Electronic Spectra and Stability of Cobalt Halide Complexes in Molten Calcium Nitrate Tetrahydrate

István J. Zsigrai, Slobodan B. Gadzuric, Ruzica Nikolic[a], and László Nagy[b]

Department of Chemistry, Faculty of Science, University of Novi Sad, Trg D. Obradovica 3, 21000
Novi Sad, Serbia & Montenegro
[a] Institute of Nuclear Sciences “Vinca”, POB 522, 11001 Belgrade, Serbia & Montenegro
[b] Department of Inorganic and Analytical Chemistry, Faculty of Science, University of Szeged,
Hungary

Reprint requests to Dr. I. Zs.; Fax: +381 21 454 065, E-mail: zigrai@ih.ns.ac.yu

Z. Naturforsch. **59a,** 602 – 608 (2004); received June 1, 2004

The complex formation between cobalt(II) and chloride and bromide ions in molten calcium nitrate tetrahydrate at different temperatures has been studied by a spectrophotometric technique. Addition of halide ions to cobalt(II) nitrate solution in calcium nitrate tetrahydrate caused a pronounced shift of the absorption maximum toward lower energies and a large increase of absorption intensity, indicating a change from octahedral to a tetrahedral co-ordination. The change of co-ordination depends on temperature and halide concentration. Stability constants for the $[Co(NO_3)_4]^{2-}$, $[Co(NO_3)_2X_2]^{2-}$ and $[CoX_4]^{2-}$ complexes at 40 and 70 °C and the corresponding species spectra are reported.

Key words: Cobalt(II) Halide Complexes; Calcium Nitrate Tetrahydrate; Stability Constants.

1. Introduction

The formation of stepwise complexes of cobalt(II) ions with halide ligands in various aqueous and non-aqueous solvents has long been known. The co-ordination number of cobalt(II) and the structure of its complexes often depend on the ligand used [1]. The wellknown octahedral – tetrahedral equilibria in aqueous solutions is best illustrated by addition of concentrated hydrochloric acid to aqueous cobalt(II) salt, when the pale red octahedral $[Co(H_2O)_6]^{2+}$ is changing to intense blue tetrahedral $[CoCl_4]^{2-}$ [2]. Similar changes in co-ordination occur when chloride or bromide is added to cobalt(II) solution in nitrate melts. Tananaev and Dzhurinskii [3, 4] ascribed the changes in cobalt(II) absorption spectra in lithium nitrate – potassium nitrate eutectics to successive cobalt(II) halide complex formation and to the change in Co(II) co-ordination from octahedral in pure nitrate to tetrahedral in halide containing melts. Later, on the basis of X-ray diffraction measurements [5], the spectrum of Co(II) in pure nitrate melts was attributed to dodecahedral $[Co(NO_3)_4]^{2-}$ species [6]. Analogous spectral changes were observed upon addition of chloride into cobalt(II) solution in molten ammonium nitrate [7]. Hemmingsson and Holmberg [8] determined the stepwise stability constants of $[CoCl_j]^{2-j}$ and $[CoBr_j]^{2-j}$ $(0 < j < 4)$ and the corresponding resolved species spectra in molten eutectic $(K, Li)NO_3$. However, they could not judge where the change from dodecahedral to tetrahedral co-ordination occurred. The stepwise formation of cobalt(II) chloride complexes in molten acetamide has been studied by Savovic et al. [9]. Stability constants for $[CoCl_j]^{2-j}$ $(j = 1-4)$ are reported. The increase of chloride concentration changed the co-ordination geometry from octahedral through severely distorted octahedral to tetrahedral. The cobalt(II) halide complex formation equilibria in hydrous salt melts $x\mathrm{NH_4NO_3} \cdot y\mathrm{Ca(NO_3)_2} \cdot z\mathrm{H_2O}$ were studied by Kerridge et al. [10]. They have found that addition of chloride or bromide changed the cobalt(II) co-ordination by both nitrate and water from near-octahedral to a tetrahedral (or severely distorted octahedral) symmetry with between two or three halide ligands.

The absorption spectra of cobalt(II) chloride were also investigated in molten mixtures of acetamide – calcium nitrate tetrahydrate [11]. A large increase of the molar absorption coefficient with increasing chloride concentration and with temperature in melts containing a large excess of chloride over cobalt(II) was observed.

