Contribution from the Department of Chemistry,
The Florida State University, Tallahassee, Florida 32301

Lanthanide Croconate Complexation in Solution

G. R. CHOPPIN* and E. OREBAUGH

Received February 3, 1978

The thermodynamic parameters of complexation of lanthanide cations by croconate ligands have been measured in aqueous solution using potentiometry and calorimetry. Comparison of experimental and calculated (with a modified Born equation) values of ΔG indicates the presence of aromatic π systems in the carbon rings of the ligands in squarate, croconate, and tropolonate complexes but of a nonaromatic π system in the cyclic ether rings of kojate and maltolate complexes.

Introduction

Squaric and croconic acids are strong oxocarbon acids which form symmetrical, planar, dinegative anions with extended π-electron systems. An earlier publication[1] has reported the thermodynamic parameters of complexation of the trivalent lanthanide cations by squarate. In this paper we describe the results of a study of the complexation of these cations by croconate. A calorimetric titration technique was used to obtain the free energy and enthalpy of complexation simultaneously since the strong acidity of croconic acid did not allow determination of the stability constants by potentiometric titration. Our earlier paper[1] showed that such an "entropy" titration technique provided values of ΔG and ΔH of complexation by squarate that agreed with the values obtained by independent potentiometric and calorimetric titrations.

Experimental Section

Lanthanide perchlorate stock solutions were prepared by dissolving reagent grade oxides or carbonates in hot perchloric acid. Appropriate quantities of the pH 4–5 lanthanide stock solutions and 2 M $NaClO_4$ were diluted with deionized water to produce working solutions whose concentrations were about 5 mM in Ln(III) and 70 mM in Na(I). The working solutions were analyzed for the lanthanide cation concentration by EDTA complexometric titration using xylenol orange indicator and for total cation concentrations by passage through an acid-form cation exchange resin (Dowex 50) followed by base titration of the eluate to ascertain the concentration of H^+ released.

The croconate ligand was synthesized from potassium rhodizonate following the procedure of Yamada and Hirata.[2] The anhydrous disodium salt was purified by repeated crystallizations from water, checked for impurities by paper chromatography, and analyzed for sodium by passage through H^+-form cation exchange resin and titration of the released H^+. The titrant solution in the calorimetric titrations was a 0.0333 M aqueous solution of the disodium croconate at pH 4–5. The ionic strength of the solutions was adjusted to 0.10 M with $NaClO_4$.

The calorimeter, the titration procedures, and the calculations used in this study have been described in the squarate paper.[1] The technique of entropy titration is based on the relationship of the observed heat change in the calorimeter vessel after each titration increment and the extent of complexation of all significant species and their reaction enthalpies. We assumed that heats of dilution were negligible for small changes in ionic strength. The mathematical analysis of the integral (or differential) calorimetric titration curves yielded the values for the thermodynamic parameters.

Results

The equilibria and associated thermodynamic parameters of interest in this study are

$$Ln^{3+}(aq) + Cc^{2-}(aq) \xrightleftharpoons{\beta_1,\ \Delta H_1,\ \Delta S_1} LnCc^{+}(aq)$$

$$Ln^{3+}(aq) + 2Cc^{2-}(aq) \xrightleftharpoons{\beta_2,\ \Delta H_2,\ \Delta S_2} Ln(Cc)_2{}^{+}(aq)$$

where Ln is the lanthanide cation and Cc is the croconate anion. Only the 1:1 and 1:2 lanthanide complexes were considered since there was no evidence in our experiments for complex formation of a 1:3 complex. At the pH of the titration, we could assume the croconate existed only as Cc^{2-} and protonation equilibria were insignificant.

Table I. Entropy Titration Data for the Praseodymium–Croconate System Integral Heat Curve[a]

titer vol, mL	Q_i, mcal obsd	Q_i, mcal calcd	$10^3[L]$, M	$\bar{n}$	$10^2\mu$
0.50	10.47	10.55	0.0510	0.079	9.75
1.00	20.77	20.90	0.1079	0.157	9.54
1.50	31.14	31.02	0.1720	0.232	9.35
2.00	40.95	40.84	0.2448	0.306	9.16
2.50	50.44	50.32	0.3282	0.376	8.99
3.00	59.48	59.37	0.4240	0.443	8.83
4.00	75.93	75.93	0.6611	0.565	8.56
5.00	89.46	90.00	0.9686	0.667	8.35
6.00	101.54	101.40	1.3474	0.749	8.20
7.00	110.54	110.29	1.7844	0.810	8.10
8.00	117.97	117.29	2.2598	0.858	8.04
9.00	123.32	123.19	2.7557	0.895	8.01
10.00	127.54	127.92	3.2592	0.924	8.00

