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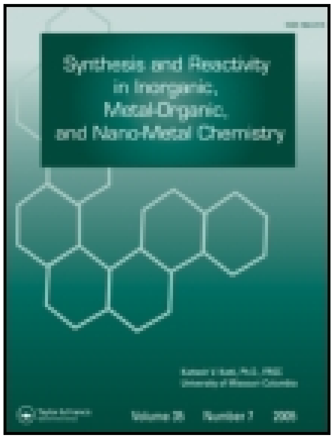

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SYNTHESIS AND CHARACTERIZATION OF SOME 3-PHENYL-4-ARYLAZO-5-PYRAZOLONES WITH La(III), Ce(III), Th(IV), AND UO_2(VI) COMPLEXES

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SYNTHESIS AND CHARACTERIZATION OF SOME 3-PHENYL-4-ARYLAZO-5-PYRAZOLONES WITH La(III), Ce(III), Th(IV), AND UO_2(VI) COMPLEXES

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ABSTRACT

La(III), Ce(III), Th(IV) and UO_2(VI) chelates with 3-phenyl-4-arylazo-5-pyrazolones have been synthesized and were characterized by several analytical tools such as elemental analyses, IR, NMR, TG and molar conductance techniques. The data obtained show that all of the prepared complexes contain water and/or alcohol molecules in their coordination sphere and the ligands form 1:1 and 1:2 complexes which are in good agreement with the proposed formulae. The NMR data of the prepared ligands show the existence of the ketonic structure rather than the enolic form. The TG data revealed no crystal water outside the coordination sphere. The azo-pyrazolone ligands act as neutral bidentate ligands bonded to the metal ions through the oxygen atom of the carbonyl group and the α nitrogen of the arylazo group. All solid chelates prepared behave as non-electrolytes in DMF solution.

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The coordination numbers of the prepared chelates are ranging from 6 to 12 for 1:1 and from 7 to 12 for 1:2 chelates.

INTRODUCTION

The importance of the pyrazolone azo dyes in industry as well as their analytical applications and excellent ability to act as ligands attracted the attention of coordination chemists to study their reactions with transition metal ions[1,2]. Pyrazolones and pyrazol derivatives such as 5-pyrazolones are formed by the reaction between hydrazines and β-ketonic esters *e.g.*, 3-methyl-1-phenyl pyrazolone was prepared from phenylhydrazine and ethyl acetoacetate. This, on methylation gives antipyrine which is used in medicine as an antipyretic[3]. Pyrazolin-5-ones have attracted much attention as ligands for a large number of metal ions[4–6]. The metal chelates produced are well known for their analytical and biological uses. The azo derivatives of 5-pyrazolones, as well as their metal complexes, have wide applications in the dye industry and as analytical reagents for the micro determination of metals[7]. Various methods were reported for the synthesis of 4-arylazo-5-pyrazolone[8]. Dissociation constants of some azo pyrazolin-5-one derivatives were obtained and the stability constants of their chelates with Th(IV), Zr(IV), Ce(III), Y(III), La(III) and UO_2(VI) were determined potentiometrically[9]. The order of stabilities were: Zr(IV) $>$ Th(IV) $>$ UO_2(VI) $>$ Y(III) $>$ Ce(III) $>$ La(III). The reaction of La(III), Ce(III), Th(IV) and UO_2(VI) ions with some heterocyclic azo pyrazolones was studied spectrophotometrically and by IR spectra[10]. All solid chelates prepared behave as non-electrolytes in DMF solution. Metal chelates of pyridine azopyrazolin-5-one derivatives with Zr(IV), La(III), Y(III) and UO_2(VI) have been prepared and characterized by electronic, IR, ^{1}H NMR spectra and thermogravimetric analyses[1]. The results revealed the possibility of both 1:1 and 1:2 metal ion to ligand adducts. Trivalent rare earth β-diketonate antipyrine coordination compounds were synthesized[11]. Their properties were studied by conductimetry, thermal, IR, UV and ^{1}H NMR spectra. Pd(II) complexes with some 1-phenyl-5-pyrazolone derivatives were prepared[12]. The complexes were characterized by IR spectra and magnetic susceptibility measurements. The structure of the ligands is shown in Fig. 1.

EXPERIMENTAL

All chemicals used were of the highest purity available from BDH. These included $La(NO_3)_3.6H_2O$, $Ce(NO_3)_3.6H_2O$, $Th(NO_3)_4.6H_2O$ and

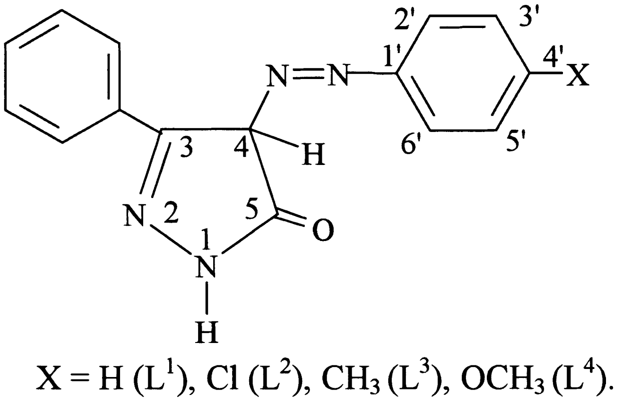

Figure 1. Structure of 3-phenyl-4-arylazo-5-pyrazolone derivatives.

$UO_2(NO_3)_2.6H_2O$. The solvents used were ethanol and deuterated dimethyl sulfoxide (DMSO).