The present study was undertaken in order to get more detailed insight into the changes of cobalt(II) coordination in calcium nitrate tetrahydrate melt, occurring with temperature and halide concentration. We have also aimed at a determination of the complex formation constants and the corresponding resolved species spectra. The solvent calcium nitrate tetrahydrate was chosen because, due to its high latent heat storage capacity and to the reversible optical properties of the dissolved cobalt halide complex compounds with temperatue, it has been considered as suitable material for simultaneous control of temperature and insolation in solar heated agricultural greenhauses [12]. Moreover, complex formation constants for cobalt(II) chloride complexes obtained in an our previos work [13] will be recalculated with new experimental data.

2. Experimental

All chemicals were reagent grade and used as received. The water content of the solvent calcium nitrate tetrahydrate (Merck) was determined gravimetrically, by slow dehydration up to 220 °C, or volumetrically, by analysis of the calcium, employing standard EDTA titration. The water content was then adjusted to the stoichometric value by drying at 120 °C or by addition of distilled water. The cobalt(II) content of cobalt nitrate hexahydrate (Merck) was checked by EDTA titration. The composition of $CaCl_2 \cdot 6H_2O$ (Kemika, Zagreb) and $CaBr_2 \cdot xH_2O$ (Merck) was determined by analysis for chloride and bromide, respectively, by titration with standard $AgNO_3$ solution. Stock solutions of cobalt(II) nitrate, calcium chloride and calcium bromide in calcium nitrate tetrahydrate were prepared. The water content of each solution was adjusted to the constant mole ratio of $n(H_2O)/n(Ca^{2+}) = 4$. Appropriate quantities of stock solutions were added into premelted calcium nitrate tetrahydrate to obtain solutions of desired cobalt(II) and halide concentration.

The solutions were prepared on the molality scale by weighing the appropriate amounts of substances, but the concentrations were converted to molarities (mol dm^{-3}), so that molar absorption coefficients could be calculated. The density of the melt required for conversion of molality units into molarities was determined picnometrically at different temperatures and different calcium halide concentration, the variation of density with the cobalt(II) concentration being negligible. The dependence of the melt density on the calcium halide molality and temperature in the range 40 – 70 °C can be rationalized according the equations

$$\begin{aligned} d/\mathrm{g\,cm^{-3}} = {} & 1.973 - 7.56 \cdot 10^{-4} T \\ & - (0.0625 + 4.4 \cdot 10^{-5} T) m \qquad (1a) \\ & \text{for chloride solutions} \end{aligned}$$

and

$$\begin{aligned} d/\mathrm{g\,cm^{-3}} = {} & 1.973 - 7.56 \cdot 10^{-4} T \\ & + (0.107 - 8.96 \cdot 10^{-5} T) m \qquad (1b) \\ & \text{for bromide solutions,} \end{aligned}$$

where T is the absolute temperature and m is the molality ($\mathrm{mol\,kg^{-1}}$) of $CaCl_2 \cdot 4H_2O$ or $CaBr_2 \cdot 4H_2O$.

Procedure

Absorption spectra were recorded on a Hewlett Packard 8452 A Diode Array spectrophotometer with a thermostated cell compartment, connected to a Vectra 386s/25 computer. The temperature was kept constant to ±0.5 °C. Rectangular quartz or glass spectrophotometric cells of 10-mm path length with Teflon stoppers were used. The reference cell was filled with calcium nitrate tetrahydrate containing an appropriate concentration of calcium halide. Spectra were recorded in the wavelength range between 400 and 800 nm. The baseline was checked immediately before the spectra were recorded.

3. Results and Discussion

3.1. The Absorption Spectra

This paper reports results derived from spectra of 25 chloride and 36 bromide solutions at different temperatures. As our experimental data are too extensive to be tabulated in this paper, only reduced sets of nine

Table 1. The composition of melts $Ca(NO)_2 \cdot 4H_2O$, Co–Cl, Br of which spectra are presented in Figs. 2 and 3.

