Chem. Soc. Rev., 1990, **19**, 21–28

Chemical Reactions in Molten Salts and their Classification

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1 Introduction

Intense interest in molten salt systems as reaction media is a result of several characteristic properties of these systems, including (a) the ability to dissolve many inorganic and organic compounds, attaining high concentrations of reagents, (b) the possibility to support oxidation states of ions not readily obtained in conventional solutions, (c) complete elimination of water as solvent and reagent, (d) fast chemical reaction rates owing to high temperature. Other characteristics include the possibility to enhance processes through the higher mass transfer, thermal conductivity, and heat emission coefficients of melts, their relatively low viscosity and density and, as a rule, easy separation of reaction products from the reaction medium and hence high yields.

It is from the standpoint of chemical synthesis that we shall review chemical reactions in molten salts to offer a general classification of these reactions and examine their characteristic features.

Several attempts at classification have been made previously. For instance, Sundermeyer[1] classifies the chemical reactions for the synthesis of *organic* substances into reactions in which the melt acts as catalyst, as simple solvent, and as precipitation reagent. Kerridge[2] distinguishes reactions of organic compounds along with exchange reactions, coordination equilibria, and redox reactions.

2 Classification and Definitions of Chemical Reactions

Chemical reactions can, in our opinion, be divided into three *main* types: acid–base-type reactions, redox reactions, and solvation reactions. All other chemical reactions fall in whole or in part into these three classes. Acid–base-type reactions include as particular cases: acid–base reactions proper (with solvolysis–hydrolysis reactions that are their reverse), exchange and complexation reactions. Redox reactions include autoxidation–autoreduction reactions, in particular disproportionation reactions. Autosolvation reactions (*i.e.* association reactions) are particular cases of solvation reactions. This classification marks out the basic reactions. Chemical reality is both wider and more diverse, *e.g.* charge-transfer complex formation reactions combine the features of complexation, redox, and solvation reactions.

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[1] W. Sundermeyer, *Z. Anorg. Allg. Chem.*, 1961, **313**, 290.

[2] D. H. Kerridge, *Pure Appl. Chem.*, 1975, **41**, 355.

We can formulate the following distinguishing features of each type of chemical reactions and give them appropriate definitions.

Redox reactions (including *disproportionation reactions*) are in the simplest case characterized by the redistribution of one, two, or *n* consecutive electrons among the reaction components.

Solvation reactions (including *association* reactions) are characterized by the clustering of the reaction components which are themselves under the action of intercomponent interaction forces.

Exchange reactions are characterized by the redistribution of reaction component particles (atoms, ions) without considerable change in electronic, and sometimes geometric structure.

Acid–base reactions (reverse solvolysis, hydrolysis reactions) are characterized by the redistribution of the electron pairs and atoms (groups) of the reaction components provided that the number of the transferred electron pairs does not exceed the formal oxidation state of the element.

Complexation reactions are characterized by the collectivization of the electron pairs and groups (atoms) of the reaction components provided that the number of collectivized electron pairs and particles exceeds the formal oxidation state of the central complexing atom.

The following examples of mostly new chemical reactions which occur in molten salts support the proposed classification.

3 Types of Chemical Reactions in Molten Salts

A. Acid–base reactions.—The extension, by Lux, of the Lewis–Usanovich ideas of acids and bases to ionic melts allows numerous acid–base equilibria to be studied, involving nitrate, carbonate, sulphate, phosphate, chromate, molybdate, and other ions.

An example of new acid–base reactions is confirmed by the spectra (Figure 1) of the products of reactions of molten sodium methaphosphate with some bivalent 3*d* metal oxides. The polyhedra formed by the products is illustrated for both melt and glass.[3–5] As seen from the electronic absorption spectra, each 3*d* metal ion forms in the melt its most typical polyhedron: cobalt(II) forms a tetrahedron and nickel(II) mostly an octahedron. These polyhedra are also retained in the quenched vitreous state but transform into other states when the melt cools slowly down, *e.g.* T_d transforms into O_h. In the end, complex polyphosphates of the general formula $Na_{15-nz}Me^{z}_{n}P_7O_{25}$ and others are formed[6] (Scheme 1).

B. Exchange Reactions.—Exchange of SCl_4 for $SeCl_4$ and $TeCl_4$ ligands in a

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[3] S. V. Volkov, N. I. Buryak, and V. A. Bandur, *Zh. Neorg. Khim.* (*Russ. Ed.*), 1987, **32**, 2634.