[a] Experimental conditions: metal solution: [Pr] = 0.00461 M, [Na] = 0.07020 M, volume = 40.0 mL; titer: total ligand = 0.0333 M, ionic strength = 0.10 M; $T = 25.00$ °C. Computed overall thermodynamic parameters: $\beta_1 = 1644$, $\beta_2 = 28500$, $\Delta H_1 = 0.722$ kcal/mol, $\Delta H_2 = 2.0$ kcal/mol.

Table I shows a set of sample data as well as the computed free-ligand concentrations and average ligand number ($\bar{n}$) calculated from the integral heat change by iteration using a nonlinear regression routine.[3] The ionic strength, μ, was recalculated for each iteration in order that the stability constants could be adjusted for the prevailing ionic strength. This adjustment in the stability constants was made by using the ratio of activity coefficients computed from the Debye–Hückel equation. For the 1:1 complexation, for example, the correction was of the form

$$\beta_1{}^{ss} = \beta_1{}'\gamma_\pm{}^{ss}/\gamma_\pm{}'$$

where "ss" indicates 0.1 M ionic strength as the standard state and the prime indicates values at a different ionic strength. The correction was as large as 30% for β_1 and 50% for β_2.

Table II shows the computed thermodynamic parameters obtained by combination and/or averaging of two or more data sets for each of the lanthanides. Data for the 1:2 complexes of Nd, Sm, Eu, and Gd are included although the integral heat curve could be fitted as accurately without including the 1:2 complexes in the calculations. This is reflected in the values listed for 1:2 complexation which are somewhat out of line with the rest of the series. The correlation factor for these data also indicated they were less reliable than the rest. The errors quoted in Table II represent one standard deviation.

Discussion

Munze[4] has shown that an extended Born equation gave

0020-1669/78/1317-2300$01.00/0

Table II. Thermodynamic Parameters[a] for the Lanthanide-Croconate System ($T = 25.0$ °C; $\mu = 0.10$ M ($NaClO_4$))

lanthanide	$10^{-3}\beta_1$	$-\Delta G_1$[b]	ΔH_1[b]	ΔS_1[c]	$10^{-3}\beta_2$	$-\Delta G_2$[b]	ΔH_2[b]	ΔS_2[c]
La	1.13	4.17	0.97	17.2	31.3	1.96	1.08	10.3
Ce	1.26	4.23	0.82	16.9	24.9	1.77	1.05	9.5
Pr	1.64	4.39	0.72	17.1	28.5	1.69	1.28	10.0
Nd	1.70	4.41	0.63	16.9	(27.1)	(1.63)	(0.77)	(6.0)
Sm	1.21	4.23	0.86	17.1	(6.8)	(1.00)	(−0.81)	(−2.3)
Eu	1.48	4.21	1.25	18.3	(15.0)	(1.48)	(0.00)	(0.8)
Gd	0.96	4.07	1.73	19.5	(16.2)	(1.67)	(0.58)	(7.5)
Tb	0.878	4.01	2.39	21.5	85.0	2.71	0.44	10.6
Dy	0.759	3.93	2.57	21.8	44.0	2.40	0.85	10.9
Ho	0.791	3.95	2.62	22.1	48.0	2.43	1.12	11.9
Tm	0.819	3.97	2.64	22.2	39.0	2.29	1.68	13.3
Yb	0.845	3.99	2.61	22.2	37.5	2.25	1.88	13.8
Lu	0.823	3.98	2.58	22.0	28.0	2.09	2.37	15.0
Y	0.612	3.80	2.71	21.8	29.1	2.29	1.20	11.7

[a] Errors (1σ): $\beta_1 = \pm 10\%$; $\Delta G_1 = \pm 0.005$ kcal/mol, $\Delta H_1 = \pm 0.005$ kcal/mol; $\Delta S_1 = \pm 0.2$ cal/(deg mol). $\beta_2 = \pm 25\%$; $\Delta G_2 = \pm 0.15$ kcal/mol, $\Delta H_2 = \pm 0.17$ kcal/mol; $\Delta S_2 = \pm 0.4$ cal/(deg mol). [b] In kcal/mol. [c] In cal/(deg mol).