No	Cobalt(II) chloride $c(Co^{2+})$ /mol kg^{-1}	$c(Cl^-)$ /mol kg^{-1}	Cobalt(II) bromide $c(Co^{2+})$ /mol kg^{-1}	$c(Br^-)$ /mol kg^{-1}
1	0.01400	0.0280	0.05181	0.000
2	0.00831	0.841	0.00247	0.854
3	0.00747	1.018	0.00646	0.944
4	0.00442	1.434	0.00221	1.163
5	0.00108	1.840	0.00524	1.378
6	0.00125	2.044	0.00238	1.546
7	0.00106	2.492	0.00129	1.912
8	0.00119	2.779	0.00134	3.195
9	0.00124	3.139	0.00352	3.334

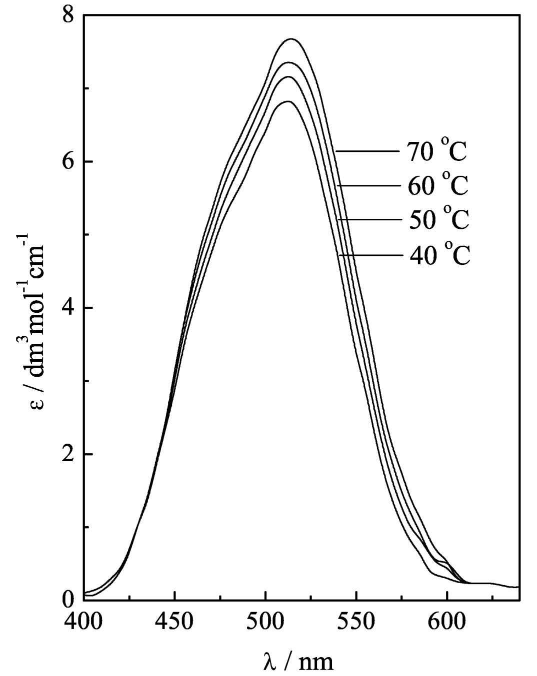

Fig. 1. Absorption spectra of cobalt(II) nitrate in molten $Ca(NO)_2 \cdot 4H_2O$ at different temperatures. c(Co) = 0.01426 mol kg^{-1}.

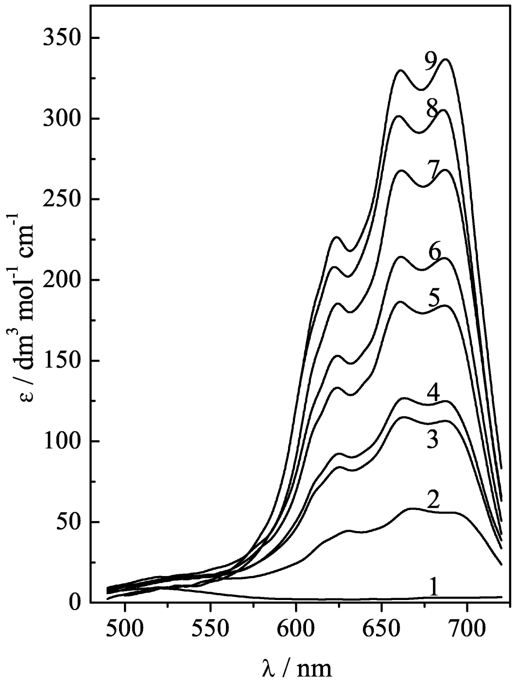

Fig. 2. Variation of the spectra of cobalt(II) with chloride concentration in molten $Ca(NO)_2 \cdot 4H_2O$ at 70 °C. The corresponding melt compositions are given in Table 1.

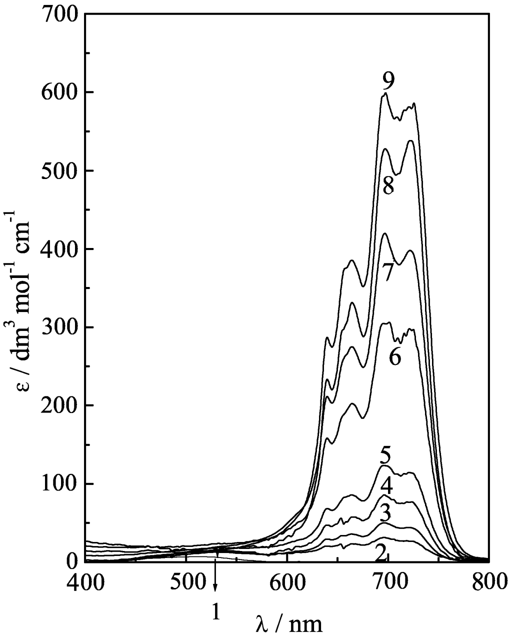

Fig 3. Variation of the spectra of cobalt(II) with bromide concentration in molten $Ca(NO)_2 \cdot 4H_2O$ at 70 °C. The corresponding melt compositions are given in Table 1.

spectra for the chloride system and nine spectra for the bromide system with different halide concentrations covering the whole concentration range are presented here as examples. The composition of the solutions corresponding to the spectra presented here are given in Table 1. The complete experimental results can be obtained upon request from the authors.

