An X-ray and NMR Study on Cerium(III) and Magnesium(II) Perchlorate Solutions

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Metal-perchlorate solutions have been investigated by the X-ray scattering technique and 35Cl NMR spectroscopy. The aim of this work was to obtain structural information on the complex formation between the Cerium and the perchlorate group and on the ClO₄⁻ — H₂O interactions. The NMR data, the correlation functions and the analysis of the structure functions agree with the literature information about the Ce — (OCIO₄)₃ species present in aqueous solutions. Good agreement with experimental data is achieved through a model in which the perchlorate ions are bonded as monodentate ligands to the Cerium(III). No complex formation is confirmed for Mg(II). The cations also possess a second coordination shell of water molecules. Some indications have been obtained supporting the presence of ClO₄⁻ — H₂O contacts.

I. Introduction

In a previous study [1] on a concentrated aqueous Ce(NO₃)₃ solution the existence of complex-formation between cation and anion was proven and the inner sphere water coordination number was determined. Two alternative models were tested and the coordination number of Ce(III) resulted between 7.5–8.5. Recently Habenschuss and Spedding [2–4] presented results of an extensive X-ray study for ten rare earth (except the Ce³⁺ ion) chloride solutions, indicating that the inner sphere water coordination of the rare earth ions in aqueous solutions decreases from nine to eight, due to the decreasing rare earth ionic radii. Information on the hydration of the Nd³⁺ ion has been obtained directly and unambiguously by neutron diffraction [5]. A well-defined hydration sphere of 8.5 ± 0.2 water molecules has been estimated.

In perchlorate solutions of Ce(III), Fratiello et al. [6] declare that “the spectral evidence for inner-shell complex formation leads to the possibility of a greater maximum hydration number than 6 for this species”. As regards complex-formation, a survey of the literature [7] on the behaviour of Ce(III) in perchlorate solutions points to Ce—OCIO₄ contacts. This phenomenon has been studied in sulphate, phosphate and nitrate solutions of divalent and trivalent cations [8–11]; in these, the presence of a peak in the correlation function G(r), attributable to the cation-X (with X = S, P, N from sulphate, phosphate and nitrate, respectively) interaction (in the range 3.1–3.6 Å), has been crucial to show the inner-complex formation. In the range 3.5–3.9 Å can also fall the contributions due to the ClO₄⁻ — H₂O interactions (distances between chloride atom and H₂O molecules). To determine the behaviour of the perchlorate ion in different conditions we analyzed also a solution of Mg(ClO₄)₂ in which the concentration of the ClO₄⁻ anion is similar to that of the Ce(ClO₄)₃ solution. In case of Mg(ClO₄)₂ no contacts between cation and anion were expected in aqueous solutions [12]. In water the perchlorate ion is weakly solvated compared with magnesium. For contact ion association, a solvent molecule must be removed from the cation and replaced by a ClO₄⁻ anion. Solvents with high donor numbers are difficult to replace, and therefore a high donor number inhibits ion association. As far as the anion is concerned, diffraclometric studies generally lead to the conclusion that the ClO₄⁻ — H₂O interactions are weak. In presence of bi- and trivalent cations, as in solutions of Fe(ClO₄)₃ [13], Ni(ClO₄)₂ and Co(ClO₄)₂ [14] they can be masked by the strong cationic contributions. Magnesium solutions were investigated since, due to the low weight of this ion (10 electrons in the atom in comparison to the 17 of chloride), a decrease of the Mg(H₂O)₇ peak is expected and therefore a better definition of the

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Cl–H₂O one. The choice of magnesium was made also because, from previous studies carried out on this ion, well defined first and second coordination shells were obtained [15, 16]. Nuclear magnetic resonance spectroscopic studies also can provide significant structural information on aqueous electrolyte solutions; in particular, the relaxation time of the ³⁵Cl nucleus in the perchlorate ion reveals the presence of contact ion pairs, while it is insensitive to solvent-separated ion aggregation [12]. This technique has been used for studying perchlorate complexes with transition metal ions in aqueous solution [17] and gave evidence of the existence of a weak inner-sphere complex of Mn(II) ion in perchlorate acid solution.