Preparation of 3-Phenyl-5-pyrazolone

A mixture of ethyl benzoylacetate (9.6 g, 49.94 mmole) and hydrazine hydrate (1.6 g, 31.96 mmole) was heated at 120 °C (oil-bath, temp. 120–130 °C) for 1 h. The resulting oil was cooled and stirred with diethyl ether (50 mL) until solidification occurred and the crude product was then filtered off. The final product was crystallized from 50% ethanol water and collected as white powder of 3-phenyl-5-pyrazolone[13]; yield 6.8 g (85%); m.p. 250 °C.

Preparation of 3-Phenyl-4-arylazo-5-pyrazolone Derivatives

A well-stirred solution of aniline, 4-chloroaniline, *p*-toluidine or *p*-anisidine 0.01 mole in 40 mL ethanol and 20 mL 2 M HCl was cooled in an ice salt bath and diazotized with an aqueous sodium nitrite solution (20 mL, 0.01 mole). The cooled (0–5 °C) diazonium solution was added slowly to a well-stirred solution of 3-phenyl-5-pyrazolone (1.6 g, 0.01 mole) in ethanol (100 mL) containing sodium hydroxide (10 g). The reaction mixture was stirred for 1 h at room temperature, then acidified with diluted HCl (100 mL, 2.5 M) to neutralize the reaction mixture and precipitate the azopyrazolone derivatives. The products were recrystallized from ethanol to give the 3-phenyl-4-arylazo-5-pyrazolone derivatives as reddish orange crystals[14].

Preparation of the Complexes

The 1:1 or 1:2 chelates were prepared by mixing hot alcoholic solutions (100 mL) of the ligands (2 or 4 mmole) with the calculated amount of metal salt (2 mmole) in 100 mL ethanol. The pH of the solution was maintained at 5.0–6.0 by addition of 1:10 dilute ammonia solution. The reaction mixture was then refluxed for 4 h on a water bath and evaporated on a steam bath, with occasional stirring. The solid product was washed several times with ethanol till a colorless filtrate was obtained. The solid was dried *in vacuo* and finally kept in a vacuum desiccator.

Measurements

The IR spectra were recorded on a Shimadzu FTIR 8201 PC spectrophotometer in KBr discs. The NMR spectra were measured using a Varian-Mercury 300 MHz spectrometer. The solvent used was deutrated dimethyl sulfoxide (DMSO) and the spectra were recorded from 0–15 ppm using TMS as internal standard. Thermal analyses (TG) were obtained using a type TGA 50 Shimadzu Derivatograph. The molar conductivities were carried out using a Jenway 4310 conductivity meter. Mass spectra were obtained using a Shimadzu QP-5000 mass spectrometer coupled with a Shimadzu GC-17A gas chromatograph.

RESULTS AND DISCUSSION

The elemental analyses of the ligands are given in Table I and were confirmed by ^{1}H NMR, IR and mass spectra. The results of the elemental analyses of the chelates derived from 3-phenyl-4-arylazo-5-pyrazolone derivatives are recorded in Table II. The data obtained show that the ligands form 1:1 and 1:2 complexes and are in good agreement with the proposed formulae.

Infrared Spectra

The infrared spectra of the investigated ligands show the presence of a band at 3197–3186 cm^{-1} corresponding to ν(NH). The strong

Table I. Analytical Data of Azopyrazolone Derivatives

Cpd.	Empirical Formula	Formula Weight	% Yield	Color[a]	M.p., °C	%C (Calcd.) Found	%H (Calcd.) Found	%N (Calcd.) Found	%Cl (Calcd.) Found
L[1]	$C_{15}H_{12}N_4O$	264	70	o.	211	(68.2)	(4.6)	(21.2)	–
						68.7	4.5	21.9	
L[2]	$C_{15}H_{11}N_4OCl$	298	80	o.	243	(60.3)	(3.7)	(18.7)	(11.9)
						60.4	3.4	18.8	11.8
L[3]	$C_{16}H_{14}N_4O$	278	75	o.	229	(69.1)	(5.1)	(20.3)	–
						69.8	5.4	20.7	
L[4]	$C_{16}H_{14}N_4O_2$	294	70	r.	197	(65.3)	(4.8)	(19.0)	–
						65.8	4.7	18.9	

[a] o.: orange, r.: red

Table II. Analytical Data of La(III), Ce(III), Th(IV), and UO_2(VI) Azopyrazolone Complexes