The spectra of cobalt(II) nitrate solution in pure calcium nitrate tetrahydrate of Fig. 1 show an absorption maximum at 512 nm, very close to 510 nm, ascribed to hexa-co-ordinated cobalt(II) aqua-complexes in aqueous solutions [2] and at a somewhat shorter wavelength than in aqueous ammonium nitrate – calcium nitrate melts (525 nm) [10]. In Fig. 1 the overall molar absorption coefficient ε, defined as

$$e = Al^{-1}c_{\mathrm{M}}^{-1}, \qquad (2)$$

where A is the absorbance, l the light pathway and c_{M} the total metal ion concentartion; is plotted against the wawelength. The position of the maximum and the value of the overall molar absorption coefficient ($\varepsilon_{\max} = 7.7$ dm^3 mol^{-1} cm^{-1} at 70 °C) indicate octahedral co-ordination of cobalt as suggested earlier [2, 10, 11, 14, 15]. The overall molar absorption coefficient increases with temperature as expected for octahedral co-ordination.

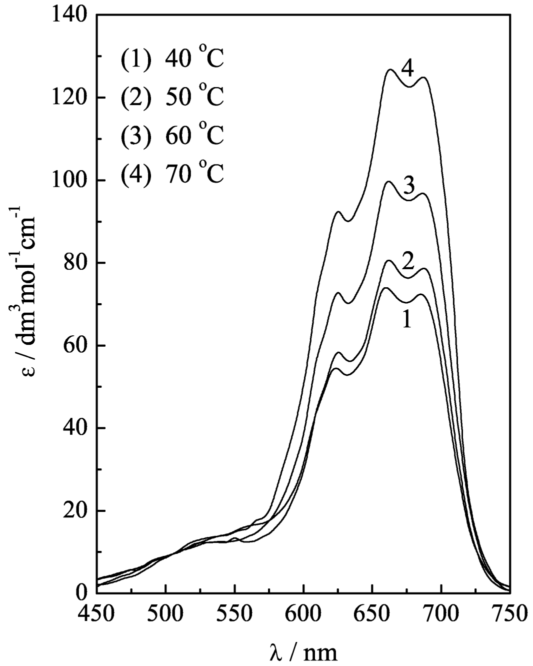

Fig. 4. Variation of the spectra of cobalt(II) with temperature in melt containing 0.90 mol kg^{-1} chloride, *c*(Co) = $3.25 \cdot 10^{-3}$ mol kg^{-1}.

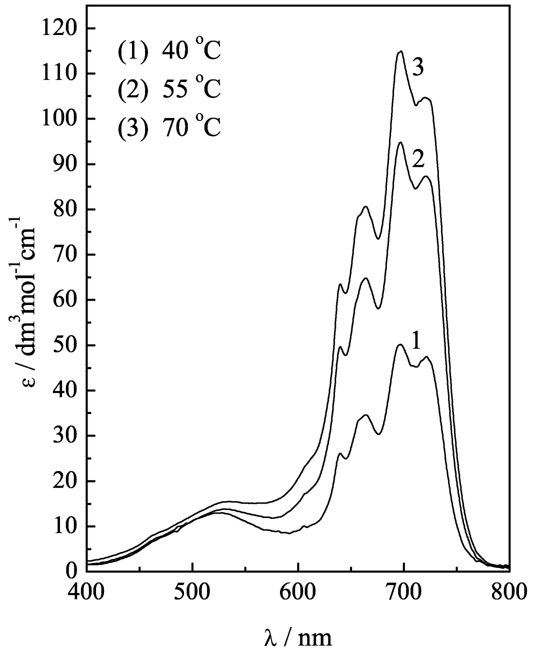

Fig. 5. Variation of the spectra of cobalt(II) with temperature in melt containing 0.79 mol kg^{-1} bromide, *c*(Co) = $9.80 \cdot 10^{-3}$ mol dm^{-3}.