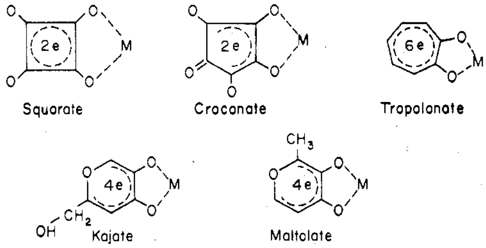

Figure 1. Structures of complexes with the number of π electrons indicated in the ring.

good agreement between experimental and calculated values of the free energy of formation of the monoacetate complexes of trivalent lanthanides and actinides. The equation contains a Coulombic term, a term to account for the change in the number of species upon complexation (i.e., a cratic term) and a term for the activity coefficients at the experimental ionic strength. The same equation was applied with equal success to the calculation of the free energy of formation of monofluoride complexes of di-, tri-, and tetravalent cations.[5] The Munze equation is

$$\Delta G = \frac{Ne^2 Z_1 Z_2}{(4.187 \times 10^2) D d_{12}} - \ln \nu 55.51 + RT\Sigma \ln f(\mu) \qquad (1)$$

where N is Avogadro's number, e is the unit charge (4.80×10^{-10} esu), Z_1 and Z_2 are the ionic charges of the metal and the ligand, respectively, D is the dielectric constant, d_{12} is the distance between charge centers, ν is the change in number of reacting species (= −1), and $\sum \ln f(\mu) = -((\sum \Delta Z^2) \cdot 0.511\mu^{1/2}/(1 + B å \mu^{1/2})) - C\mu^{1/2} - E$ ($B = 0.33$, $C = 0.75$, $E = -0.15$, $å = 4.3$).

Munze used $D = 78.5$, but in the fluoride study, we allowed D to be a parameter which varied with the cation charge. For trivalent cations agreement was obtained between eq 1 and experiment when D had a value of about 57. Using this value, setting $d_{12} = 2.5$ Å (estimated for Sm(III) complexes), and assuming squarate and croconate have $\sum Z_2 = -2$, we calculate $-\Delta G$ to be +10.9 kcal/mol compared to the experimental values of 3.83 ($SmSq^+$) and 4.23 ($SmCc^+$). The complexation of lanthanides by maltolate,[6] kojate,[7] and tropolonate[8] has been measured and the free energies of formation of the 1:1 Sm(III) complexes ($\mu = 0.1$ M) are 8.88, 8.19, and 9.41 kcal/mol. Assuming $\sum Z_2 = -1$ for these ligands and, again, setting $D = 57$ and $d_{12} = 2.5$ Å lead to a calculated $-\Delta G$ of 3.50 kcal/mol. Obviously, the calculations are in serious disagreement for all these complexes.

When resonance structures are considered, other values of Z_2 result. An added stabilization is provided by aromaticity in the ring structures. Since such aromaticity, according to Hückel's rule,[9] is present when the π systems have $4n + 2$ electrons ($n = 0, 1, 2$, etc.), our ligands must have 2 or 6 π electrons to be aromatic. For squarate and croconate, a two-electron π system is possible. This would result in the structures in Figure 1 which would lead to $\sum Z_2 = 2(-0.5)$ for both of these oxocarbon ligands. Tropolonate would have a six-electron aromatic π structure (Figure 1) with $\Sigma Z_2 = 2(-6/7)$. Using these values for $\sum Z_2$ (i.e., −1 for squarate and croconate and −1.72 for tropolonate) with $D = 57$ and $d_{12} = 2.4 \pm 0.1$ Å gives calculated values of $-\Delta G = 3.8 \pm 0.3$ kcal/mol for squarate and croconate and 9.2 ± 0.5 kcal/mol for tropolonate (vs. $-\Delta G_{\text{exptl}}(\text{SmX})$ of 3.8, 4.2, and 9.4 kcal/mol, respectively).

This change in anion structure also explains the relative orders of $-\Delta G(\text{LnCc}^+) > -\Delta G(\text{LnSq}^+)$ vs. $\text{p}K_{a_2}(\text{HSq}^-)$[10] $> \text{p}K_{a_2}(\text{HCc})$.[11] Monoprotonation of Cc^{2-} allows retention of the "symmetric" structure so the bonding oxygen is only −0.4 compared to −0.5 for squarate. Only in chelation do the canonical resonance structures lead to the presence of the C=O groups as in Figure 1.

