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SPECTROSCOPIC STUDIES ON COORDINATION COMPOUNDS FORMED IN MOLTEN SALTS

K.B. Yatsimirskii

Institute of Physical Chemistry, Ukrainian Academy of Sciences, Prospect Nauki 97, Kiev 28, U.S.S.R.

Abstract - Using Raman and electronic absorption spectroscopic methods the symmetries and geometries of coordination have been examined for transition metal ions in melts of alkali metal salts. The species $MnCl_4^{2-}$, $CoCl_4^{2-}$ and $NiCl_4^{2-}$ have T_d, and $CrCl_4^{2-}$, $FeCl_4^{2-}$ and $CuCl_4^{2-}$ have D_{2d} symmetries. $FeCl_4^{2-}$ is nearly tetrahedral but $CrCl_4^{2-}$ and $CuCl_4^{2-}$ are close to square structures. In thiocyanate melts, Mn^{2+} and Ni^{2+} ions show a coordination number of 6, and Co^{2+} one of 4. Coordination is through the N-atom, except for $Zn(NCS)_4^{2-}$ in which both thiocyanate bridging and isothiocyanate coordination occurs. Modes of coordination of NO_3^- with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} in alkali nitrate melts are also discussed.

INTRODUCTION

Ionic melts are solvents of special type. Unlike molecular solvents they contain separate mobile ions with opposite charges which may interact with each other to yield "ionic pairs" and more complex associates of the R_pX_q type. The formation, composition and structure of such associates are determined by the nature of R^{z+} cations and X^{w-} anions.

By introducing other metal cations into an ionic melt the formation of "complexes-solvates" of the $[M_mX_n]$ type is observed. The compositions of these "complexes-solvates" is certain to depend on the concentration of the M^{z+} cations. At high dilution (such conditions will be considered in the present paper) m is likely to be unity and the melt will involve uninuclear clusters of the $[MX_n]$ type. As X^{w-} anions usually have some lone electron pairs and their effective negative electric charges are only partially neutralized, they are capable of coupling with other cations, in particular, cations of a melt-solvent, R^{z+}. Therefore, a cluster of a more complex structure $[MX_nR_p]$ is actually formed in melt. As a rule, there is no direct interaction (with orbital overlap) between R^{z+} and M^{z+} cations. Therefore, some workers call M^{z+} and X^{w-} innersphere, and R^{z+} outersphere ions, though such terminology is, to a great extent, conventional.

Some other anions/ligands, A^{y-}, may be introduced into the ionic melt differing from the anions of a melt in composition. In this case, a melt-solvent is only a medium in which complexes of the $[MA_n]$type or, to be more correct, clusters of the $[MA_nR_p]$ type involving "outersphere" cations are formed.

It should be noted that ionic melts exist solely at relatively high temperatures ranging from 100 to 1000° C and above. This makes research with such media by routine methods and conventional equipment difficult, resulting in some apparent abnormalities in the thermodynamics of such reactions and the structure of the complexes formed (i.e., great tendency towards the dissociation of "exothermic" complexes and an increase in the stability of "endothermic" complexes, an appreciable role of vibrational excited states, etc.).

The aim of studying melts involving metal complexes is to elucidate the composition of the above clusters, to establish their geometry and electronic structure, and to determine their thermodynamic and kinetic characteristics. So far geometry and electronic structure of clusters in melts have mainly been studied by spectroscopic techniques; absorption spectroscopy in the u.v./visible region of the spectrum, absorption electronic spectroscopy (AES) and vibrational spectroscopy (VS). The last may be classified into infra-red (IR) and Raman spectroscopy (RS). The present work primarily concerns absorption electronic spectra and Raman spectra (RS) of melts.

Electronic absorption spectra of ionic melts are measured in the frequency range 5000 to 50,000 cm^{-1} (2000 to 200 nm). The low frequency limit is governed by the frequency range of spectrophotometers while the high frequency range limit is determined by the light absorption of a molten salt itself.

