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SPECTROPHOTOMETRIC AND THERMOGRAVIMETRIC STUDIES ON NEW COORDINATION COMPOUNDS OF LANTHANIDE(III)-4-ACETYLPYRIDINE *N*-OXIDE

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ABSTRACT

A series of rare earth complexes of 4-acetylpyridine *N*-oxide have been isolated and characterized. Characterization involves elemental analysis, molar conductance, thermogravimetric analysis (TGA), UV and IR spectrometry. The suggested formulae of these complexes are $ML_n(ClO_4)_3 \cdot x\ H_2O$ where L = 4-acetylpyridine *N*-oxide, $n = 8$, $x = 1$–3 and M = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Y but for Pr complexes the suggested formula is $PrL_7 \cdot H_2O(ClO_4)_3 \cdot H_2O$, based on chemical analysis. Thermogravimetric analysis of selected complexes have already indicated the different nature and/or modes of interaction between various types of ligands comprising water molecules and a central metal ion. The UV and IR spectra analyses already indicate that coordination of the ligand to central metal ions is via oxygen atoms of the N–O groups and confirms the presence of water molecules in the moiety of these complexes.

In conclusion, the ionic nature of all perchlorate ions was proved based on molar conductivity measurements, as well as established from the present IR studies.

INTRODUCTION

Different preparative and characteristic natures of the transition metal-ion complexes of 2-acetylpyridine *N*-oxide have been recently reported [1]. As indicated, there is a small tendency for the 2-acetylpyridine *N*-oxide to bind these metal ions by both the *N*-oxide and the acetyl functions hence acting as a bidentate ligand. Further, some recent investigations [2,3] have been previously reported on the complexes of 4-acetylpyridine *N*-oxide with first row transition series elements, in which the ligand is considered as a monodentate one, and in turn no more studies have been reported for the complexes of the lanthanide series with the 4-acetylpyridine *N*-oxide ligand.

As an ultimate goal of this investigation, the preparation and characterization of these lanthanide complexes with 4-acetylpyridine *N*-oxide are pre-

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sented and discussed in view of some UV and IR spectral studies, electrical conductivity measurements and chemical analysis, as well as thermogravimetric studies.

Occasionally, these lanthanide complexes exhibit an abnormal yellow colouration, which is not directly related to the colour of the respective hydrated lathanide(III) ions [4–6]. Therefore, the present investigation throws light on the coordination chemistry of such types of complexes which are formed by these tripositive lanthanides via their anomalous interaction with the 4-acetylpyridine *N*-oxide ligand.

EXPERIMENTAL

Reagent grade chemicals (Merck) of 4-acetylpyridine were used in the preparation of the 4-acetylpyridine *N*-oxide ligand (4-AcPYO) by a method reported by Kanno [7].

In order to prepare the hydrated lanthanide perchlorates, dropwise, perchloric acid solution (70%) was added to an amount of the lanthanide oxides (Koch Light) until completely dissolved, and the mixture heated and continuously stirred. The resulting solution was filtered and the filtrate allowed to evaporate to dryness, and the obtained solid lanthanide perchlorates preserved in a vacuum desiccator.

For preparation of lanthanide(III) complexes of 4-AcPYO, two solutions of this ligand (1 g/10 ml ethanol) and the lanthanide perchlorate (0.25 g/10 ml ethanol) were boiled separately, mixed, thoroughly stirred and left for 2–3 days, a semi-solid product being formed. The obtained slimey precipitate was filtered off, added to 40 ml petroleum ether (40–60), and 10 ml cold ethanol added with continuous stirring and scratching in order to solidify this product. The obtained solid complexes were yellow in colour, hygroscopic, slightly soluble in organic solvents but completely soluble in dimethylformamide (DMF).

Partial elemental analysis for C, H, N and Cl were perfomed by Microanalytics, Cairo University. The analysis of metal content was performed spectrophotometrically by the recommended procedure [8]. The content of perchlorate in the complexes was determined by the cationic exchange method [9], through titration of the obtained perchloric acid in the effluent.

The termogravimetric analysis TGA of Pr and Y were recorded on a Shimadzu TGA system Shimadzu 30 series thermal analysis instrument. The weight losses in 10 mg sample were measured in the temperature range 20–400°C at a heating rate 10°C min^{-1}.

