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Synthesis, Crystal and Molecular Structure of Light Lanthanide Complexes with a New 1:1 Open Phenolic Schiff Base Acetal

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Abstract

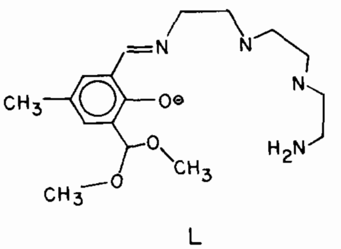
The compounds $LnL(NO_3)_2X$, Ln = Pr, L = phenolic Schiff base acetal, X = CH_3OH and Ln = La, Nd, X = H_2O have been prepared, but Ln heavier than Nd failed to give similar compounds. $PrL(NO_3)_2(CH_3OH)$ crystals are monoclinic with space group $P2_1/c$, $Z = 4$ and decacoordinate Pr^{3+}. The Pr–O(phenolate) distance of 2.263 Å is the shortest contact Pr^{3+} makes indicating a strong Pr^{3+}-phenolate interaction. The angle subtended by the terminal amino nitrogen and phenolate oxygen at Pr^{3+} is much larger than the others subtended by other members of the equatorial near-pentagon defined by the ligating atoms of L, indicating that the 14-membered cavity defined by the pentagon is small for Pr^{3+}. The NMR, TG, and UV–Vis spectral features of complexes of L and those of the homodinuclear complexes of the 2:2 ligand (L″) formed by 2,6-diformyl-*p*-cresol and triethylenetetramine differ substantially.

Introduction

A variety of Schiff base complexes with trivalent lanthanides have been reported over the last few years [1, 2]. While there is some information about trivalent lanthanide complexes with neutral ligands derived from 2,6-dicarbonylpyridines including four crystal structures [2–5], little is known about complexes of negatively charged ligands such as those derived from 2,6-dicarbonylphenols [1], or 2-carbonylphenols [6]. Our successful syntheses of homodinuclear lanthanide complexes of a 2:2 phenolate Schiff base derived from 2,6-diformyl-*p*-cresol and triethylenetetramine [1], has demonstrated the versatility of anionic ligands for the preparation of lanthanide complexes in which trapping of Ln^{3+} cations in close proximity is desired. Our failure to obtain similar complexes from dicarbonylpyridine precursors suggests that it is a strong interaction between the phenolate anion with the Ln^{3+} cations which may serve to offset Ln^{3+}–Ln^{3+} repulsive interactions, thereby enabling Ln^{3+} cations to be trapped in close proximity by phenolate Schiff bases. If this is true then the phenolate moiety may have the potential to impact lanthanide complexation chemistry as importantly as the pyridine moiety has dominated the complexation chemistry of the d-block elements [7, 8].

In order to evaluate this hypothesis, structural data of lanthanide–phenolate systems are essential. However, crystal structures of the homodinuclear complexes or any other closely related lanthanide phenolate Schiff base complex have not been determined. The closest structures available are those of trinuclear Cu–Ln–Cu complexes, Ln = Ce [9] and Gd [10, 11], where the neutral copper phenolate Schiff base complexes participate in the coordination spheres of Ln^{3+} through the phenolate oxygens. The only crystal structure of a lanthanide Schiff base complex showing the phenolate ligand coordinated exclusively to the lanthanide cation (Ce^{4+}) is that of CeX_2, where the doubly charged open compartmental ligand X^{2-} is derived from 2 molecules of 2-formylphenol and one of 1,2 diaminobenzene [12].

To gain insight into the nature of the lanthanide cation–phenolate Schiff base interaction, we have undertaken synthetic and structural studies of those systems. We have now isolated X-ray diffraction quality crystals of complexes of an open 1:1 ligand, L, with trivalent light lanthanides. We report here the



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crystal and molecular structures of $PrL(NO_3)_2(CH_3OH)$ and a comparison of its NMR, electronic absorption, and thermogravimetric data with those of the homodinuclear complexes reported earlier [1].

Experimental

The compounds 2,6-diformyl-*p*-cresol (DFPC), triethylenetetramine (TETA), and $Ln(NO_3)_3 \cdot nH_2O$ were the same as those used previously [1]. Nitric acid was reagent grade supplied by Baker Chemical Co.

