Determination of Acid Dissociation and Stability Constants of 1:1 and 1:2 Complexes of Acid Chromium and Lanthanon Nitrilotriacetates

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Abstract: The present work describes the determination of acid dissociation and stability constants of 1:1 and 1:2 complexes of acid chromium and lanthanon nitrilotriacetates. The results obtained support our previous suggestion that NTA, in acid medium, is in the monoprotonated tridentate form $(HNTA)^{2-}$ and not the quadridentate state $(NTA)^{3-}$. This is reflected on the very high log β values obtained in neutral or slightly basic media as compared to those obtained in the present study.

Key words: pka · log β_1 · log β_2 · acid nitrilotriacetates

INTRODUCTION

Acid trivalent-metal nitrilotriacetates, especially those complexes of Al (III) and Fe (III), have several uses in different fields [1 -5]. Very little work, however, has been done on acid-NTA complexes of the lanthanons. In continuation to our work on the preparation, characterization and determination of pka and log β values of 1:1 and 1:2 acid divalent-metal nitrilo triacetates [6 -8], the present work is carried out to supplement existing data on such an important group of compounds. Literature survey reveals that no work has been carried out on acid dissociation and stability constants of acid nitrilotriacetates of the lanthanon complexes.

In neutral or slightly basic media such constants were determined by Schwarzenbach and coworkers [9, 10] and by Moeller and Ferrus [11]. Anderegg [12] was the first to claim that NTA shows a pronounced tendency to from 1:2 complexes. There is however some controvercy as to whether NTA is a tri or quadridentate ligand [13, 14].

For monobasic acids, pka values are simply determined by potentiometric titration of a known weight of the acid against standard potassium hydroxide solution. The method of calculation is also simple [15]. The link between acid dissociation and stability constants is the fact that those ionic species which combine with a hydrogen cation have an affinity, also, for the cations of metals. The principal difference is that ionization is commonly regarded as dissociation, whereas metal binding is seen as an association. The present work is an attempt to apply the KONST program [16], to calculate log β values for the acid chromium and the acid lanthanon nitrilotriacetates, also to determine pka values of these acid complexes, both categories were not determined before.

MATERIALS AND METHODS

All chemicals used are of the A.R. or extra pure grade.

Determination of the pka_1 values of the 1:1 and 1:2 acid M^{III} complexes together with log β_1 and log β_2 for metal- NTA complexes present in these acid were carried out by potentiometric titration against standard 0.05 N potassium hydroxide solution using a Fischer pH meter as follows: the metal chloride and nitrilotriacetic acid in the molar ratios 1:1 and 1:2 were mixed together in a breaker, about 10 ml of bidistilled water and 10 ml of 1 M KNO_3 solution were then added and the mixture heated to allow the reaction to go to completion. The solution was then cooled, completed to 50 ml with bidistilled water and the temperature adjusted to 25°C ± 0.02. The solution was then titrated against standard 0.05 N KOH solution. The pH values measured were converted to pC_H by subtracting the conversion factor for HCl. The pka values are then calculated by Albert and Sergeant's method [15] and the log β values by applying the KONST program [16].

RESULTS AND DISCUSSION

pka values for acid 1:1 and 1:2 chromium and the lanthanon nitriloacetates are given in Table 1.

There are no literature acid dissociation constant values for comparison, the pka values obtained in the present study are determined for the first time. However,

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Table 1: pka_1 values for 1:1 and 1:2 M^{III} acid complexes

M^{3+}	1:1 complex	1:2 complex
Cr	2.08	2.92
Ce	5.65	4.99
Pr	5.47	4.97
Nd	5.40	4.96
Sm	5.34	4.93
Eu	5.25	4.91
Gd	5.19	4.72
Tb	5.13	4.61
Dy	5.00	4.54
Ho	4.96	4.53
Er	4.83	4.49
Yb	4.75	4.46
Lu	4.14	4.02

Table 2: $\log \beta_1$ values for the acid 1:1 M^{III} nitrilotriacetate complexes

M^{3+}	$\log \beta_1$	M^{3+}	$\log \beta_1$
Cr	9.10	Tb	6.75
Ce	6.42	Dy	6.77
Pr	6.53	Ho	6.91
Nd	6.61	Er	6.92
Sm	6.63	Yb	6.92
Eu	6.68	Lu	6.93
Gd	6.74		