An earlier publication[12] reported the thermodynamics of complexation of Eu(III) by methylhydroxycyclobutenedione, which resembles squaric acid with methyl replacing a hydroxy group. On the basis of ΔH and ΔS values, it was proposed that an outer-sphere complex was formed. Such a complex would have $\sum Z_2 = -1$ and $d_{12} = (2.4 + 1.8) \pm 0.1$ Å. The calculated $-\Delta G$ with these values is 0.5 ± 0.2 kcal/mol while $-\Delta G_{\text{exptl}}$ is 0.89 ± 0.06 kcal/mol.

If kojate and maltolate have aromatic π systems (six electrons), $\sum Z_2 = 2(-1)$. This results in a calculated $-\Delta G$ of 11.3 kcal/mol compared to the experimental values of 8.2 and 8.9 kcal/mol. However, Palmer[13] cites evidence for only four π electrons in these cyclic ether rings. This implies that one of the pairs of nonbonding electrons does not occupy a p orbital since such occupation leads to a $4n + 2$ aromatic system. Such nonaromatic four-π-electron structures lead to $\sum Z_2 = (-1) + (-^2/_3)$ or −1.67. Using this value we calculate $-\Delta G = 8.9 \pm 0.5$ kcal/mol, in good agreement with the experimental values.

The agreement between values of ΔG calculated from eq 1 and from experiment is evidence of the validity of such a calculation for lanthanide complexes. Equation 1 is based on ionic bonding which is quite dominant in lanthanide complexes. Moreover, the agreement between calculation and experiment allows us to propose electronic structures for the ligands. It would seem that the squarate and croconate ligands have aromatic systems with two π electrons. This requires the presence of a carbonyl (>C=O) group in croconate. Tro-

Table III. Comparison of Entropy and Enthalpy Changes of Sm(III) Complexation

ligand	ΔH, kcal/mol	ΔS, cal/(deg mol)	ΔH,^{c} kcal/mol	ΣZ_2
squarate	+2.00	19.6	+1.25	−1.00
croconate	+0.86	17.1	+0.86	−1.00
kojate	−0.50	25.8	−3.11	−1.67
tropolonate	−2.81	22.2	−4.34	−1.72

polonate has an aromatic ring of six π electrons. However, the cyclic ether rings of the kojate and maltolate ligands are nonaromatic with four π electrons.

Table III compares the enthalpies and entropies of complexation of Sm(III) with croconate and related ligands. The overall complexation reaction can be described in two steps:

$$\begin{array}{ll} M(H_2O)_x \rightarrow M(H_2O)_y + (x-y)H_2O & \qquad (2a) \\ & \Delta H_H, \Delta S_H \\ L(H_2O)_n \rightarrow L(H_2O)_m + (n-m)H_2O & \qquad (2b) \end{array}$$

$$M(H_2O)_y + L(H_2O)_m \rightarrow ML(H_2O)_{y-m} \quad \Delta H_R, \Delta S_R \tag{3}$$

In general, in lanthanide reactions involving inner-sphere complexation, $\Delta H_H > \Delta H_R$ and $\Delta S_H > \Delta S_R$.[14] Since ΔH_R and ΔS_R should be negative whereas ΔH_H and ΔS_H should be positive, the experimental positive values are in agreement with these relationships. Moreover, there is good evidence for a compensation in these dehydration terms such that $\partial\Delta H_H = T\partial\Delta S_H$.[14,15] If we assume that the differences in the entropies in Table III reflect differences in ΔS_H (since the ligands are all bidentate, we would expect ΔS_R to be very similar), we can correct the enthalpies to constant entropy values such that the differences in the corrected enthalpies, ΔH^c, reflect differences in the ΔH_R terms only. The correction is $\Delta H^c = \Delta H - T\partial\Delta S$, where $\partial\Delta S = \Delta S - 17.1$ cal/(deg mol) (this uses croconate as the base for correction).

The ΔH^c values are listed in Table III. The ΔH^c values have a linear correlation with $\sum Z_2$ which is expected if $\Delta H^c \propto \Delta H_R$ and is related by ligand only to ΔH_R. We ascribe the differences in the experimental ΔH values of complexation for the different ligands primarily to the relationship between the ΔH_R terms and the ligand charge and secondarily to the (smaller) differences due to different dehydration rates.

Acknowledgment. We wish to acknowledge valuable discussions with Professor H. Walborsky in the interpretation of these results. This research was supported by a contract with the U.S. Energy and Development Agency (now DOE).