Syntheses of $LnL(NO_3)_2X$

To one mmol of $Ln(NO_3)_3$, was added 10 ml of methanol followed by three drops of concentrated nitric acid. Solid 2,6-diformyl-*p*-cresol (1 mmol) was then added and the resulting solution was cooled in an ice bath. After 10–15 min a pre-cooled solution of triethylenetetramine (2 mmol) in 5 ml of methanol was added. If a precipitate forms then a little triethylenetetramine is added until it just dissolves. The mixture was transferred to a freezer operating at −17 °C and crystals were deposited in two days. After four days, the mixture was filtered, washed with methanol and ether, and air dried. The compound isolated is $PrL(NO_3)_2(CH_3OH)$. Yield 53%. *Anal.* Found: C, 33.71; H, 5.30; N, 13.51; ash (Pr_6O_{11}), 26. Calc.: C, 34.4; H, 5.20; N, 13.2; ash (Pr_6O_{11}), 27%. If the mole ratio of reactants Pr^{3+}:DFPC:TETA is 1:1:1 and the temperature is about 0 °C the yield is 29%.

If seven drops of concentrated nitric acid are used, the complexes obtained are small quantities of $LnL(NO_3)_3 \cdot H_2O$: for example, for Ln = Nd. *Anal.* Found: C, 32.97; H, 5.20; N, 13.54. Calc.: C, 32.7; H, 5.01; N, 13.5%.

The instruments used to obtain thermogravimetric, electronic absorption, NMR and IR data were described previously [1].

X-ray Structure Determination

Intensity data were obtained from a yellow crystal of dimensions 0.12 × 0.24 × 0.38 mm (sealed in a thin-walled glass capillary, since crystal damage on prolonged exposure to the atmosphere was observed) on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Cell dimensions and crystal orientation were obtained from the setting angles of 25 reflections having $18° < 2\theta < 22°$. Crystal data are: $PrC_{18}H_{33}N_6O_{10}$, formula weight = 634.4, monoclinic space group $P2_1/c$, a = 10.5475(12), b = 32.121(4), c = 7.8432(14) Å, β = 97.871(13)°, V = 2632.2(12) Å^3, Z = 4, D_c = 1.601 g cm^{-3}, μ(Mo Kα) = 19.0 cm^{-1}, T = 21 °C. Data were collected by ω–2θ scans of variable speed 1.8–4.0 deg min^{-1} in order to measure all significant data with approximately equal relative precision. All data in one quadrant having $1° < \theta < 25°$ were measured in this fashion. Data reduction included corrections for background, Lorentz, polarization, and absorption. The absorption corrections were based on ψ scans of reflections near χ = 90°, and the minimum relative transmission coefficient was 84.26%. Of 4629 unique data, 3026 had $I > 3\sigma(I)$, and were used in the refinement.

The structure was solved by heavy atom methods and refined by full matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs [13]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located in difference maps and included as fixed contributions with isotropic B = 5.0 Å^2. The H atoms of the coordinated methanol molecule were not located. Convergence was achieved with R = 0.035, R_w = 0.037, goodness of fit (GOF) = 1.448 for 316 variables, and the maximum residual density was 0.67 e Å^{-3}, near the metal position.

Results and Discussion

The Structure of $PrL(NO_3)_2(CH_3OH)$

The compound isolated from a low temperature acid catalyzed condensation of DFPC (1 mol) and TETA (*ca.* 2 mol) with Pr^{3+} (1 mol) as the template cation was determined from elemental analysis and single crystal X-ray crystallography to be $PrL(NO_3)_2(CH_3OH)$, where L is a 1:1 open condensation product with the non-condensed carbonyl having been acetalated under the mild acid conditions [14]. Compounds of La and Nd isolated from more acidic solutions have a water molecule substituting for a methanol molecule to give: $LnL(NO_3)_2 \cdot H_2O$. The atomic coordinates of non-hydrogen atoms are given in Table I while a selection of bond lengths and angles is given in Table II.

The decacoordination scheme around Pr^{3+} is constituted by one phenolate oxygen, an imine nitrogen and three amino nitrogen atoms from L, two bidentate nitrate anions and a molecule of methanol as shown in Fig. 1, which also shows the numbering scheme. This decacoordination geometry is of approximate C_2 symmetry with the local twofold axis bisecting angle N2–Pr–N3. This geometry maybe viewed as a distorted D_{4d} bicapped square antiprism with the pseudo fourfold axis lying along the N1–Pr–N4 axis. The pseudo square faces are O1, O1A, N2, O5A with capping by N1 and O1M, O4A, N3, O2A with capping by N4. The geometry also may be viewed as a distorted bicapped dodecahedron of D_2 symmetry with one pseudo-twofold axis bisecting the angle N2–Pr–N3, the second lying along the N1–Pr–N4 axis and the third lying along the central line joining the nitrate anions.

