Inorganica Chimica Acta, 145 (1988) 309–314

Thermodynamics of Complexation of Lanthanides by Methoxybenzoates

G. R. CHOPPIN, Q. LIU and E. N. RIZKALLA
Chemistry Department, Florida State University, Tallahassee, Fla. 32306-3006, U.S.A.

(Received October 15, 1987)

Abstract

The thermodynamic parameters of complexation of lanthanide cations by *ortho*-, *meta*- and *para*-methoxybenzoates have been measured using potentiometric and calorimetric techniques at 25 °C and an ionic strength of 0.10 M ($NaClO_4$). The values of $\log\beta_{101}$ correlate well with the ligand acid values of pK_a, reflecting the strongly ionic nature of the metal–ligand interaction. No evidence is found for extra charge polarization in these aromatic ligands due to the lanthanide complexation.

Introduction

In an earlier paper [1] it was shown that isophthalic acid has a larger stability constant, β_{101}, for complexation with lanthanide cations than would be expected from the correlation of $\log\beta_{101}$ with ligand pK_a which has been demonstrated for metal–ligand ionic interaction. By contrast, the stability constants for 1:1 lanthanide–benzoic acid complexation fit the $\log\beta_{101}$ *vs.* pK_a correlation very well. The interpretation proposed for the enhanced binding by isophthalate was polarization of the electronic charge from the unbonded carboxylate group through the pi system of the aromatic nucleus to the bonded carboxylate. It was further noted that the $\log\beta_{101}$ values for lanthanide–isophthalate complexation corresponded to an 'effective pK_a' of *ca.* 5.5, which is the maximum value recorded for the pK_a of monocarboxylic acids. This suggests that the charge transmission saturates the carboxylate group.

This possibility led to the study of other aromatic ligands [2, 3] where charge polarization via resonance and/or inductive effects would alter the basicity of the bonding carboxylate group. In this paper, we report the extension of these studies to complexation of lanthanides by the isomers of methoxybenzoic acid. These ligands can allow transmission of charge, via inductive and/or mesomeric effects, from the methoxy group which, however, cannot bind directly to the lanthanide cations.

Experimental

Reagents and Solutions

Stock solutions of lanthanide perchlorates were prepared and analyzed as described previously [1]. Commercial *ortho*-, *meta*- and *para*-methoxybenzoic acids (Aldrich, ⩾98% purity) were used directly. The stock solution of the *o*-methoxybenzoate buffer for the potentiometry was prepared by dissolving the appropriate weight of the acid in known amounts of 1 M NaOH, adjusting the [HL]/[L] ratio (~0.3) with standardized $HClO_4$ and dilution to the desired concentration (0.04–0.06 M). For the calorimetric titrations, the sodium salts of the ligands were used (0.05–0.10 M). All solutions were adjusted to 0.10 M ionic strength with $NaClO_4$.

Procedures

The pH measurements were obtained using a Radiometer PHM 84 Research pH meter fitted with a combined glass-calomel electrode. The potentiometer allows an accuracy of ±0.001 pH unit. The electrode was calibrated with standard 'BuffAR' of pH 4.01 and 7.00. Corrections for hydrogen ion activity in solutions of 0.10 M ionic strength were made by using a value of 0.782 for the activity coefficient [4]. The acid protonation constants of the ligands were obtained by titrating the sodium salt solutions with standard $HClO_4$.

Stability constants of the lanthanide–*o*-methoxybenzoate complexes were obtained by pH-titration of the metal solution (50 ml of *ca.* 2–3 mM) with the ligand buffer solution (*ca.* 0.05 M).

The complexation of all three methoxybenzoate isomers with the lanthanides were studied by calorimetric titration. The sodium salt solutions of the ligands were titrated into the metal solutions (pH 5–6) and the heat was detected using an adiabatic calorimeter fitted with a Radiometer ABU 80 autoburette and interfaced to an Ohio Scientific microcomputer [5]. The heats of dilution of the ligands and the lanthanide solutions were determined by titrating the respective solution with 0.10 M $NaClO_4$. The enthalpy of protonation of *ortho*- and *meta*-methoxybenzoate were determined calori-

0020-1693/88/$3.50

TABLE I. Thermodynamics of Protonation of Benzoate Anions; I = 0.10 M ($NaClO_4$); T = 298 K

Anion	$\log K_{011}$	ΔH_{011} (kJ mol^{-1})	ΔS_{011} (J K^{-1} mol^{-1})
Benzoate	3.99 ± 0.05 [1]	−0.87 ± 0.05 [1]	74 ± 1
o-Methoxybenzoate	3.83 ± 0.04	2.00 ± 0.20	80 ± 1
m-Methoxybenzoate	3.82 ± 0.04	−1.38 ± 0.15	69 ± 1
p-Methoxybenzoate	4.26 ± 0.10	−2.38 ± 0.10 [6, 7][a]	74 ± 2

[a] Zero ionic strength.