II. Experimental Results

A) X-ray Scattering Measurements and Data Treatment

The solutions studied were obtained by dissolving a weighed amount of Ce(ClO₄)₃·6H₂O (G. Frederick Smith Chemical Company) in a solution of HClO₄, and Mg(ClO₄)₂·6H₂O (BDH) in distilled water. Cation and anion contents were determined by standard methods [18, 19]. The composition of the solutions investigated is given in Table 1. X-ray scattering data were obtained at 20 ± 1 °C on a Θ−Θ diffractometer equipped with a Mo X-ray tube (wavelength = 0.7107 Å). The observed range of scattering angles (2θ) was from 3° to 120°, corresponding to the range 0.5 < s < 15.28 Å⁻¹, where s = (4 sin θ/λ) is the scattering variable. The measured intensities were corrected for background, polarization and absorption [20], and smoothed by fourth differences [21]. The absolute scale for the intensities was established by a semiempirical method proposed by Habenschuss and Spedding [2–4] and previously used [22]. Briefly, the corrected intensities Iₖ(s) were fitted to

\[ I_k(s) = K L_k(s) \left[ \sum_{i=1}^{m} x_i f_i^2(s) + \sum_{i=1}^{m} x_i I^{inc}_i(s) \right] \cdot [A + \sum B_j \exp(-C_j s^D j)]/[A + \sum B_j] , \]

where the second term is an empirical function that, according to Habenschuss and Spedding [2–4] absorbs unknown errors in the experimental data and any inadequacies in the corrections to the data. A, B_j, C_j and D_j are parameters determined by the least squares fit. The structure function i(s) was calculated from

\[ i(s) = K L(s) \left[ \sum_{i=1}^{m} x_i f_i^2(s) + \sum_{i=1}^{m} x_i I^{inc}_i(s) \right] \]

\[ \cdot [A + \sum B_j \exp(-C_j s^D j)]/[A + \sum B_j] , \]

where k = 1/[A + \sum B_j] is the scaling constant, xᵢ are the stoichiometric coefficients in a structural unit containing m kinds of atoms, fᵢ(s) are the scattering factors [23–26] corrected for anomalous dispersion and I^{inc}_ᵢ(s) is the Compton radiation corrected for electron recoil. The experimental correlation function G(r) was obtained from i(s) by Fourier transformation according to

\[ G(r) = 1 + \left( 2\pi^2 q_0 r \right)^{-1} \int_{s_{min}}^{s_{max}} i(s) M(s) \sin(sr) ds \]

at 0.05 Å increments. r is the interatomic distance, s_{min} and s_{max} used are respectively 0.0 and 15.28 Å⁻¹, q_0 is the bulk number density of the stoichiometric units, and the modification functions M(s) is equal to \( \left( \sum_{i=1}^{m} x_i f_i \right)^{-2} \). Before calculating the final correlation functions, the structure functions s_i(s) were corrected for residual systematic errors by means of a procedure described by Levy, Danford and Narten [27]. The method is based on the removal of the peaks present in G(r) at small values of r, and is more effective if a sufficiently extended range of distances can be used to this end. Therefore, in addition to unphysical ripples, the peak due to the Cl–O (from ClO₄⁻ group) distance was also removed from G(r), following a proce-

<table>
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<th>[H⁺]</th>
<th>[H₂O]</th>
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<th>μ (cm⁻¹)</th>
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<th>[ClO₄⁻]</th>
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</tr>
<tr>
<td>HClO₄</td>
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</table>
Fig. 1. Observed structure functions (-----) for the two studied solutions compared with those calculated with the parameters reported in Table 3.

Fig. 2. Observed (-----) and model (----) distance spectra obtained from Fourier transformation of the corresponding structure functions reported in Figure 1.

The procedure used elsewhere [1, 22], since this contribution is obvious and not very important for the interpretation of the results. The O_{Cl}—O_{Cl} contribution, obviously, was not removed because it is not a resolved peak but its contribution is present under the peak due to Ce—O_{Cl} distances. No convergence factor was used in calculating the Fourier transformation.

