); $\text{ACl}-\text{ANO}_3$ (b); and ACl (c) (A = Li, Na, K, Rb, Cs)

cillator strength (f) to the overlap of metal 3d-orbitals and ligand orbitals, is applied to the intensity of EAS bands for complex ions in melts, the dependence of oscillator strength on the degree of metal-ligand bond covalence as a function of outer-sphere cation is clearly seen from the known equation:

$$f = \frac{1 - \alpha^2}{1 - 2S\alpha(1 - \alpha^2)^{0.5}} 16.32 \times 10^{11} \text{ A}^2 \quad (S = \text{overlap integral, } A = \text{ligand-ligand interaction integral}).$$

It is maximal for the CoCl_4^{2-} complex in the aqueous solution of HCl, where we have to do with completely hydrated ions: both complex and background ones, occupies an intermediate position in $\text{ANO}_3\text{-ACl}$ melts owing to the partial solvation of outer-sphere cations by a large number of ANO_3 solvent melt ions and is minimal in ACl melts due to the direct interaction of outer-sphere cations with the CoCl_4^{2-} complex. It is evident that the degree of interaction, i.e. the covalency of the bond between CoCl_4^{2-} complex and outer-sphere cations increases in the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$. (It is interesting to point out here the rather important fact that the proton in the system $\text{HCl-H}_2\text{O}$ does not act as the outer-sphere A^+ cation of the CoCl_4^{2-} complex but belongs to dynamic water-structure of hydroxonium ions.)

Thus, although the molten salt systems under discussion show a complex formation region, it is more correct to regard the existing complex anions as quasi-heteronuclear, quasi-binuclear systems of the type $\text{A}_n[\text{MX}_m]$. The parameters of these complex species in melts differ from the characteristics of analogous species in aqueous and nonaqueous solutions because of the direct interaction between complexes and outer-sphere cations competing "for ligand", due to which the existing theoretical and experimental relations for normal complexes cannot be simply extended to them. Therefore, the necessity arises to develop theories of structure, electronic, vibrational and radio-spectral transitions for such coordination systems in molten salts.

III. STRUCTURE AND SPECTROSCOPIC RADIATIVE TRANSITIONS OF COORDINATION COMPOUNDS IN MOLTEN SALTS

The aim of this section of the paper is to briefly describe the main theses of the quantum chemistry of condensed coordination systems which are developed by us for complexes in molten salts. Let us discuss here such properties as radiative quantum transitions: electronic, vibrational, electronic and nuclear spin transitions as a function of the composition and structure (symmetry of such a quasi-binuclear complex (ref. 2)).

1. Electronic structure of d-metal coordination compounds and spectra of electronic transitions in molten salts (ref. 5)

As is seen from Fig. 10, the electronic absorption spectra (frequencies and intensities) of the CoCl_4^{2-} complex in molten salts undergo regular changes depending on outer-sphere cations. Table 2 summarizes, for greater clearness, the EAS parameters (transition energies, assignment of absorption bands, their intensities) and the electronic structure parameters (parameter of crystal field theory (CFT), $10 Dq$, nephelauxetic parameter, β , reflecting bond ionicity) of the MnCl_4^{2-} complex in binary MnCl_2 (1 M)-ACl melts ($A = \text{Li, Na, K, Rb, Cs}$). It is evident that the parameter $10 Dq$ and the ionicity β of the MnCl_4^{2-} complex decrease regularly when passing from the outer-sphere cation Li^+ to Cs^+ .