[4] S. V. Volkov and N. I. Buryak, *Koord. Khim.* (*Russ. Ed.*), 1983, **9**, 803.

[5] S. V. Volkov and N. I. Buryak, *Koord. Khim.* (*Russ. Ed.*), 1977, **3**, 1860.

[6] Y. K. Delimarskii, 'Chemistry of Ionic Melts' (Russ. Ed.), Kiev, 1980, p. 327.

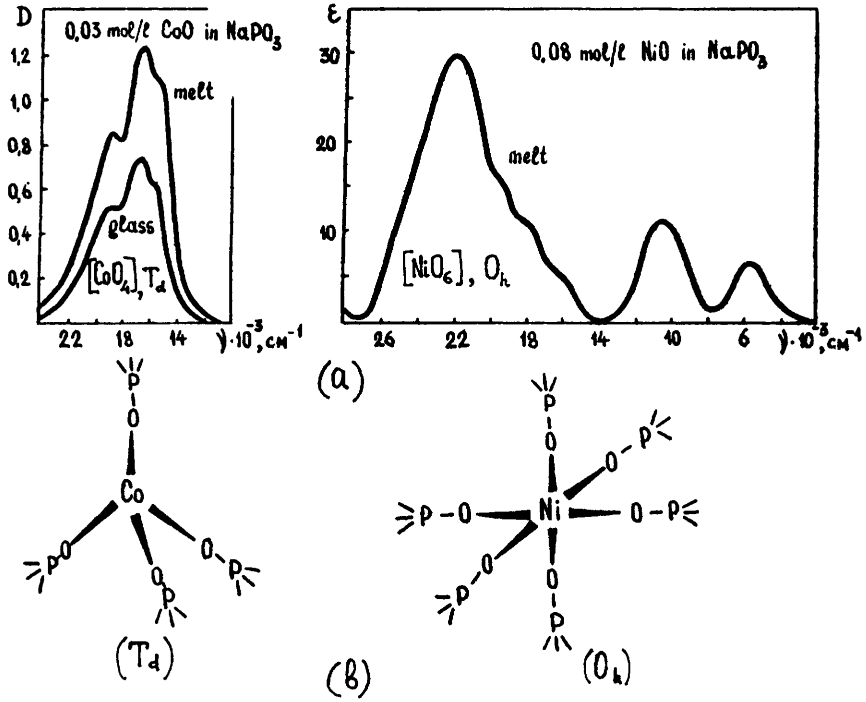

Figure 1 *Electronic absorption spectra of* CoO *and* NiO *in the* $NaPO_3$ *melt* (a), *and coordination polyhedra of* Co^{II} *and* Ni^{II} *formed in them* (b)

$$PO_3^- + MO \xrightarrow[650\,°C]{NaPO_3} PO_4^{3-} + M^{2+} \xrightarrow{NaPO_3} Na_{15-nz}M_n^{2+}P_7O_{25}$$

(M = Co, Ni, Cu)

Scheme 1

$$AuCl_3{\cdot}SCl_4 + SeCl_4 \xrightarrow[100\,°C]{SCl_2} AuCl_3{\cdot}SeCl_4 + SCl_4$$

$$OsCl_4{\cdot}(SCl_4)_2 + 2TeCl_4 \longrightarrow OsCl_4{\cdot}(TeCl_4)_2 + 2SCl_4 \quad \textit{etc.}$$

Scheme 2

molecular sulphur dichloride melt, at 100 °C, of gold and osmium coordination compounds may serve as an example of the new exchange reactions[7] (Scheme 2). The same reactions have been also studied for complexes of other platinum metals.[8]

Exchange reactions in melts for organic compounds are well established.

[7] Z. A. Fokina, V. F. Lapko, S. V. Volkov, E. M. Mashkova, and N. G. Alexandrova, *Ukr. Khim. Zh* (*Russ. Ed.*), 1985, **51**, 573.