35Cl has been observed on a Varian FT-80A pulse spectrometer at a nominal frequency of 7.793 MHz, using 10 mm sample tubes and a SW: 4000 Hz, an AT = 1 s, a Pw = 30 μs and a number of transients ranging from 10 to 200, depending on concentration and line width. Proton decoupler was off. The probe temperature was 30 ± 1°C. 35Cl spectra of different solutions of Mg(ClO_{4})_{2}, Ce(ClO_{4})_{3} and HClO_{4} have been recorded. In Table 2 the concentrations of the cations and of ClO_{4} in the examined solutions are reported.

III. Analysis of the Results

A) Correlation Functions

The experimental structure functions s_{i}(s) and the resulting correlation functions G(r) are plotted in Figs. 1 and 2, respectively (points). An inspection of
the $G(r)$ functions allows the first qualitative information to be obtained. In the case of the Cerium solution four well-resolved peaks can be distinguished with their maxima centered at about 2.50–2.55, 3.00, 3.65 and 4.60 Å.

The first peak is diagnostic of the Ce$^{3+}$–O$_1$ distances (with O$_1$ oxygen atoms deriving from water molecules or from perchlorate anions) on the basis of the ionic radii of the species and as found in aqueous solution [1] and in the crystal structures of CeCl$_3$(H$_2$O)$_7$, [28]. A contribution to this peak arise also from O–O interactions within the perchlorate anion, their mean values being in the solid structure ~ 2.36 Å.

The peak centered at about 3.00 Å is certainly caused by nearest-neighbour interactions H$_2$O–H$_2$O.

The attribution of the large peak at about 4.6 Å is less direct than that of the two preceding peaks. In the Ce(NO$_3$)$_3$ solution [1] the mean contribution to this peak resulted from the second hydration shell around the Ce(III) ion. Obviously further contributions to this peak also arise from H$_2$O–H$_2$O second distances 4.5–4.7 Å).

The very significative peak present at about 3.65 Å indicates the presence of cation-anion contact phenomena in our solution. The origin of this peak are the Ce–Cl interactions, the value of the Ce–Cl distance depending on the ClO$_4^-$ orientation.

In the Mg(ClO$_4$)$_2$ solution three peaks are present at about 2.25, 2.9 and 4.20 Å.

The first derives from Mg–H$_2$O$_\text{II}$ interactions (contributions at about 2.1 Å, as found in [15] and [16]) and O–O interactions within the perchlorate anion (contributions at about 2.36 Å).

The second peak is certainly caused by nearest-neighbour interactions H$_2$O–H$_2$O. Contributions could also come from interactions between the oxygen atoms of the perchlorate anion and anionic hydration water molecules.

The peak at 4.20 Å derives from Mg–H$_2$O$_\text{II}$ (H$_2$O$_\text{II}$ = second shell molecules as found previously [15, 16]).

A small hump at about 3.80 Å is also present in the correlation function; it can be ascribed to the Cl–H$_2$O interactions.

Peaks from larger intermolecular distances are absent. As in previous investigations on concentrated solutions, the order phenomena observable in the experimental correlation curves concern ionic hydration exclusively.

B) NMR Data

HClO$_4$ and Mg(ClO$_4$)$_2$ Solutions

The $^{35}$Cl spectra of ClO$_4^-$ in HClO$_4$ at various concentrations in the range 1–11 M show a slight

![Fig. 3. Halfline width of the $^{35}$Cl NMR signal of the perchlorate-anion for three different series of solutions vs. perchlorate anion concentration: (–, △) pure Ce(ClO$_4$)$_3$ solution of varying concentration; (–, ○) a solution of fixed 1 M Ce(III) concentration and ClO$_4^-$ varying for added perchloric acid; (–, ○) HC104 at varying concentration.](image-url)
increase of linewidth only for the solutions with concentrations greater than 8 M (Fig. 3), and this should be ascribed to viscosity effects.

