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Spectroscopy and Structure of Neodymium Complexes with EDTA

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Abstract

The spectral properties of Nd^{3+}–EDTA solutions were investigated at different Nd^{3+} and EDTA concentrations within a broad pH region. The analysis of the oscillator strength values of the 'hypersensitive' $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition and of the Judd-Ofelt intensity parameters was performed in order to investigate the formation and the type of bonding in the Nd^{3+}–EDTA species. The correlation of these results with NMR and kinetic data has made it possible to suggest a relatively complete model of the Nd^{3+}–EDTA coordination. The X-ray data in the solid phase confirmed the proposed model.

Introduction

Lanthanide complexes with polyaminoacids have found wide application as NMR shift reagents in the investigation of biological systems. The problem of lanthanide ion coordination with N and O donor atoms is also important for further progress in the lanthanide coordination chemistry.

We decided therefore to investigate precisely the spectroscopic properties of the Nd^{3+}–EDTA system, considering the Nd^{3+} ion as a typical light lanthanide ion convenient for spectral measurements. Our recent studies on the spectroscopy and structure of lanthanide complexes with monocarboxylic and α-hydroxycarboxylic aliphatic acids were helpful [1–3].

Several potentiometric and calorimetric data are available for the lanthanide complexes with polyaminocarboxylic ligands. The concentration stability constants were determined and the thermodynamic formation functions were measured for lanthanide compounds with different polyaminoacids [4, 5] under the same conditions. The influence of different ligand structure modifications on the entropy and enthalpy changes of these systems provide valuable information about the structure of the solution, as well as the hydration energy of the lanthanide ion. Those results however did not solve the important problems of the formation mechanism and of the lanthanide polyaminoacid complex structure.

Extensive studies on NMR lanthanide polyaminoacids were published by Baisden *et al.* [6]. The pattern of ^1H NMR spectra indicated coordination by the nitrogen and carboxylate groups in alkaline solutions. Moreover, for Lu^{3+} and Y^{3+} EDTA compounds the AB pattern for acetate protons indicates that at least the nitrogen inversion is slow for these complexes. The ^1H NMR spectrum of the $LaEDTA^-$ seems to be intermediate between the spectra of Lu^{3+}, Y^{3+} and alkaline earth EDTA complexes.

An explanation of the lanthanide polyaminoacids formation mechanism was given by Southwood-Jones and Merbach, using NMR [7], and by Brücher and others [8, 9], using pH-metric and spectrophotometric methods.

Recent electronic spectroscopy measurements of the Ln^{3+}–EDTA systems are very incomplete and aim only at establishing the relation between the nephelauxetic effect value and such parameters as the oscillator strength of 'hypersensitive' transitions or the $U^{(2)}$ matrix elements [10, 11]. According to the opinion of some authors this can give some idea about the covalency of the bonds in those complexes. Generally, all investigations of $LnEDTA^-$ systems are far from complete, because the results obtained by different methods have been considered separately.

Experimental

Reagents

The stock solution of neodymium perchlorate was prepared from 99.9% neodymium oxide (Merck). The Nd^{3+} ion concentration was determined gravimetrically. Commercial EDTA was applied as sodium salts (Na_2H_2EDTA). A carbonate-free NaOH solution was used to adjust the pH of the ligand solutions to appropriate values.

Measurements and Calculations

All spectral measurements were made with a Cary 14 spectrophotometer within the region 11,000–30,000 cm^{-1}. All the measured solutions were prepared with the same ionic strength 2 M $NaClO_4$. The pH values of the solutions investigated

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spectroscopically were measured with a Radelkis pH-meter (with the accuracy ±0.05 pH unit). Experimental oscillator strength values were obtained by a graphic integration of the area under the absorption curves, after appropriate corrections for the base line. The τ_λ parameters were calculated from the experimental oscillator strengths and the Judd-Ofelt equation written in the following modified form:

$$\mathbf{P} = \sum_{\lambda} \frac{\tau_\lambda \sigma(\mathbf{f}^{N}{}_{\psi_J} \| \mathbf{U}^{(\lambda)} \| \mathbf{f}^{N}{}_{\psi'_{J'}})^2}{2\mathbf{J} + 1} \qquad (1)$$