TABLE II. Potentiometric Data for the Sm(III)–*o*-Methoxybenzoic Acid System[a]; I = 0.10 M ($NaClO_4$); T = 298 K

Titrant (ml)	$10^5[H^+]_{exptl}$ (M)	$10^5[H^+]_{calc}$ (M)	$10^3[Sm^{3+}]$ (M)	$10^3[L^-]$ (M)	$\bar{n}$
0.2	7.635	7.742	2.243	0.123	0.015
0.4	7.777	7.916	2.202	0.244	0.030
0.6	7.849	8.003	2.161	0.365	0.044
0.8	7.903	8.049	2.122	0.485	0.057
1.0	7.976	8.073	2.084	0.604	0.070
1.2	7.995	8.083	2.048	0.724	0.083
1.6	8.013	8.081	1.978	0.963	0.108
2.0	8.031	8.063	1.912	1.200	0.131
2.5	8.013	8.030	1.834	1.496	0.158
3.0	8.031	7.991	1.762	1.790	0.183
3.5	8.031	7.951	1.695	2.082	0.207
4.0	8.013	7.911	1.633	2.372	0.229
4.5	7.976	7.871	1.574	2.660	0.250
5.0	7.958	7.832	1.519	2.944	0.269
6.0	7.885	7.760	1.419	3.506	0.305
7.0	7.813	7.694	1.330	4.055	0.337
8.0	7.759	7.634	1.252	4.593	0.365
9.0	7.705	7.579	1.181	5.117	0.391
10.0	7.688	7.529	1.118	5.630	0.413

[a] Experimental conditions: Cup solution: $[Sm^{3+}]$ = 2.287 mM; pH = 4.242; volume = 50.0 ml. Titrant: [oMB] = 0.0557 M; $[H^+]$ = 0.0173 M. Calculated constant; $\log \beta_{101}$ = 2.10.

metrically by titrating their salt solutions with standard perchloric acid. The literature values [6, 7] of the protonation enthalpy of the *para* isomer was used.

Carbon-13 magnetic resonance spectra were recorded with the Florida State University Bruker 270 MHz spectrometer using the pulsed Fourier transform mode with a deuterium lock. All measurements were obtained at ambient temperature with DSS (sodium 4,4-dimethyl-4-silapentanesulfonate) as internal standard.

Results

Table I lists the thermodynamic parameters for protonation of the three methoxybenzoate isomers. Stability constants for the lanthanide–*o*-methoxybenzoate complexes were calculated by the computer program 'BETA' written to evaluate pH data. This program is based on a simplex [8] nonlinear regression algorithm for refinement of the equilibrium constants and a Newton–Raphson [9] algorithm for calculation of the equilibrium concentrations of all solution species. The best fit was obtained by minimizing the residuals of the observed and calculated hydrogen ion concentrations for a particular set of fitted stability constants. Under the present experimental conditions, only one complex species, LnL^{2+}, is formed ($\bar{n}$ = 0–0.5). A typical set of potentiometric data is presented in Table II; the 'calc' columns are the values calculated for each titration point with the final constants of Table IV.

Enthalpies of complexation of the lanthanides with the *ortho* ligand were computed by fitting the observed heat changes, after correction for dilution effects, to the number of moles of complex formed. The latter was calculated by the nonlinear simplex program (DELTA-H) written in this laboratory based on the same algorithm as in ref. 8. A sample set of calculations is shown in Table III.