[8] V. I. Pekhnyo, Z. A. Fokina, and S. V. Volkov, *Zh. Neorg. Khim.* (*Russ. Ed.*), 1988, **33**, 1214.

$$\mathrm{MF_{melt} + Cl_2 + CH_4 \xrightarrow{700-900\,^{\circ}C} MCl_{melt} + HCl + CH_xF_{4-x}}\ (x = 1-3)$$

$$\left(\begin{array}{l}\text{yield} \sim 92\% \\ \text{selectivity} \sim 87\%\end{array}\right)$$

$$\left\{\begin{array}{l}\mathrm{MF_{melt} + Cl_2 \longrightarrow MCl_{melt} + ClF} \\ \mathrm{ClF + CH_4 \longrightarrow CH_xF_{4-x} + HCl}\end{array}\right.$$

Scheme 3

Whereas organic fluorine derivatives are known to be produced by bubbling organochlorine compounds through fluoride melts, direct methane fluorination to chlorine-free freons is produced by bubbling methane with chlorine through fluoride salt melts.[9] The reaction is represented in Scheme 3. Formation of chlorine(I) fluoride was confirmed spectroscopically and by gas chromatography. High product yields were obtained, for example, the yield of monofluoromethane was 92% with 87% selectivity.

C. Complexation Reactions.—Complexation reactions are typical of molten salt systems and have been studied in detail. To date, practically all complexing metals of the periodic system have been investigated, and their complex formation has been established in melts with such ligands as halides, nitrate, sulphate, bisulphate, thiocyanate, cyanide, bromate, chromate, phosphate, molybdate ions and other ions, both in the solvent salt medium and in the molten salt of the ligand. A comprehensive characterization of such complexes in terms of composition, structure, stability constants, application, *etc.* is given in our book 'Coordination Chemistry of Salt Melts'.[10] Here we comment on the formation of several new complex types.

Heteronuclear complexes were first found in melts of 3*d* metal compounds by Øye and Gruen and by the present author and coworkers; by the former in $AlCl_3$-based melts[11] and by the latter in melts containing $SnCl_2$, $CsZnCl_4$, and $CsCdCl_3$.[12–14] Their formation reactions are represented as follows (Scheme 4):

$$\begin{array}{lll}\mathrm{M^{2+} + 2AlCl_7^-} & \longrightarrow & \mathrm{M(Al_2Cl_7)_2}, \text{ where M is a } 3d \text{ metal} \\ \mathrm{Mn^{2+} + 2CdCl_3^-} & \longrightarrow & \mathrm{Mn(CdCl_3)_2}, \\ \mathrm{Fe^{2+} + 2SnCl_3^-} & \longrightarrow & \mathrm{Fe(SnCl_3)_2}\end{array}$$

Scheme 4

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[9] S. V. Volkov, V. A. Bandur, and N. I. Buryak, 'Ionic Melts and their Application in Science and Technology' (Russ. Ed.), Kiev, 1984.

[10] S. V. Volkov, V. F. Grishchenko, and Y. K. Delimarskii, 'Coordination Chemistry of Salt Melts' (Russ. Ed.), Kiev, 1977, p. 331.

[11] H. A. Øye and D. M. Gruen, *Inorg. Chem.*, 1964, **3**, 836.

[12] K. B. Yatsimirskii, S. V. Volkov, I. I. Maslovska, and N. I. Buryak, *Rozch. Chim.*, 1972, **46**, 1999.

[13] S. V. Volkov and N. I. Buryak, *Zh. Neorg. Khim.* (*Russ. Ed.*), 1973, **18**, 2382.

[14] S. V. Volkov and N. I. Buryak, *Teor. Eksper. Khim.* (*Russ. Ed.*), 1974, **10**, 523.

At present, such heteronuclear complexes as $NbAlCl_8$, $Zn(AlCl_4)_2$, $Mg(AlCl_4)_2$, and some others, have been obtained in melts.

Hydrocomplexes are distinguished by the fact that the complexing agent is not an individual atom but an intermetallic cluster;[15] formation reactions for such coordination compounds may be written as shown in Scheme 5.

$$Na_3Bi + nNaOH \longrightarrow [Na_3Bi(OH)_x(NaOH)_{n-x}]^{x-} + xNa^+,$$
$$Na_3Bi + nMCl \longrightarrow [Na_3Bi(Cl)_x(MCl)_{n-x}]^{x-} + xM^+$$

Scheme 5

The presence of these complex types in the above melts produces interesting electrochemical behaviour in which the metal migrates from cathode to anode.[6,16]

The third complex ion type (Scheme 6) includes chalcogenide complexes,[15]

$$MS + nNa_2S \longrightarrow [MS_{n+1}]^{2n-} + 2nNa^+$$
$$(M = 3d\,\text{metal})$$