$\lambda = 2, 4, 6$

where σ is the wavenumber in $[\mathrm{cm}^{-1}]$, $\mathbf{U}^{(\lambda)}$ are the matrix elements of the unit tensor calculated by Carnall *et al.* [12] in the intermediate coupling scheme, $\mathbf{f}^{N}{}_{\psi_J}$, $\mathbf{f}^{N}{}_{\psi_{J'}}$ are the initial and final states of electronic transitions respectively, and $\mathbf{J}$ is the total quantum number. The τ_λ parameters values were fitted to the experimental oscillator strength values of the 9 Nd^{3+} ion absorption bands within the range 11,000–30,000 cm^{-1}. The identification of the electronic levels and wave number values are listed in [1].

The appropriate system of computer programs (ICH-30) was used in the calculations.

Results and Discussion

The absorption spectrum of the Nd^{3+} aquoion changed systematically with increasing concentration of the EDTA ligand added. Particularly distinct changes have been observed for the 'hypersensitive' transition $^2G_{7/2}$, $^4G_{5/2}$ ← $^4I_{9/2}$ (Figs. 1–3). This transition is also strongly affected in acid solutions and the changes in both the shape and intensity are related to the concentration of the partially deprotonated ligand.

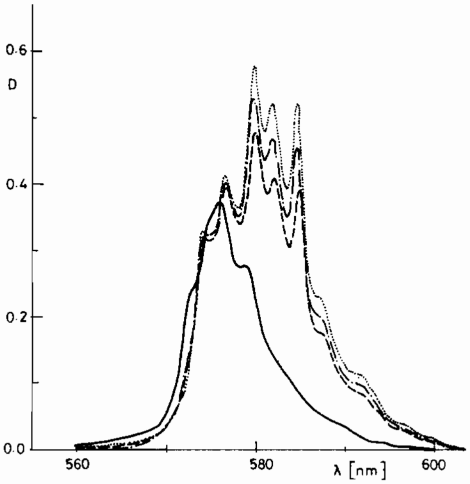

Fig. 1. The effect of the EDTA concentration on the 'hypersensitive' transition $^2G_{7/2}$, $^4G_{5/2}$ ← $^4I_{9/2}$ in the absorption spectrum of the Nd^{3+} ion ($c_M = 9.96 \times 10^{-3}$ M). $Nd(ClO_4)_3$ (pH = 3.52) ———; $Nd(ClO_4)_3$ + 0.0104 M EDTA (pH = 1.68) – – – –; $Nd(ClO_4)_3$ + 0.0152 M EDTA (pH = 1.72) – · – · –; $Nd(ClO_4)_3$ + 0.0248 M EDTA (pH = 1.90) ……..

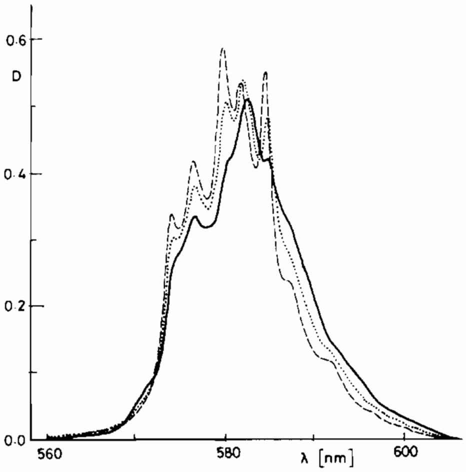

Fig. 2. The effect of pH on the 'hypersensitive' transition $^2G_{7/2}$, $^4G_{5/2}$ ← $^4I_{9/2}$ in the absorption spectrum of the Nd^{3+} ion for the Nd^{3+}: EDTA ratio of 1:1 ($c_M = 9.96 \times 10^{-3}$ M, $c_{EDTA} = 1.04 \times 10^{-2}$ M). $Nd(ClO_4)_3$ + EDTA (pH = 2.86) – – – –; $Nd(ClO_4)_3$ + EDTA (pH = 9.88) …….; Nd-$(ClO_4)_3$ + EDTA (pH = 10.21) ———.