TABLE III. Calorimetric Entropy Titration Data for the Nd(III)–*m*-Methoxybenzoic Acid System[a]; $I = 0.10$ M ($NaClO_4$); $T = 298$ K

Titrant (ml)	$-\Sigma Q_c{}^{*}$ [b] (mJ)	$-\Sigma Q_{\mathrm{calc}}$ (mJ)	$10^3[Nd^{3+}]$ (M)	$10^3[L^-]$ (M)	$10^6[H^+]$ (M)	$\bar{n}$
0.1	51	51	10.945	0.080	5.379	0.011
0.2	103	101	10.811	0.162	3.966	0.021
0.3	153	152	10.675	0.245	3.129	0.031
0.4	199	201	10.541	0.330	2.577	0.042
0.5	249	251	10.408	0.415	2.185	0.052
0.6	303	300	10.277	0.501	1.893	0.062
0.7	350	348	10.147	0.587	1.667	0.072
0.8	402	396	10.019	0.675	1.487	0.082
0.9	454	443	9.893	0.764	1.340	0.092
1.0	502	490	9.769	0.853	1.218	0.101
1.1	556	536	9.646	0.944	1.115	0.111
1.2	600	582	9.526	1.035	1.028	0.120
1.3	642	627	9.406	1.127	0.952	0.130
1.4	681	671	9.289	1.220	0.885	0.139
1.5	730	715	9.173	1.314	0.827	0.148
1.6	771	759	9.059	1.409	0.775	0.157
1.7	811	802	8.946	1.504	0.729	0.166
1.8	855	844	8.835	1.601	0.687	0.174
1.9	898	886	8.725	1.698	0.650	0.183
2.0	937	927	8.618	1.796	0.616	0.192
2.1	971	968	8.511	1.895	0.585	0.200
2.2	1007	1009	8.407	1.994	0.557	0.208
2.3	1042	1048	8.304	2.095	0.531	0.217
2.4	1079	1087	8.202	2.196	0.507	0.225
2.5	1118	1126	8.102	2.297	0.485	0.233
2.6	1155	1164	8.003	2.400	0.465	0.241
2.7	1192	1202	7.906	2.503	0.446	0.248
2.8	1228	1239	7.811	2.607	0.428	0.256
2.9	1260	1276	7.717	2.712	0.411	0.264
3.0	1295	1312	7.624	2.818	0.396	0.271

[a] Experimental conditions. Cup solution: $[Nd^{3+}] = 11.087$ mM; pH = 5.19; Vol. = 50.0 ml. Titrant: $[mMB] = 0.100$ M; $[H^+] = 1 \times 10^{-7}$ M. Computed constants: $\log \beta_{101} = 2.12$; $\Delta H_{101} = 6.09$ kJ mol^{-1}. [b] $\Sigma Q_c{}^{*}$ is the observed heat corrected for dilution.

TABLE IV. Thermodynamics Parameters of Complexation of Lanthanide Ions by *o*-Methoxybenzoic Acid; $I = 0.10$ M ($NaClO_4$) $T = 298$ K

Ion	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
La	1.78 ± 0.04	10.16 ± 0.23	7.97 ± 0.6	61 ± 2
Pr	1.96 ± 0.01	11.18 ± 0.06	8.74 ± 0.3	69 ± 1
Nd	2.08 ± 0.06	11.87 ± 0.34	6.62 ± 0.5	63 ± 2
Sm	2.10 ± 0.02	11.98 ± 0.11	6.85 ± 1.1	63 ± 4
Eu	2.05 ± 0.04	11.70 ± 0.23	6.83 ± 0.6	62 ± 2
Gd	1.95 ± 0.06	11.13 ± 0.34	8.42 ± 1.3	66 ± 5
Tb	1.93 ± 0.01	11.01 ± 0.06	9.03 ± 0.3	67 ± 1
Dy	1.89 ± 0.03	10.78 ± 0.17	9.85 ± 0.5	69 ± 2
Ho	1.85 ± 0.06	10.56 ± 0.34	10.60 ± 0.7	71 ± 3
Er	1.82 ± 0.01	10.38 ± 0.06	10.57 ± 1.0	70 ± 3
Tm	1.83 ± 0.01	10.44 ± 0.06	10.73 ± 0.8	71 ± 3
Yb	1.85 ± 0.06	10.56 ± 0.34	9.79 ± 1.3	68 ± 5
Lu	1.88 ± 0.01	10.73 ± 0.06	10.59 ± 0.2	72 ± 1
Y	1.66 ± 0.02	9.47 ± 0.11	9.32 ± 0.5	63 ± 2