The edges of the light absorption bands for various molten salts are shown in Table 1 for those ionic melts which have been examined as solvents.

TABLE 1. The edges of light absorption bands for molten alkali metal salts

Salt	Temperature, °C	Long wave edge of salt absorption	Reference	Salt	Temperature, °C	Long wave edge of salt absorption	Reference
LiCl	644	277	(1)	KNCS	233	220	(1)
NaCl	850	280	(2)	$LiNO_3$	287	335	(1)
KCl	850	282	(2)	$NaNO_3$	328	340	(1)
RbCl	850	283	(2)	KNO_3	338	304	(3)
CsCl	850	284	(2)	$RbNO_3$	300	267	(4)
KNCS	180-215	220	(1)	$CsNO_3$	420	285	(4)

The absorption bands of the metal halogenides are broadened and localized in the UV region of the spectra. So far their origin has not been completely elucidated. Two possible explanations are available from the literature:

1) a Rydberg-type electron transfer is realized in the halogenide ion: $np \rightarrow (n + 1)s$

2) an electron transfer from a halogenide ion to a vacant orbital of an alkali metal.

A regular absorption band shift towards longer wavelength in the series of alkali metal halogenides attracts attention: LiCl < NaCl < KCl < RbCl < CsCl

Absorption bands of nitrates and thiocyanates seemed to occur as a result of the electron transfer from one to another molecular orbital of the same polyatomic ion. In this case, too, one can observe that the position of the absorption band depends upon the nature of the alkali metal ion, though the melt is certain to involve some individual polyatomic ions (thiocyanate, nitrate, etc.). Comparing absorption band positions in the crystal and the melt one can usually observe a pronounced bathochromic shift. This phenomenon accounts for the position disordering of ions in the lattice on crystal melting. Crystal melting is known to be accompanied by a decrease in the mean coordination number of the ion.

Clusters of the M_pX_q type with different p and q values are likely to remain in melts of other metal halogenides (AgCl, $ZnCl_2$, $CdCl_2$, $SnCl_2$, $AlCl_3$, etc) having pronounced bond covalency.

The present paper concerns coordination compounds formed from uniatomic ligands (chloride-ions), the polyatomic linear anion, NCS^-, and polyatomic planar anions of oxygen acids, NO_3^-, formed in melts.

The coordination compounds of 3*d* transition metals with chloride are characterized by chromophores of two types, MCl_6 (a regular or distorted octahedron), and MCl_4 (a tetrahedron, a square or a distorted tetrahedron).

The coordination number of metal in the MCl_n group depends upon the nature of a melt-solvent.

The coordination number 4 is realized in typical ionic melts (alkali metal halogenides and their mixtures), higher coordination numbers of 6 can be observed in molten chlorides in the presence of covalent bonding e.g., $AlCl_3$, $HgCl_2$, $SnCl_2$, $PbCl_2$, $ZnCl_2$ and even $MgCl_2$.

Such a phenomenon can be explained by two factors. The electrostatic interligand repulsion should be greater in octahedral complexes than in tetrahedral ones. At the same time, the absolute values of effective charges on chlorine atoms in melts of type II (halogenides with a covalent bond) are far less than those in melts of type I (ionic halogenides of alkali metals). The second reason why the coordination numbers of complex halogenides of transition metals differ is a purely geometric factor; the ionic and covalent radii for a chlorine atom are 1.81 and 0.99 Å, respectively. (Ref.5).

In compounds involving an intermediate chemical bond, chlorine atoms appear also to be characterized by intermediate values of effective radii. Chloride ions in the coordination sphere occupy more space than chlorine atoms displaying small negative effective charges. The great role of the geometric (three-dimensional) factor is also illustrated by the fact that the coordination number in the complex fluorides of transition metals is 6.