The $^{35}\text{Cl}$ spectra of ClO$_4^-$ in the studied solutions (Table 2, Fig. 4) of Mg(ClO$_4$)$_2$ show no significant change of spectral parameters with respect to the solutions of HClO$_4$ at the same concentrations; therefore no complex formation is remarked, in agreement with previous work [12, 29].

Ce(III) Solutions

In the observed series, the first with increasing concentration of Ce(ClO$_4$)$_3$, the second with fixed Ce$^{3+}$ concentration 1 M and varying ClO$_4^-$ concentration, two phenomena are observed:

i) the occurrence of a new resonance downfield with respect to that of the free ClO$_4^-$;

ii) a remarkable increase of linewidth of the signals with ClO$_4^-$ concentration (as can be seen from Figs. 3 and 4) in a non linear way, that leads to a collapse of the two signals.

The first point is indicative of the formation of a complex between ClO$_4^-$ and Ce(III). The new peak is at ~11 Hz downfield with respect to that of free ClO$_4^-$; the two forms are in a slow exchange situation, as can be seen from the halfline width of the peak of the free form, unchanged in comparison with ClO$_4^-$ at the same concentration in HClO$_4$ solutions.

In order to attribute this peak the spectra were analyzed in terms of Lorentzian lineshapes whose parameters (chemical shift, halfline width and height) were optimized by a least squares procedure: the resultant populations of the two forms up to the collapse of the two signals indicate a number of bound ligands for the metal atom ranging from 1 to 2; these values are affected by a large error due to the noticeable superimposition of the two signals of different broadness. Nevertheless they indicate the presence of complexes of different stoichiometry, since only 1:1 and 1:2 complexes would have a constant so large that with Ce(ClO$_4$)$_3$ we would have the principal signal due to bound ClO$_4^-$.

Concerning the point ii), the remarkable increase of linewidth with ClO$_4^-$ concentration can be explained with different concomitant causes:

1) an increase of the viscosity of medium
2) the formation of higher than 1:3 complexes, with a cooperative effect, whose linewidths are larger than those of lower stoichiometry adducts;
3) an intermediate exchange situation between ClO$_4^-$ in the lower and higher stoichiometry adducts; a similar situation has been pointed out in our study [30] on complexes of Al$^{3+}$, in which a quantitative determination of the rate parameters was possible.

Our data do not allow the discrimination between the various effects nor furthermore a quantitative evaluation.

The formation constants cannot be reliably evaluated for the following reasons:

![Fig. 4. NMR signals of $^{35}\text{Cl}$ for perchlorate anion in four different environments: a) perchloric acid 5.85 M; b) Mg(ClO$_4$)$_2$ 2.5 M; c) Ce(III) 1.21 M, ClO$_4^-$ 5.02 M; d) Ce(III) 1 M, ClO$_4^-$ 10.8 M. The solutions b) and c) are those examined by X-ray. The clear second peak for curve c is to be remarked, while curve b shows only a slight broadening, that should be ascribed to viscosity effects.](image-url)
There is no possibility of varying the ClO₄⁻ concentration freely: in fact, if one uses Ce(CIO₄)₃ the starting ClO₄⁻ concentration is three times that of Ce(III); if a different Ce(III) salt is used we should have to consider mixed complexes because presumably any other anion should have greater complexing ability than ClO₄⁻ toward Ce(III). Consequently, the range of concentrations where \( \bar{n} \) can be measured is too narrow, being limited by the stoichiometry of the used salt and by the broadening of signals, that forbids a clear distinction, respectively, for low and high concentrations. Only one signal is observable for the bound forms, which is to ascribe, as the least-squares evaluated population pointed out, to at least 1:1, 1:2 and 1:3 stoichiometry adducts, whose relative population cannot be separately evaluated.

Nevertheless an important conclusion can be drawn from the spectra in which the two signals are well separated, i.e. the existence of stable adducts between ClO₄⁻ and Ce(III) and a mean value of bound ligands for the metal atom of about two for the X-ray studied solution.