Complex	Empirical Formula	M:L	F.W.	% Yield	Color^a	C% (Cald.) Found	H% (Cald.) Found	N% (Cald.) Found	Cl% (Cald.) Found	M% (Cald.) Found
$[La(L^1)(NO_3)(OH)_2(EtOH)_2]$	$C_{19}H_{26}LaN_5O_8$	1:1	591	65	p.o.	(38.58) 38.8	(4.06) 4.0	(11.84) 11.8	–	(23.50) 23.7
$[La(L^1)_2(NO_3)_2(OH)(H_2O)_2]$	$C_{30}H_{29}LaN_{10}O_{11}$	1:2	844	70	o.	(42.65) 42.9	(3.44) 3.5	(16.59) 16.3	–	(16.46) 16.5
$[Ce(L^1)(NO_3)(OH)_2(H_2O)(EtOH)]$	$C_{17}H_{22}CeN_5O_8$	1:1	564	70	o.	(36.17) 36.2	(3.9) 3.7	(12.41) 12.5	–	(24.82) 24.9
$[Ce(L^1)_2(NO_3)_2(OH)(EtOH)_3]$	$C_{36}H_{43}CeN_{10}O_{12}$	1:2	947	80	p.o.	(45.62) 45.9	(4.54) 4.5	(14.78) 14.7	–	(14.78) 14.6
$[Th(L^1)(NO_3)_4(EtOH)_2]$	$C_{19}H_{24}ThN_8O_{15}$	1:1	836	65	o.	(27.27) 27.1	(2.87) 2.7	(13.39) 13.2	–	(27.75) 28.0
$[Th(L^1)_2(NO_3)_4(H_2O)(EtOH)_2]$	$C_{34}H_{38}ThN_{12}O_{17}$	1:2	1118	70	p.o.	(36.49) 36.6	(3.39) 3.4	(15.03) 15.0	–	(20.75) 20.1
$[UO_2(L^1)(OH)_2(H_2O)_4(EtOH)]$	$C_{17}H_{28}UN_4O_{10}$	1:1	686	80	y.o.	(29.74) 29.4	(4.08) 4.0	(8.61) 8.3	–	(34.69) 34.8
$[UO_2(L^1)_2(OH)_2(H_2O)_4(EtOH)_2]$	$C_{34}H_{46}UN_8O_{12}$	1:2	996	65	y.o.	(34.17) 34.4	(4.62) 4.6	(11.24) 11.2	–	(23.89) 23.7
$[La(L^2)(NO_3)_2(OH)(H_2O)_2(EtOH)_3]$	$C_{21}H_{35}LaN_6O_{13}Cl$	1:1	752	85	o.	(3.51) 33.2	(4.38) 4.2	(11.17) 11.2	(4.65) 4.8	(24.82) 24.6
$[La(L^2)_2(NO_3)(OH)_2(H_2O)_2]$	$C_{30}H_{30}LaN_5O_9Cl$	1:2	867	70	o.	(41.52) 41.5	(3.22) 3.5	(14.53) 14.4	(8.07) 8.1	(14.78) 14.9
$[Ce(L^2)(NO_3)(OH)_2(H_2O)_2(EtOH)]$	$C_{17}H_{24}CeN_5O_9Cl$	1:1	616	80	o.	(33.11) 33.3	(3.9) 3.7	(11.36) 11.5	(5.76) 5.6	(22.27) 22.4
$[Ce(L^2)_2(NO_3)(OH)_2(H_2O)_2(EtOH)_2]$	$C_{34}H_{43}CeN_9O_{11}Cl$	1:2	960	65	o.	(45.0) 45.3	(4.17) 4.0	(13.12) 13.3	(3.69) 3.7	(14.58) 14.3

$[Th(L^2)(NO_3)_4(H_2O)_2(EtOH)_4]$	$C_{23}H_{40}ThN_8O_{19}Cl$	1:1	998	70	o.	(27.66) 27.6	(3.91) 3.8	(11.22) 11.3	(3.55) 3.4	(23.24) 23.4
$[Th(L^2)_2(NO_3)_2(OH)_2(EtOH)_4]$	$C_{38}H_{50}ThN_{10}O_{14}Cl$	1:2	1170	85	o.	(38.97) 38.9	(4.10) 4.2	(11.97) 12.0	(3.03) 3.1	(19.83) 19.6
$[UO_2(L^2)(OH)_2(H_2O)_2]$	$C_{15}H_{17}UN_4O_7Cl$	1:1	638	80	y.o.	(28.21) 27.9	(2.57) 2.4	(8.77) 8.9	(6.56) 6.4	(37.3) 36.8
$[UO_2(L^2)_2(OH)_2(H_2O)]$	$C_{30}H_{26}UO_7Cl$	1:2	918	70	y.o.	(39.22) 39.0	(2.83) 2.8	(12.2) 12.3	(3.86) 3.7	(29.92) 29.8
$[La(L^3)(NO_3)_3(H_2O)_2(EtOH)_2]$	$C_{20}H_{30}LaN_7O_{14}$	1:1	731	65	o.	(32.83) 32.4	(4.01) 4.0	(13.4) 13.1	–	(19.0) 18.8
$[La(L^3)_2(NO_3)(OH)_2]$	$C_{32}H_{30}LaN_9O_7$	1:2	791	80	o.	(48.55) 48.4	(3.79) 3.9	(15.93) 15.9	–	(17.56) 17.8
$[Ce(L^3)(NO_3)(OH)_2(EtOH)]$	$C_{18}H_{22}CeN_5O_7$	1:1	560	85	o.	(38.57) 38.4	(3.92) 4.0	(12.5) 12.3	–	(25.0) 24.9
$[Ce(L^3)_2(NO_3)_2(OH)(H_2O)_4]$	$C_{32}H_{37}CeN_{10}O_{13}$	1:2	909	70	o.	(42.24) 42.3	(4.04) 3.9	(15.4) 15.7	–	(15.4) 15.6
$[Th(L^3)(OH)_4(H_2O)_6]$	$C_{16}H_{30}ThN_4O_{11}$	1:1	686	65	o.	(27.99) 27.9	(4.37) 4.4	(8.16) 8.1	–	(33.82) 33.6
$[Th(L^3)_2(OH)_4(H_2O)_4]$	$C_{32}H_{40}ThN_8O_{10}$	1:2	928	65	o.	(41.37) 41.2	(4.31) 4.3	(12.06) 11.8	–	(24.52) 24.7
$[UO_2(L^3)(NO_3)_2(H_2O)_8]$	$C_{16}H_{30}UN_6O_{17}$	1:1	816	80	y.o.	(22.31) 22.3	(3.8) 3.6	(14.1) 14.1	–	(29.16) 29.3
$[UO_2(L^3)_2(NO_3)_2(H_2O)_4]$	$C_{32}H_{36}UN_{10}O_{12}$	1:2	1022	70	y.o.	(37.6) 37.6	(3.52) 3.4	(13.69) 13.4	–	(23.28) 23.1
$[La(L^4)(NO_3)_3(H_2O)_2(EtOH)]$	$C_{18}H_{24}LaN_7O_{14}$	1:1	701	85	o.	(30.81) 30.5	(3.42) 3.2	(13.98) 14.0	–	(19.81) 19.9
$[La(L^4)_2(NO_3)_2(OH)(H_2O)(EtOH)]$	$C_{34}H_{37}LaN_{10}O_{13}$	1:2	932	80	o.	(43.77) 43.8	(3.97) 4.0	(15.02) 15.2	–	(14.90) 14.7