In "covalent" melts e.g., $SnCl_2$, $PbCl_2$, $HgCl_2$, $AlCl_2$, etc., groups of the $SnCl_3^-$ type can be considered to be unique ligands in which chlorine atoms are bound to tin atoms. Such groups may act as bidentate ligands.

The coordination numbers of 3*d* transition metal complexes in the ionic melts of alkali metals generally proved to be 4. The symmetry of the chlorine atoms within the chromophore was determined by the electronic structure of the central metal ions. Table 2 lists some spectral data for the chloride complexes studied.

TABLE 2. Symmetry and spectral data on transition metal complexes molten alkali metal chlorides at 400-600°C in the concentration range 0.003 to 1.0 M (Refs. 6,7,8,9,10).

Symmetry and spectral parameters of electronic structure	Coordination compound					
	$CrCl_4^{2-}$	$MnCl_4^{2-}$	$FeCl_4^{2-}$	$CoCl_4^{2-}$	$NiCl_4^{2-}$	$CuCl_4^{2-}$
Symmetry	D_{2d}	T_d	D_{2d}	T_d	T_d	D_{2d}
$\Delta(10Dq)\,cm^{-1}$	9500	4000-5000	4500	3600	3800	7400
B	-	700-780	-	600	720	-
β	-	0.73-0.77	-	0.62	0.69	-
ε max	50	2	30	320	100	150
$\varepsilon_{Cl^-}/\varepsilon_{H_2O}$	8	50	20	60	20	17

The Δ(10Dq) parameter of the *d*-level splitting in the ligand field characterized the symmetry and the type of coordination in the chromophore. Its magnitude in the tetrahedral field is known to be only 4/9 of that in the octahedral field. Thus, the tetrahedral symmetry of $MnCl_4^{2-}$, $CoCl_4^{2-}$ and $NiCl_4^{2-}$ may be considered to be proved. The symmetry in the $FeCl_4^{2+}$ complex seems also to be very close to tetrahedral.

Meanwhile, the highly overestimated values of Δ(10Dq) in the chromium(II) and copper(II) complexes suggest a tetra-coordinate structure with a much distorted, flattened tetrahedron of D_{2d} symmetry).

The B value (Racah's parameter) in coordination compounds involving chloride differs markedly from that in gaseous free ions of transition metals, which points to covalent bonding(with transfer of some electron density from the central atom on to the ligands). Further evidence lies in the large deviation in the nephelauxetic ratio from unity (0.62-0.77). The bond covalence is especially pronounced in a $CoCl_4$ complex (β = 0.62).

For tetrahedral complexes, some information on bond covalency may be obtained by comparing the intensities of absorption bands. The bond covalence in tetrahedral complexes results in a marked overlapping of the *d* and *p* atomic orbitals with an increased molar extinction coefficient in the absorption band maximum (ε_{max}). Its highest value is observed for the $CoCl_4^{2-}$ complex. $MnCl_4^{2-}$ has a low ε_{max} value because it refers to a spin restricted transfer (from a sextet to a quartet level).

Comparable information on different transitions may be obtained from Table 2 which lists the ratios of molar extinction coefficients for chloride and aquo-complexes. The changes in value of this ratio over the series of complexes under discussion is relatively small. The highest value of the $\varepsilon_{Cl^-}/\varepsilon_{H_2O}$ ratio is again found to be for $CoCl_4^{2-}$.

The structures of the $CrCl_4^{2-}$ and $CuCl_4^{2-}$ complexes closely resemble a square. Quantum-chemical calculations on the $CuCl_4^{2-}$ complex using the most modern computation techniques show that the positive charge is localized on the copper atom and equal to + 1.28. The effective charges on chlorine atoms (assuming that they are equal on all four atoms) are then - 0.82. Each chlorine ion seems to "give" 0.18 of its electronic charge by transfer to the copper ion (Ref.11).

The symmetry of chloride complexes may also be determined from vibrational spectra (skeletal M-Cl vibrations). Raman spectra were observed for MCl_4^{2-} complexes in molten alkaline halogenides using a laser excitation source.