**C) Models**

In order to get more detailed information than that directly deducible from the experimental correlation functions, the usual analysis based on the calculation of a model structure function, which was systematically refined against experimental data, has been used. This synthetic structure function was constructed according to the formula proposed by Debye

\[
i(s) = \sum_{i=1}^{m} \sum_{j=1}^{n_i} x_i f_i f_j \left( \sum_{i=1}^{m} x_i f_i \right)^{-2} \exp\left(-\frac{1}{2} \sigma_{ij} s^2 \right) \frac{\sin(s r_{ij})}{s r_{ij}},
\]

where \( m \) = number of atoms in the stoichiometric unit, \( n_i \) = number of atoms of discrete structure "seen" by an origin atom of \( i \) type, \( r_{ij} \) = mean radial distance of the \( j \)th atom from an origin atom of the \( i \) type, \( \sigma_{ij} \) = root-mean-squares deviation for the distance \( r_{ij} \). The least squares refinements were carried out using the s intervall 1.5–15.28 Å⁻¹, the function

\[
U = \sum_{s_{\text{min}}}^{s_{\text{max}}} (i(s)_{\text{calc}} - i(s)_{\text{obs}})^2
\]

being minimized by means of the LSHS program [1]; this is based on the classical Gauss-Newton linearization method as modified by Marquardt [31].

The quantitative analysis has been made in different steps. Since the structural information about the first and second hydration shells of the Cerium(III) ion in perchlorate solutions is poor, a first preliminary calculation has been carried out. In it only six independent parameters have been introduced, i.e. the first distance Ce–O(r₇CeHO₂), the root-mean-squares deviation of the distance (σ₇CeHO₂), the coordination number (n₇CeHO₂), the second distance Ce–O(r₈CeHO₄), the root-mean-squares deviation of the distance (σ₈CeHO₄), and the coordination number (n₈CeHO₄). A number of calculations were carried out with \( s_{\text{min}} \) and \( s_{\text{max}} \) fixed. Only four parameters have been fitted; the \( n_{\text{Ce-H}_2\text{O}_1} \) and \( n_{\text{Ce-H}_2\text{O}_1} \) values in each calculation were fixed. The \( n_{\text{Ce-H}_2\text{O}_1} \) values vary from 6 to 12 with steps of 1, and the \( n_{\text{Ce-H}_2\text{O}_1} \) values vary from 14 to 18 with steps 2. The function U reaches its minimum at \( n_{\text{Ce-H}_2\text{O}_1} = 10 \) and \( n_{\text{Ce-H}_2\text{O}_1} = 14 \). The U value is equal to 1.67 with these contributions. At this point, on the basis of the qualitative analysis of the \( G(r) \) and the results of the NMR data the ulterior parameters added in the model are the following:

a) The O–O contacts from the perchlorate group (the distance \( r_{\text{Cl-O}_1} \) and its root-mean-squares deviation \( \sigma_{\text{Cl-O}_1} \) are independent parameters).
b) The Ce–OClO₄ contacts from the complex; the Ce–Cl, Ce–O₂ = Ce–O₃ and Ce–O₄ distances (Scheme 1) are parameters, while a root-mean-squares deviation for all three distances is introduced \( (\sigma_{\text{complex}}) \). The average number of coordinated perchlorate groups is also an independent parameter \( (z_{\text{Ce-ClO}_4}) \). As far as the Ce–O₁ distance we used the same value Ce–H₂O₁, and the parameter \( n_{\text{Ce-H}_2\text{O}_1} \) (reported in Table 3) indicates the total coordination number for Ce(III), i.e. the sum of H₂O₁ water molecules around the ion and the \( z \) perchlorate groups.

