

Ethylenediamine Complexes of Rare-Earth Trichlorides*

C. Castellani Bisi

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Complexes of the type: $M(En)_xCl_3$ (where $M = Y$ and all lanthanides except Pm, and $En =$ ethylenediamine) have been isolated; preparation and properties are reported.

Introduction

As F. A. Hart and F. P. Laming¹ pointed out, the isolation of lanthanide complexes based upon neutral ligands containing only nitrogen donors has been generally very infrequent. Recently, however, several very stable complexes of lanthanides with polycyclic nitrogen bases like *o*-phenanthroline, bipyridyl, and terpyridine, have been isolated.¹⁻⁶

All these species are useful in studying the coordination numbers of the rare-earth metals. It has been noted that the number of neutral ligands attached to the metal ion strictly depends on the coordinating ability of the anion as well as on the nature of the neutral ligand itself. For a given neutral ligand the maximum number of groups bonded to the metal ion is attained using the poorly-coordinating perchlorate as anion.³ For instance, with *o*-phenanthroline the metal to ligand ratio in the perchlorate complexes is 1:4, while in the nitrate complexes it is 1:2, suggesting the coordination number eight for the former and nine for the latter compounds. With several lanthanide chlorides, *o*-phenanthroline used in excess gives complexes of the formula: $LnCl_3 \cdot (C_{10}H_8N_2)_2$ for which a coordination number of six has been suggested.¹

Using terpyridine as a ligand for lanthanide perchlorates, complexes of the type: $M(terpy)_3(ClO_4)_3$ are formed, which show the highest coordination number of nitrogen donor atoms with any metal ion;⁴ for the lanthanide chlorides, only $MCl_3 \cdot terpy \cdot (H_2O)_n$ and $MCl_3 \cdot (terpy)_2(H_2O)_n$, have been reported.^{5,6}

It seems thus, that the presence of the chloride anion hinders the formation of complexes with a high number of neutral nitrogen ligands attached to the metal ion; however rare-earth chlorides form well known ammoniates, containing a high number of ammonia molecules,⁷ and according to A. J. Popov and W. W. Wendlandt⁸ it is quite likely that corresponding methylamino compounds can be prepared at temperatures lower than 0°C. Thus it is to be expected that using a strong polydentate nitrogen base with a small bulk the lanthanide chlorides would form some other complexes, in addition to the ammoniates, containing a high number of neutral nitrogen ligands. Consequently an investigation on the rare-earth chloride complexes with ethylenediamine was undertaken.

Results and Discussion

When an alcoholic solution of anhydrous rare-earth trichloride is treated with a large excess of ethylenediamine (about ten molecular proportion) in completely anhydrous conditions, the tetrakisethylenediamine complex for Y and all lanthanides (except Pm) is formed.

Treatment of alcoholic solutions of rare-earth chlorides with a deficiency of ethylenediamine leads to precipitates of ill defined composition, always containing some percentage of alcohol (5-10%). This amount of alcohol strictly depends on working conditions, such as temperature, stirring, time of standing etc., and cannot be removed by cautious heating *in vacuo* because the complexes undergo decomposition. This strongly indicates that in deficiency of ethylenediamine, alcohol also acts as a ligand.

In order to obtain a high yield of the tetrakisethylenediamine complexes in a well crystallized form, it is advisable to slowly pour the saturated alcoholic solution of rare earth trichloride with constant shaking, into a much bigger volume of a solution of ethylenediamine in anhydrous CCl_4 . Using anhydrous alcohol as is generally done for similar complexes, a lower yield of precipitates containing a small amount

(* Preliminary results of this work have already been reported by A. Moggi: Doctoral Dissertation-Istituto di Chimica Generale della Università di Pavia 1967; and by C. Castellani Bisi: X Cong. Naz. Soc. Chim. It., Padova, 17-21 giugno 1968. Riassunto delle Comunicazioni Sect. IX-12; 11° Convegno Naz. Chim. Inorg. Bressanone 20-23 luglio 1969. Riassunti delle Comunicazioni pg. 117.

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Table I. The tetrakisethylenediamine rare-earth trichlorides

Metal	Colour	Decomp. point (°C) ^a	Metal (%)		Chlorine (%)		Ethylenediamine (%)	
			Found	Calc.	Found	Calc.	Found	Calc.
Y	colourless	260	20.3	20.4	24.1	24.4	55.0	55.2
La	colourless	330	28.4	28.55	22.2	21.9	49.2	49.5
Ce	dark-cream	215	28.7	28.8	21.55	21.85	49.15	49.4
Pr	pale-green	260	28.75	28.9	21.6	21.8	49.6	49.3
Nd	pale-lilac	265	29.2	29.4	21.9	21.7	48.95	48.95
Sm	very pale-cream	230	30.1	30.25	21.35	21.5	48.1	48.35
Eu	pale-cream	220	30.45	30.5	21.6	21.3	48.35	48.2
Gd	very pale-cream	200	31.1	31.2	20.9	21.1	47.7	47.7
Tb	cream	200	31.25	31.4	21.2	21.0	47.45	47.5
Dy	colourless	267	31.9	31.9	20.7	20.9	47.4	47.2
Ho	pale-pink	263	31.9	32.2	20.65	20.8	46.8	47.0
Er	pink	270	32.6	32.5	21.0	20.7	46.9	46.8
Tm	colourless	260	32.8	32.75	21.0	20.6	47.0	46.6
Yb	colourless	259	33.1	33.3	20.6	20.5	45.9	46.2
Lu	colourless	270	33.35	33.5	20.7	20.4	45.75	46.1

^a Diffuse and difficult to observe. Temperatures of incipient decomposition are shown.

of basic chlorides is obtained, especially in the case of Y and heavier lanthanides. These precipitates are very difficult to filter.