The IR spectra were recorded as KBr discs on a Pye Unicam SP 1100 IR spectrophotometer in the range 400–4000 cm^{-1}. The UV spectra of the ligand and its complexes were measured in water, DMF, methanol, ethanol and 1,4-dioxane using a recording Pye Unicam SP 1750 spectrophotometer; a Nujol mulls Technique [10] was also used.

The electrical conductivities were measured for 1 mM solutions in water and DMF with a D 812 conductivity meter Model LBR (cell constant = 0.741) at 25 ± 0.1°C.

RESULTS AND DISCUSSION

From the microanalytical data presented in Table 1 of the separated solid complexes for the elements C, H, N, Cl and metal (M), the suggested formulae are $ML_n(ClO_4)_3 \cdot x\ H_2O$ where L = 4-AcPYO, M = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er or Yb and $x = 1$–3; exceptionally, for Pr complexes, the formula is $PrL_7 \cdot H_2O\ (ClO_4)_3 \cdot H_2O$. Obviously, all these solid complexes are isolated with solvent water molecules and are considerably hygroscopic.

UV spectra

In order to study the effect of solvent on the stability of such similar complexes, it is of importance to study the effect of different solvents on both the ligand and the complexes spectrophotometrically. The polar solvents used were water, DMF, ethanol, and methanol, Nujol was used as a non-polar solvent.

To study the effect of polar solvents on the ligand, the presence of two bands at 220–240 and 290–320 nm was established. The first band was assigned to π–π^* local transitions within the pyridine ring (ϵ of the order of 10^4), whilst the second band was assigned to π–π^* transitions influenced by intramolecular charge transfer interactions. In the case of pyridine and pyridine *N*-oxide [11], the presence of only one band at 257–265 nm supports the first band obtained for the 4-AcPYO ligand. Therefore, the second band located at 255–326 nm might be attributed to the presence of acetyl group interactions.

The obtained weak band at 410 nm, using Nujol as a nonpolar solvent (cf., Fig. 1), was attributed to n–π^* electronic transitions in the N–O group. Therefore, going from non-polar to polar solvents, the two main bands were blue shifted and the n–π^* transition completely disappeared. This behaviour is attributed to the oxygen $2p$ non-bonding orbital in the N–O group being energetically stabilized by hydrogen-bond formation with the polar solvent molecules.

Comparing the UV spectra of 4-AcPYO in polar solvents with that of its lanthanide(III) complexes, it was found that there is a great similarity between their behaviour in such solvents and hence the ligand showed less tendency to form these complexes. This behaviour is attributed to the

TABLE 1

Elemental analyses of some lanthanide complexes of 4-acetylpyridine *N*-oxide

Complex [a]	Found (%)						Calc. (%)					
	M	ClO_4	C	H	N	Cl	M	ClO_4	C	H	N	Cl
$LaL_8(ClO_4)_3 \cdot H_2O$	8.94	18.82	43.6	3.8	6.8	7.2	8.95	19.24	43.32	3.77	7.22	6.90
$PrL_7H_2O(ClO_4)_3 \cdot H_2O$	9.94	20.39	40.7	3.8	6.9	7.4	9.82	20.81	40.99	3.70	6.83	7.43
$NdL_8(ClO_4)_3 \cdot 2\,H_2O$	9.31	18.43	42.7	3.8	6.8	6.7	9.16	18.95	42.68	3.81	7.11	6.76
$SmL_8(ClO_4)_3 \cdot 3\,H_2O$	9.72	18.16	41.6	3.8	7.1	6.8	9.41	18.67	42.03	3.88	7.01	6.66
$EuL_8(ClO_4)_3 \cdot 2\,H_2O$	9.89	18.23	42.5	3.8	6.9	6.6	9.60	18.86	42.47	3.87	7.08	6.73
$GdL_8(ClO_4)_3 \cdot H_2O$	10.21	19.33	42.9	4.1	6.8	6.9	10.0	19.02	42.81	3.73	7.14	6.79
$DyL_8(ClO_4)_3 \cdot H_2O$	10.28	18.76	43.0	3.8	7.4	6.7	10.3	18.95	42.70	3.71	7.11	6.76
$HoL_8(ClO_4)_3 \cdot H_2O$	10.90	20.00	42.3	4.0	6.8	7.1	10.5	19.14	42.60	3.71	7.10	6.75
$ErL_8(ClO_4)_3 \cdot 2\,H_2O$	10.78	19.50	42.0	3.8	6.6	7.1	10.5	18.68	42.06	3.79	7.00	6.67
$YbL_8(ClO_4)_3 \cdot 2\,H_2O$	11.00	19.20	41.8	3.7	6.7	7.0	10.8	18.62	41.91	3.77	6.98	6.64
$Y\,L_8(ClO_4)_3 \cdot 2\,H_2O$	5.99	19.50	43.8	4.1	7.5	7.2	5.9	19.65	44.23	3.95	7.37	7.01