Table 3: $\log \beta_1$ and $\log \beta_2$ values for acid 1:2 M^{III} complexes

M^{3+}	$\log \beta_1$	$\log \beta_2$
Cr	9.74	19.00
Ce	6.92	13.27
Pr	6.92	13.27
Nd	7.14	13.68
Sm	7.19	13.80
Eu	7.21	13.82
Gd	7.23	14.05
Tb	7.23	14.05
Dy	7.32	14.21
Ho	7.40	14.33
Er	7.45	14.34
Yb	7.46	14.38
Lu	7.83	14.48

comparing the pka_1 values for the chromium complex with those for the lanthanons reveals that the ionic radius is a determining factor being 0.55 Å for Cr^{3+} ion and ranges from 0.88-1.07 for the lanthanons [17]. Results in Table 1 also show that the smaller the radius of the central metal atom the stronger is the complex as an acid.

It may be suggested that during the potentiometric titration the reactions proceed as follows for the 1:1 and 1:2 complexes respectively;

$$[M^{III}(HNTA).3H_2O]Cl + KOH \rightarrow [M^{III}(NTA).2H_2O] + KCl + H_2O$$

$$H[M^{III}(HNTA)_2] + KOH \rightarrow K[M(NTA)_2] + 2H_2O$$

It must be remembered that the most reliable readings for pka calculation are those of the almost horizontal part of the titration curve; i.e. from 20-80% ionization.

The constants (βi's) are computed using the KONST [16] program with its uncertainties and some statistical parameters necessary for the correctness of the fit. Moreover, the data are weighted, i.e a smaller weight is given to the less accurate regions of the titration curve in which the change of dE (mV) / dV (ml) is large. $\log \beta_1$ for the 1:1 complexes are given in Table 2.

Comparing these values with those previously recorded in the literature measured in neutral or slightly basic media, it will be observed that those for the lanthanons, determined in the present study, range from 6.42-6.93 while those previously determined range from 10.70-12.40 [9]. This, again supports our previous suggestion that the ligand in the complexes of the present study is the tridentate $(HNTA)^{2-}$ and not the quadridentate $(NTA)^{3-}$ [8].

The effect of ionic radius of the central metal is best shown by the marked difference in $\log \beta_1$ between the chromium and the lanthanon complexes. $\log \beta_1$ and $\log \beta_2$ values for acid 1:2 trivalent-metal nitrilotriacetates are given in Table 3.

These results show that the smaller the ionic radius of the central metal atom the more stable is the complex formed.

Again the reported values for $\log \beta_2$ in the literature are around 20[18] which is explained as being due to charge and dentation of the ligand as described in the above text.

REFERENCES

1. Ebina, Y., S. Okada, S. Hamazaki and Y. Toda, 1991. Calcified tissue International 48: 28.
2. Liu, M., S. Okada and T. Kawabata, 1991. Acta Medica Okayama, 45: 401.
3. Toyokuni, S. and J.L. Sagripauti, 1993. Carcinogenesis, 4: 2.
4. Deguchi, J., T. Kawabati, A. Rando and S. Okada, 1993. Japanese Journal of Cancer Research, 84: 649.

5. Uchida, K., A. Fukuda, S. Kawakiski and S. Toyokuni, 1995. Febs. Letters, 357: 165.
6. Souaya, E.R., W.G. Hanna, E.H. Ismail and N.E. Milad, 2000. Molecules, 5: 1121.
7. Souaya, E.R., W.G. Hanna, E.H. Ismail and N. E Milad, 2002. J. Coordination Chemistry, 55: 999.
8. Ibid, 2004. J. Coordination Chemistry, 57: 825.
9. Schwarzenbach, G. and W. Biederman, 1940. Helv. Chim. Acta, 31: 331.
10. Schwarzenbach, G. and R. Gut, 1956. Helv. Chim. Acta, 34: 1589.
11. Moeller, T. and R. Ferrus, 1962. Inorg. Chem., 1: 55.
12. Anderegg, V.G., 1960. Hel. Chim. Acta, 43: 825.
13. Uehara, A., E. Kyuno and R. Tsuchiya, 1967. Bull. Chem. Soc. Japan, 40: 2317.
14. Koine, N., J. Bianchini and I. Legg, 1986. Inorg. Chem., 25: 2835.
15. Albert, A. and E.P. Serjeant, 1984. The determination of Ionization constants.
16. Stunzi, H. and G. Anderegg, 1978. J. Coord. Chem., 7: 239.
17. Wilkinson, G., R.D. Gillard and J.A. Mclverty, 1987. Comprehensive Coordination Chemistry, 2: 789.
18. Sillen, L.G., 1971. Stability constants of metal - Ion complexes, Chemical Soc., Special Publication, 25.