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Complexes of 1,8-Naphthyridines. X. Complexes of 1,8-Naphthyridine with Rare Earth Nitrates[1a]

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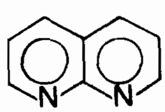
Rare earth nitrate complexes of the type $M(napy)_3(NO_3)_3$ where M = La-Nd and napy is 1,8-naphthyridine, and $M(napy)_2(NO_3)_3$ where M = Y, Sm-Yb have been synthesized. The compounds have been characterized by elemental analyses, molar conductances, magnetic moments, and infrared (4000-200 cm^{-1}) *spectra. The molar conductance and infrared spectral data show that all nitrate groups are coordinated. Both nitrate and napy are known to produce complexes which exhibit high coordination numbers, and there is crystallographic evidence of twelve-coordination in $Ce(NO_3)_6^{3-}$. Therefore, the $M(napy)_3(NO_3)_3$ complexes appear to be twelve-coordinate, and the $M(napy)_2(NO_3)_3$ complexes are apparently ten-coordinate.*

Introduction

The coordination chemistry of the rare earths has been developed only recently.[2-4] In the past decade numerous lanthanide complexes of the nitrogen-donor ligands phenanthroline and bipyridyl have been successfully isolated using non-aqueous solvents and anhydrous lanthanide salts as starting materials.[5-12] These chelating ligands produce five-membered rings when coordinated to a metals, whereas 1,8-napthyridine forms a four-membered ring in its complexes.



napy

Considering the large size of the tripositive lanthanide ions relative to the first row transition metal ions, higher coordination numbers for the lanthanides are expected. Crystallographic studies have shown several lanthanide nitrate species to be ten-coordinate.[13-16] We have previously reported the syntheses of ten-coordinate complexes $M(2,7\text{-dmnapy})_2(NO_3)_3$ where M = Y, La-Yb, and 2,7-dmnapy is 2,7-dimethyl-1,8-naphthyridine.[17]

However, a coordination number greater than ten for the lanthanide ions is considerably less common. Two twelve-coordinate species which contain six bidentate nitrate groups have been verified by crystallography.[18,19] The ability of the nitrate group to attain unusually high coordination numbers with first row transition metals is well known.[20,21] Likewise, napy has also exhibited the ability to form eight-coordinate first row transition metal complexes.[22-25]

As a continuation of our studies of the coordination chemistry of naphthyridines with the tripositive rare earth ions, and in view of the fact that both nitrate and napy tend to give high coordination numbers in their complexes, we have synthesized rare earth nitrate complexes of napy in an effort to achieve complexes wherein the coordination number is greater than ten.

Experimental

Materials. Lanthanum nitrate hexahydrate was purchased from Fisher Scientific Co. and used without further purification. Rare earth oxides (99.9%

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Table I. Analytical Data and Physical Properties for $M(napy)_n(NO_3)_3$.

Compound M, n =		%C	Analysis %N	%H	Color	Conductivity [a] Λ(molar cm²-mho)	Concn. $M \times 10^3$
Y, 2	c.	35.90	18.32	2.26	white	24	0.66
	f.	35.78	18.04	2.09			
La, 3	c.	40.29	17.62	2.54	white	11	0.89
	f.	40.22	17.36	2.58			
Ce, 3	c.	40.22	17.60	2.54	yellow	13	0.75
	f.	40.45	17.37	2.58			
Pr, 3	c.	40.18	17.58	2.53	lt. green	14	0.56
	f.	40.42	17.33	2.54			
Nd, 3	c.	39.99	17.49	2.52	lt. violet	16	0.63
	f.	40.09	17.24	2.41			
Sm, 2	c.	32.20	16.44	1.85	white	15	0.46
	f.	32.26	16.26	1.88			
Eu, 2	c.	32.12	16.39	2.03	white	14	0.76
	f.	32.06	16.10	1.91			
Gd, 2	c.	31.84	16.25	2.01	white	13	0.89
	f.	31.60	16.04	2.11			
Tb, 2	c.	31.75	16.20	2.00	white	15	0.67
	f.	31.69	15.99	1.97			
Dy, 2	c.	31.56	16.11	1.99	white	19	0.81
	f.	31.38	16.02	1.92			
Ho, 2	c.	31.44	16.04	1.98	lt. orange	14	0.69
	f.	31.38	15.93	1.90			
Er, 2	c.	31.32	15.98	1.98	pink	19	0.95
	f.	31.14	15.65	1.95			
Tm, 2	c.	31.23	15.94	1.97	white	23	0.90
	f.	31.02	15.65	1.95			
Yb, 2	c.	31.02	15.83	1.96	white	25	0.72
	f.	30.98	15.68	1.86			