(*continued*)

Table II. Continued

Complex	Empirical Formula	M:L	F.W.	% Yield	Color[a]	C% (Cald.) Found	H% (Cald.) Found	N% (Cald.) Found	Cl% (Cald.) Found	M% (Cald.) Found
$[Ce(L^4)(NO_3)(OH)_2(H_2O)(EtOH)]$	$C_{18}H_{24}CeN_5O_9$	1:1	594	75	o.	(36.36) 36.4	(4.04) 3.9	(11.78) 11.8	–	(23.56) 23.7
$[Ce(L^4)_2(NO_3)(OH)_2(H_2O)_2]$	$C_{32}H_{34}CeN_9O_{11}$	1:2	860	70	o.	(44.65) 44.5	(3.95) 3.9	(14.65) 14.7	–	(16.27) 16.4
$[Th(L^4)(NO_3)_2(OH)_2(EtOH)_4]$	$C_{24}H_{40}ThN_6O_{14}$	1:1	868	65	o.	(33.17) 33.0	(4.61) 4.5	(9.68) 9.8	–	(26.72) 26.5
$[Th(L^4)_2(OH)_4(EtOH)_3]$	$C_{38}H_{40}ThN_8O_{11}$	1:2	1026	80	o.	(44.44) 44.4	(4.87) 4.8	(10.91) 10.8	–	(22.61) 22.7
$[UO_2(L^4)(OH)_2(H_2O)_3(EtOH)]$	$C_{18}H_{28}UN_4O_{10}$	1:1	698	75	y.o.	(30.94) 30.9	(4.01) 4.1	(8.02) 8.0	–	(34.09) 34.0
$[UO_2(L^4)_2(OH)_2(H_2O)_3(EtOH)]$	$C_{34}H_{28}UN_8O_{12}$	1:2	992	70	y.o.	(41.13) 41.3	(4.23) 4.2	(11.29) 11.6	–	(23.99) 24.1

[a] o.: orange, y.o.: yellow orange, p.o.: pale orange

bands appearing at the range 1660–1650 cm^{-1} are assigned to ν(C=O). The ν(N=N) bands are observed in the range 1496–1488 cm^{-1} and are conjugated with the aromatic ring skeletal vibrations[15] [ν(C=C)] at 1604–1600 cm^{-1}.

The infrared spectra of the solid chelates display interesting changes that may give a reasonable idea about the structure of these chelates. The main IR bands of the solid chelates are given in Table III. A comparison of the IR spectra of the ligands with those of their metal chelates indicates that changes are occurring as a result of the involvement of the ligands with various coordination sites with the metal ions. The absence of the C=O group indicates that it is a center of chelation as it loses its double bond character (-C-O-M). The OH stretching frequency appears in the spectra of all the complexes as a broad band within the range 3201–3570 cm^{-1} and is due to the presence of water/or alcohol and OH^- which neutralizes the charge on the metal ion. Most of the La(III), Ce(III), Th(IV) and UO_2(VI) complexes were characterized by four bands which may be assigned to the nitrato ion C_{2v} symmetry[16]: 1515–1552 (ν_1), 1259–1315 (ν_4), 1004–1051 (ν_2) and 800–831 (ν_6) cm^{-1}. The spectra of the metal chelates exhibit mainly bands in the ranges 520–590 and 430–497 cm^{-1} which may be assigned to ν(M-N) and ν(M-O) stretching frequencies, respectively. These bands are possibly due to the formation of coordinate bonds between the donor atoms (O and N) and the central metal ion[17].

Nuclear Magnetic Resonance

Further support for the results obtained from the IR spectra is gained by considering the changes in the NMR spectra of the investigated chelates (Table IV). The ^{1}H NMR spectra of the investigated ligands exhibit a singlet at 2.51–2.52 ppm which were assigned to the aliphatic proton H^4. The signals observed at 8.1–7.4 ppm are assigned to the aromatic protons. The integration curves show 9 protons for each ligand except for the ligand L^1 which exhibits 10 protons. For the ligand L^3 a singlet observed at 2.33 ppm is assigned to the CH_3 protons (the integration curve shows 3 protons). Also for the ligand L^4 a singlet observed at 3.81 ppm is assigned to the OCH_3 protons. For all of the investigated ligands a singlet observed at 12.06–12.15 ppm is assigned to the NH proton. The keto structure of the free ligands was confirmed by ^{1}H NMR data which revealed that there is no signal for the OH proton. Also this is confirmed by the absence of a singlet at 12.16–12.15 ppm upon investigating the ^{1}H NMR spectrum of 1,3-diphenyl-4-phenylazo-5-pyrazolone in which the signal at 12.14 ppm was not observed. For the La chelates with the ligands L^1, L^2, L^3 and L^4 (1:1 and