Scheme 6

which are produced in melts by mixing chalcogenides of different conductivity types (metallic conductivity, semiconductivity) of, say, $3d$ metals and a heteropolar sodium chalcogenide addition. In this case, we observe a suppression of the electronic conductance component and the appearance of electrode polarization and negative temperature-coefficient of conductance, *i.e.* evidence of transition to ion transfer as a result of the formation of complex ions shown in Scheme 6.[17]

Of special interest is a new type of coordination compound (Scheme 7) containing organic substances, *viz.* individual molten complexes, *e.g.* $3d$ metal β-diketonate complexes $M(\beta\text{-dik})_2$ and their adducts $Me(\beta\text{-dik})_2{\cdot}2L$, where L is CH_3CN, DMFA, DMSO, Py, Phen, which were synthesized and investigated by us for the first time in molten state.[18] ESR spectra of molten copper β-diketonate adducts pointed us to the presence of stereoisomers in melts and showed that oxygen-coordinated bases (L) yield, independent of their donor strength, with $Cu(DFG)_2$ only axial-type adducts (I); conversely nitrogen-coordinated ones (L) yield equatorial-type adducts (II). The thermal destruction of the former (Scheme 7, I) involves consecutive detachment of L from complexes and takes place at lower temperatures than with the equatorial-type adducts, which are thermally more stable. Rearrangement of the equatorial-type structure with rising temperature involves opening of the β-diketonate chelate rings. As a consequence, there is

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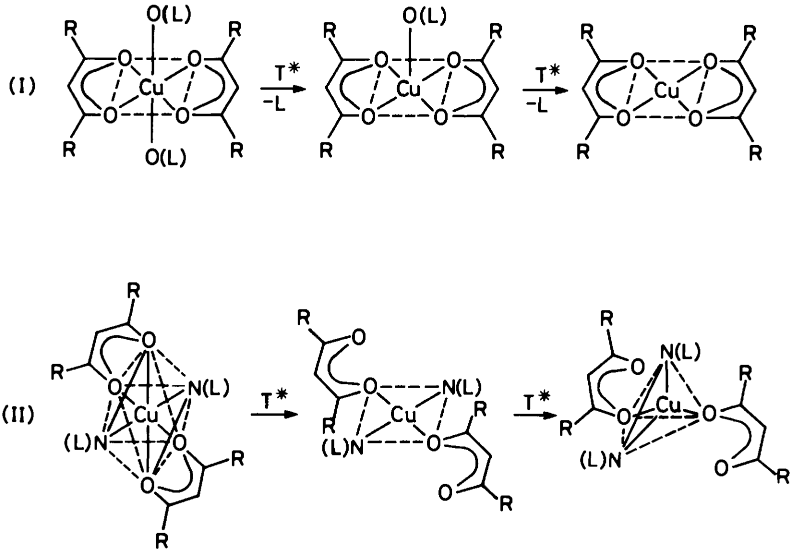
[15] S. V. Volkov, in 'Ionic Melts' (Russ. Ed.), Kiev, 1975.

[16] Y. K. Delimarskii and O. G. Zarubitskii, 'Electrochemistry and Melts' (Russ. Ed.), Moscow, 1974.

[17] A. A. Velikanov, 'Electrochemical Investigation of Chalcogenide Melts' (Russ. Ed.), Ph.D. thesis, Kiev, 1972.

[18] S. V. Volkov, V. Y. Zub, Y. A. Mazurenko, and G. M. Larin, *Dokl. Akad. Nauk USSR (Russ. Ed.)*, 1987, **295**, 904.



Scheme 7

a transition from a octahedral to a tetrahedral structure, which is more temperature-stable (Scheme 7, II).

D. Redox Reactions.—This reaction type is the most widespread in, and unique to molten salts.[2] In some melt systems it is possible to stabilize the lowest oxidation states, *e.g.* Bi_8^{2+}, Se_8^{2+}, Te_4^{2+}, and others, whereas in other melt systems ($KBrO_3$, KIO_4)–(alkali nitrate, alkali hydroxide) the highest stable oxidation states of Np^{VII} ions, *e.g.* NpO_6^{5-}, have been obtained. Such reactions have been reviewed,[2] and some of them have great practical importance.