[a] Values obtained in nitromethane solutions at 25°. The conductivity of the 1:1 electrolyte $[(CH_3(CH_2)_3)_4N]NO_3$ in nitromethane at 25° is 90.

pure) were purchased from Molycorp, Louviers, Colorado. Triethyl orthorformate and spectral grade nitromethane were obtained from Eastman Chemical Co. Commercially available ethyl acetate and absolute ethanol, stored over molecular sieves, were used in the preparation of the complexes. Purity of 1,8-naphthyridine, prepared by the method of Paudler and Kress,[26] was verified by pmr spectroscopy.

Instrumentation. The infrared spectra (4000-200 cm^{-1}) were obtained with a Perkin-Elmer Model 621 double-beam grating spectrophotometer on Nujol-Fluorolube mulls supported between sodium chloride or polyethylene windows. All spectra were calibrated with polystyrene film. An Industrial Instruments Model RC-16B2 conductance bridge was used to determine the conductivity of nitromethane solutions of the complexes. The Sargent Model S-29885 cell was calibrated with a standard KCl solution prepared with conductance water. Magnetic moments were obtained at 24.7° using the Faraday apparatus described by DuBois and Meek.[27] Diamagnetic corrections for the metal and nitrate ions were obtained from Selwood.[28] A value of -86.8×10^{-6} cgsu was measured for napy. Carbon, hydrogen and nitrogen analyses were ascertained by combustion.

Preparations. Hydrated rare earth nitrates were prepared by dissolving the corresponding oxides in concentrated nitric acid and evaporating the solution to dryness. The requisite amount of hydrated rare earth nitrate (0.3 mmol) was dissolved in 20 ml of hot ethyl acetate and dehydrated by adding 5 ml of triethyl orthoformate and refluxing with stirring for 12 hr. To this solution was added napy (1.8 mmol) which had been dissolved in 10 ml of hot ethyl acetate. The complexes precipitated gradually over a period of a few hours. Prior to isolating the complexes by filtration, the solution was refluxed with stirring for two days. The product was recrystallized from a 3:1 ethyl acetate-absolute ethanol solution, washed with 60 ml of anhydrous ethyl ether under helium flush, and dried *in vacuo* for one week.

Results and Discussion

The analytical and conductance data for the newly synthesized complexes listed in Table I indicate that three molecules of ligand are associated with La-Nd, and two molecules of ligand are associated with the smaller Y, Sm-Yb, and in addition that all three nitrate groups are also coordinated to the metals. The tris-napy complexes exhibit a slight increase in conductivity with decreasing size of the cation, and the bis-napy complexes also show the same general trend. This is expected since steric crowding should cause a higher degree of dissociation with the smaller ions. Notably, the conductivities of the tris complexes are equal to or even less than the bis complexes. This may indicate that the larger rare earth ions can accommodate three napys and three nitrate groups as easily as the smaller ions can accomodate two napys

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Table II. Magnetic Data for $M(napy)_n(NO_3)_3$ at 24.7°.