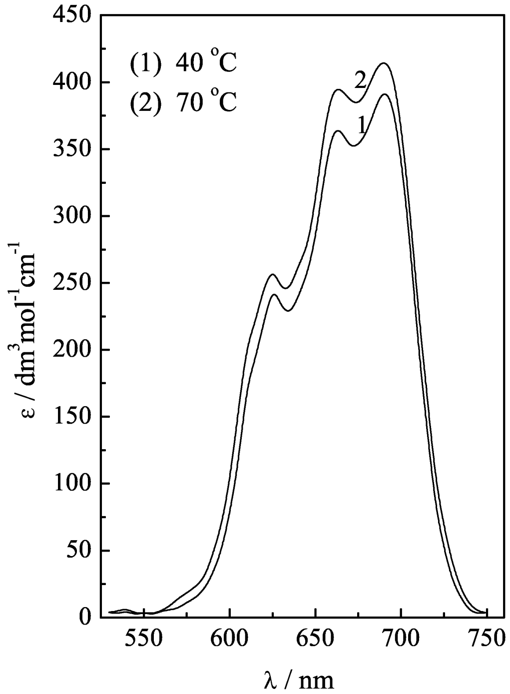

Fig. 6. Spectra of cobalt(II) in molten $CaCl_2 \cdot 6H_2O$ at 40 and 70 °C. *c*(Co) = $3.77 \cdot 10^{-3}$ mol kg^{-1}.

Addition of chloride or bromide caused a pronounced shift of the absorption maximum toward lower energies and a large increase of absorption intensity. Chloride containing melts, Fig. 2, show three maxima, at 623, 660 and 690 nm. The position of this multiple absorption band is the same as that for $[CoCl_4]^{2-}$ in 12 mol dm^{-3} aqueous HCl solution, in dimethylformamide [16] and in aqueous ammonium nitrate – calcium nitrate melt [10]. The position of the maxima and the size of the overall molar absorption coefficient indicate tetrahedral co-ordination of cobalt(II), although it could also be attributed to severely distorted octahedral species [9, 17]. The "tetrahedral" maximum is at a slightly shorther wavelength than in pure chloride melts [17], but at the same position as in eutectic melt of $LiNO_3$ – KNO_3 [3, 8]. This indicates some coordination by nitrate ions.

Bromide containing melts show four maxima, at 640, 665, 695 and 725 nm, Fig. 3, in good agreement with the cobalt(II) bromide spectra in aqueous ammonium nitrate – calcium nitrate [10] and $LiNO_3$ – KNO_3 [3, 4] melts. The maximum at 725 nm agrees well with 720 nm for tetrahedral cobalt(II) bromide in pure bromide melt [18], indicating, again, tetrahedral co-ordination.

An increase in temperature also caused an increase in the overall molar absorption coefficient, both for chloride and bromide containing melts (Figs. 4 and 5). The increasing intensity in the multiple absorption maxima, referred as “tetrahedral”, is opposite to the normally expected behaviour of tetrahedral species. Moreover, cobalt(II) chloride spectra in pure $CaCl_2 \cdot 6H_2O$, in which the tetrahedral $[CoCl_4]^{2-}$ is the predominant species, showed only a small increase in the absorption coefficient, Figure 6. Therefore the cause of the increasing absorption intensity in $Ca(NO_3)_2 \cdot 4H_2O$ may either be due to the presence of lower octahedral or severely distorted octahedral mixed complexes with halide and nitrate ions, or to higher stability of the tetrahedral ones and mixed at higher temperature [10].

Stability Constants of the Complexes

The complex formation equilibrium in a mixed ligand system

$$\mathrm{M} + p\mathrm{A} + q\mathrm{B} \rightleftharpoons \mathrm{MA}_p\mathrm{B}_q \tag{3}$$

can be characterized by a set of stability constants,

$$\beta_{pq} = [\mathrm{MA}_p\mathrm{B}_q]/[\mathrm{M}][\mathrm{A}]^p[\mathrm{B}]^q. \tag{4}$$

On the basis of the cobalt(II) co-ordination by halide ions in other solvents, we assumed that the complexes were mononuclear in cobalt(II), and that the maximum ligand co-ordination for cobalt(II) was 4.