Attempts to determine the stability constants of lanthanide complexes with the *meta-* and *para-*isomers using the pH titration technique were unsuccessful. The extremely low solubilities of the free acids did not allow measurements in the buffer regions necessary to study the competition between the proton and the metal cation for the ligand anion. Consequently, the thermodynamics of complexation by these two ligands were obtained from entropy titrations. The observed heat data together with the information on the volume and concentration of the titrant and titrand were used in program 'ET' [10] to fit for the unknowns β_{101} and ΔH_{101} given by the relationship;

$$Q_c = Q_{LnL} = \beta_{101} V\{[Ln]_f[L]_f - [Ln]_i[L]_i\}\Delta H_{101}$$

where Q_c is the heat observed corrected for dilution; V is the total volume of the reaction mixture, [ ] denotes concentration (f = final and i = initial values) and β_{101} and ΔH_{101} are the formation constant and enthalpy for the reaction;

$$Ln^{3+} + L^- \rightleftharpoons LnL^{2+}$$

Corrections for ligand protonation were unnecessary, since under the present experimental conditions of concentration and pH, the estimated concentration of HL species is $\leqslant 10^{-5}$ M.

All measurements were repeated two or more times and the error limits given for the final values are 3σ of the average deviation between the individual runs. A summary of all the thermodynamic parameters obtained in this study is shown in Tables IV–VI.

Discussion

Comparison of the lanthanide complexation of the methoxybenzoate isomers with that of other substituted benzoate ligands is shown in Figs. 1 and 2. Figure 1 reflects the strongly ionic nature of the bonding in these complexes in the good correlation between the values of $\log \beta_{101}$ and pK_a of the ligand. Such a correlation is typical of hard acid (lanthanide cations) and hard base (carboxylate group) interaction. This plot provides no evidence for perturbing steric effects, even for the *o*-methoxy isomer. Moreover, if $\log \beta_{101}$ values for samarium complexation with aliphatic carboxylate ligands were included in Fig. 1, they would fit the correlation equally well [3]. From this we can deduce that the lanthanides do not polarize additional charge from the aromatic ring in the complexation reaction.

The linear relation of ΔH_{101} and ΔS_{101} of Fig. 2 is a common feature of lanthanide complexation. This correlation (and the positive values of both ΔH_{101} and ΔS_{101} for this monodentate complexing) has been attributed to the dehydration of the metal and the ligand when they complex. Greater dehydration in a particular metal–ligand system results in a more endothermic enthalpy change which is compensated by a more positive entropy effect [11]. The agreement of the enthalpy and entropy data with the other data in Fig. 2 is further evidence for no unusual charge polarization in these ligands as this would be expected to be evidenced by a more exothermic ΔH_{101} without a compensating change in ΔS_{101}.

TABLE V. Thermodynamics Parameters of Complexation of Lanthanide Ions by *m*-Methoxybenzoic Acid; I = 0.10 M ($NaClO_4$); T = 298 K

Ion	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
La	1.96 ± 0.09	11.18 ± 0.51	5.41 ± 1.2	56 ± 4
Pr	2.00 ± 0.03	11.41 ± 0.17	9.78 ± 1.1	71 ± 4
Nd	2.12 ± 0.03	12.10 ± 0.17	8.61 ± 0.5	69 ± 4
Sm	2.24 ± 0.05	12.78 ± 0.29	8.25 ± 0.6	71 ± 2
Eu	2.21 ± 0.03	12.61 ± 0.17	9.08 ± 0.9	73 ± 3
Gd	2.07 ± 0.03	11.81 ± 0.17	9.62 ± 0.5	72 ± 2
Tb	2.02 ± 0.05	11.53 ± 0.29	11.19 ± 1.8	76 ± 6
Dy	2.01 ± 0.05	11.47 ± 0.29	11.98 ± 1.8	79 ± 6
Ho	1.97 ± 0.04	11.24 ± 0.23	12.35 ± 2.2	79 ± 7
Er	2.01 ± 0.03	11.47 ± 0.17	12.77 ± 0.7	81 ± 2
Tm	2.05 ± 0.04	11.70 ± 0.23	11.94 ± 0.3	79 ± 1
Yb	2.01 ± 0.10	11.47 ± 0.57	11.82 ± 0.5	78 ± 2
Lu	2.03 ± 0.03	11.58 ± 0.17	11.88 ± 0.3	79 ± 1
Y	1.87 ± 0.04	10.67 ± 0.23	11.62 ± 0.6	75 ± 2

TABLE VI. Thermodynamics Parameters of Complexation of Lanthanide Ions by *p*-Methoxybenzoic Acid; $I = 0.10$ M ($NaClO_4$); $T = 298$ K