TABLE I. Coordinates for Pr Complex $Pr(C_{17}H_{29}N_4O_3)(NO_3)_2CH_3OH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pr	0.03497(3)	0.11893(1)	0.30923(4)	C2	0.4046(5)	0.1560(2)	0.0898(8)
O1	0.2105(4)	0.1375(1)	0.1906(5)	C3	0.5056(6)	0.1835(2)	0.0927(8)
O2	0.4159(4)	0.0827(1)	0.0839(6)	C4	0.5163(6)	0.2190(2)	0.1923(7)
O3	0.4810(4)	0.1172(2)	−0.1407(6)	C5	0.6256(6)	0.2493(2)	0.1873(9)
O1A	−0.0788(5)	0.1822(2)	0.1604(6)	C6	0.4226(6)	0.2266(2)	0.2938(8)
O2A	−0.0529(5)	0.1350(1)	−0.0239(6)	C7	0.3185(5)	0.1992(2)	0.2991(7)
O3A	−0.1687(7)	0.1877(2)	−0.1000(7)	C8	0.2321(6)	0.2089(2)	0.4251(8)
O4A	−0.0224(4)	0.0583(2)	0.5071(6)	C9	0.0717(6)	0.2027(2)	0.6020(8)
O5A	0.1210(4)	0.0991(2)	0.6352(6)	C10	−0.0697(6)	0.2007(2)	0.5471(9)
O6A	0.0693(5)	0.0433(2)	0.7642(6)	C11	−0.2474(6)	0.1532(2)	0.4646(8)
O1M	0.2272(4)	0.0623(2)	0.3251(6)	C12	−0.2830(6)	0.1102(2)	0.4023(9)
N1	0.1406(5)	0.1862(2)	0.4639(6)	C13	−0.2434(6)	0.0573(2)	0.1868(9)
N2	−0.1080(5)	0.1568(2)	0.5193(6)	C14	−0.1621(7)	0.0479(2)	0.0494(9)
N3	−0.2188(5)	0.1001(2)	0.2499(6)	C15	0.3919(5)	0.1180(2)	−0.0223(8)
N4	−0.0263(5)	0.0513(2)	0.1194(6)	C16	0.3890(8)	0.0452(2)	−0.0099(12)
N1A	−0.1010(6)	0.1687(2)	0.0081(7)	C17	0.4358(8)	0.1374(3)	−0.2957(10)
N2A	0.0555(5)	0.0664(2)	0.6388(7)	C1M	0.2851(9)	0.0285(3)	0.4244(12)
C1	0.3066(5)	0.1632(2)	0.1961(7)				

TABLE II. Selected Bond Distances and Angles

Distances		Angles (e.s.d. = 0.1)	
Pr–O1	2.263(3)	O1–Pr–N1	69.9
Pr–N1	2.647(4)	O1–Pr–N2	134.1
Pr–N2	2.673(4)	O1–Pr–N3	146.0
Pr–N3	2.722(4)	O1–Pr–N4	97.8
Pr–N4	2.661(4)	O1–Pr–O1A	87.8
Pr–O1A	2.558(4)	O1–Pr–O2A	75.1
Pr–O2A	2.700(4)	O1–Pr–O4A	135.3
Pr–O4A	2.612(4)	O1–Pr–O5A	105.5
Pr–O5A	2.671(4)	O1–Pr–O1M	63.1
Pr–O1M	2.714(4)	N1–Pr–N2	65.4
O1–C1	1.302(6)	N1–Pr–N3	127.0
O2–C15	1.410(7)	N1–Pr–N4	167.6
O2–C16	1.419(7)	N1–Pr–O1A	72.7
O3–C15	1.409(6)	N1–Pr–O2A	110.8
O3–C17	1.402(9)	N1–Pr–O4A	116.9
N1–C8	1.279(6)	N1–Pr–O5A	71.9
N1–C9	1.483(6)	N1–Pr–O1M	105.1
N2–C10	1.474(7)	N2–Pr–N3	65.3
N2–C11	1.479(7)	N2–Pr–N4	127.0
N3–C12	1.488(7)	N2–Pr–O1A	69.6
N3–C13	1.471(7)	N2–Pr–O2A	111.2
N4–C14	1.466(7)	N2–Pr–O4A	77.1
C1–C2	1.433(7)	N2–Pr–O5A	70.4
C1–C7	1.407(7)		
C2–C3	1.382(7)		
C2–C15	1.498(7)	N2–Pr–O1M	139.2
C3–C4	1.379(7)	N3–Pr–N4	64.2
C4–C5	1.512(7)	N3–Pr–O1A	73.1
C4–C6	1.373(7)	N3–Pr–O2A	71.2
C6–C7	1.412(7)	N3–Pr–O4A	68.5
C7–C8	1.465(7)		
C9–C10	1.496(8)	N3–Pr–O5A	107.9
C11–C12	1.496(8)	N3–Pr–O1M	124.7
C13–C14	1.497(8)	N4–Pr–O1A	109.3
N1A–O1A	1.262(6)	N4–Pr–O2A	65.8
N1A–O2A	1.234(6)	N4–Pr–O4A	70.5
N1A–O3A	1.199(6)	N4–Pr–O5A	111.4
N2A–O4A	1.256(6)	N4–Pr–O1M	66.5
N2A–O5A	1.259(6)	O1A–Pr–O2A	47.9
N2A–O6A	1.224(6)	O1A–Pr–O4A	136.9
O1M–C1M	1.423(8)	O1A–Pr–O5A	134.7
		O1A–Pr–O1M	148.6
		O2A–Pr–O4A	129.8
		O2A–Pr–O5A	177.2
		O2A–Pr–O1M	109.1
		O4A–Pr–O5A	47.9
		O4A–Pr–O1M	72.9
		O5A–Pr–O1M	69.0