For the computation of the stability constants β_{pq} and species spectra $\varepsilon_{pq}(\lambda)$ the non-linear regression program STAR [19] was used. On the basis of the absorption spectra one should expect overlapping of species spectra and formation of various complex species with halide ligand including complexes with associated nitrate ions. For that reason it is necessary to have a properly assumed chemical model including the number of complexes formed and good estimates of starting values of the parameters in order to achieve proper convergence toward a minimum of the squared residuals sum. The number of absorbing species has been determined by factor analysis using the program STAR/FA [19] and the program MRA [20] that applies matrix rank analysis. From a large number of trials to obtain the most relevant complexation model it was concluded that the following species were formed: $[Co(NO_3)_4]^{-2}$, $[Co(NO_3)_2X_2]^{-2}$ and $[CoX_4]^{-2}$. The stability constant for the complex $[Co(NO_3)_4]^{-2}$ should be independent of the type of halide ligand, since it refers to the halide free melt. Thus, in the calculation of the stability constants for the other two complexes the same value of β_{40} can be used both for the chloride and bromide systems. Therefore, as a starting value of β_{40} in the calculation of the stability constants of the bromide complexes we used the value obtained from chloride data in our previous work [13]. This value was then refined together with the other two constants. The new β_{40} value was then used to recalculate the stability constants of the chloride complexes. Finally, the mean value of β_{40} obtained in the refinement procedure of the chloride and bromide system, respectively, has been used in the calculation of the stability constants of $[Co(NO_3)_2X_2]^{-2}$ and $[CoX_4]^{-2}$. The stability constants of these complexes, calculated at 40 and 70 °C, are given in Table 2.

Table 2. Stability constants for $Co(NO_3)_pX_q$ in molten $Ca(NO_3)_2 \cdot 4H_2O$.

	log β_{pq}	
Complex	$t = 40$ °C	$t = 70$ °C
$[Co(NO_3)_4]^{2-}$	1.78 ± 0.23	$1.92 \pm 0{,}03$
$[Co(NO_3)_2Cl_2]^{2-}$	3.83 ± 0.22	$4.10 \pm 0{,}04$
$[CoCl_4]^{2-}$	5.21 ± 0.22	$5.68 \pm 0{,}04$
$[Co(NO_3)_2Br_2]^{2-}$	2.74 ± 0.12	$1.80 \pm 0{,}47$
$[CoBr_4]^{2-}$	4.53 ± 0.05	$5.07 \pm 0{,}03$

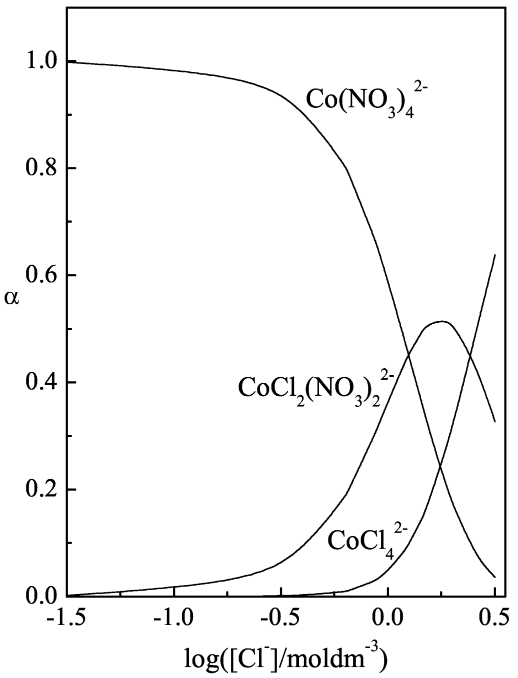

Fig. 7. The fraction α of Co(II) in different complexes $Co(NO_3)_pCl_q$ in molten $Ca(NO)_2 \cdot 4H_2O$ at 40 °C.

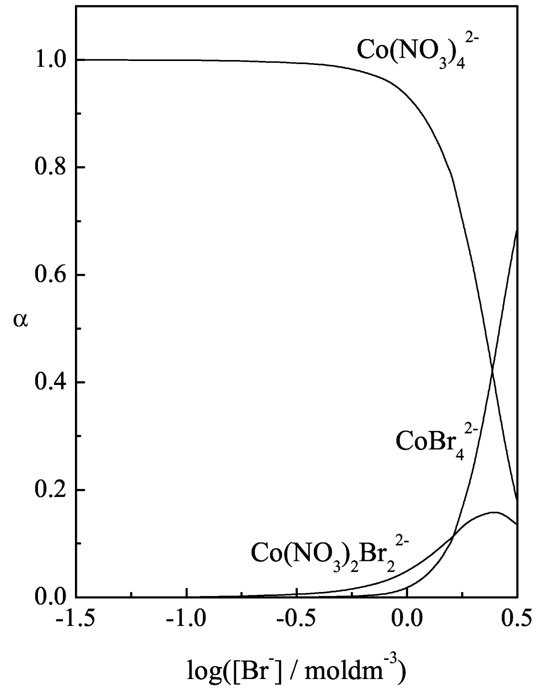

Fig. 8. The fraction α of Co(II) in different complexes $Co(NO_3)_pBr_q$ in molten $Ca(NO)_2 \cdot 4H_2O$ at 40 °C.