For each tetrahedral ion only one polarized line was detected in the Raman spectra as follows: $MnCl_4^{2-}$, 240 cm^{-1}; $CoCl_4^{2-}$, 280 cm^{-1}; $NiCl_4^{2-}$, 260 cm^{-1}; $ZnCl_4^{2-}$, 275 cm^{-1}. These lines are assigned to the symmetric stretching vibration A (ν_1). These data confirm the symmetry for the above ions as regular (T_d) tetrahedral (Ref.12). At least three weak bands were detected in the Raman spectrum of $CuCl_4^{2-}$ at 270, 150 and 125 cm^{-1}, respectively. It follows that a $CuCl_4^{2-}$ ion has far lower symmetry than T_d, and the ion is assigned to the point-group D_{2d} (Ref. 12).

The effect on the spectral parameters of the nature of melt cations R^+, involved in $[M_nCl_4R_n]$ clusters, has been observed in all transition metal complexes and is most pronounced in clusters containing $CoCl_4^{2-}$. This effect is especially marked in comparing the intensities of analogous absorption bands in $CoCl_4^{2-}$ complexes. It is illustrated by the data listed in $CoCl_4^{2-}$ complexes. It is illustrated by the data listed in Tables 3 and 4

TABLE 3. Molar extinction coefficients, ε, for $CoCl_4^{2-}$ complexes in different media and 800°C.

Spectral transitions (frequency range) cm^{-1}	Molten salts					
	CsCl (Ref.14)	RbCl (Ref.14)	KCl (Ref.13)	NaCl (Ref.13)	LiCl (Ref.13)	$MgCl_2$ (Ref.13)
14100-14400	292	250	249	223	173	154
14800-15100	289	250	245	223	179	156
16300-16800	178	250	152	140	117	101

TABLE 4. The effect of alkali metal cations upon the spectral parameters of a $CoCl_4^{2-}$ complex in a molten $LiNO_3$-KNO_3 mixture at 200°, at a molar $CoCl_2$: KCl ratio 1:500 (Ref.10).

Cation R^+	cm^{-1} (10 Dq)	ε $^4A_2 - {}^4T_1(p)$	Oscillator strength $f.10^3$ $^4A_2 - {}^4T_1(p)$
Cs^+	3600	333	2.97
Rb^+	3600	324	2.80
K^+	3600	323	2.79
Na^+	3650	311	2.68
Li^+	3680	306	2.65

The intensity of the absorption band of the *d-d* transition is determined by two factors; the symmetry of the complex, and the distance between the band and that of a charge transfer band from which the intensity is borrowed. The less the distance, the more intense the spectral transition is. The data in Table 4 suggest that the distance between the visible spectral absorption - band and the charge transfer band should decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. In this sequence the bond polarity R^+Cl^-, increases. The presence of a Mg^{2+} ion in a $[CoCl_4R_n]$ cluster results in a further "borrowing" of some part of the effective charge from the chloride ion.

Tetrahedral symmetry (T_d) of a $CoCl_4^{2-}$ fragment seems to occur in all the systems shown in Tables 3 and 4. A change in the 10 Dq parameter depending upon the nature of R^+ is less pronounced, Table 4. The increase in 10 Dq for $[CoCl_4R_n]$ clusters across the alkali metal ions, Cs^+ to Li^+, can be interpreted both on the basis of the crystal field theory (for octahedral symmetry by additional electrostatic field originating from alkali metal cations - which increases 10 Dq), and of molecular orbital theory (by an increase in the "antibonding effect" in a three-centre Co-C-R fragment on passing from Cs^+ to Li^+).

Data on the chloride complexes of transition metal ions in the melts permit one to draw conclusions about complexing in melts: 1) a transition metal ion coordinates a large number of anions (4-6), unlike their coordination behaviour in aqueous and some other molecular solvents; 2) the "cluster" involves alkali metal cations which greatly affect the spectral parameters of $CoCl_4^{2-}$.

