Asian Journal of Chemistry Vol. 9, No. 3 (1997), 341–344

Rare Earth Complexes of Some Substituted Chalcones

S.K. AKUSKAR, A.G. SHANKARWAR; T.K. CHONDHEKAR* and D.G. DHULEY
Department of Chemistry
Dr. Babasaheb Ambedkar Marathwada University
Aurangabad-431 004, India

The present paper reports (a) the synthesis of a series of chalcones from *ortho*-hydroxy acetophenones with *p*-nitromethyl/-benzoic acid and benzaldehyde/anisaldehyde, (b) the determination of their pK values and the study of their complexation with some metal ions in lanthanide series.

INTRODUCTION

Chalcones are reported to exhibit germicidal[1], bacteridcidal[2], fungicidal and carcinogenic activities.[3] Complexes of chalcones are widely used in biological systems.[4, 5] In view of the analytical, biological importance and manifold uses of metal complexes with chalcones, a study of their stability is, therefore, an important factor in determining the effectiveness of these chelates in above mentioned fields. The most stable lanthanide complexes of polyamide carboxylic acids, β-diketones and β-diketoesters have already been reported.[6, 7]

The literature survey revealed that no systematic study of the binary complexes of rare earth metal ions with present substituted chalcones has been reported. Hence the study of their complexes with rare earth metal ions like La(III), Ce(III), Pr(III), Nd(III), Sm(III), Cu(III), Gd(III), Tb(III), Dy(III) and Ho(III) was undertaken.

EXPERIMENTAL

All the chemicals such as phenols, acetic anhydride, aluminium chloride, hydrochloric acid, pyridine, ethanol, rare earth salts, $HClO_4$, $NaClO_4$ etc. were of analytical grade. The concentrations of metal ions in solutions were determined by standard procedures.[8–10]

Preparation and characterisation of chalcones

The chalcones were prepared and characterised by the procedure reported in earlier communications.[11]

RESULTS AND DISCUSSION

Chalcones used in the present study are:

R_1 = 1-(2′-hydroxyphenyl)-2-(4′-nitrobenzoyl)-3-(phenyl)-2-propen-1-one

R_1 = 1-(2′-hydroxyphenyl)-2-(4′-methylbenzoyl)-3-(phenyl)-2-propen-1-one

Proton ligand and metal-ligand stability constants

The acid + ligand curve deviates from acid curve at pH 9.5 indicating the deprotonation of phenolic group in this pH range. From these curves, values of $\bar{n}_A$ for various pH were calculated and they are found to be in the range 0.2 to 0.8 indicating the presence of only one pK of each chalcone. The pK values calculated by pointwise calculation and half integral methods were found to be in good agreement.

The displacement of metal titration curve with respect to ligand titration curve along volume axis indicates the formation of complex species and lies in the pH region where hydrolysis is not expected. The probability of formation of polynuclear complexes was ruled out as metal concentrations were very dilute.

The pL values were calculated and plotted against $\bar{n}_A$ to get the fomation curve. The metal-ligand stability constant (log K) was obtained by pointwise calculation, half integral and least-squares methods. The pK and log K values are listed in Table-1.

o-Hydroxy chalcones and their substituted derivatives may be considered as monobasic acids having only one dissociable proton from —OH group and hence there is only one pK value. This is confirmed by $\bar{n}_A$ values which were less than one for each ligand.

The pK values of parent *ortho*-hydroxy acetophenones were also determined for the purpose of comparison with the pK values of chalcones prepared from them. It is found that pK values of chalcones were lower than the corresponding acetophenone. The overall decrease in pK values of chalcones is attributed to the presence of phenyl ring at 2 and 3 positions which act as electron withdrawing group and reduce the strength of intermolecular hydrogen bonding due to which the ligand becomes more acidic. It is observed from Table-1 that the pK value of ligand R_1 is relatively lower than R_2. This may be due to the combined negative inductive effect (–I) of phenyl and *para*-nitrophenyl groups, which act as electron sink.

The larger pK value of R_2 is due to the presence of electron releasing, —CH_3 group present at *para* position. The introduction of methyl group at *para* position increases the charge density on phenyl ring by positive inductive effect (+I) and opposes the charge transfer from —OH group which causes bonding of proton to oxygon atom.

The interaction of chalcones with metal ions like La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Ho(III) was studied in 60% (v/v) ethanol-water medium at an ionic strength 0.1 M and the log K values are set out in Table 1.

The stability constants of lanthanide complexes with chalcones were determined by pointwise calculation method and half integral method and the average values are presented in Table 1. The observed values of stability constants of these complexes have been explained on the basis of basicity of ligands, atomic number and gadolinium break.