[a] L: 4-AcPYO, M: lanthanide(III) metal ion.

competition between polar solvents—which form a hydrogen bond with the N–O group—and the metal ion which forms an N–O ··· M bond. Consequently, to avoid such competition, the UV spectra of these types of complex were studied in Nujol as a non-polar solvent (cf., Fig. 1). In Nujol, the first band at 320 nm of the ligand shifted to shorter wavelength during the formation of lanthanide(III) complexes, this shift being somewhat pronounced at 240–280 nm in case of Yb. This was found to be in good agreement with the fact that the tendency of complex formation increases with the decrease in ionic size in the lanthanide series (La^{3+} to Yb^{3+}). This shift is attributed to the perturbation of the π electron configuration of the pyridine ring as a result of bonding of the N–O group to the metal ion. Due to such perturbation, it is also noticeable that the second band at 230 nm—which is attributed to acetyl group interactions—becomes a group of sharp individual peaks during complex formation. The very weak band of the ligand at 410 nm appears as shoulders at shorter wavelength in the region 330–350 nm. This blue shift is also attributed to the formation of an N–O ··· M bond with the lanthanide metal ions, and consequently the change in the π electron system of the ligand, during the complex formation.

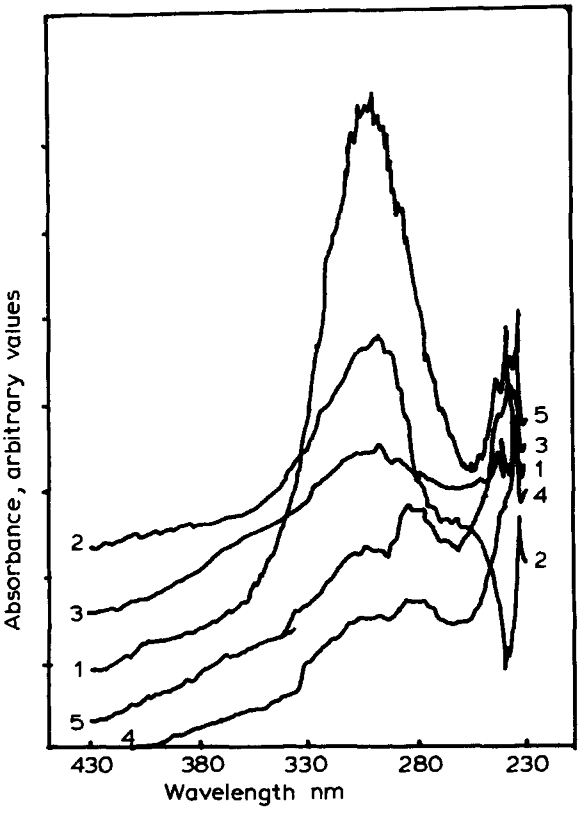

Fig. 1. UV spectra of (1) 4-acetylpyridine *N*-oxide and its complexes with (2) La, (3) Ho, (4) Er, (5) Yb ions in Nujol mulls.

Molar conductance

The molar conductivity values of 1 mM solutions in DMF and water of the given lanthanide(III) complexes are listed in Table 2. The obtained values are 226–262 and 370–471 Ω^{-1} cm^2 mol^{-1} in DMF and water, respectively. These anomalous conductivity values are of the same order of magnitude as the previously stated values [12,13] and this is attributed to ionic association rather than the coordination of perchlorate groups to lanthanide(III) cations in a way analogous to that found with other similar complexes [11,13,14]. These results also indicate that all perchlorate groups in these complexes are ionic in nature, behaving as 1 : 3 electrolytes.

Thermogravimetric analysis

The thermogravimetric data for Pr and Y complexes, as typical examples, are listed in Table 3. In the case of the Pr complex, the water loss of 1.40% at 110–140°C indicates the loss of one mole of water (theoretically, in gram%, 1.42), which could be water of hydration. The weight loss of 1.40% continues to 160°C which is referred to the loss of one coordinate water molecule.