Registry No. Squaric acid, 2892-51-5; croconic acid, 488-86-8; kojic acid, 501-30-4; tropolone, 533-75-5; maltol, 118-71-8; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; Y, 7440-65-5; La, 7439-91-0.

References and Notes

(1) E. Orebaugh and G. R. Choppin, *J. Coord. Chem.*, **5**, 123 (1976).

(2) K. Yamada and Y. Hirata, *Bull. Chem. Soc. Jpn.*, **31**, 550 (1958).

(3) A complete description of the mathematical analysis is presented in E. Orebaugh, "Complexation Thermodynamics of Lanthanide Oxocarbon Systems", Ph.D. Dissertation, The Florida State University, 1972.

(4) R. Munze, *J. Inorg. Nucl. Chem.*, **34**, 661 (1972).

(5) G. R. Choppin and R. J. Unrein, "Transplutonium 1975", W. Muller and R. Linder, Ed., North-Holland Publishing Co., Amsterdam, 1976, p 97.

(6) N. K. Dutt and U. V. M. Sharma, *J. Inorg. Nucl. Chem.*, **32**, 1035 (1970).

(7) R. Stampfli and G. R. Choppin, *J. Coord. Chem.*, **1**, 173 (1972).

(8) D. L. Campbell and T. Moeller, *J. Inorg. Nucl. Chem.*, **32**, 945 (1970).

(9) J. D. Roberts, R. Stewart, and M. C. Caserio, "Organic Chemistry", W. A. Benjamin, New York, N.Y., 1971, p 145.

(10) L. W. Schwartz and L. O. Howard, *J. Phys. Chem.*, **74**, 4374 (1970).

(11) R. I. Gelb, L. M. Schwartz, D. A. Laufer, and J. O. Yardley, *J. Phys. Chem.*, **81**, 1268 (1977).

(12) S. S. Yun and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **38**, 332 (1976).

(13) M. H. Palmer, "The Structures and Reactions of Heterocyclic Compounds", St. Martin's Press, New York, N.Y., 1967, p 213.

(14) G. R. Choppin, *Pure Appl. Chem.*, **27**, 23 (1971).

(15) G. R. Choppin, M. P. Goedkin, and T. F. Gritmon, *J. Inorg. Nucl. Chem.*, **39**, 2025 (1977).

Contribution from Ames Laboratory—USDOE and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Polarized Electronic Absorption Spectra for Potassium Tetrabromoplatinate(II) Dihydrate. Spectral Effects of a Platinum(IV) Component

TIMOTHY J. PETERS, ROY F. KROENING, and D. S. MARTIN, JR.*

Received December 27, 1977

Crystals of the metastable compound $K_2PtBr_4{\cdot}2H_2O$ have an orthorhombic structure, space group *Pbam*, with $a{:}b{:}c$ = 8.31 (2):13.73 (3):4.84 (1) Å and $Z = 2$. The $PtBr_4^{2-}$ ion occupies a crystallographic site of C_{2h} symmetry but retains essentially a D_{4h} molecular symmetry with the z axis directed along c. The absorption spectra in the d ← d region were recorded for a, b, and c polarizations. Band maxima lie at 300–800 cm^{-1} higher energies than in anhydrous K_2PtBr_4. The $^1A_{2g} \leftarrow {}^1A_{1g}$ transition, forbidden in z polarization, was not observed in c polarization. Vibrational components were resolved in the $^3B_{1g}$ shoulder and in the $^1A_{2g}$ peak. Striking differences in intensities which occurred in the a and b polarization indicated that crystal effects were important in the vibronic excitation process. Red sections, in some crystals, were attributed to a dipole-allowed band, completely c polarized, for a mixed-valence electron-transfer transition involving a $PtBr_6^{2-}$ impurity defect.

Introduction

When a solution of potassium tetrabromoplatinate(II) evaporates at room temperature, some crystals of anhydrous K_2PtBr_4 are formed. The structure, determined by X-ray diffraction, and polarized crystal absorption spectra of these crystals were described previously.[1] However, the formation of a hydrate can also occur. This hydrate, characterized as $K_2PtBr_4{\cdot}2H_2O$, was described by Biilman and Anderson[2] as black crystals which were very rapidly dehydrated when exposed to laboratory air. However, they reported angles between well-developed faces of these crystals and concluded that they were orthorhombic.

In anhydrous K_2PtBr_4 the square-planar $PtBr_4^{2-}$ occupies a site of full D_{4h} symmetry, and the polarized crystal spectra

0020-1669/78/1317-2302$01.00/0