Table III. IR Spectral Data of La(III), Ce(III), Th(IV), and UO_2(VI) Azopyrazolone Complexes

Complex	M:L	ν(OH)	ν(C=C)	ν(N=N)	ν(C-O)	ν(M-N)	ν(M-O)
$[La(L^1)(NO_3)(OH)_2(EtOH)_2]$	1:1	3548 s	1604 s, 1552 s	1494 s	1249 m	590 m	440 m
$[La(L^1)_2(NO_3)_2(OH)(H_2O)_2]$	1:2	3546 m	1595 s, 1552 m	1494 s	1247 m	590 m	430 m
$[Ce(L^1)(NO_3)(OH)_2(H_2O)(EtOH)]$	1:1	3520 m	1596 s, 1550 m	1485 m	1245 s	586 w	466 w
$[Ce(L^1)_2(NO_3)_2(OH)(EtOH)_3]$	1:2	3518 s	1596 s, 1550 m	1485 s	1245 s	586 w	466 w
$[Th(L^1)(NO_3)_4(EtOH)_2]$	1:1	3375 s	1595 s, 1552 m	1477 s	1247 s	586 m	491 m
$[Th(L^1)_2(NO_3)_4(H_2O)(EtOH)_2]$	1:2	3375 m	1595 s, 1552 m	1479 s	1247 m	590 m	474 m
$[UO_2(L^1)(OH)_2(H_2O)_4(EtOH)]$	1:1	3565 s	1595 m, 1552 m	1492 m	1253 m	530 m	457 m
$[UO_2(L^1)_2(OH)_2(H_2O)_4(EtOH)_2]$	1:2	3570 s	1595 s, 1552 s	1492 m	1247 m	590 m	447 w
$[La(L^2)(NO_3)_2(OH)(H_2O)_2(EtOH)_3]$	1:1	3543 s	1591 m, 1546 s	1491 m	1240 m	520 m	491 w
$[La(L^2)_2(NO_3)(OH)_2(H_2O)_2]$	1:2	3544 s	1591 m, 1546 m	1489 m	1240 s	520 w	491 m
$[Ce(L^2)(NO_3)(OH)_2(H_2O)_2(EtOH)]$	1:1	3342 m	1591 s, 1542 m	1489 s	1240 s	520 w	451 m
$[Ce(L^2)_2(NO_3)(OH)_2(H_2O)_2(EtOH)_2]$	1:2	3340 m	1591 s, 1542 s	1489 s	1240 s	520 m	451 m
$[Th(L^2)(NO_3)_4(H_2O)_2(EtOH)_4]$	1:1	3463 m	1589 s, 1546 s	1485 m	1240 m	530 m	461 w
$[Th(L^2)_2(NO_3)_2(OH)_2(EtOH)_4]$	1:2	3464 s	1589 s, 1546 s	1489 s	1240 m	530 m	461 w
$[UO_2(L^2)(OH)_2(H_2O)_2]$	1:1	3224 s	1589 s, 1545 m	1490 m	1238 m	520 w	462 w

$[UO_2(L^2)_2(OH)_2(H_2O)]$	1:2	3227 s	1591 m, 1547 m	1491 m	1240 s	520 w	461 m
$[La(L^3)(NO_3)_3(H_2O)_2(EtOH)_2]$	1:1	3548 m	1595 m, 1548 m	1496 m	1247 s	560 w	491 m
$[La(L^3)_2(NO_3)(OH)_2]$	1:2	3555 s	1595 m, 1546 m	1496 s	1244 s	560 m	491 m
$[Ce(L^3)(NO_3)(OH)_2EtOH]$	1:1	3549 m	1591 s, 1548 s	1494 s	1245 s	536 m	491 m
$[Ce(L^3)_2(NO_3)_2(OH)(H_2O)_4]$	1:2	3520 m	1591 s, 1546 m	1496 s	1244 m	536 w	595 w
$[Th(L^3)(OH)_4(H_2O)_6]$	1:1	3541 s	1591 m, 1548 m	1494 m	1245 m	536 w	497 w
$[Th(L^3)_2(OH)_4(H_2O)_4]$	1:2	3541 s	1591 m, 1548 s	1496 s	1245 s	536 m	491 m
$[UO_2(L^3)(NO_3)_2(H_2O)_8]$	1:1	3228 m	1591 m, 1546 m	1494 m	1244 s	536 w	461 w
$[UO_2(L^3)_2(NO_3)_2(H_2O)_4]$	1:2	3201 s	1591 s, 1546 m	1496 s	1244 s	536 m	461 m
$[La(L^4)(NO_3)_3(H_2O)_2(EtOH)]$	1:1	3548 m	1585 s, 1544 s	1494 m	1242 m	549 w	440 m
$[La(L^4)_2(NO_3)_2(OH)(H_2O)(EtOH)]$	1:2	3400 m	1585 m, 1546 s	1494 m	1242 s	540 m	450 w
$[Ce(L^4)(NO_3)(OH)_2(H_2O)(EtOH)]$	1:1	3396 m	1604 m, 1546 s	1496 m	1240 m	545 m	445 m
$[Ce(L^4)_2(NO_3)(OH)_2(H_2O)_2]$	1:2	3398 s	1602 s, 1544 m	1492 s	1242 m	547 m	441 m
$[Th(L^4)(NO_3)_2(OH)_2(EtOH)_4]$	1:1	3460 s	1602 s, 1546 m	1494 s	1240 s	547 w	441 w
$[Th(L^4)_2(OH)_4(EtOH)_3]$	1:2	3400 s	1602 m, 1546 m	1494 s	1240 s	547 w	441 w
$[UO_2(L^4)(OH)_2(H_2O)_3(EtOH)]$	1:1	3226 m	1604 s, 1544 s	1494 m	1242 s	549 m	461 m
$[UO_2(L^4)_2(OH)_2(H_2O)_3(EtOH)]$	1:2	3232 s	1604 s, 1544 s	1492 s	1242 m	549 m	462 m

s: strong, m: medium, w: weak

Table IV. Proton NMR Spectral Data of the Azopyrazolone Ligands and Their La(III) Complexes