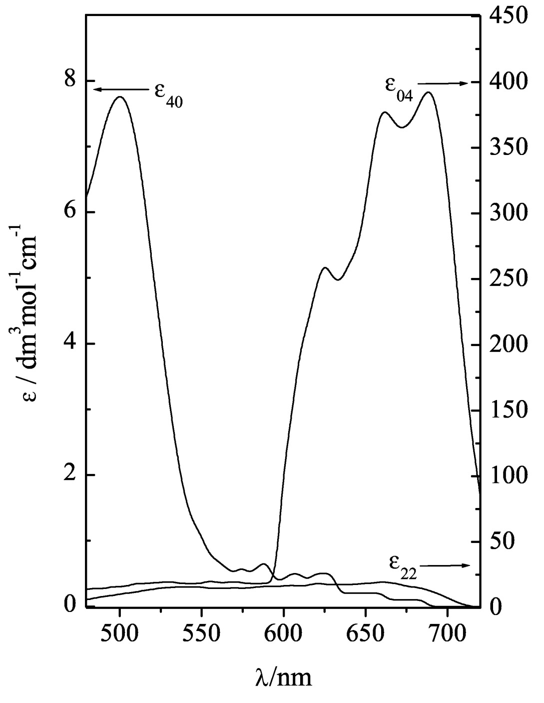

Fig. 9. Resolved species spectra for $Co(NO_3)_pCl_q$ in molten $Ca(NO)_2 \cdot 4H_2O$ at 40 °C.

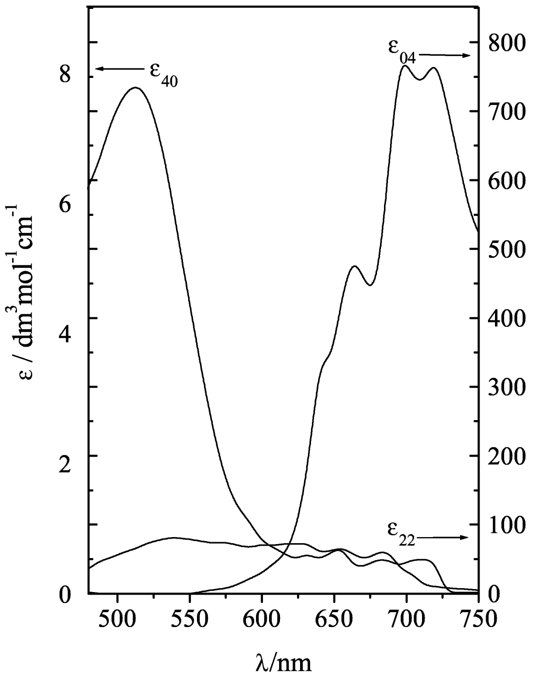

Fig. 10. Resolved species spectra for $Co(NO_3)_pBr_q$ in molten $Ca(NO)_2 \cdot 4H_2O$ at 40 °C.

As seen from Table 2, the chloride complexes are more stable than the corresponding bromide complexes, in accordance with the data for eutectic $(K,Li)NO_3$ at 160 °C. The results support the assumptions that mixed complexes are formed and that the stability constants increase with temperature, except in one case, for $[Co(NO_3)_2Br_2]^{2-}$, but the value at 70 °C seems to be too low.

Figures 7 and 8 display the fraction of Co(II) present in different complexes as a function of $\log([X]/\text{mol dm}^{-3})$ for the Co(II) – Cl and Co(II) – Br system, respectively. From the figures it can be seen that the fraction of $[CoX_4]^{2-}$ amounts about 62% in case of chloride and about 68% in case of bromide at maxiumum halide concentration $[X] = 3.2\ \text{mol dm}^{-3}$. It is interesting that the ratio of the intermediate species $[Co(NO_3)_2Cl_2]^{2-}$ is much higher than that of $[Co(NO_3)_2Br_2]^{2-}$. Moreover, it is evident that the only species spectrum that can be obtained by direct measurements is that of $[Co(NO_3)_2]^{4-}$.

