Proc. Indian natn. Sci. Acad., **63**, A, No. 5, 1997, pp. 421-426.
© Printed in India.

COORDINATION COMPOUNDS OF POTENTIAL BIOINORGANIC INTEREST: SYNTHESIS, MAGNETIC AND SPECTRAL STUDIES OF SOME NOVEL LANTHANUM (III) CHELATES OF SCHIFF BASES DERIVED FROM A PYRAZOLONE BASED HETEROCYCLIC β-DIKETONE

R C MAURYA

Coordination Chemistry Laboratory, Department of P.G. Studies and Research in Chemistry, R.D. University, Jabalpur-482 001

(*Received 04 July 1996; Revised 24 January 1997; Accepted 21 April 1997*)

Seven novel chelates of lanthanum (III) with Schiff bases derived from a pyrazolone based heterocyclic β-diketone, viz., 4-benzoyl- 3-methyl-1-phenyl-2-pyrazolin-5-one and aromatic amines, viz., N- (4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one) *p*-anisidine(I,BMPHP-PAH), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one) *m*-phenetidine(II,BMPHP-MPH), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one) *m*-toluidine-(III,BMPHP-MT), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5-one) *o*-phenylenediamine(IV,BMPHP-OPHDH$_2$), N-(4-benzoylidene-3-methyl-1-phenyl-2-pyrazolin-5-one) *m*-phenylenediamine(V,BMPHP-MPHDH$_2$), N-(4'-benzoylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one) *p*-phenylenediamine(VI,BMPHP-PPHDH$_2$) and N-(4'-benzoylidene-3'-methyl-1-phenyl-2'-pyrazolin-5'-one)benzidine (VII, BMPHP-BZH$_2$), have been prepared. The complexes, which have been characterized by analytical data, electrical conductances, magnetic measurements, electronic and infrared spectral studies have the compositions, [La(L)$_3$(LH)] (where LH = I, II or III), [La(L)(LH)] (where LH$_2$=IV, V, VI or VII). Suitable coordination modes of ligands in the complexes have been suggested.

Key Words : Coordination Compounds; Bioinorganics; Synthesis; Lanthanum (III) Chelates; Schiff Bases; Heterocyclic β-Diketone

Introduction

Lanthanide and actinide complexes with Schiff bases have been widely studied due to their manifestation of noval structural features and relevance to biological processes[1, 2]. Some aspects of the bioinorganic chemistry of the actinides and lanthanides have been recently reviewed by Bulman[3]. Pyrazolone derivatives are well known for their different biological activities[4] and as potential extractants for actinides and lanthanides[5]. Previous reports from our laboratory[6] described the preparation and characterization of monometallic complexes of dioxouranium (VI) with a series of multidentate Schiff bases derived from hetero- cyclic β-diketones of pyrazolone family. Owing to very little work done on coordination complexes with pyrazolone Schiff bases, in view of potential interest in the biologically important pyrazolone derivatives, and further the bioinorganic importance of lanthanide compounds, it was thought of interest to synthesize and characterize the lanthanum (III) chelates with the Schiff bases derived from a pyrazolone based heterocyclic β-diketone, viz., 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one(BMPHP) with *p*-

anisidine, *m*-phenetidine, *m*-toluidine, *o*-phenylenediamine, *m*- phenylenediamine, *p*-phenylenediamine or benzidine.

Materials and Method

Benzidine (B.D.H. Chemicals, Bombay), *p*-anisidine and *m*-phenetidine (Aldrich Chemical Co., U.S.A.), *m*-toluidine (Sarabhai M. Chemicals, Baroda) *o*-, *m*- and *p*-phenylenediamine (Fluka A.G. Switzerland) and 3-methyl-1-phenyl-2-pyrazolin-5-one (Johnsons Chemical Co., Bombay) were used as supplied. All other chemicals used were of analytical reagent grade.

Synthesis of BMPHP and its Schiff Bases

BMPHP was prepared by the interaction of 3-methyl-1-phenyl-2- pyrazolin-5-one in dioxane with calcium hydroxide and benzoyl chloride by the reported method[7]. The Schiff bases were prepared by refluxing stoichiometric amount of 4-benzoyl-3-methyl-1- phenyl-2-pyrazolin 5-one and the appropriate aromatic amine in ethanol by the method reported by Maurya *et al.*[8,9].

Synthesis of the Schiff Base Complexes

The complexes were prepared by the following general method. Lanthanum (III) nitrate hexahydrate (0.002 mol) was dissolved in 20 mL ethanol. The warm ethanolic solution of the respective Schiff base (0.008 mol in case of Schiff base I-III and 0.004 mol in case of Schiff bases IV-VII) was added into it. The resulting solution was then refluxed over a hot plate at 80°C for 5-7 hours, and then concentrated to a small volume. The solid product thus obtained was suction filtered and washed several times with ethanol. The product was dried *in vacuo* over anhydrous $CaCl_2$ to a constant weight. The analytical data are given in Table I.

Analyses

The carbon, hydrogen and nitrogen elements of the complexes were determined by microanalytical method on a Carbo Erba 1108 Heraeus elemental analyser at C.D.R.I., Lucknow. The lanthanum content of each of the complexes was determined gravimetrically by oxalate-oxide method[10].