A bicapped dodecahedral geometry was assigned to similar arrangements in the complexes $Nd(EO5)(NO_3)_3$ where EO5 is tetraethyleneglycol [15], $Nd(EO6)(NO_3)_3$ where EO6 is pentaethyleneglycol [16] and $La(bpy)_2(NO_3)_3$ where bpy = bipyridine [17]. In the case of the glycols, EO5 and EO6 form a pentagon and hexagon respectively around Nd^{3+} in the equatorial plane as does L, which forms a distorted pentagon with deviations from planarity (O1, N1, N2, N3, N4, Pr) being within 0.5 Å.

The angle O1–Pr–N4 is large, (97.77(13)°), compared to O1–Pr–N1 (69.89(13)°, and N1–Pr–N2, N2–Pr–N3, and N3–Pr–N4 (64–65°), which suggests that the open 14-membered cavity defined by the ligand L is small for Pr^{3+} and thus the angle O1–Pr–N4 opens up to provide more room. Since the (closed) cavity defined by a completely cyclized 1:1 ligand L':

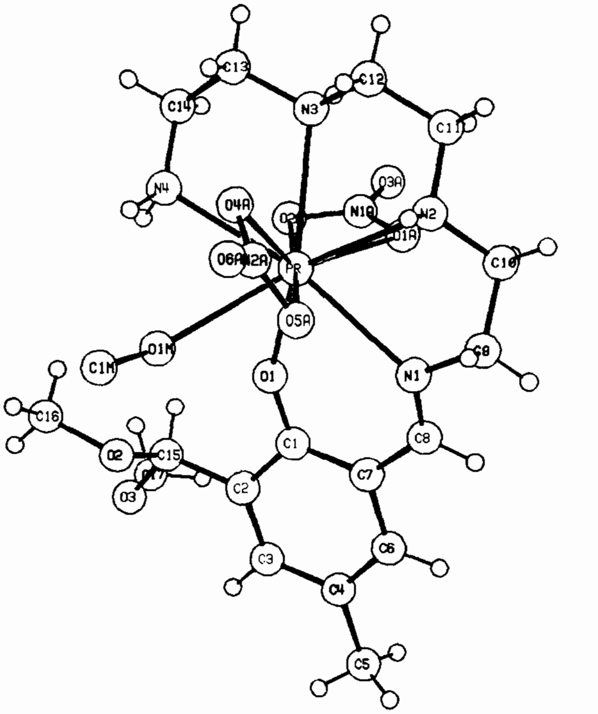
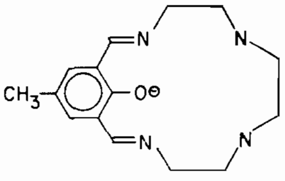
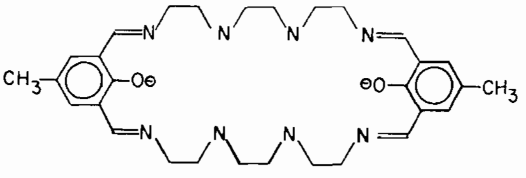


Fig. 1. The ORTEP drawing of a molecule of $PrL(NO_3)_2$-CH_3OH showing the numbering scheme.