We have developed a quantum-chemical theory of the effect of the outer-sphere environment of complexes in molten salts on their electronic structure and spectral characteristics in terms of CFT as well as ICAO and ICMO (ref. 2). The problem of the effect of outer-sphere cations on the electronic terms of d-metal complexes in terms of CFT was solved by superimposing the corresponding fields of the next cation-coordination-sphere on the known fields of complexes. For example, Fig. 11 shows the splitting of the atomic term 2D in the octahedral (A) and tetrahedral (B) ligand fields with allowance for the surrounding of these complexes by cations of different exter-

TABLE 2. Effect of outer-sphere alkali metal cations on the electronic structure parameters of the complex MnCl_4^{2-} ion in molten alkali chlorides

Outer-sphere cation	Observed transitions from the 6A_1 level (cm $^{-1}$)					$\epsilon_{\text{rel.}}$	10Dq (cm $^{-1}$)	β
	${}^4T_1(G) \leftarrow {}^4T_2(G)$	4A_1	${}^4E(D) \leftarrow {}^4T_2(D)$	${}^4E(D)$				
Li $^+$	20100	21800	23200	25850	27800	0.37	5000	0.715
Na $^+$	19800	21600	22700	26000	27500	0.41	4870	0.735
K $^+$	19600	21000	22600	25850	27600	0.42	4730	0.725
Rb $^+$	19500	20800	22400	25600	27500	0.45	4630	0.720
Cs $^+$	19400	20600	22400	25700	27700	0.47	4350	0.710

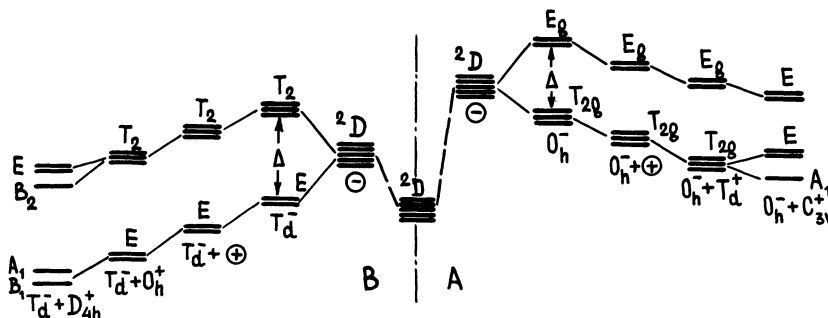


Fig. 11. Splitting of the atomic term 2D in octahedral (A) and tetrahedral (B) ligand-fields with allowance for outer-sphere environment

nal symmetry: tetrahedral and lower one (C_{3v}) in the former case and octahedral and lower one (D_{4h}) in the latter case.

If we now consider only fields of high cubic symmetry, we can write the following expressions for the overall parameter $10 Dq$ (Δ) in the inner-complex (Δ)/outer-sphere environment (Δ') fields:

$$\begin{aligned} \sum \Delta_{\text{oct/tetr(cub)}} &= \Delta_{\text{oct}} \pm \Delta'_{\text{tetr(cub)}}; & \sum \Delta_{\text{oct/oct}} &= \Delta_{\text{oct}} \mp \Delta'_{\text{oct}}; \\ \sum \Delta_{\text{tetr(cub)/oct}} &= \Delta_{\text{tetr(cub)}} \pm \Delta'_{\text{oct}}; & \sum \Delta_{\text{tetr/tetr}} &= \Delta_{\text{tetr}} \mp \Delta'_{\text{tetr}} \end{aligned}$$

The subscripts "oct", "tetr", "cub" here denote octahedral, tetrahedral, cubic fields; the order of writing them corresponds to the order of superimposing the internal and external fields on the central metal ion; the signs (+) and (-) correspond to superimposing cations and anions respectively.

Thus, the term splitting rules for d-metals in complexes in crystals (strictly) and in melts (less strictly) are (due to the less definite symmetry of the outer-sphere environment): the combination of the tetrahedral and cubic fields of the first inner sphere and the octahedral field of outer-sphere cations (and possibly anions) as well as the combination of the octahedral field of the first sphere and the tetrahedral and cubic fields of the second sphere of cations (or anions) increase (decrease for anions) the splitting parameter $10 Dq$ (Δ), and the combination of fields of the same symmetry (tetrahedron/tetrahedron, octahedron/octahedron) decreases this parameter with outer-sphere cations and increases it with anions. In the outer-sphere ion series Li $^+$, Na $^+$, K $^+$, Rb $^+$, Cs $^+$ or F $^-$, Cl $^-$, Br $^-$, I $^-$ these effects become weaker with increasing distance to the outer-sphere ion, which is observed in the experiment (Fig. 10, Table 2).