The thiocyanate-ion available in relatively low temperature melts of alkali metal thiocyanates, was chosen as a polyatomic ligand with a linear structure. Thiocyanate coordination is known to occur in thiocyanate M-SCN, isothiocyanate M-NCS and binuclear M-SCN-M (bridging) forms. The mode of coordination can be determined from the vibrational modes which characterize a linear thiocyanate ion. Table 5 shows three such types of vibrations.

TABLE 5. Typical vibrational frequencies of thiocyanate ion in different modes of coordination (Refs. 16,17)

Mode of coordination	ν_{CN} (A_1) cm^{-1}	ν_{CS} (A_1) cm^{-1}	ν_{NCS} (E_1) cm^{-1}
Free ion NCS^-	2050-2060	740-750	470-475
Isothiocyanate coordination M - NCS	2080-2120	780-860	470-490
Thiocyanate coordination M - SCN	2100-2130	680-740	410-460
Bridge coordination M - SCN-M	2130-2180	700-800	-

To obtain vibrational spectral information concerning thiocyanate coordination compounds, the Raman spectra were measured in molten alkali metal thiocyanates. The vibrational frequencies observed for thiocyanates in complexes of the $M(NCS)_n^{2-n}$ type (n=4 or 6) for all 3 transition metals suggest isothiocyanate coordination. The exception is with $Zn(NCS)_4^{2-}$, in which case bridging coordination may be assumed to occur together with isothiocyanate coordination. Isothiocyanate coordination has also been confirmed by the visible absorption spectral data shown in Table 7.

In the case of isothiocyanate coordination, the magnitude of 10 Dq must equal that of aquo-ions.* It holds for all cases studied. A high nephelauxetic effect value suggests a pronounced covalent bond in $M(NCS)_n^{2-n}$ complexes. It is also confirmed by high values of maximum molar extinction coefficients (a hyperchromic effect).

The presence of isothiocyanate coordination may be qualitatively interpreted on the basis of the Pearson (Refs. 21,22) theory of hard and soft acids. The metal cations under examination may be regarded as hard acids or, more exactly, may take an intermediate position between soft and hard acids. A thiocyanate ion is a typical ambidentate ligand involving two different

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* $\{\Delta_{NCS}/\Delta_{H_2O} \simeq 1.02$ (Ref. 20)}

TABLE 6. Vibration frequencies of thiocyanate in M(NCS)$_n^{(2-n)-}$ complexes in molten alkali metal thiocyanates at 200°C (Refs. 17.18,19).

Ion	Raman Vibrational frequencies, cm^{-1}		
	ν_{CN} (A_1)	ν_{CS} (A_1)	ν_2 δ_{NCS} (E)
Mn(NCS$_6^{4-}$	2095	775	480
Co(NCS$_4^{2-}$	2095	830	470
Ni(NCS)$_6^{4-}$	2105	800	495
Zn(NCS)$_4^{2-}$	2100-2155	825,710	470,435

TABLE 7. Symmetry and spectral parameters of transition metal complexes in molten alkali metal thiocyanates at 200°C (Refs. 6,7,8,19).

Symmetry and spectral parameters of electronic structure	Complexes					
	Cr(NCS)$_6^{4-}$	Mn(NCS)$_6^{4-}$	Fe(NCS)$_6^{4-}$	Co(NCS)$_4^{2-}$	Ni(NCS)$_6^{4-}$	Cu(NCS)$_4^{2-}$
Symmetry	D_{4h}	O_h	O_h	T_d	O_h	D_{2d}
Δ(10 Dq)cm^{-1}	9800	8200	8150	5000	8500	9800
β	-	0.72	-	0.60	0.65	-
ε_{max}	6	0.3	15	600	100	150

terminal donor atoms; the "soft" donor sulphur atom, and the "intermediate" (close to "hard") donor nitrogen atom. On this basis isothiocyanate coordination would be expected for the donors and acceptors ought to match each other in softness and hardness.