\[
\text{Scheme 1. Model assumed for the bonding of the perchlorate group to the Cerium(III). The model has a mirror plane containing the cerium, the bridging oxygen O₁, the Cl atom, and the O₄ atom.}
\]
Table 3. Mean distances $r$(Å) and root-mean-squares deviation $\sigma$ (Å) for the discrete interactions used in the final calculation of the synthetic functions from the models. Standard errors for the refined parameters are given in parentheses. $n$ is the coordination number. $z$ is the average number of perchlorate bonded to cerium.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ce</th>
<th>Mg</th>
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<tr>
<td>$r_{\text{Me}-\text{H}_2\text{O}}$</td>
<td>2.574(4)</td>
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<td>$\sigma_{\text{Me}-\text{H}_2\text{O}}$</td>
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<td>0.129(7)</td>
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<td>6</td>
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<tr>
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<td>4.28 (1)</td>
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<tr>
<td>$\sigma_{\text{Me}-\text{H}<em>2\text{O}</em>{\text{H}}}$</td>
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<td>0.23 (1)</td>
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<tr>
<td>$n_{\text{Me}-\text{H}<em>2\text{O}</em>{\text{H}}}$</td>
<td>19.5 (7)</td>
<td>12.0 (7)</td>
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In this model are reported in Table 3. With the parameter values obtained in the least-squares refinements we calculated the structure function reported in Fig. 1 (solid line), and with the same procedure used for the Cerium solution we calculated the theoretical correlation function $G(r)$ reported in Fig. 2 (solid line).

IV. Discussion and Conclusions

The qualitative analysis of the experimental correlation functions has shown cerium-perchlorate contacts and ClO$_4^-$–H$_2$O contacts in the Mg(ClO$_4$)$_2$ solution. This is in line with literature, which points out cerium-perchlorate complex formation. The existence of anion-solvent interactions is also visible, but the $G(r)$ functions are mainly characterized by metal–water and water–water interactions. The NMR measurements supported the X-ray findings on the Cerium–ClO$_4^-$ contacts. The values of the parameters obtained in the quantitative analysis of the $si(s)$ functions by the least-squares fitting with the used models suggest the same conclusions.

As concerns the parameters of the hydration shells of magnesium, they are in agreement with those previously obtained [15, 16]. The number of contacts ClO$_4^-$–H$_2$O is high, indicating weak hydrogen bonds between the perchlorate anion and the water molecules in agreement with the literature.

As for the average number of first contacts Ce–O (sum of water molecules H$_2$O and oxygen O from perchlorate groups), it is between 9 and 10. The number of ClO$_4^-$ ions bonded to Ce(III) resulted to be about 2.

The agreement between our model and the experimental data is not a proof that this model is apposite; in fact the selected orientation, reported in Scheme 1, for the perchlorate group with respect the Ce(III) is one of the many possible ones. Obviously we can built up other models with slightly different orientations, and these give us good agreements with the experimental data.

The detailed analysis of the partial contributions of our model to the total structure function, shown in Figs. 5a–l, and the respective contributions to the radial distribution function in the differential form, reported in Figs. 6a–l, point out the reliability of the different parameters used in our model.

The use of two different complementary techniques was useful in obtaining more information on the behaviour of perchlorate in different cation solutions.
Fig. 5. Observed structure functions (-----) and partial structure functions (----) for the solution of Ce(ClO$_4$)$_3$. a) Ce-O contacts; b) O-O (from perchlorate groups) contacts; c) sum of the a and b contributions; d) Ce-H$_2$O contacts; e) sum of the a, b and d contributions; f) H$_2$O-H$_2$O contacts; g) sum of a, b, d and f contributions; h) Ce-Cl contacts; i) Ce-O$_2$, Ce-O$_3$, Ce-O$_4$ contacts; j) sum of h and i contributions.

Fig. 6. Observed radial distribution function in the $D(r)-4\pi r^2 g_0$ form (-----) and peak shapes (----) for the cerium perchlorate solution. Peak shapes calculated for the interactions: a) Ce-O; b) O-O (from perchlorate groups); c) sum of the a and b interactions; d) Ce-H$_2$O; e) sum of the a, b and d interactions; f) H$_2$O-H$_2$O; g) sum of the a, b, d and f interactions; h) Ce-Cl; i) Ce-O$_2$, Ce-O$_3$, Ce-O$_4$ interactions; j) sum of h and i interactions. Clearly, without the Ce-Cl interaction the observed peak at ~ 3.6 Å would not exist.
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