Due to the limitations of CFT, which does not take into account the overlap of the orbitals of the central metal ion and ligands (as well as outer-sphere cations), the variation of metal-ligand bond covalency under the influence of the outer-sphere cation and other characteristics are not estimable in this theory.

TABLE 3. CFT parameter $10 Dq$ (Δ in the ligand field theory) and bond ionicity β of some complex ions in molten alkali chlorides as a function of outer-sphere alkali metal cations

Outer-sphere cation	$10 Dq$ (Δ) (cm^{-1})			$\beta = B/B_0$		
	MnCl_4^{2-}	CoCl_4^{2-}	NiCl_4^{2-}	MnCl_4^{2-}	CoCl_4^{2-}	NiCl_4^{2-}
Li^+	5000	4100	-	0.74	0.70	-
Na^+	4870	3900	4350	0.73	0.69	0.78
K^+	4730	3700	4200	0.72	0.69	0.77
Rb^+	4630	3500	4100	0.72	0.68	0.76
Cs^+	4350	3250	4000	0.71	0.67	0.74

The most general approach to take into account all the parameters of electronic complex ion structure in molten salts is the MO method: for calculating the inner complex anion in terms of LCAO and for calculating the whole cluster together with outer-sphere cations in terms of LCMO. To this end, let us define the cluster MOs (Ψ_i) through the complex MOs (Φ_i) and the group orbitals of outer-sphere ions (ϕ_i) with corresponding coefficients: $\Psi_i = a_1 \phi_i + a_2 \Phi_i$. Here ϕ_i for d-metal complex may be e- or t_2 -orbitals and Φ_i atomic group orbitals, e.g., of S type for alkali metals. In the outer-sphere cation series Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ the a_1 coefficient tends to 1 and the a_2 coefficient, which is related to a_1 by the expression $a_1 = -a_2 S + [1 - a_2^2 (1 - S^2)]^{1/2}$ and reflects the degree of covalence, tends to 0, which reflects an enhancement of bond covalency in the inner complex and a weakening of the complex anion-outer-sphere cations bond and is convincingly substantiated experimentally (Table 3).

The covalency parameter $(1 - \beta)$ increases in this series for the MnCl_4^{2-} , CoCl_4^{2-} and NiCl_4^{2-} complexes, whereas the Δ ($10 Dq$) parameter decreases.

General expression for $\sum \Delta$ in terms of the LCMO method (ref. 2) may be written as $\sum \Delta = \Delta_I + \Delta_E - \Delta_{T_2} + \delta_{T_2} - \delta_E$, where Δ_I is the splitting parameter in the first sphere of the environment, Δ_E and Δ_{T_2} are the stabilization of electron energy on the corresponding complex-orbital in the external field, δ_E and δ_{T_2} are binding effects.

Thus, with allowance for intensity discussed in the previous section all the EAS and structure parameters of complex quasi-binuclear ions in melts have been unambiguously explained and predicted theoretically in terms of the cluster approach.

2. Vibrational (IR and Raman) spectra of coordination compounds in molten salts

The experimental data on the vibrational spectra of coordination compounds in molten salts (ref. 5) indicate the vibrational frequencies of metal-ligand bonds (the data on their force constants in melts are scarce) to depend not only on the type of the central atom, its oxidation state, other characteristics and ligand nature but also (under otherwise equal conditions) on the outer-sphere environment (Table 4). The vibrational frequencies of metal (or element)-ligand bonds in a complex ion are, as a rule, higher than with the outer-sphere partner Li^+ and decrease toward the outer-sphere Cs^+ . However, taking into account the redistribution of electron density between the inner complex and the vacant orbitals of outer-sphere cations (maximal for Li^+ and minimal for Cs^+), an opposite dependence should be expected. What is the reason of this?