Some simple properties of the compounds are listed in Table I.

The complexes can be kept indefinitely in an absolutely dry atmosphere but alter very rapidly with moisture. Thermal stability is noticeable; decomposition, observed by a hot-stage microscope, occurs between 200° and 280°C for all the complexes, except for the La compound which remains unchanged over 330°C. However, by heating the compounds *in vacuo* at increasing temperatures and then carrying out the analyses, slight changes in composition can already be noted around 80°C.

The colours of the compounds are closely similar in shade to the colours of the simple salts of corresponding rare-earth metal, except in the case of the cerium complex which is dark cream. A similar phenomenon has already been noticed and explained by other Authors in other series of lanthanide complexes.^{1,3}

The complexes are highly insoluble in all common organic solvents and this unfortunately makes many physical methods of structure investigation impossible to carry out. For this reason it is impossible at present to establish with certainty the coordination number of the metal ions in the described complexes and to state whether the chlorine atoms are or not in an ionic form.

In order to clarify this point the action of an excess of ethylenediamine on anhydrous neodymium perchlorate has been studied and the compound Nd(En)₄(ClO₄)₃ has been obtained. Thus it seems quite reasonable to suppose that the coordination number of the rare earth cations in the described complexes is eight and all the chlorine atoms, as well as the perchlorate groups, are in an ionic form*.

Experimental Section

All preparations in which anhydrous materials were handled, were performed in a glove bag. Decomposition points were obtained by use of a hot-stage microscope.

Extremely dry ethyl alcohol was obtained by refluxing it first with sodium and then with an excess of ethyl formate: this was followed by distillation through a short column.⁹ Anhydrous carbon tetrachloride was obtained by refluxing over P₂O₅ and distillation. Y and lanthanides were obtained as their oxides, 99.9% pure, from the Fluka Company.

3.1. Anhydrous rare earth trichlorides. These were obtained free from oxichloride by dehydrating a mixture of hydrated rare earth chloride and NH₄Cl *in vacuo*, as described in the literature.¹⁰

3.2. Tetrakisethylenediamine rare-earth (III) chlorides. A nearly saturated solution of anhydrous rare earth trichloride in extremely dry ethyl alcohol was slowly poured with constant shaking into a solution of ethylenediamine in anhydrous CCl₄. Metal to ethylenediamine molar ratio was approximately 1:10; alcohol to carbon tetrachloride volume ratio was approximately 1:10. The complex was immediately formed as a fine crystalline powder. It was allowed to stand several minutes and then was filtered, washed with anhydrous CCl₄, roughly dried over a porous plate and then carefully desiccated *in vacuo* over CaCl₂ at room temperature.

The analytical figures are listed in Table I; in each case the calculated values correspond to the formula Ln(En)₄Cl₃. The yields for all the compounds were around 90-95%.

3.3. Anhydrous Neodymium perchlorate. This salt was obtained by dehydrating *in vacuo* the hydrated compound, as described in the literature.¹¹

(9) A. I. Vogel: Practical Organic Chemistry, III Ed., Longmans p. 169.

(10) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).

(*) Addendum. After the present paper had already been sent to the Editor for publication, the excellent work, very recently published by J. H. Forsberg and T. Moller (*Inorg. Chem.*, **8**, 883 (1969)), has come to the knowledge of the Author; in their work analogous series of complexes and five of the compounds described here have been isolated.

(11) R. I. Slawkina, Dzh. Usutaliev and V. V. Serebrennikov, *C. A.*, **61**, 7918 from, *Tr. Tomskogo Gos. Univ., Ser. Kim.*, **157**, 304 (1963).

3.4. *Tetrakisethylenediamine Neodimium (III) perchlorate*. This compound was obtained following the same procedure described for the tetrakisethylenediamine complexes of rare-earth chlorides. The analytical results were: Found: Nd, 21.2; En, 35.3. Calc. for $\text{Nd}(\text{En})_4 \cdot (\text{ClO}_4)_3$: Nd, 21.1; En, 35.2.

3.5. *Analyses*. Metals were determined as sulfates

by direct treatment of a sample (approximately 0.1 g) with diluted H_2SO_4 in a platinum crucible and successive dehydration of the lanthanide sulfate at about 350°C . The chloride, in another similar sample, was estimated by the Volhard method.

Ethylenediamine was determined by dissolving another similar sample in an excess of standard H_2SO_4 and back titrating with NaOH solution (indicator: methylorange).