L′

is about the same size, cavity size could partly explain why complexes of L′ are not obtained in favor of either the homodinuclear complexes where two Ln^{3+} may occupy adjacent 18-membered compartments of a 2:2 Schiff base L″ [1] or mononuclear complexes of L, where the uncondensed carbonyl is acetalated.



L″

The Pr–O1 bond length of 2.263(3) Å is the shortest contact Pr^{3+} makes with the ten ligating atoms. The distance is also shorter than Ln–O (phenolate) bonds in trinuclear complexes of Cu–Ln–Cu, Ln = Ce (2.45 Å, decacoordinated Ce^{3+} [9]; Ln = Gd, 2.37 Å hepta-coordinated Gd^{3+} [10, 11]; and 2.43 Å for nona-coordinated Gd^{3+} [11]). This Pr–O1 bond length is closer to the Ce–O (phenolate) distance (2.214 Å) in a Ce^{4+} phenolate Schiff base complex [12]. Other Ln–O (phenolate) distances include those of Ln = Ce(IV) (2.36 Å) in dodecahedral coordination in $Na_4[Ce(catecholate)_4]\cdot H_2O$ [18] and Ln = Sc (1.869 Å) in tris(2,6-di-tertbutyl-4-methyl-phenoxy)scandium(III) [19] where tricoordination around Sc^{3+} precludes comparison with decacoordinated Pr^{3+}. Clearly therefore Pr^{3+} bonds strongly to the phenolate center and this provides a basis for concluding that ligands based on a phenolate moiety may be very useful for studying the behavior of rare earth elements in new complexation environments.

The Pr–N distances are normal and the Pr–N (imine) bond, 2.647(4) Å, is slightly shorter than the Pr–N (amine) bonds 2.661(4)–2.722(4) Å.

One of the nitrates (N2A) bonds much more symmetrically to Pr^{3+} than the other (Table II), and in both cases the uncoordinated oxygen shows the shortest N–O distance.

The C1–O1 distance of 1.302(6) Å is shorter than found in non-Schiff base phenolates, e.g. 1.35 Å in $[Ce(catecholate)_4]^{4-}$ [18], 1.34–1.37 Å in Sm(salicylate)$_3$ [20] where less double bond character is expected [21, 22]. In the CeX_2 phenolic Schiff base complex [12], the average value of 1.32 Å is closer to that found in this study. This demonstrates the incremental influence of the C=N bond adjacent to the phenolate center on the C–O (phenolate) double bond character and supports conclusions reached on the basis of IR spectroscopy, where the peak in the 1550 cm^{-1} area in phenolate Schiff base complexes was attributed to C–O (phenolate) with double bond character [1].

Comparison of UV–Vis, NMR and TG data of Complexes of L and L″

Although the colors of the complex $PrL(NO_3)_2$-(CH_3OH) and the homodinuclear off-white form of $Pr_2L''(NO_3)_4\cdot 2H_2O$ [1] are nearly the same, their electronic absorption spectra have significant differences (Fig. 2). While the complex of L in Nujol mull has a major peak at 4200 Å and none at 3700 Å, that of L″ has a shoulder at ~4300 Å and a major peak at ~3700 Å. In DMSO the complex of L has a shoulder at ~4100 Å (peak 1) and a major peak at ~3700 Å (peak 2) as do complexes of L″. However, the intensity of peak 1 relative to peak 2 (A_1/A_2) grows slowly from 0.05 to 0.3 in about 100 h for the L complex (Fig. 3) compared to an increase from 0.01 to 0.5 in 10 h for complexes of L″ (Fig. 3, ref. 1). Therefore the complex of L is remarkably stable in DMSO and we accordingly were able to obtain a good NMR spectrum of $PrL(NO_3)_2(CH_3OH)$ where the large chemical shifts are a firm indication of the integrity

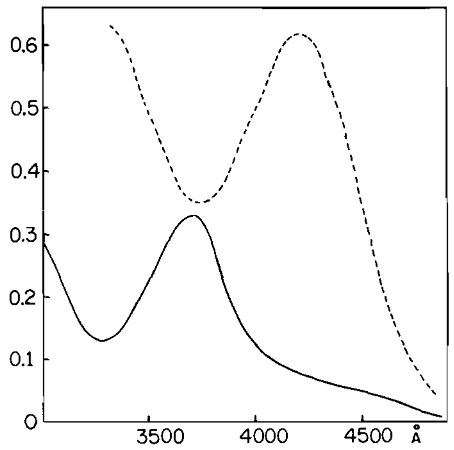


Fig. 2. The UV–Vis spectra of off-white $Pr_2L''(NO_3)_4 \cdot 2H_2O$ (solid line) and $PrL(NO_3)_2(CH_3OH)$ (dotted line) in Nujol mull.