The theoretical analysis of bond force constants strictly as a function of electron density, ρ , which varies due to outer-sphere cation parameters, gives no unambiguous answer, demonstrating both a similar and an opposite and extreme dependence (ref. 2). To account for the stubborn experimental facts, one has to include in the discussion other theoretical possibilities: contribution of outer-sphere cations to the kinematic constants of vibrational frequencies of just quasi-binuclear cluster species $A_n[\text{MX}_m]$ but,

TABLE 4. Some Raman and IR frequencies of complex species in melts as a function of outer-sphere alkali metal cations

Outer-sphere cation	Raman and IR frequencies (cm ⁻¹)									
	NO ₃ ⁻	NO ₂ ⁻	ClO ₄ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	VO ₂ Cl ₄ ²⁻	CdCl ₄ ²⁻	ZnCl ₄ ²⁻	AlCl ₄ ⁻	InCl ₄ ⁻
Li ⁺	1064-1050	1353	960	1072-1064	988	-	250	320-290	498	315
Na ⁺	1053-1048	1348	946	1050-1031	965	929	256	-	490	-
K ⁺	1047-1045	1338	937	1040-1025	955	925	258	290-280	487	320
Rb ⁺	1046-1041	1323	936	1020	943	-	-	283-280	-	-
Cs ⁺	1043-1039	1310	935	-	-	924	-	276	483	322

above all, contribution of electronic excitations to the force constants of vibrational frequencies of the complex itself. We showed in ref. 2 that vibrational frequencies (ω_d) may be described by the expression:

$\omega_d = (K_{dd}/t_{dd})^{1/2} \approx (K_{dd}/M_d)^{1/2}$, which resembles the formula for the vibrational frequency of a two-atom molecule. Here K_{dd} and t_{dd} are the force and kinematic constants, M_d is the group mass. The dependence of frequency on the kinematic constants t_{dd} is evident: the kinematic constants increase and hence the frequencies decrease with increasing group mass M_d of the atoms involved in a particular vibration.

Another objective is to elucidate the question of variation of K_{dd} constants in the symmetry coordinates by coordination cluster composition variation involving outer-sphere cations. On the basis of expanding the electronic Hamiltonian $\hat{H}(r, q)$ into a series up to the second order of the perturbation theory, an expression can be obtained for metal-ligand bond force

constant (ref. 2): $K_{dd} = (\partial^2 v_{nn} / \partial Q_d^2)_0 + [(\partial^2 v_{en} / \partial Q_d^2)]_{00} - 2 \sum_m [(\partial v_{en} / \partial Q_d)_0]_{om}^2 / (E_m^0 - E_0^0)$ that depends on the energy of electronic excitations ($E_m^0 - E_0^0$), which were discussed in the previous section. Due to a decrease in $\Delta \approx E_m^0 - E_0^0$ quantity in the outer-sphere cation series $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ under otherwise equal conditions, the K_{dd} values must decrease (like frequency values) because of an increase in the negative value of the third summand in the expression for K_{dd} . The available scanty data on the bond force constants of the complex ions MoO_4^{2-} , WO_4^{2-} , CrO_4^{2-} , PO_4^{3-} , SO_4^{2-} , CO_3^{2-} in the NaCl, KCl, RbCl, CsCl melts at 855 °C confirm fully this theoretical analysis:

	NaCl	KCl	RbCl	CsCl
SO ₄ ²⁻	7.63	7.4	7.34	7.31
CO ₃ ²⁻	7.89	7.72	7.67	7.61, mdyne/Å ⁰

The same is evidenced by the data listed in Table 4 on the vibrational frequencies of bonds in complex ions as a function of background cation.

The problem of elucidating the dependence of the vibrational spectra intensities of complex ions in molten salts on outer-sphere cations is of no less interest. The experimental data on this question have just begun to be collected and even then mainly in the form of relative IR band and Raman line intensities (Table 5) which have no clear quantitative basis.