The gradual weight losses of 2% at 160–230°C and 1% at 230–255°C are attributed to the loss of a CO group from the moiety of the 4-AcPYO ligand (theoretically, in gram%, 2.11) and the loss of a coordinated water molecule (theoretically, in gram%, 1.36), respectively. The weight loss of 8% at

TABLE 2

Molar conductance data of the rare earth complexes with 4-acetylpyridine *N*-oxide at 25°C

Complex [a]	Solvent				No. of dissociated charged species
	Water		DMF		
	Conc. (mM)	Λ (Ω^{-1} cm^2 mol^{-1})	Conc. (mM)	Λ (Ω^{-1} cm^2 mol^{-1})	
$LaL_8(ClO_4)_3 \cdot H_2O$	1.32	449	1.19	235	1:3
$PrL_7H_2O(ClO_4)_3 \cdot H_2O$	1.10	440	1.20	256	1:3
$NdL_8(ClO_4)_3 \cdot 2\ H_2O$	1.19	469	1.09	249	1:3
$SmL_8(ClO_4)_3 \cdot 3\ H_2O$	1.23	419	1.11	240	1:3
$EuL_8(ClO_4)_3 \cdot 2\ H_2O$	1.30	370	1.11	249	1:3
$GdL_8(ClO_4)_3 \cdot H_2O$	1.20	405	1.15	226	1:3
$DyL_8(ClO_4)_3 \cdot H_2O$	1.35	394	1.72	234	1:3
$HoL_8(ClO_4)_3 \cdot H_2O$	1.22	470	1.36	261	1:3
$ErL_8(ClO_4)_3 \cdot 2\ H_2O$	1.28	470	1.30	262	1:3
$YbL_8(ClO_4)_3 \cdot 2\ H_2O$	1.29	471	1.37	260	1:3
$Y\ L_8(ClO_4)_3 \cdot 2\ H_2O$	1.20	459	1.19	241	1:3

[a] L: 4-AcPYO.

TABLE 3

Percentage weight losses of 4-acetylpyridine *N*-oxide complexes

Compound [a]	Temp. range (°C)	Loss of solvate water (%) [b]	Temp. range (°C)	Loss of coordinate water (%) [b]	Temp. range (°C)	Further decomposition (%) [b]
$PrL_7 \cdot H_2O(ClO_4)_3 \cdot H_2O$	110–120	est. 1 calc. 1.36	230–255	est. 1 calc. 1.36	160 230	est. 2 calc. 2.11
					260–400	est. 8 calc. 8.46
$YL_8(ClO_4)_3 \cdot 2\,H_2O$	95–150	est. 2 calc. 2.4			170–400	est. 9 calc. 8.79

[a] L: 4-AcPYO.

[b] Estimated values from the respective TGA measurements. Calculated values based on the results of chemical analysis.

TABLE 4

Functional group and perchlorate vibrations of 4-acetylpyridine *N*-oxide (L) and its lanthanide complexes (cm^{-1})

Mode	Ligand	La	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb
ν_{CO}	1680vs	1700vs	1700vs	1700vs	1698vs	1703vs	1700vs	1700vs	1698vs	1700vs	1702vs
ν_{C-H}	3090w	3105w	3135w	3140w	3137w	3130w	3135w	3100w	3107w	3110w	3110w
ν_{NO}	1267vs,sh	1238vs	1243vs,sh	1235vs,sh	1243vs,sh	1250vs,sh	1245vs	1235vs	1238vs	1240vs	1240vs
$\nu_3(ClO_4^-)$	*	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s	1108–1150s
$\nu_4(ClO_4)$	*	620m	620m	620m	620m	620m	620m	620m	620m	620m	620m
δ_{NO}	843vs	847vs	849vs	852vs	851vs	850vs	850vs	850vs	850vs	850vs	850vs

Abbreviations: s = strong; vs = very strong; m = medium; w = weak; sh = shoulder; * = not observed.

260–400°C is attributed to the loss of 4 CO groups (theoretically, in gram%, 8.46) which dissociate from the acetyl groups of the ligand molecules.