Compound M, n =	$\chi \cdot 10^6$ cgsu	$\chi_m \cdot 10^3$ cgsu	$\chi'_m \cdot 10^3$ [a] cgsu	Experimental μ_{eff}(BM)	Theoretical [b] μ_{eff}(BM)
Y, 2	Diamagnetic				
La, 3	Diamagnetic				
Ce, 3	3.02	2.16	2.50	2.44	2.56
Pr, 3	6.12	4.39	4.73	3.37	3.62
Nd, 3	6.25	4.50	4.85	3.40	3.68
Sm, 2	1.73	1.04	1.29	1.75	1.55-1.65
Eu, 2	7.93	4.78	5.00	3.45	3.40-3.51
Gd, 2	47.0	28.4	28.6	8.2	7.94
Tb 2	71.3	43.2	43.4	10.2	9.7
Dy, 2	81.8	49.8	50.1	10.9	10.6
Ho, 2	84.1	51.4	51.7	11.1	10.6
Er, 2	62.4	38.3	38.5	9.6	9.6
Tm, 2	39.5	24.3	24.6	7.6	7.6
Yb, 2	13.16	8.15	8.41	4.47	4.5

[a] χ'_m corrected for diamagnetic contribution of metal, nitrate and napy. [b] Values are the theoretical μ_{eff}(BM) for Ln^{3+} ions. L.N. Mulay, « Magnetic Susceptibility », Interscience Publishers, Inc., New York, N.Y., 1963, p. 1776.

Table III. Vibrational Modes For Bidentate C_{2v} NO_3 in $M(napy)_n(NO_3)_3$.

Compound M, n =	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_2(A_1)$	$\nu_3(B_1)$	$\nu_5(A_1)$	$\nu_6(B_2)$	ν_1-ν_4
La, 3	1454vs, br [a]	1316vs	1039vs	821s	738s	706w	138
Ce, 3	1454vs, br	1316vs	1037vs	819s	736s	706vw	138
Pr, 3	1453vs, br	1316vs	1037vs	819s	737s	706vw	137
Nd, 3	1453vs, br	1314vs	1040vs	819s	740vs	707vw	139
Sm, 2	1469vs, br	1296vs	1027vs	813s	745s, 737vs	705w	173
Eu, 2	1468vs, br	1315vs	1022vs	818s	746s, 740vs	705w	153
Gd, 2	1470vs, br	1317vs	1022vs	816s	746s, 739vs	705w	153
Tb, 2	1470vs, br	1319vs	1022vs	816s	747s, 742vs	704m	151
Dy, 2	1470vs, br	1317vs	1026vs	818s	748s, 744vs	707w	153
Ho, 2	1469vs, br	1317vs	1026vs	817s	748s, 744vs	707w	152
Er, 2	1470vs, br	1322vs	1025vs	816s	752s, 747vs	705m	148
Tm, 2	1469vs, br	1310vs	1025vs	814s	752sh, 747vs	705m	159
Yb, 2	1470vs, br	1317vs	1027vs	817s	752s, 747vs	707vw	153
Y, 2	1470vs, br	1317vs	1029vs	820s	751sh, 746vs	708vw	153

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

and three nitrates. The compounds are indefinitely stable, but they were stored over $CaSO_4$ *in vacuo* as a precaution against any possible adsorption of water.

The magnetic moments of the complexes are listed in Table II. They compare favorably with the theoretical values, as is expected for the well-shielded 4f electrons of lanthanide ions. The moments of the napy complexes Ce-Gd and Er-Yb are less than or equal to the moments of the 2,7-dmnapy complexes, but the Tb-Ho moments are higher in the napy complexes.[17] Except for Tb-Ho, the magnetic moments of the napy series correspond quite closely to the values for the similar $Ln(phen)_2(NO_3)_3$ complexes.[13]

The infrared (4000-200 cm^{-1}) spectra of the complexes were recorded and analyzed to detect the possible presence of coordinated or lattice water, and to determine whether the nitrate groups are coordinated or ionic in nature. No bands which could be attributed to water were found in any of the spectra, establishing that the complexes are anhydrous.