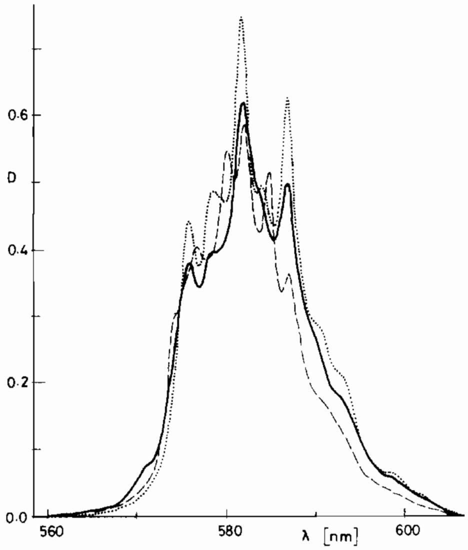

Fig. 3. The effect of pH on the 'hypersensitive' transition $^2G_{7/2}$, $^4G_{5/2}$ ← $^4I_{9/2}$ in the absorption spectrum of the Nd^{3+} ion for the Nd^{3+}: EDTA ratio of 1:2.5 ($c_M = 9.96 \times 10^{-3}$ M, $c_{EDTA} = 2.48 \times 10^{-2}$ M). $Nd(ClO_4)_3$ + EDTA (pH = 5.50) – – – –; $Nd(ClO_4)_3$ + EDTA (pH = 9.10) …….; $Nd(ClO_4)_3$ + EDTA (pH = 10.48) ———.

We have tried to find more quantitative spectral characteristics related to the changes of the lanthanide ion coordination state in the solution. The absorption spectra were recorded for four different

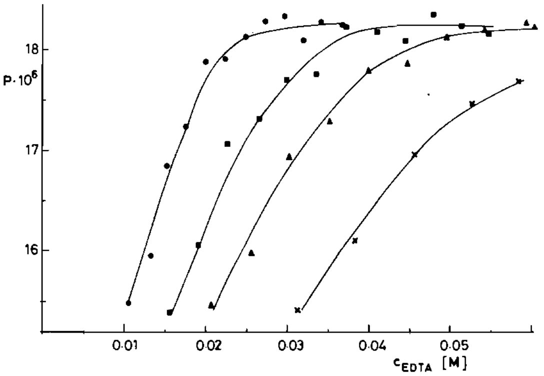

Fig. 4. The oscillator strength value of the ${}^2G_{7/2}$, ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ 'hypersensitive' transition of Nd^{3+} as function of EDTA concentration. $c_M = 9.96 \times 10^{-3}$ M, ●; $c_M = 1.494 \times 10^{-2}$ M, ■; $c_M = 1.993 \times 10^{-2}$ M, ▲; $c_M = 2.989 \times 10^{-2}$ M, ×.

Nd^{3+} ion concentrations (9.96×10^{-3}, 1.494×10^{-2}, 1.993×10^{-2}, 2.989×10^{-2} M) with: (1) different ligand concentrations (1×10^{-2}–6×10^{-2} M); (2) different pH values and a constant metal to ligand ratio of 1:1; (3) different pH values and a constant metal to ligand ratio of 1:2.5. For all the solutions investigated, the experimental values of the oscillator strength of 'hypersensitive' transition ${}^2G_{7/2}$, ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ were calculated (Fig. 4).

All the absorption spectra of Nd^{3+}–EDTA solutions with $c_{Nd^{3+}} = 1.993 \times 10^{-2}$ M were analysed by the Judd-Ofelt method of the intensity analysis. The results are given in Tables I–III. For all analysed spectra only the τ_2 parameter values change significantly as a function of the ligand concentration, whereas τ_4 and τ_6 parameter values remain constant (within the limit of experimental error). In such a case, intensity changes of the 'hypersensitive' transition are mainly responsible in the fitting procedure for the changes of τ_2 parameter values. So, as in recent investigations, we can consider oscillator strength of 'hypersensitive' transitions as proof of the coordination state of solution. Moreover, for polyaminoacetate ligands, the feature changes of the 'hypersensitive' transition bands are very typical. For the different ligand concentrations changes both in the energy values and intensities of particular band components are observed (Figs. 1–3).