A zinc ion alone (the softest acid in the series of metals under consideration) can coordinate the thiocyanate ion through the sulphur atom, as well as by bridge coordination. The mercury ion, Hg^{2+}, coordinates a thiocyanate ion through the sulphur atom exclusively.

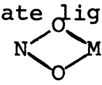
The effective electronic charges on the atoms in free thiocyanate ion are arranged approximately symmetrically as: $q_N = -0.51$; $q_S = -0.48$; $q_C = -0.01$. (Ref.23). Since, on sulphur and nitrogen atoms, they are less than unity and approximately equal to 0.5, to characterize the volume of S and N atoms their covalent radii should be compared. The ionic radii, S^{2-} and N^{3-}, are very close but the covalent radii are markedly different; 0.70 for a nitrogen atom and 1.04 for a sulphur atom (Ref.5). If the effective charge for a nitrogen atom is -0.5, its effective radius does not differ much from 1.0 Å

The small volume of a nitrogen atom accounts for the coordination number 6 in all the complexes except Co(NCS)$_4^{2-}$. The 4-coordinate nature of the latter is due to some peculiarities in the electronic structure of the *d*^{7}

cobalt(II) ion and the high stability of the non-degenerate tetrahedral electronic distribution, $(e)^4\ (t_2)^3$.

As an example of a polyatomic nonlinear ligand, we can consider a NO_3^- ion which has a planar structure with a nitrogen atom at the centre of an equilateral triangle whose vertices contain oxygen atoms (D_{3h} symmetry).

If a chloride ion is regarded as a soft base, (a thiocyanate ion contains a "soft" sulphur atom and an "intermediate" nitrogen atom as terminal donor atoms), a nitrate ion may undoubtedly be classed as a hard base. In this anion, the oxygen atoms located at the vertices of a triangle act as donors. Their interaction with the acceptor orbitals of a metal ion can produce σ- and π-bonds.

Unlike the other ligands a nitrate ion can also act as a bidentate ligand. In this case, a somewhat unstable four-membered ring is formed 

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In melts at high temperatures, however, the stability of such rings increases. One may assume that in some cases M-O bonds in nitrate complexes may prove unequal.

The mode of coordination for nitrate ions may be established from the vibrational spectra of $M(NO_3)_n^{(2-n)-}$ complex ions. Table 8 shows the vibrational frequencies for differently coordinated nitrate ions.

TABLE 8. Approximate range of vibrational frequencies for nitrate ions differently coordinated to metal ions. (Ref.24).

Mode of coordination	Nitrate ion Symmetry	Frequency range cm^{-1}	Observed in spectra
Free NO_3^-	D_{3h}	$\nu_3 = 1390$	IR, Raman
Monodentate	C_{2v} or C_s	$\nu_1 = 1250\text{-}1300$ $\nu_4 = 1480\text{-}1530$	IR, Raman
Bidentate	C_{2v}	$\nu_1 = 1565\text{-}1600$ $\nu_4 = 1170\text{-}1270$	IR, Raman
Bridge	C_{2v}	$\nu_1 > 1590$, $\nu_4 < 1200$	IR, Raman

Coordination of the NO_3^- ion decreases its symmetry from D_{3h} to C_{2v} (in some cases even to C_s) and the number of frequencies observed in the vibrational spectrum increases from 4 to 6.

The N-O vibrational frequencies (both symmetric and antisymmetric) produced by the splitting of the ν_3 frequency (1390 cm^{-1}) proved to be especially significant in establishing the mode of coordination. In molten alkali metal nitrates all transition 3*d* metals form $M(NO_3)_4^{2-}$ complexes. However, the mode of coordination of the nitro group in these and the symmetries of the clusters turned out to be different.