The highest value of $\bar{n}$ obtained was about 2.0 which clearly indicates the formation of both 1 : 1 and 1 : 2 complexes. Due to shielding effect ionic

TABLE-1

pK AND log K VALUES IN 60% (v/v) ETHANOL-WATER MEDIUM

Temp. = 25 ± 0.1°C; $\mu = 0.1$ M ($NaClO_4$)

Ligand		R_1	R_2
pK		10.830	11.210
La(III)	log K_1	8.742	8.542
	log K_2	7.384	7.098
	log β	16.126	15.640
Ce(III)	log K_1	8.852	8.652
	log K_2	7.400	7.341
	log β	16.253	15.994
Pr(III)	log K_1	8.150	9.007
	log K_2	8.053	8.758
	log β	17.203	17.758
Nd(III)	log K_1	9.221	9.021
	log K_2	7.861	7.720
	log β	17.082	16.753
Sm(III)	log K_1	9.260	9.071
	log K_2	7.904	8.872
	log β	17.165	17.943
Eu(III)	log K_1	9.301	9.001
	log K_2	8.001	7.718
	log β	17.303	16.719
Gd(III)	log K_1	9.071	8.863
	log K_2	7.688	7.560
	log β	16.760	16.423
Tb(III)	log K_1	9.219	9.012
	log K_2	7.920	7.708
	log β	17.131	16.721
Dy(III)	log K_1	9.481	9.270
	log K_2	8.198	9.971
	log β	17.680	19.241
Ho(III)	log K_1	9.324	9.125
	log K_2	8.024	7.830
	log β	17.359	16.955

compounds are generally formed by lanthanides. Possibility of covalent interaction, however, cannot be completely excluded. According to Born, if the bond in lanthanide complexes is ionic, $E = (e_2/2r)\ (1 - 1/D)$ relation should be followed for the ions. Since stability constant is related directly to this energy, it is expected for the complexes of various rare earths that the log K values should increase linearly with e_2/r. It has been observed that the stability constants of metal complexes increase with increasing atomic numbers (*i.e.* decrease in ionic radius) from La(III) to Eu(III). There is, however, a discontinuity found at Gd(III) (gadolinium break). From Gd(III), the plot shows maxima and minima in log β values of these complexes indicating their greater stability which may be attributed to the increased covalent character.[12]

It is also concluded from the observed nature of graphs that the present chalcone complexes are predominantly ionic in the first part *i.e.* from La(III) to Gd(III) and covalent in character in second part *i.e.* after Gd(III).

Validity of log K = a pK + b relation

When log β values were plotted against pK values of chalcones, a linear relationship was observed. The values of slopes are in the range of 0.75 to 1.46 for all the metals. The calculated slope values are listed below.

La(III) = 0.80
Ce(III) = 0.75
Pr(III) = 0.90
Nd(III) = 0.95
Sm(III) = 0.95
Eu(III) = 1.05

Gd(III) = 1.01
Tb(III) = 1.25
Dy(III) = 1.41
Yb(III) = 1.43
Ho(III) = 1.46

According to Ernst and Meenashi,[13] the effect of substituent in ligand on stability of metal complexes, as compared to that on proton-ligand complex, will be greater if the slope is greater than 1.0. The calculated values of slopes are found to be approximately equal to or less than one up to Gd(III). The higher values of slopes for the complexes after Gd(III) may be explained by considering the possibility of covalent character in the present complexes.

REFERENCES

1. J. Russel and H. Clarke, *J. Am. Chem. Soc.*, **61**, 3651 (1939).
2. N.P. Buu-Hai and N.D. Xuong, *J. Org. Chem.*, **23**, 39 (1958).
3. S.C. Kushwaha, Dinker and J.B. Lal, *Indian J. Chem.*, **13**, 844 (1967).
4. K. Syamsunder, *Proc. Indian Acad. Sci.*, **4**, 241 (1964).
5. D.N. Dhar, The Chemistry of Chalcones and Related Compounds, Wiley Interscience, New York (1981).
6. S.P. Tondon and P.C. Mehta, *Z. Naturforsch*, **B25**, 139 (1970).
7. N.K. Datta and S. Rahutgi, *J. Inorg. Nucl. Chem.*, **33**, 1725 (1971).
8. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Pergamon Green and Co. Ltd.
9. G. Scharembeek, Complexometric Titrations, Methuen and Co. Ltd., London (1957).
10. N.V. Thakur, S.M. Jogdev and R.C. Kanekar, *J. Inorg. Nucl. Chem.*, **28**, 2297 (1966).
11. S.K. Akuskar, T.K. Condhekar and D.G. Dhuley, *Asian J. Chem.*, **9**, 336 (1997)
12. L.C. Thomson, *J. Inorg. Nucl. Chem.*, **24**, 1089 (1962).
13. Z.L. Ernst and Meenshi, *J. Trans. Farad. Soc.*, **591**, 2838 (1983).

(*Received:* 2 July 1996; *Accepted:* 10 January 1997) AJC-1209