Ligands and Complexes	M:L	Chemical Shift	Assignment
L^1		12.14 s	H^1 (NH)
		8.1–7.2 m	Aromatic C-H
		2.51 s	H^4 (aliphatic)
$[La(L^1)(NO_3)(OH)_2(EtOH)_2]$	1:1	12.14 s	H^1 (NH)
		8.1–7.2 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
$[La(L^1)_2(NO_3)_2(OH)(H_2O)_2]$	1:2	12.14 s	H^1 (NH)
		8.1–7.2 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
L^2		12.15 s	H^1(NH)
		8.1–7.4 m	Aromatic C-H
		2.51 s	H^4(aliphatic)
$[La(L^2)(NO_3)_2(OH)(H_2O)_2(EtOH)_3]$	1:1	12.14 s	H^1 (NH)
		8.09–7.5 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
$[La(L^2)_2(NO_3)(OH)_2(H_2O)_2]$	1:2	12.14 s	H^1 (NH)
		8.09–7.5 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
L^3		12.07 s	H^1(NH)
		8.1–7.2 m	Aromatic C-H
		2.52 s	H^4(aliphatic)
		2.33 s	CH_3 protons
$[La(L^3)(NO_3)_3(H_2O)_2(EtOH)_2]$	1:1	12.11 s	H^1 (NH)
		8.1–7.2 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
		2.34 s	CH_3 protons
$[La(L^3)_2(NO_3)(OH)_2]$	1:2	8.1–7.2 m	Aromatic C-H
		3.35 s	H_2O of coordination
		2.52 s	H^4 (aliphatic)
		2.34 s	CH_3 protons
L^4		12.06 s	H^1 (NH)
		8.1–7.0 m	Aromatic C-H
		2.51 s	H^4 (aliphatic)
		3.81 s	OCH_3 protons

Table IV. Continued

Ligands and Complexes	M:L	Chemical Shift	Assignment
[La(L^4) $(NO_3)_3(H_2O)_2$(EtOH)]	1:1	12.06 s	H^1 (NH)
		8.1—7.06 m	Aromatic C-H
		3.8 s	OCH_3 protons
		3.35 s	H_2O of coordination
		2.51 s	H^4 (aliphatic)
[La$(L^4)_2(NO_3)_2$(OH)(H_2O)(EtOH)]	1:2	12.06 s	H^1 (NH)
		8.1—7.05 m	Aromatic C-H
		3.8 s	OCH_3 protons
		3.35 s	H_2O of coordination
		2.51 s	H^4 (aliphatic)

1:2), coordinated water molecules were observed in the region at 3.35 ppm. These signals obviously were not seen in the spectra of the free ligands. The aromatic protons were observed at 8.1—7.05 ppm. The aliphatic H^4 proton was observed at 2.52—2.51 ppm for the 1:1 and 1:2 chelates, respectively. For the La-L^3 (1:1 and 1:2) chelates, the singlet observed at 2.34 ppm corresponds to the aliphatic CH_3 protons. For the La-L^4 (1:1 and 1:2) chelates, a singlet observed at 3.8 ppm was assigned to the OCH_3 protons. For all of the investigated chelates a singlet observed at 12.14—12.06 ppm was assigned to the NH proton which means that NH at position 1 is not involved in chelation and the investigated ligands act as neutral bidentate ligands[7].

The data obtained from the ^1H NMR spectra confirm the results obtained from the IR spectra. The difference between the 1:1 and 1:2 chelates is that the integration curves show twice as many aromatic protons in case of the 1:2 chelates. In addition, for the La-L^3 1:2 and for the La-L^4 1:2 chelates the integration curves show twice as many methyl protons, corresponding to two methyl groups or two methoxy groups.

Mass Spectra

Mass spectra are a powerful tool in elucidating and confirming the structure of chemical compounds. It is known from the standard concepts of physical organic chemistry that cyclic structures, double bonds, aromatic and specially heteroaromatic rings, stabilize the parent ion and thus increase the probability of its appearance in the mass spectra. The mass spectral pattern of the ligand L^1 shows a main peak of 264 (calcd. M. Wt. = 264).

The fragmentation pattern of this ligand can be regarded as a general scheme showing the main fragmentation paths involved. The differences in the other ligands (L^2, L^3 and L^4) results from the effects of the electronegativities of the substituent attached to the aromatic ring. For the ligand L^2, the main peak is observed at 298 (calcd. M. Wt. = 298). As it is known from the concepts of mass spectral analysis, a compound that contains one chlorine atom will have a p+2 peak approximately one-third the intensity of the parent peak because of the presence of molecular ions containing the ^{37}Cl isotope (relative abundance 34.8%). From the mass spectral presentation of the ligand L^2, it is apparent that there is one chlorine atom in the molecule, the intensity of the M+2 peak (m/z 300, 34.8%) is almost one-third the intensity of the parent peak (m/z 298, 100%). For the ligand L^3, the main peak is observed at 278 (calcd. M. Wt. = 278). For the ligand L^4, the main peak is observed at 294 (calcd. M. Wt. = 294). From the data obtained we concluded that the molecular weights are in good agreement with the calculated one.