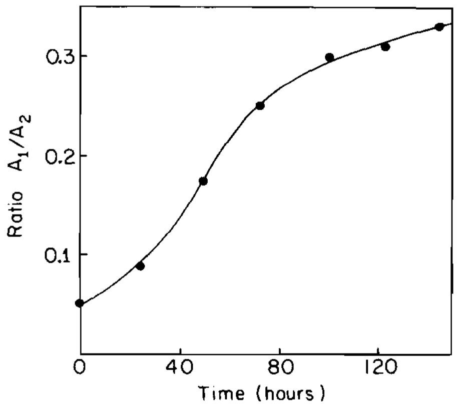
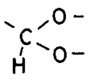
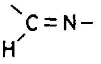


Fig. 3. Variations in the intensity ratio of Peak 1 (4200–4300 Å) (A_1) and Peak 2 (~3700 Å) (A_2) with time, at ~24 °C, for $PrL(NO_3)_2CH_3OH$ in DMSO.

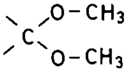
of the complex [20]. On the basis of intensity and line width we assign the singlets at 27 and 21 ppm to



and

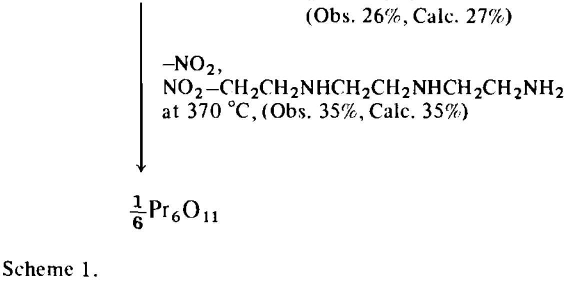


protons, and the broadest singlet at −17 ppm to methanolic O–H which is expected to be a triplet. The peaks at 10 and 8 ppm have triple intensity and are probably due to



methyl protons. The double intensity broad peak at 9 ppm is probably due to aromatic protons which should have given a doublet. The features in the region 2–6 ppm are probably due to $-CH_2-$ and $-CH_3$ protons. NMR spectra of complexes of L″ were intractable.

Finally the TG curves of complexes of L and L″ are substantially different, showing a stepwise decomposition of $PrL(NO_3)_2(CH_3OH)$ and a rapid single stage decomposition for the anhydrous off-white $Pr_2L''NO_3)_4$ complex (Fig. 4). The proposed decomposition stages for $PrL(NO_3)(CH_3OH)$ in air with weight losses in parentheses are shown in Scheme 1. Where L* is L with an aldehyde instead of an acetal, A is an azido–aldehyde phenol presumed



Scheme 1.

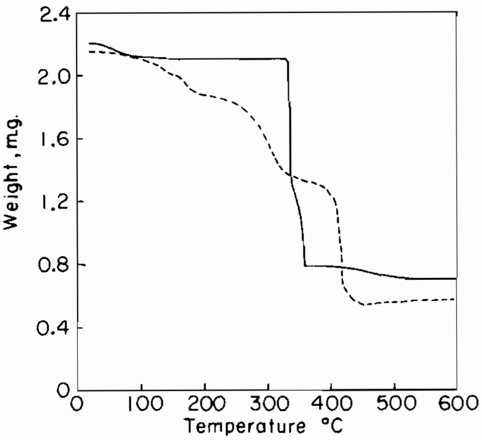


Fig. 4. The thermogravimetric curves of off-white $Pr_2L''(NO_3)_4\cdot 2H_2O$ (solid line) and $PrL(NO_3)_2(CH_3OH)$ dotted line) run in dynamic air atmosphere (7.2 l/h) and heating rate 20 °C/min.

to form when the single C–N(imine) bond ruptures leading to loss of hydrogen atom and constitution of a C≡N triple bond. L** is probably anionic: $^-O_3NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, since a neutral fragment, $CH_3CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, produced when the azido-aldehyde group A is lost at 200–350 °C, is not expected to coordinate to Pr^{3+} that strongly (dec. 370 °C).

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