Table 9 lists the N-O symmetric and antisymmetric vibrational frequencies and the O'NO" symmetric and antisymmetric deformation frequencies across the row of transition metals. All vibration frequencies given in Table 9 were obtained from the Raman spectra of complexes in molten nitrates (Refs. 18,24, 25).

TABLE 9. Some vibration frequencies in $M(NO_3)_4^{2-}$ complexes in molten alkali metal and ammonium nitrates at 150-250°C, at concentrations ranging between 1 and 5 mol % (Refs. 18,24, 25).

Metal	Symmetry of complex	Coordination number	$\nu_1(A_1)$ ν_sNO	$\nu_4(B_1)$ ν_{as} NO	$\nu_3(A_1)$ ν_s ONO	$\nu_5(B_1)$ as ONO
Mn(II)	$D_{2\underline{d}}$	8	1535 bi	1135 bi	810	720
Co(II)	$D_{4\underline{h}}(D_{2\underline{d}})$	6	1590 bi 1348 mono	1230 bi -	780	725
Ni(II)	$D_{4\underline{h}}$	6	1565-bi 1300 mono	1270-bi 1485-mono	765	725
Ci(II)	$D_{4\underline{h}}$	6	1630-bridge 1535-bi 1325-mono	1185 bridge 1280 bi	750	725
Zn(II)	$T_{\underline{d}}$	4	1330-mono	1475-mono	720	675

Bidentate coordination for the NO_3^- with dodecahedral symmetry is observed only with the $Mn(NO_3)_4^{2-}$ complex. In this case the $\mathrm{Mn}{<}^{O}_{O}$ bonds may be unequal and two tetrahedra of Mn-O_4' and Mn-O_4'' may be formed. In one of them the Mn-O bond is shorter than in the other.

The second extreme case of coordination of a nitrate ion takes a $Zn(NO_3)_4^{2-}$ complex; all these are mono-coordinated. Thus the symmetry of the immediate environment of Zn^{2+} is tetrahedral, each vertex of the tetrahedron being occupied by the oxygen atoms of an NO_3^- ion.

Two modes of coordination, monodentate and bidentate, are found in $Co(NO_3)_4^{2-}$ $Ni(NO_3)_4^{2-}$, and $Cu(NO_3)_4^{2-}$ complexes. Two bidentate nitrate ion ligands may be assumed to be located in these compounds in the equatorial plane while two other monodentate nitrate ion ligands occupy the apices of a tetragonally elongated bipyramid.

The conclusions drawn about the geometry of $M(NO_3)_4^{2-}$ complexes are also confirmed from the analysis of the skeletal vibrations of the M-O bonds.

The electronic absorption spectra of nitrate complexes of the $M(NO_3)_4^{2-}$ type are given in Table 10.

The data in Table 10 suggest a high field force produced by the nitrate ions. An underestimated 10Dq value is observed only for $Mn(NO_3)_4^{2-}$ which is evidence of the inequality of the Mn-O bonds and the formation of a tetrahedral MnO_4 structure with somewhat shortened Mn-O distances compared to those in the other MnO_4'' tetrahedron.

High β values and relatively small ε_{max} values suggest a highly ionic metal ion—nitrate ion bond.

The symmetry of $M(NO_3)_4^{2-}$ complexes given in Table 10 is confirmed by broad Absorption bands of the fine structure, indicating tetragonal distortion of of coordinated polyhedra (their shape resembles a tetragonal bipyramid).

TABLE 10. Symmetry and Spectral data of coordination compounds of transition metals in molten alkali metal nitrates at 200°C at concentrations 0.002-1.0 M (Refs., 8,26,27).

Symmetry and spectral parameters of electronic structure	Coordination compounds of the $M(NO_3)_4^{3-}$ type			
	Mn(II)	Co(II)	Ni(II)	Cu(II)
Symmetry	D_{2d}	D_{4h}	D_{4h}	D_{4h}
(10 Dq) in cm^{-1}	6000	8600	7800	10000
β	0.74	0.74	0.78	-
ε_{max}	2	90	32	90

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