Thermogravimetric Analyses (TG)

TG analyses of the La(III) complexes with the investigated ligands (1:1) (Table V) were performed. The weight loss being measured from ambient temperature up to 800 °C at a rate of 10 °C min^{-1}. The weight loss for each chelate, obtained from the thermographs was used to calculate the number of coordinated water and/or alcohol molecules present, since no hygroscopic water or moisture was observed up to the 135–192 °C range. For the $[La(L^1)(NO_3)(OH)_2(EtOH)_2]$ (1:1) chelate, two alcohol molecules are coordinated to the metal ion; these are expelled within the temperature range 192–293 °C corresponding to a loss of 15.64% (calcd. 15.56%). In the temperature range 295–438 °C a weight loss of 22.86% (calcd. 22.44%) is observed corresponding to the formation of an intermediate species through the decomposition and combustion of the organic part with the loss of a phenyl group and two hydroxy groups used for neutralization. Above this temperature another loss occurred within the temperature range 438–597 °C which corresponds to a loss of 12.54% (calcd. 13.43%) corresponding to two carbon and two nitrogen atoms followed by another loss at 598–749 °C corresponding to 4.52% (calcd. 4.77%) for an oxygen atom. At the end of the thermogram the metal contents were calculated from the residual weight of 23.33% (calcd. 23.52%), which is in good agreement with the calculated values obtained by determination of the metal content after decomposition of the chelate applying the method described by Macdonald[18] and with the result of elemental analysis (Table II).

Table V. Thermogravimetric Analysis of the La(III) Azopyrazolone (1:1) Complexes

Complex	M. Wt.	Temp. °C	Calcd. loss %	Found Loss %	Assignment
$[La(C_{15}H_{12}N_4O)(NO_3)(OH)_2(EtOH)_2]$	591	192–293	15.56	15.64	2EtOH
$[La(C_{15}H_{12}N_4O)(OH)_2(NO_3)]^+$	499	295–438	22.44	22.86	C_6H_6, 2OH
$[La(C_9H_9N_4O)(NO_3)]^+$	387	438–597	13.43	12.54	2C, 2N
$[La(C_7H_9N_2O)(NO_3)]^+$	335	598–749	4.77	4.52	O atom
		751–800	23.52	23.33	La_2O_3
$[La(C_{15}H_{11}N_4OCl)(NO_3)_2(OH)(H_2O)_2(EtOH)_3]$	752	146–316	20.74	19.88	3EtOH, H_2O
$[La(C_{15}H_{11}N_4OCl)(NO_3)_2(OH)(H_2O)]^+$	596	318–471	18.46	19.71	$2NO_3$, H_2O
$[La(C_{15}H_{11}N_4OCl)(OH)]^+$	486	473–607	16.05	15.97	C_6H_6
$[La(C_9H_5N_4OCl)(OH)]^+$	408	609–802	17.40	17.65	Cl, 3C
		802–1000	23.52	23.48	La_2O_3
$[La(C_{16}H_{14}N_4O)(NO_3)_3(H_2O)_2(EtOH)_2]$	731	161–331	40.49	40.57	2EtOH, $3NO_3$, H_2O
$[La(C_{16}H_{14}N_4O)(H_2O)]^+$	435	331–437	10.57	10.19	H_2O, CO
$[La(C_{15}H_{14}N_4)]^+$	389	440–626	30.84	30.51	$-N{=}N-C_6H_4-CH_3$
		626–800	19.01	18.40	La_2O_3
$[La(C_{16}H_{14}N_4O_2)(NO_3)_3(H_2O)_2(EtOH)]$	701	135–289	15.40	14.64	EtOH, NO_3
$[La(C_{16}H_{14}N_4O_2)(NO_3)_2(H_2O)_2]^+$	593	289–398	12.14	12.71	$2H_2O$, 3C
$[La(C_{13}H_{14}N_4O_2)(NO_3)_2]^+$	521	413–661	40.69	40.73	C_6H_6, $-N{=}N-C_6H_4-OCH_3$
		661–800	19.82	19.93	La_2O_3

For the $[La(L^2)(NO_3)_2(OH)(H_2O)_2(EtOH)_3]$ (1:1) chelate, a weight loss occurred within the temperature range 146–316 °C corresponding to the loss of 19.88% (calcd. 20.74%) for three coordinated alcohol molecules and one water molecule. In the temperature range 318–471 °C a loss of 19.71% (calcd. 18.46) that corresponds to one water molecule and two nitrato groups is observed. At the higher temperature range 473–607 °C a loss of 15.97% (calcd. 16.05%) corresponds to the elimination of the phenyl group. After this temperature another loss occurred within the temperature range 609–802 °C corresponding to 17.65% (calcd. 17.40) due to the loss of chlorine and three carbon atoms which were oxidized by the atmospheric oxygen to CO_2. After this temperature a metal oxide residue was obtained from which the metal content was calculated as 18.08% (calcd. 18.48%).

For the $[La(L^3)(NO_3)_3(H_2O)_2(EtOH)_2]$ (1:1) chelate, a loss of 40.57% (calcd. 40.49%) occurs corresponding to the loss of two coordinated ethanol molecules, one water molecule and three nitrato groups which are expelled within the temperature range 161–331 °C. By raising the temperature another loss occurred within the temperature range 331–437 °C corresponding to 10.19% (calcd. 10.57%) due to the loss of one coordinated water and a carbonyl group. In the temperature range 440–626 °C decomposition and combustion of the organic ligand starts followed by the loss of 30.51% (calcd. 30.84%) which corresponds to the loss of $\text{-N=N-}C_6H_4\text{-}CH_3$. At the final stage metal oxide as residue is obtained from which the metal content is calculated to 19.00% (calcd. 19.01%).