At the measured acid solutions with varying EDTA concentrations (pH = 1.5–2), the oscillator strengths of the 'hypersensitive' transition increase

TABLE I. Oscillator Strength Values (P) of the ${}^2G_{7/2}$, ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ 'Hypersensitive' Transition and the Judd-Ofelt Parameter Values (τ_λ) of Nd^{3+} at Different Ligand Excesses and Constant Metal Concentration ($c_{Nd^{3+}} = 1.993 \times 10^{-2}$ M).

$c_{Nd^{3+}}$:c_{EDTA}	c_{EDTA} [M]	pH	P × 10^6	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0	–	2.64	9.5725	1.67 ± 0.62	5.45 ± 0.56	10.61 ± 0.81
1:1.04	0.0208	1.58	15.4582	4.45 ± 0.65	6.55 ± 0.58	12.03 ± 0.84
1:1.28	0.0256	1.60	15.9874	4.70 ± 0.80	6.67 ± 0.73	12.33 ± 1.05
1:1.53	0.0304	1.63	16.9518	5.24 ± 0.72	6.71 ± 0.65	12.53 ± 0.94
1:1.77	0.0352	1.66	17.3012	5.48 ± 0.72	6.65 ± 0.65	12.60 ± 0.94
1:2.01	0.0400	1.70	17.8061	5.35 ± 0.71	7.33 ± 0.64	12.67 ± 0.92
1:2.25	0.0448	1.74	17.8557			
1:2.49	0.0496	1.79	18.1385	5.78 ± 0.65	6.89 ± 0.59	12.87 ± 0.85
1:2.73	0.0544	1.84	18.1953			
1:2.97	0.0592	1.89	18.2512	5.81 ± 0.76	7.02 ± 0.69	12.85 ± 0.99
1:3.11	0.0620	1.95	18.2406			

TABLE II. Oscillator Strength Values (P) of the ${}^2G_{7/2}$, ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ 'Hypersensitive' Transition and the Judd-Ofelt Parameter Values (τ_λ) of Nd^{3+} for the Nd^{3+}:EDTA Ratio of 1:1 at Different pH Values ($c_{Nd^{3+}} = 1.993 \times 10^{-2}$ M, $c_{EDTA} = 2.08 \times 10^{-2}$ M).

c_{EDTA}:c_{NaOH}	pH	P × 10^6	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0	1.58	15.4582	4.45 ± 0.65	6.55 ± 0.58	12.03 ± 0.84
1:0.54	1.65	15.9868			
1:0.98	1.79	16.8266	5.04 ± 0.69	6.88 ± 0.62	12.75 ± 0.90
1:1.52	2.09	17.5322			
1:1.96	2.92	18.3119	5.53 ± 0.70	7.44 ± 0.64	13.12 ± 0.92
1:2.50	10.17	18.9542	6.15 ± 0.82	7.35 ± 0.74	11.50 ± 1.07
1:2.72	10.31	18.9925			
1;2.83	10.35	19.2051			
1:2.94	10.40	19.3034	6.35 ± 0.63	7.24 ± 0.57	12.21 ± 0.82
1:3.27	10.55	19.3659			

TABLE III. Oscillator Strength Values (P) of the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ 'Hypersensitive' Transition and the Judd-Ofelt Parameter Values (τ_λ) of Nd^{3+} for the Nd^{3+}:EDTA Ratio of 1:2.5 at Different pH Values ($c_{Nd^{3+}} = 1.993 \times 10^{-2}$ M, $c_{EDTA} = 4.96 \times 10^{-2}$ M).

c_{EDTA}:c_{NaOH}	pH	$P \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0	1.79	18.1385	5.78 ± 0.65	6.89 ± 0.59	12.87 ± 0.85
1:0.50	2.33	18.5103			
1:1.00	5.24	20.0073	6.76 ± 0.80	7.16 ± 0.72	13.63 ± 1.04
1:1.51	7.53	23.0733			
1:2.01	10.02	23.7441	8.42 ± 0.86	8.01 ± 0.78	14.55 ± 1.12
1:2.51	10.40	21.8267	7.50 ± 0.70	7.69 ± 0.63	13.29 ± 0.91
1:2.74	10.43	21.6806			
1:2.88	10.44	21.8442			
1:2.97	10.50	21.6400	7.48 ± 0.67	7.71 ± 0.61	12.30 ± 0.87
1:3.24	10.55	21.6913			

with increasing ligand concentrations up to the $c_{Nd^{3+}}$:c_{EDTA} ratio 1:2.5; then they remain constant (Table I). The τ_2 parameter values are significantly higher than those for the aquoion.