Of the greatest interest among redox reactions in molten salts of organic compounds is the activation of saturated hydrocarbons. Chemically inert molecules such as methane can be used as reactants in effecting simple single-stage and selective processes to produce valuable products. We have managed (Scheme 8) to effect partial single-stage methane oxidation, in melts with an oxygen-containing melt (a) and air oxygen (b), to formaldehyde with about 30% yield and to methanol (c) with up to about 10% yield and high selectivities (70 to 90%) using melts as catalysts.[19,20]

E. Solvation Reactions.—Solvation reactions in molten salts involve formation of molecules which undergo no subsequent chemical changes, through intercompo-

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[19] V. A. Bandur, N. I. Buryak, and S. V. Volkov, in 'Ionic Melts and Solid Electrolytes' (Russ. Ed.), Kiev, 1986.

[20] S. V. Volkov, N. I. Buryak, V. A. Bandur, and A. F. Gurko, 'New Methods for the Transformation of Saturated Hydrocarbons' (Russ. Ed.), AN USSR (Chernogolovka), 1988.

$$\text{(a) } CH_4 + MNO_3 \xrightarrow{500\text{—}700\,^\circ C} CH_2O + MOH\,(+\,NO + CO + CO_2)$$

$$\left.\begin{array}{l} MNO_3 \longrightarrow MNO_2 + \tfrac{1}{2}O_2 \\ MNO_2 \longrightarrow NO + NO_2 + M_2O \\ CH_4 + O_2 \longrightarrow CH_2O + H_2O \end{array}\right\} MOH$$

$$\text{(b) } CH_4 + O_2 \xrightarrow[850\text{—}1000\,^\circ C]{Me_xO_y\, +\, MPO_3} CH_2O\,(+\,CO + CO_2 + H_2O)$$

(yield ~ 31%)
(selectivity ~ 90%)

$$\text{(c) } CH_4 + O_2 \xrightarrow[650\text{—}800\,^\circ C]{Me_xO_y\, +\, MPO_3} CH_3OH\,(+\,CO + CO_2 + H_2O)$$

(yield ~ 10%)
(selectivity ~ 71%)

Scheme 8

$$AuCl_3 + SeCl_4 \xrightarrow{\sim 100\,^\circ C,\ S_2Cl_2} AuCl_3{\cdot}SeCl_4$$

$$AuCl_3 + TeCl_4 \xrightarrow{\sim 100\,^\circ C,\ S_2Cl_2} AuCl_3{\cdot}TeCl_4$$

$$AuCl_3 + S_2Cl_2 \xrightarrow{100\,^\circ C} AuCl_3{\cdot}SCl_2$$

$$\text{---------}\ PtCl_4(SCl_2)_2$$

$$\text{---------}\ ReCl_4{\cdot}SeCl_4$$

Scheme 9

nent interaction forces, including electrostatic interaction, of the system. Two new examples, two groups of solvate compounds obtained by us are shown in Schemes 9 and 10. The solvates (Scheme 9) $AuCl_3{\cdot}ECl_4$, $PtCl_4{\cdot}(SCl_2)_2$, $ReCl_4{\cdot}SeCl_4$, $ReCl_4{\cdot}TeCl_4$, and others, were obtained by reactions between MCl_x (M is Au, Pt, Pd, Re, and others) and ECl_y melts (E is S, Se, Te).[7,21–23]

When studying the extraction of 3*d* metal ions (M^{2+}) with tributyl phosphate (TBP) from alkali metal (A^+) nitrate and thiocyanate (X^-) melts, we demonstrated[24–26] that tributyl phosphate does not form part of the inner sphere of 3*d* metal complex but solvates the complex species together with the outer-sphere A_2MX_4 cations present in the second coordination sphere. Hence the extraction process in melts should be written as in Scheme 10.

Real chemical reactions generally do not belong to individual reaction classes but are a combination of several types.

A very interesting example of bringing about three reactions at the same time, namely solvation, complexation, and partial redox reactions occurs during the formation of charge-transfer complexes between Lewis acids such as $AlCl_3$,

[21] S. V. Volkov, Z. A. Fokina, and N. I. Timoshchenko, *Rev. Chim. Minerale*, 1983, **20**, 776.

[22] S. V. Volkov, N. I. Timoshchenko, and V. L. Kolesnichenko, Report 10th Int. Conf. Nonaqueous Solutions, Belgium, 1986, p. 62.