The species spectra for the chloride and bromide system, calculated from the experimntal spectra using fixed values of β_{pq}, are displayed in Figs. 9 and 10, respectively. The spectrum ε_{40} in Figs. 9 and 10, derived from halide containing melts, arises from $[Co(NO_3)_4]^{2-}$. This spectrum agrees very well with those derived from pure calcium nitrate melt (Fig. 1) and aqueous solutions [2], indicating again octahedral co-ordination. The resolved spectrum ε_{04} for $[CoCl_4]^{2-}$ (Fig. 9) agrees with those for tetrahedral $[CoCl_4]^{2-}$ in 12 mol dm^{-3} aqueous HCl solution, dimethylformamide [16] and molten chloride [17]. Hence, $[CoCl_4]^{2-}$ in molten $Ca(NO_3)_2 \cdot 4H_2O$ is most probably a tetrahedral species.

The spectrum of $[CoBr_4]^{2-}$ (Fig. 10) is very similar to that of $[CoCl_4]^{2-}$, but the bromide complex absorbs light at somewhat lower energies. The spectrum agrees well with spectra that have been assigned to tetrahedral $[CoBr_4]^{2-}$ in pure bromide melt [18]. It is thus concluded that both $[CoCl_4]^{2-}$ and $[CoBr_4]^{2-}$ have tetrahedral configuration.

Referring now to the species spectra ε_{22} of $[Co(NO_3)_2Cl_2]^{2-}$ and $[Co(NO_3)_2Br_2]^{2-}$, it should be noted that, due to the uncertainties in the stability constants of the mixed complexes and in the values of ε_{22}, a meaningful evaluation of the fine details of the spectra is not possible. Hence, no definite conclusions can be drawn on the structure of these mixed complexes.

Acknowledgement

This work was financially supported by the Ministry of Science and Environmental Protection of Republic of Serbia under contract no. 1399.

[1] C. J. Ballhausen and A. D. Liehr, J. Mol. Spectr. **2**, 342 (1958).

[2] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th ed. John Wiley and Sons, New York 1988.

[3] I. V. Tananaev and B. F. Dzhurinskii, Dokl. Akad. Nauk SSSR **134**, 1374 (1960).

[4] I. V. Tananaev and B. F. Dzhurinskii, Dokl. Akad. Nauk SSSR **135**, 94 (1960).

[5] F. A. Cotton and J. G. Bergman, J. Amer. Chem. Soc. **86**, 2941 (1964).

[6] J. A. Duffy and M. D. Ingram, J. Amer. Chem. Soc. **51**, 544 (1968).

[7] A. G. Keenan and J. Ferrer, J. Phys. Chem. **76**, 2844 (1972).

[8] S. Hemmingson and B. Holmberg, Inorg. Chem. **19**, 2242 (1980).

[9] J. Savović, R. Nikolić, and D. H. Kerridge, Fluid Phase Equilibria **118**, 143 (1996).

[10] D. H. Kerridge, R. Nikolić, and D. Stojic, J. Chem. Soc. Dalton Trans. 1663 (1986).

[11] J. Tripković, R. Nikolić, and D. H. Kerridge, J. Serb. Chem. Soc. **54**, 527 (1989).

[12] M. Marinković, R. Nikolić, J. Savović, S. Gadžurić, and I. Zsigrai, Sol. Energy Mater. Sol. Cells **51**, 401 (1998).

[13] I. J. Zsigrai, S. Gadžurić, and R. Nikolić in: Advances in Molten Salts: From Structural Aspects to Waste Processing (Ed. M. Gaune-Escard), Begell House Inc., New York 1999, p. 690.

[14] P. J. Proll, L. H. L. H. Sutcliffe, and J. Walkley, J. Phys. Chem. **65**, 455 (1961).

[15] J. R. Dickinson and K. E. Johnson, J. Mol. Spectrosc. **33**, 414 (1970).

[16] S. Buffagni and T. M. Dunn, J. Chem. Soc. 5105, (1961).

[17] H. A. Øye and D. Gruen, Inorg Chem. **3**, 836 (1964).

[18] B. R. Sundheim and M. Kukk, Discuss. Faraday Soc. **32**, 49 (1961).

[19] J. L. Beltrán, R. Codony, and M. D. Prat, Anal. Chim. Acta **276**, 441 (1993).

[20] G. Peintler, I. Nagypál, A. Jancsó, I. R. Epstein, and K. Kustin, J. Phys. Chem. **101**, 8013 (1997).