Further measurement results are collected in Table II. In this case, the concentration of the deprotonated ligand varied with pH within the whole region available for spectral measurements. The oscillator strengths of the 'hypersensitive' transition and the τ_2 parameter values increase with increasing pH of the investigated solutions within the pH range 1.5–3. Above that pH value, very small amounts of OH^- ions cause a sharp increase of the pH value in the solution up to pH = 10. In strongly alkaline solutions both the oscillator strength and the τ_2 parameter values remain constant.

The same spectroscopic quantities were also measured for the solutions with the molar ratio $c_{Nd^{3+}}$:c_{EDTA} = 1:2.5 (Table III). Those measurements were possible within the whole pH region (1.5–11). A systematic increase in the oscillator strength values was observed together with increasing pH values of the solutions up to pH = 10. For pH > 10 oscillator strengths and τ_2 parameter values decrease.

Electronic spectroscopy measurements made it possible to observe the effect of coordination in the Nd^{3+}–EDTA system. Significant changes of both the complicated structure and intensity of the 'hypersensitive' transition suggest that more than one species can exist in this system.

Solutions of Nd^{3+}–EDTA at Low pH Values

As the first step we considered the spectral behaviours of Nd^{3+}–EDTA solutions at low pH values for different Nd^{3+}:EDTA ratio (Table I, Fig. 1). In these conditions mainly H_3EDTA^- (with possibly some amount of H_2EDTA^{2-}) species exist. The changes both of the oscillator strength and the shape of the 'hypersensitive' transition suggest the existence of species bounded only by carboxylic groups. The small changes of the oscillator strengths suggest that the concentration of these species is not very high, and some possible equilibria between carboxylic-bounded species can exist.

In this case, the NMR spectroscopy does not give any information. As it was proved, the exchange of protons between the coordinated and uncoordinated ligand molecules is too fast [7]. Brücher [9], who calculated formation rate constants for $LnEDTA^-$, observed that even for $HEDTA^{3-}$ solutions the first step of the lanthanide ion coordination should be coordination to the carboxylic group. In our case, at very low pH values where predominantly H_3EDTA^- exists, coordination by carboxylic groups is the only reasonable explanation.

Solutions with Ratio of Nd^{3+}:EDTA = 1:1

For this system (Table II, Fig. 2) at low pH values similarity with previously discussed data can be observed, suggesting that carboxylic-bounded species also exist in these conditions. In alkaline solutions at pH ~ 10 the species $NdEDTA^-$ bounded by the iminodiacetic group is formed. Some changes of oscillator strengths at slightly higher pH values could be caused by the formation of some monohydroxo-species $Nd(OH)EDTA^{2-}$.

Solutions with Ratio of Nd^{3+}:EDTA = 1:2.5

Because of the small ligand deprotonation in acidic solutions (pH < 2.5), the spectral picture at an excess EDTA concentration is identical with that considered previously for the Nd^{3+}–EDTA (1:1) system at lower pH values. A more complex picture is observed when the system with an excess of EDTA is considered within a higher pH region. A significant increase in the spectral intensities at 5 < pH < 10 is typical. As mentioned above, this pH region is available for spectral measurements only at excess ligand concentrations. This can be explained by the formation of the $Nd(EDTA)_2^{5-}$ species in which the ligands are bound exclusively by the oxygen atoms of the acetate group. In the alkaline solutions (pH > 10), the oscillator strengths are higher than for the 1:1 chelate complex but lower than for the species existing within the intermediate pH region. Because of the 1:1 chelate high stability, those higher oscillator strengths cannot be caused by the higher concentration of the chelate.