Of much greater value may be theoretical relations having a predicting character, one of which is the proposed formula for the dependence of the IR band intensity (absorption coefficient) of a cluster in a condensed

TABLE 5. Relative intensity of some IR and Raman frequencies of complex species in melts as a function of alkali metal outer-sphere cations

Outer-sphere cation	Relative intensity of IR and Raman frequencies					
	in IR spectra				in Raman spectra	
	NO ₃ ⁻	SO ₄ ²⁻	MoO ₄ ²⁻	ClO ₃ ⁻	NO ₃ ⁻	AlCl ₄ ⁻
Li ⁺	0.36	66	-	104.6	64	0.85
Na ⁺	0.32	66	73	107.8	63	-
K ⁺	0.33	71	78	88.9	73	0.59
Rb ⁺	-	-	-	-	-	-
Cs ⁺	-	-	-	-	-	0.60

phase (ref. 2). Since the IR band absorption coefficient \mathcal{E} is determined by the square of the derivative of dipole moment, μ , with respect to normal coordinate Q_α : $\mathcal{E} \approx (\partial \bar{\mu} / \partial Q_\alpha)_0^2$, the determinantal function of cluster can be constructed by defining the top level orbitals as inner-complex LCMO and outer-sphere cation group orbitals. As a result we obtain:

$$(\partial \bar{\mu} / \partial Q_\alpha)_0 = (\partial \bar{\mu}_0 / \partial Q_\alpha)_0 + \sum_{ikr} n_{ik} (a_{ik}^2 - 1 + a_{ik} a_{ikr} s_{ikr}) \times$$

$(\partial \langle \varphi_{ik} | \vec{r} | \varphi_{ik} \rangle / \partial Q_\alpha)_0$. Due to the fact that in the case of maximally ionic interaction of the inner complex with the outer-sphere cation Cs⁺ a_{ik} tends to 1 and the product $(a_{ik} a_{ikr})$ to 0, and in the case of maximally covalent bond between the inner complex and the outer-sphere cation Li⁺ $a_{ik}^2 = (a_{ik} a_{ikr}) \rightarrow 1/\sqrt{2}$, the absorption coefficient \mathcal{E} must decrease with increasing degree of covalence of the complex-outer sphere cation bond in the order Cs⁺...Li⁺, which is observed experimentally in a number of instances (Table 5).

3. ESR spectra of coordination compounds in molten salts (ref. 5)

From the equation for the g-factor (ref. 2):

$$g_{\alpha\beta} = g_{Se} (\delta_{\alpha\beta} - \lambda \sum_{n \neq 0} \langle \psi_0 | \hat{1}_{\alpha\alpha} | \psi_n \rangle \langle \psi_n | \hat{1}_{\beta\beta} | \psi_0 \rangle / (E_n - E_0))$$

where $(E_n - E_0)$ may be approximately replaced by the difference $(\mathcal{E}_n - \mathcal{E}_0)$ of one-electron levels, which correspond to the MOs ψ_0 and ψ_n in the products of ground and excited states, a dependence of the g-factor on the degree of electron delocalization (degree of bond covalence) and on electronic-excitation energy $(\mathcal{E}_n - \mathcal{E}_0)$ is seen.

In terms of the problem under discussion, the effect of the outer-sphere cations Li⁺...Cs⁺ on the g-factor of metal clusters reduces itself to the allowance for the delocalization of inner-complex electrons to these cations. To this end, one must also consider (as MOs of the cluster) φ_i , MOs of the complex, and Φ_i , group orbitals of these cations, whose contributions should be taken with the sign (+) due to the bonding character of the MOs of the whole cluster. Since the covalency of this bond decreases in the order Li⁺...Cs⁺, this must cause an increase in g-factor values for dⁿ < 5 metal clusters, i.e. with d-electron shell filled less than to a half ($\lambda > 0$), and a decrease for dⁿ > 5 metal clusters ($\lambda < 0$). However, this would be only the case if $(\mathcal{E}_n - \mathcal{E}_0) = \text{const}$.