Physical Methods

Infrared spectra (4000-600 cm^{-1}) of the ligands and complexes were recorded in KBr at 298K on FT-IR (Bio-Rad) at C.S. & M.C.R.I., Bhavnagar. The room temperature magnetic susceptibilities of the complexes were measured by vibrating sample magnetometer using PAR/VSM-155 at Regional Sophisticated Instrumen-

Table I

Analytical data and important IR spectral bands (cm^{-1}) of the synthesized complexes

Sl. No.	Complex (Empirical Formula)	Found/(Calc.) % C	H	N	La	ν(C=N) Azometh.	ν(C=N) Azometh.	ν(C-O) Ring	ν(C=O) Ring
1.	[(La(BMPHP-PA)$_3$ (BMPHP-PAH)] ($C_{96}H_{81}N_{12}O_8La$)	75.04 (69.06)	5.60 (4.85)	10.88 (10.07)	7.81 (8.33)	—	1571	1165	1629
2.	[(La(BMPHP-MP)$_3$ (BMPHP-MPH)] ($C_{100}H_{89}N_{12}O_8La$)	71.08 (69.60)	5.96 (5.16)	9.26 (9.74)	7.52 (8.06)	—	!570	1170	1631
3.	[(La(BMPHP-MT)$_3$ (BMPHP-MTH)] ($C_{96}H_{81}N_{12}O_1La$)	72.45 (71.82)	5.82 (5.05)	10.12 (10.47)	8.18 (8.66)	—	1575	1160	1628
4.	[(La(BMPHP-OPHD) (BMPHP-OPHDH)] ($C_{80}H_{61}N_{12}O_1La$)	70.39 (68.96)	5.18 (4.38)	12.68 (12.06)	9.42 (9.98)	—	1589	1170	1631
5.	[(La(BMPHP-MPHD) (BMPHP-MPHDH)] ($C_{80}H_{61}N_{12}O_1La$)	71.50 (68.96)	5.23 (4.38)	12.68 (12.06)	10.32 (9.98)	1647	!583	1172	1630
6.	[(La(BMPHP-PPHD) (BMPHP-PPHDH)] ($C_{80}H_{61}N_{12}O_1La$)	71.35 68.96	5.18 (4.38)	12.53 (12.06)	9.45 (9.98)	1645	1588	1174	1633
7.	[(La(BMPHP-BZ) (BMPHP-BZH)] ($C_{92}H_{69}N_{12}O_1La$)	74.40 (71.50)	5.38 (4.46)	11.69 (10.88)	9.38 (9.00)	1645	1590	1175	1634

tation Centre, I.I.T., Madras. Room Temperature molar conductivities in 10^{-3}M solutions in analytical grade dimethylformamide were measured using a Digisun Electronics Conductivity bridge. Electronic spectra of the complexes were recorded in 10^{-3} solution in dimethylformamide on a Shimadzu, model UV-160 spectrophotometer.

Results and Discussion

All the complexes are non-hygroscopic coloured solids (see Table II for colours). They are completely soluble in dimethylformamide but sparingly soluble in other common organic solvents.

Infrared Spectra

The Schiff base ligands, BMPHP-PAH, BMPHP-MPH and BMPHP-MTH exist

Table II

Some physical properties of synthesized complexes

Sl. No.	Complex	Colour	Decomp. Temp °C	Yield %	μeff (B.M.)	Λ_M ($ohm^{-1}cm^2mol^{-1}$) (in DMF)
1.	[(La(BMPHP-PA)$_3$ (BMPHP-PAH)]	Lemon yellow	145	60	D*	1
2.	[(La(BMPHP-MP)$_3$ (BMPHP-MPH)]	Cream yellow	140	60	D	1
3.	[(La(BMPHP-MT)$_3$ (BMPHP-MTH)]	Yellow	128	55	D	2
4.	[(La(BMPHP-OPHD) (BMPHP-OPHDH)]	Shiny Orange	205	65	D	1
5.	[(La(BMPHP-MPHD) (BMPHP-MPHDH)]	Yellow	190	60	D	2
6.	[(La(BMPHP-PPHD) (BMPHP-PPHDH)]	Creamish yellow	310	65	D	1
7.	[(La(BMPHP-BZ) (BMPHP-BZH)]	Yellow	295	65	D	1

D* = Diamagnetic

in enolic form[8]. These three ligands, therefore, contain two potential donor sites: (i) enolic oxygen and (ii) azomethine nitrogen. The ligands BMPHP-$OPHDH_2$ and BMPHP-$PPHDH_2$ also exist in enolic form[10]. They contain four potential donor sites : (i) the two enolic oxygens and (ii) the two azomethine nitrogens. The remaining two Schiff base ligands BMPHP-$MPHDH_2$(VI) and BMPHP- BZH_2-(VII) exist in ketonic form[9] and contain four potential donor sites : (i) the two ring carbonyl oxygens and (ii) the two azomethine nitrogens.