Ion	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
La	2.06 ± 0.04	11.77 ± 0.23	6.88 ± 0.4	63 ± 2
Pr	2.09 ± 0.05	11.95 ± 0.29	8.95 ± 2.2	70 ± 7
Nd	2.18 ± 0.08	12.41 ± 0.46	8.28 ± 1.5	69 ± 5
Sm	2.24 ± 0.03	12.78 ± 0.17	9.01 ± 1.6	73 ± 5
Eu	2.14 ± 0.02	12.18 ± 0.11	9.83 ± 1.2	74 ± 4
Gd	2.12 ± 0.03	12.10 ± 0.11	10.30 ± 0.4	75 ± 1
Tb	2.00 ± 0.08	11.41 ± 0.46	11.19 ± 0.9	76 ± 3
Dy	2.00 ± 0.08	11.41 ± 0.46	12.59 ± 0.3	81 ± 2
Ho	2.04 ± 0.06	11.66 ± 0.34	13.59 ± 1.2	85 ± 4
Er	2.00 ± 0.04	11.41 ± 0.23	15.31 ± 0.3	90 ± 1
Tm	2.02 ± 0.03	11.51 ± 0.17	14.51 ± 0.5	87 ± 2
Yb	2.01 ± 0.10	11.47 ± 0.57	15.29 ± 1.0	90 ± 3
Lu	2.01 ± 0.08	11.47 ± 0.46	13.43 ± 0.9	84 ± 3
Y	2.01 ± 0.03	11.47 ± 0.17	14.16 ± 1.0	86 ± 3

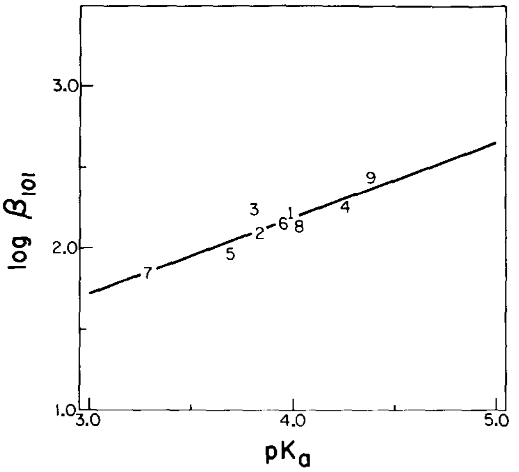

Fig. 1. Correlation of $\log \beta_{101}$ for Sm(III) complexation and pK_a of the ligand: 1, benzoate [1]; 2, *o*-methoxybenzoate; 3, *m*-methoxybenzoate; 4, *p*-methoxybenzoate; 5, *m*-fluorobenzoate [3]; 6, *p*-fluorobenzoate [3]; 7, *m*-nitrobenzoate [3]; 8, *m*-hydroxybenzoate [11]; 9, *p*-hydroxybenzoate [11].

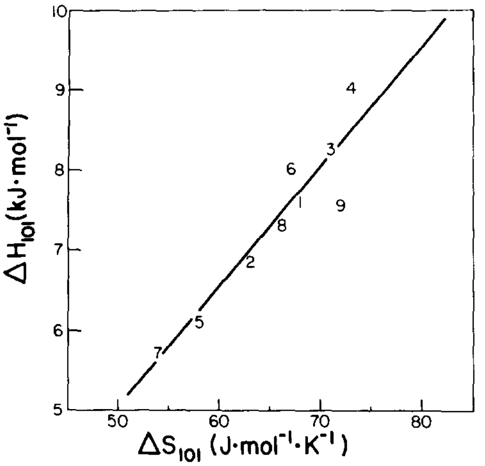

Fig. 2. Plot of the enthalpy change, ΔH_{101}, and entropy change, ΔS_{101}, for Sm(III) complexation. The numbers refer to the same ligands as in Fig. 1.

Earlier measurements of the stability constants for the complexation of the methoxybenzoate isomers with lanthanide cations had given somewhat larger values than the present [12]. This led to the proposal that a degree of charge polarization to the carboxylate group was responsible. To further investigate this question, we have measured the ^{13}C NMR spectra of these methoxy benzoate isomers in solution when ionized and when complexed with La^{3+} (1:1 complex). The chemical shifts of the carboxylate carbon for the lanthanum complex differed from those of the ionized (sodium salt) form by less than 0.1 ppm for all three isomers as well as for benzoate. This indicates that lanthanide complexation does not cause any significant disturbance to the charge distribution in the aromatic nucleus. Similar conclusions were inferred from other investigations [13, 14] including Raman, IR and UV spectroscopic measurements which indicated that the number, frequency and intensity of the aromatic system bands for both lanthanide benzoates and the parent acid are very similar.