When deprotonation of the ligand occurs, practically all the Nd^{3+} ions are coordinated. The only reasonable explanation is the appearance of $Nd(EDTA)_2^{5-}$ species beside $NdEDTA^-$. Since the possibility of two EDTA molecules arrangement around the small lanthanide ion is limited, it seems very likely that at least one Ln–O bonding is broken in each EDTA molecule. This should be reflected in the symmetry lowering of the lanthanide ions immediate environment, and leads to higher oscillator strength values. Another possible explanation, as assumed by Southwood-Jones [7] and Brücher [8], is that formation of the binuclear species $Nd_2(EDTA)_3^{6-}$ is possible in these conditions. The spectral effect should be very similar in this case, so we are unable to differentiate between these two alternatives.

It is interesting to correlate the properties of $NdEDTA^-$ species in solutions with the structure of solid lanthanide ethylenediaminetetraacetates. Extensive data are available for the $LnEDTA^-$ systems. In the $K[Ln(EDTA)]\cdot 8H_2O$ (where Ln = La, Nd, Gd, Tb, Er) the coordination number is 9 and the coordination polyhedron is formed by EDTA and three water molecules [13]. Another isolated compound is $[La(HEDTA)]\cdot 7H_2O$ where the coordination number of the metal ion is 10 [14]. In both of these structures EDTA occupies the neighbouring coordination positions located on one side of the aquoion polyhedron, while water molecules remain on the opposite side. The bond lengths Ln–N and Ln–O in both these compounds are as below:

	C.N.	M–N[A]	M–O[A]	$M–OH_2$[A]
$La(EDTA)(OH_2)_3$	9	2.755	2.507	2.580
$La(EDTA)(OH_2)_4$	10	2.865	2.537 2.609	2.592

The distances between the lanthanide ion and the nitrogen atom are larger than those between the lanthanide ion and the oxygen atoms both of the acetate group and of the water molecules. It is difficult to compare the solid state structure with that in the solution. For the stable species $NdEDTA^-$ which exists in alkaline solution it seems reasonable, however, to assume coordination similar to that existing in a solid state. Some rigidity of chelate-bounded rings should be preserved in solution. Thus in solution, Ln–N distances could be longer than those between Ln–O. Such a case can be considered as an example of weak Ln–N bond, where conditions of the steric arrangement around the lanthanide ion enforced the formation of this bonding.

From the above results it may be concluded that the electron spectroscopy method is able to elucidate some problems of structure and formation of lanthanide complexes, especially when the spectroscopic results are compared with those obtained by other physical methods.

References

1 K. Bukietyńska and A. Mondry, *Bull. Acad. Pol. Chim., 28,* 215 (1980).
2 K. Bukietyńska and E. Osmeda, *Bull. Acad. Pol. Chim., 28,* 227 (1980).
3 K. Bukietyńska and A. Mondry, *Inorg. Chim. Acta, 72,* 109 (1983).
4 T. F. Gritmon, M. P. Goedken and G. R. Choppin, *J. Inorg. Nucl. Chem., 39,* 2021 (1977).
5 G. R. Choppin, M. P. Goedken and T. F. Gritmon, *J. Inorg. Nucl. Chem., 39,* 2025 (1977).
6 P. A. Baisden, G. R. Choppin and B. B. Garrett, *Inorg. Chem., 16,* 1367 (1977).
7 R. V. Southwood-Jones and A. E. Merbach, *Inorg. Chim. Acta, 30,* 77 (1978).
8 E. Brücher, R. Király and I. Nagypál, *J. Inorg. Chem., 37,* 1009 (1975).
9 G. Laurenczy and E. Brücher, *Inorg. Chim. Acta, 95,* 5 (1984).
10 N. S. Poluektov, *Dokl. Acad. Nauk SSSR, 235,* 5 (1977).
11 N. S. Poluektov, *Zh. Prikl. Spektrosk., 28,* 101 (1978).
12 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys., 49,* 4424 (1968).
13 J. L. Hoard, B. Lee and M. D. Lind, *J. Am. Chem. Soc., 87,* 1612 (1965).
14 M. D. Lind, B. Lee and J. L. Hoard, *J. Am. Chem. Soc., 87,* 1611 (1965).