[23] Z. A. Fokina, S. V. Volkov, I. B. Baranovskii, N. I. Timoshchenko, and V. I. Pekhnyo, *Zh. Neorg. Khim.* (*Russ. Ed.*), 1981, 7, 1835.

[24] S. V. Volkov, O. B. Babushkina, and N. I. Buryak, *Zh. Neorg. Khim.* (*Russ. Ed.*), 1980, **25**, 2228.

[25] S. V. Volkov, O. B. Babushkina, and N. I. Buryak, *Koord. Khim.* (*Russ. Ed.*), 1980, **6**, 101.

[26] O. B. Babushkina, S. V. Volkov, and F. I. Lobanov, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1983, **49**, 229.

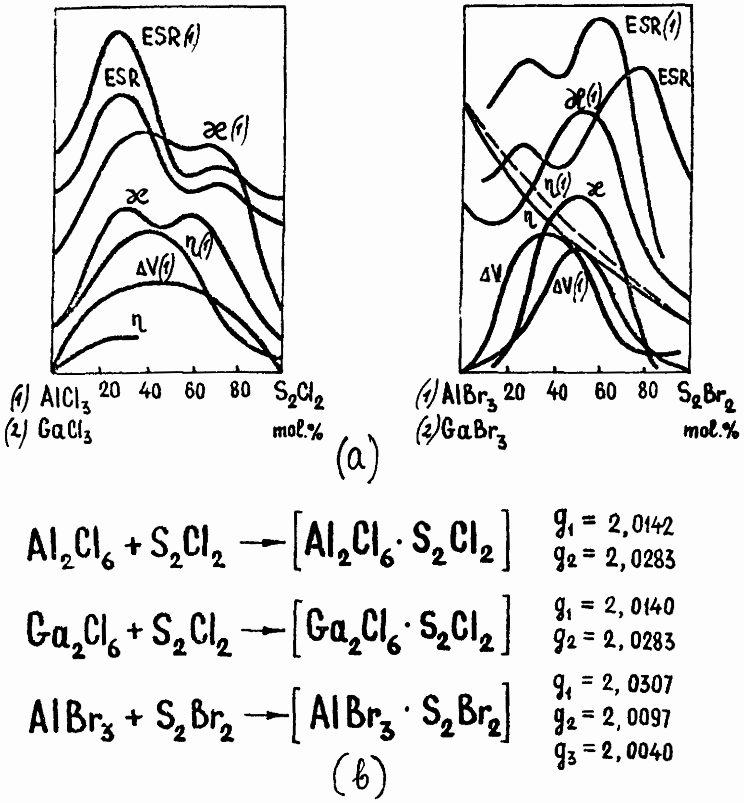

Figure 2 *Conductivity* (κ), *viscosity* (η), *molar volume* (*V*) *and intensities of ESR isotherms for the* $AlCl_3$–S_2Cl_2, $GaCl_3$–S_2Cl_2, $AlBr_3$–S_2Br_2, *and* $GaBr_3$–S_2Br_2 *melts* (a) *and composition of the charge-transfer complexes with g-factors formed by them* (b)

$$M^{2+} + 4X^{-} + 2A^{+} + n\mathrm{TBP} \longrightarrow A_2[MX_4]\cdot n\mathrm{TBP}$$

$$(M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; X^{-} = NO_3^{-}, NCS^{-}; A^{+} = Li^{+}, K^{+}, Na^{+})$$

Scheme 10

$AlBr_3$, $GaBr_3$, $GaCl_3$ (MX_3) and sulphur monochloride and monobromide (S_2X_2). Charge-transfer complexes are formed in melts of the composition MeX_3:S_2X_2 = 2:1, 1:1, 1:2 with formation of paramagnetic molecules (Figure 2).[26–31]

[27] S. V. Volkov, I. V. Matyashchuk, V. V. Trachevskii, and Z. A. Fokina, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1978, **43**, 5.

[28] I. V. Matyashchuk and Z. A. Fokina, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1978, **43**, 97.

[29] I. V. Matyashchuk and S. V. Volkov, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1986, **51**, 1235.

[30] I. V. Matyashchuk, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1978, **43**, 516.

[31] S. V. Volkov, V. V. Trachevskii, and I. V. Matyashchuk, *Dokl. Akad. Nauk USSR* (*Russ. Ed.*), 1977, **232**, 1336.