For the $[La(L^4)(NO_3)_3(H_2O)_2(EtOH)]$ (1:1) chelate, a weight loss occurred within the temperature range 135–298 °C corresponding to the loss of 14.64% (calcd. 15.40) for one coordinated ethanol and one nitrato group. In the temperature range 289–398 °C a loss of 12.71% (calcd. 12.14%) occurs corresponding to the loss of two coordinated water molecules and three carbon atoms which are oxidized by atmospheric oxygen to CO_2. At the higher temperature range of 413–661 °C decomposition and combustion of the organic ligand starts followed by a loss of 40.73% (calcd. 40.69%) which corresponds to the phenyl group and $\text{-N=N}C_6H_4\text{-O}CH_3$. At the final stage metal oxide as residue is obtained from which the metal content is calculated as 19.93% (calcd. 19.82%).

Molar Conductance

The molar conductivities of the solid chelates were measured in DMF solution (10^{-3} M), the conductance values (Λ_M) were found to be in the range 30–60 $\Omega^{-1}\,cm^2\,mol^{-1}$. For $[La(L^1)(NO_3)(OH)_2(EtOH)_2]$ (1:1),

$[La(L^2)(NO_3)_2\text{-}(OH)(H_2O)_2(EtOH)_3]$ (1:1), for $[La(L^3)(NO_3)_3(H_2O)_2(EtOH)_2]$ (1:1) and for $[La(L^4)(NO_3)_3(H_2O)_2(EtOH)]$ (1:1) the conductivities are 40, 60, 30 and 50 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively. These values are small for the ionic complexes of lanthanum metal ions and may be attributed to the coordination of the nitrato ion in the above complexes rather than the ionic association to the lanthanum ions during complex formation[19]. These molar conductance values show that there are no anions present outside the coordination sphere *i.e.*, there are no nitrato groups outside this sphere and the obtained chelates are neutral.

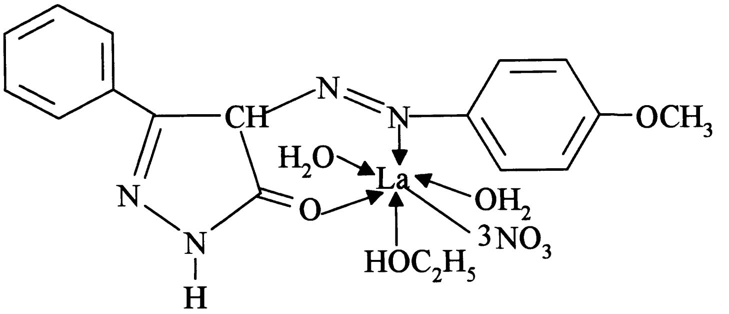

Figure 2. Suggested structure of the 1:1 complex formed by La(III) ions and 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone.

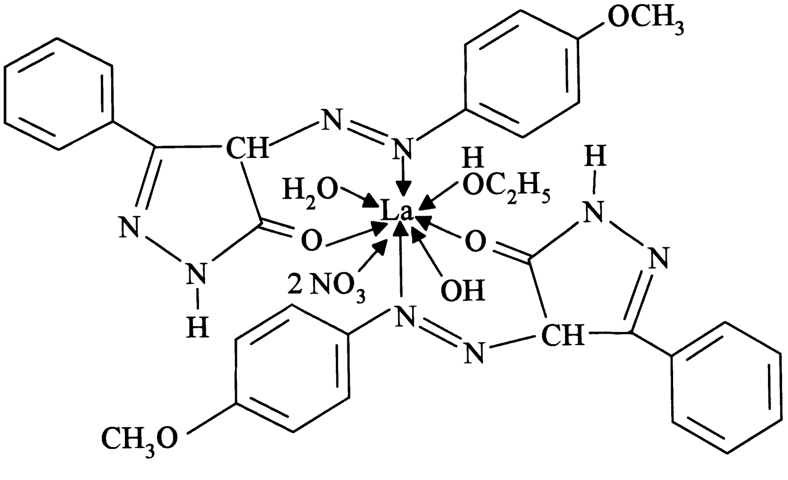

Figure 3. Suggested structure of the 1:2 complex of La(III) ions with 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone.

CONCLUSION

Based on the results gained from the elemental analyses, IR, NMR, molar conductance as well as TG analyses, a suggested structure of the La(III) chelates with 3-phenyl-4-(p-methoxyphenylazo)-5-pyrazolone for 1:1 chelates is shown in Fig. 2 and for the 1:2 complexes in Fig. 3. The coordination numbers of the prepared chelates (1:1) are 7, 10[20], 9[21] and 8[22] for La(III) ions, 7, 8[23], 6 and 7 for Ce(III) ions, 8, 12, 12[19] and 10 for Th(IV) ions and 9, 6, 12[19] and 8[24] for UO_2(VI) ions, respectively, while for the 1:2 chelates the coordination numbers are 9, 9, 7 and 9 for La(III) ions, 10, 11, 11 and 9 for Ce(III) ions, 11, 12, 12 and 11 for Th(IV) ions and 12, 7, 10 and 10 for UO_2(VI) ions with the azopyrazolone ligands (L^1), (L^2), (L^3) and (L^4), respectively.

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