But the fact is, as is shown in section III,1, that the value of $(\mathcal{E}_n - \mathcal{E}_0) \approx 10 Dq \neq \text{const}$ decreases also for d-metal clusters in the outer-sphere cation series Li⁺...Cs⁺ (or Mg²⁺...Ba²⁺). The fact that this quantity appears in the denominator of the second negative term of the equation leads to

a g-factor decrease in this order for $d^n < 5$ metals ($\lambda > 0$) and to an increase for $d^n > 5$ metals ($\lambda < 0$). It is owing to this that the experimental g-factor values for 3d-metal clusters in crystals confirm this relation (ref. 2):

	MgO	CaO	SrO		LiCl	NaCl	KCl	CsCl
v^{2+}	1.98	1.968	1.959	Cu^{2+}	2.178	2.16	2.18	2.217
Cr^{3+}	1.978	1.973	-		2.039	2.07	-	2.013
Ni^{2+}	2.215	2.327	-			2.06		

Unfortunately, there are no data on such g-factor relations for clusters in molten salts, and to confirm the effect of outer-sphere cations on the parameters of their ESR spectra, we can only cite line-width (ΔH) measurement data for manganese(II) ESR spectra in the octahedral clusters of the following molten fluorides:

	MnF_2	$KMnF_3$	$RbMnF_3$	$CsMnF_3$
$\Delta H_{T_{melt.}}$, Gs	205	180	150	110
$\delta \Delta H / \delta T$, mGs/K		-180...-50	-150...-70	-110

The signal (line-width) narrowing is due to a decrease in the dipole-dipole interaction of $A_n[MnF_6]$ clusters in melts when passing from systems with the K^+ cation just in the second coordination sphere to systems with large Cs^+ and Rb^+ cations that are more ionically bonded to complexes.

The magnetic susceptibility measurements of molten salt systems $MnCl_2-ACl$ ($A = Li, Na, K, Rb, Cs$) bear indirectly an analogous information. If the magnetic criterion of Pauling bond type is used, it is seen from Fig. 5 that an obvious decrease in $MnCl_4^{2-}$ complex paramagnetism is observed in the case of molten systems with the outer-sphere cations Li^+, Na^+, K^+ but not with Rb^+, Cs^+ , which results just from complex-outer sphere cation bonds being more covalent in the former case than in the latter.

4. NMR spectra of ionic associates in molten salts (ref. 5)

Whereas in dilute aqueous solutions there is, as a rule, no variation of the chemical shift of the NMR spectrum of atomic nuclei with $I \neq 0$ by the replacement of the background cations of the medium, such a relation is evident in molten salt systems (Fig. 12). It is due just to a variation of the covalency of the bond, e.g., $^{205}Tl-X$ ($X = Cl, Br, I$), under the influence of melt cations A^+ ($Li^+ \dots Cs^+$), whose X^-A^+ bond covalency varies, in its turn, contrary to the first relation (Fig. 12a). The order of ^{205}Tl chemical shifts: $Cl^- < Br^- < I^-$ indicates a variation just of the covalent bond component and not of polarization.