The weight loss of 2% at 95–160°C in the case of the Y complex is attributed to the loss of two moles of water (theoretically, in gram%, 2.43), which are probably water of hydration. The higher weight loss of 9%, extending from 170 to 400°C, is attributed to the loss of one mole of 4-AcPYO (theoretically, in gram%, 8.79) from the moiety of the complex; consequently, the coordination number of Y becomes 7. The other lanthanide(III)–4-AcPYO complexes show similar behaviour. Therefore, it is concluded that water molecules are present either as water of hydration in the outer spheres or as coordinated water in the inner shields of these complexes. It is also concluded that the loss of CO groups, in the case of Pr complexes, starting from 160°C, is a result of dissociation from acetyl groups of the ligands and this is in good agreement with recent results for 2-AcPYO complexes already published [15].

IR spectra

The assignment of the IR bands is presented in Table 4. It seems necessary to understand the nature of bonding in these complexes.

The band at 620 cm^{-1} is assigned as ν_4 of the perchlorate group and the broad band at 1150–1080 cm^{-1} is assigned as ν_3 of the same group since they do not appear in the IR spectra of the ligand. The breadth of the band assigned as ν_3 is most probably caused by the lattice requirements and their hydrogen bonding to water molecules rather than a significant bonding of the perchlorate groups with the lanthanide(III) ions. In other similar complexes, when ν_3 and ν_4 bands for the perchlorate groups are recorded in KBr discs, both of these bands are significantly split, indicating an extreme pressure used in forming these discs, distorting the perchlorate ions measurably from the pure tetrahedral symmetry [15]. It is apparent that such splitting does not occur in the lanthanide complexes under test. However, the breadth of the band assigned as ν_3 establishes the distortion of the tetrahedral symmetry of the pure perchlorate group, via hydrogen bonding with water molecules of hydration, during the process of complex formation. It is concluded that the perchlorate groups are all ionic in nature and not entirely involved in the complex formation.

The band at 1267 cm^{-1} is attributed to ν_{NO}; in the IR spectra of the ligand, this is somewhat shifted to lower energy (1267–1235 cm^{-1}) during the formation of the resultant complexes. This shift is attributed to the bonding of the N–O group to the metal ion [12]. This bonding results in a decrease in the contribution of the resonating structures II (cf., Fig. 2) and consequently a decrease of the N = O contribution.

It was found that in the case of 2- and 4-substituted pyridine *N*-oxides, the electron-releasing substituents enhance the contribution of structures III,

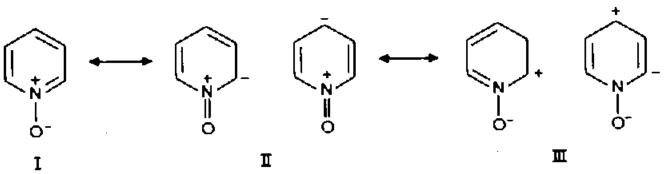

Fig. 2. Resonating structures of the pyridine *N*-oxide molecule.

while the electron-withdrawing substituents (e.g., acetyl group) enhance the contribution of structures II. Consequently, using 4-AcPYO as a ligand, the NO stretching is influenced by two opposing factors: the effect of coordination to the lanthanide ion, which decreases the contribution of structures II, and, in turn, the effect of the electron-withdrawing acetyl group which helps contribution of structures II. Therefore, the coordination would result in a small decrease in the contribution of structures II and, accordingly, in a small shift of ν_{NO} ($\sim$ 25 cm^{-1}). The shift is a measure of the strength of the M–O bond and is considered less than those obtained for the complexes of trivalent transition metal ions (40–60 cm^{-1}) [15]. For this reason, such lanthanide complexes are less stable than those obtained in the case of the trivalent metal ions with pyridine *N*-oxides.

The ν_{CO} band appears at 1680 cm^{-1} in the spectrum of the 4-AcPYO ligand. Despite the shift of this band in some cases to 1700 cm^{-1} during complex formation, it is attributed to the increase of electron-withdrawing effect of the NO group during coordination to the lanthanide(III) ions. This shift is somewhat small and measurably less in magnitude as expected for the coordination of carbonyl oxygen [2]. Consequently, there is no complex formation via oxygen atoms of CO groups in the given complexes.

The band at 3090 cm^{-1} is assigned to the stretching mode of the C–H bond in the spectra of the ligand. This band is shifted to 3105–3140 cm^{-1} in complex formation. The shift is attributed to the decrease of electron density on the ring of the ligand, resulting from the smaller contribution of the resonating structures II as a consequence of the formation of the N–O $\cdots$ M bond.

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