Complexes with Potentially Bidentate Schiff Base Ligands

The appearance of a sharp spectral bands at 1592, 1591 and 1581cm^{-1} in the uncoordinated BMPHP-PAH, BMPHP-MPH and BMPHP-MTH, respectively, is due to ν(C=N)of the azomethine group. Shifting of this mode towards lower wave numbers in the complexes (*see* Table I) is indicative of the coordination of the Schiff bases to the metal ion through the azomethine nitrogen[9]. ν(C-O) (enolic) peak observed at 1144, 1144, and 1137cm^{-1} in the uncoordinated BMPHP-PAH, BMPHP- MPH and BMPHP-MTH, respectively, is shifted to higher wave numbers at 1165, 1170 and 1160cm^{-1} in their respective complexes. This suggests the bonding of the enolic oxygen after deprotonation[9]. All the complexes exhibit a strong band at 1628- 1631cm^{-1} assignable to ν(C=O)owing to the coordination of atleast one cyclic carbonyl group in the keto form[11]. Thus the overall infrared results in recapitulation with the non-electrolytic nature of the complexes (vide infra) indicate that out of the four ligand molecules, three coordinate as uninegative bidentate (N,O-donor) and one as a neutral bidentate (N,O-donor).

Complexes with Potentially Tetradentate Ligands

The Schiff base BMPHP-$OPHDH_2$ displays a strong band due to azomethine group at 1615cm^{-1} which undergoes a low energy shift in its complex and appears

at 1589cm^{-1}. This indicates the coordination of both the azomethine nitrogens to lanthanum. In the ligands, V, VI, and VII, one of the azomethine nitrogens is unable to coordinate to the lanthanum in their respective complexes due to their *meta/para* position. This is shown by the presence of a ν(C=N) band at 1645-1647 cm^{-1} (as in the ligands) and the appearance of a new band at 1583-1590 cm^{-1} due to coordinated ν(C=N) in complexes, 5-7. The appearance of a medium band at 1172-1175cm^{-1} in all the complexes is attributed to ν(C-O)due to coordination of enolic oxygen after deprotonation. All the complexes display a strong band at 1630-1634cm^{-1} assignable to ν(C=O)due to the coordination of atleast one cyclic carbonyl group in the keto form. These observations along with non-electrolytic nature of these complexes (vide infra) conclude that out of the two ligand molecules in the complex 4, one molecule coordinates in binegative tetradentate (ONNO-donor) and other molecule as uninegative tetradentate fashion while in the complexes 5-7, one molecule of the ligand coordinates as a binegative tridentate and the other molecule in mononegative tridentate way.

Electronic Spectra

The electronic spectra of the ligands in acetone exhibit two bands at 327-347nm and 410nm, which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The absence of the band at 327-347nm and retention of the band at 410nm in the spectra of all the complexes indicate the coordination of the ligands to lanthanum(III). A shoulder band is observed at 419nm in the spectra of all the complexes, which may be due to ligand to metal charge transfer transitions[9]. An additional band in the region 430-444nm with relatively increased intensity in all the complexes is attributed to metal to ligand charge transfer transition[9].

Conductance Measurements

The observed molar conductances (^m = 1-2 ohm^{-1} cm^{2}mol^{-1}) of all the complexes in the 10^{-3}M DMF solutions suggest the non-electrolytic nature of these complexes[12].

Magnetic Measurements

The magnetic moments observed at room temperature show that all the complexes are diamagnetic, as expected for lanthanum(III) complexes.

The satisfactory analytical data all the above results suggest that the heterochelates may be formulated as [La(L)$_3$(LH)], where 2H = I, II or III and [La(L)(LH)], where LH_2 = IV, V, VI or VII. Thus it is reasonable to assign a coordination number eight for complexes 1, 2, 3 and 4, and coordination number six for the complexes, 5, 6 and 7.

Acknowledgement

The author is thankful to Professor D D Mishra, Head of the Department, for laboratory facilities and Professor J P Shukla, Vice-Chancellor of this University, for encouragement.

References

1 D E Fenton *Inorg Chim Acta* **95** (1984) 187
2 D E Fenton and R L Lintvedt *J Am Chem Soc* **100** (1978) 6367
3 R D Bulman *Coord chem Rev* **31** (1980) 221
4 R H Wiley and P Wiley Heterocyclic Compounds : Pyrazolones, Pyrazolidines and Derivatives Interscience New York (1964)
5 Yu A Zolotov and N M Kuzmin Metal Extraction with Acylpyrazolones Izdat Nauka-Moscow (1977)
6 R C Maurya, M Pandey and P Shukla *Synth react Inorg met - org Chem* **23** (1993) 161
7 B S Jensen *Acta Chem Scand* **13** (1959) 1347
8 R C Maurya, D D Mishra S Rao and N N Rao *Polyhedron* **11** (1992) 2837
9 R C Maurya, D D Mishra, S Rao and N N Rao *Polyhedron* **12** (1993) 2045
10 M N Jayaswal *Ph. D Thesis*, R D Univ. Jabalpur (1993)
11 A Syamal and K S Kale *Indian J Chem* **16** (1978) 46
12 W J Geary *Coord chem Rev* **1** (1971) 81