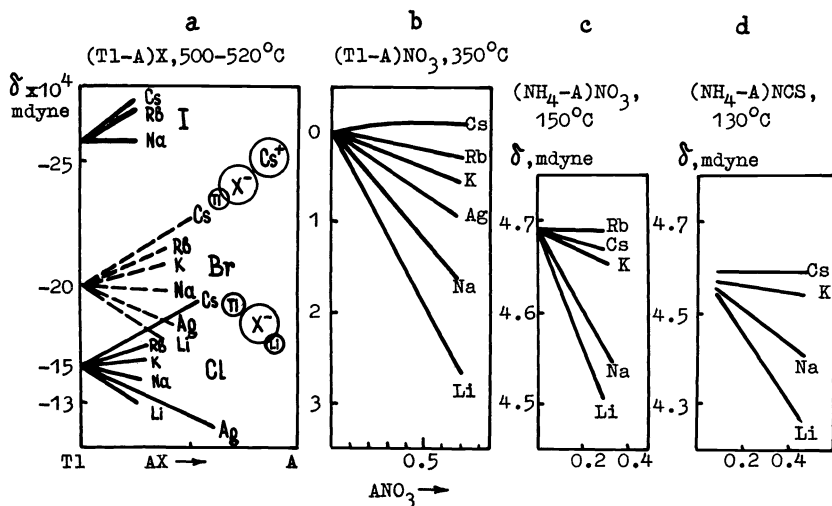


Fig. 12. ^{205}Tl and 1H chemical shifts in molten salt systems as a function of background cations

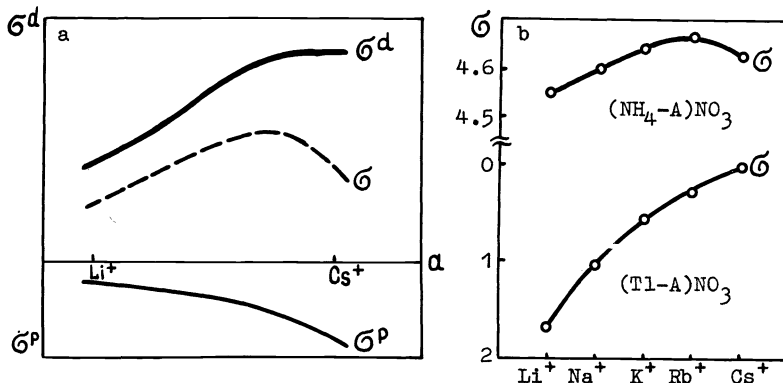


Fig. 13. Theoretical (a) and experimental (b) chemical shift - background melt-cation relations

The quantum-chemical interpretation of chemical shift (magnetic shielding of nuclei) relations in such systems as a function of melt background ions is more complicated due to the necessity to take into account their effect on both the diamagnetic (σ^d) and paramagnetic (σ^p) components of overall shift (σ). In the general form, one must also take into account the delocalization of electron density from the upper MOs ψ_i of covalently bonded associate groups to the group orbitals ϕ_i of competitive background partners - melt cations A^+ , composed of vacant outer orbitals, leading to cluster MOs of the form: $\psi_i = a_{ik} \phi_{ik} + \sum_k a_{ik'} \phi_{ik'}$. Thus, as was shown in ref. 2, the overall chemical shift is expressed by the general formula:

$$\sigma = \sigma^d + \sigma^p = 1/2 \int \psi_i \frac{1}{r_I^3} \psi_i dv - 1/(E_n - E_0) \int \psi_i \times \sum_{kk'} L_k L_{k'} / r_I^3 \psi_i dv.$$

It follows from this that both the diamagnetic and paramagnetic (in magnitude) shielding-components increase with decreasing degree of associate-competitive cation bond covalence in the order Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ (these components approach limiting values in the case of purely ionic interaction).

In the order $\text{Li}^+ \dots \text{Cs}^+$, the paramagnetic shielding-component must increase not only due to a decrease in the degree of associate-competitive cation bond covalence but also as a result of a decrease in electronic-excitation energies ($E_n - E_0$) in the same order (section III, 1).

Thus, the overall shielding $\sigma = \sigma^d + \sigma^p$ in the background melt-cation series from Li^+ to Cs^+ may increase, assume extreme values and even decrease depending on the ratio of diamagnetic and paramagnetic (in magnitude) shielding component increase rates (Fig. 13a). The analysis of the experimental data shown in Fig. 12 (Fig. 13b) confirms unambiguously just such theoretical relations as were derived by us.

Thus, we would have liked to attract, by this paper, investigators' attention to the fact that the quantum-chemical concept of cluster approximation is promising for the theoretical description of the spectra and structure of molten salt systems with complex formation and, above all, for the prediction of intercorrelation between the structure and properties of such condensed coordination systems.

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