An additional support for an absence of unusual polarizing effects in lanthanide complexation with these ligands is obtained from the linear correlation of the stability constants and the Hammett σ con-

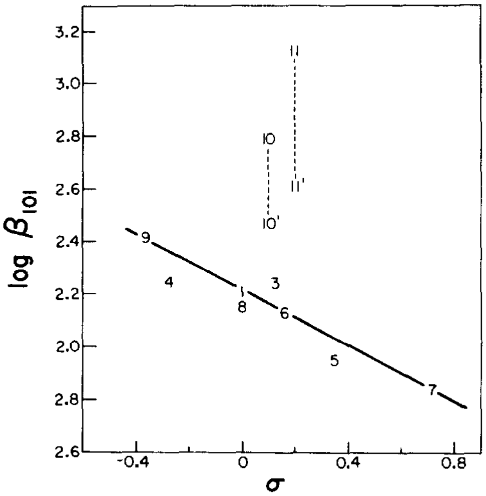

Fig. 3. The relation between log β_{101} for Sm(III) complexes and the Hammett σ values of substituted benzoic acid ligands. The numbering system of 1–9 is the same as in Fig. 1; 10, isophthalate [1]; 11, 1,3,5-benzenetricarboxylate [16].

stants. The plot of log β_{101} *vs.* values of σ from ref. 15 is shown in Fig. 3. The correlation is good, within experimental uncertainties, when the substituent group is neutral. For charged, non-coordinating substituents, such as iso-phthalate [1] and 1,3,5-benzenetricarboxylate [16], the stabilities of the complexes formed, even after correction of the statistical factors [17] as indicated by the prime numbers in Fig. 3, are greater than predicted. This deviation can possibly be due to some polarization of charge from the non-bonding carboxylate group(s) to the bonded one. Raman and NMR studies are underway to check this interpretation.

Acknowledgement

This research was supported by a contract with the Division of Chemical Sciences, USDOE-OBES.

References

1 G. R. Choppin, P. A. Bertrand, Y. Hasegawa and E. N. Rizkalla, *Inorg. Chem., 21*, 3722 (1982).
2 G. R. Choppin, L. Qingliang and N. Chunji, *Lanthanides Actinides Res.*, in press.
3 G. R. Choppin and L. H. J. Lajunen, *Inorg. Chem., 25*, 3512 (1986).
4 C. W. Davies, *J. Chem. Soc.*, 2093 (1938).
5 M. S. Caceci and G. R. Choppin, *Comput. Chem., 6*, 161 (1982).
6 T. W. Zawidski, H. M. Papee and K. J. Laidler, *Trans. Faraday Soc., 55*, 1743 (1959).
7 T. Matsui, H. C. Ko and L. G. Hepler, *Can. J. Chem., 52*, 2906 (1974).
8 M. S. Caceci and W. P. Cacheris, *Byte, 5*, 340 (1984).
9 H. Margenau and R. M. Murphy, 'The Mathematics of Physics and Chemistry', Van Nostrand, New York, 1943, p. 476.
10 M. S. Caceci, G. R. Choppin and Q. Liu, *Solvent Extraction Ion Exchange, 3*, 605 (1985).
11 L. H. J. Lajunen, M. Lajunen, G. R. Choppin and K. Yao, *Inorg. Chim. Acta*, accepted for publication.
12 G. R. Choppin, *J. Less-Common Met., 112*, 193 (1985).
13 H. Trwing and H. Rossotti, *Acta Chem. Scand., 10*, 72 (1956).
14 (a) W. Lewandowski and H. Baranska, *J. Raman Spectrosc., 17*, 17 (1986); (b) W. Lewandowski, *J. Mol. Struct., 101*, 93 (1983).
15 J. March, 'Advanced Organic Chemistry', 2nd edn., McGraw-Hill, New York, 1977, pp. 251–258.
16 W. R. Bradley, *M.Sc. Thesis*, The Florida State University, 1986.
17 J. Bjerrum, 'Metal Ammine Formation in Aqueous Solution', Haase, Copenhagen, 1941, 1957.