Nitrate assignments based on the symmetry group C_{2v} for bidentate coordinated nitrate[29,30] are reported in Table III. Infrared spectra can aid in establishing if a nitrate group is ionic or coordinated in nature. When a nitrate group is coordinated in either a mono – or bidentate manner, the symmetry of the free nitrate group is reduced from D_{3h} to C_{2v}. Therefore, the number of vibrational modes observed in the infrared spectra alone is not sufficient to distinguish between the two forms of coordinated nitrate. Raman data, which we lack the facility to obtain, in conjunction with infrared data would provide an unequivocal assignment. However, the magnitude of separation of certain infrared active modes of nitrate appears to provide a reasonable basis for distinguishing between mono– and bidentate coordination.[31-33]

The absorption attributed to ν_3 (813-821 cm^{-1}), ν_2 (1022-1040 cm^{-1}) and ν_4 (1296-1322 cm^{-1}) are all in general agreement with the assignments of numerous authors who have synthesized various oxygen– and nitrogen-donor complexes of lanthanide nitrates, including those which contain phenanthroline, bipyr-

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Table IV. Combination Bands for $(M(napy)_n(NO_3)_3$.

Compound M, n =	$\nu_2+\nu_5$ obs.	$\nu_2+\nu_5$ calc. [a]	$\nu_2+\nu_6$ obs.	$\nu_2+\nu_6$ calc. [a]	Separation obs.	Separation calc.
La, 3	1769	1777	1739	1745	30	32
Ce, 3	1771	1773	1740	1743	31	30
Pr, 3	1771	1774	1740	1743	31	31
Nd, 3	1774	1780	1741	1747	33	33
Sm, 2	1764	1768	1730	1732	34	36
Eu, 2	1763	1765	1728	1727	35	38
Gd, 2	1774	1764	1736	1727	38	37
Tb, 2	1770	1766	1730	1726	40	40
Dy, 2	1776	1772	1736	1733	40	39
Ho, 2	1776	1772	1735	1733	41	39
Er, 2	1774	1774	1733	1730	41	44
Tm, 2	1774	1774	1731	1730	43	44
Yb, 2	1772	1776	1733	1734	39	42
Y, 2	1777	1777	1737	1737	40	40

[a] Calc. values are the sum of appropriate bands listed in Table III. Where a doublet was observed for ν_5, an average value was used.

idyl and 2,7-dmnapy as ligands.[8,10,11,17,34-39] Both ν_3 and ν_4 can be observed without ligand interference. In the tris-napy complexes, the ν_2 absorption has combined with a ligand mode to produce a very intense band. However, the ν_2 absorption in the bis-napy complexes and the ligand mode occur as a distinct doublet. The lower frequency band of the doublet is assigned to ν_2 nitrate since the sum of this band and the observed ν_5 and ν_6 nitrate modes which are clear of ligand interferences, more closely corresponds to the observed nitrate combination bands in the 1700-1800 cm^{-1} region.

This 1700-1800 cm^{-1} region which is also free from interfering ligand bands in these complexes is viewed by some authors as the key to differentiating between mono– and bidentate nitrate groups.[31,32] Ionic nitrate exhibits one band in the 1700-1800 cm^{-1} region due to the combination of the A_1' and E' modes (D_{3h} symmetry). When the nitrate group coordinates, the E' mode is split into two components, A_1 and B_2 (C_{2v} symmetry), which results in two combination bands ($A_1 + A_1$ and $B_2 + A_1$). For the same metal center it is expected that distortion of the 120° O-N-O angles of D_{3h} nitrate will be greater for bidentate rather than monodentate coordination. Thus the A_1 and B_2 modes arising out of E' and their combination bands should undergo greater separation for bidentate rather than monodentate coordination.

Mixed mono– and bidentate coordination results in a very broad band with more than two peaks in the 1700-1800 cm^{-1} region.[32] Although in all cases two distinct bands free of ligand interferences are observed in this region for our complexes, the amount of fine structure is noticeably greater for the bis– than tris-napy complexes. All bis-napy complexes exhibit a doublet ν_5 band, while no fine structure is observed on the single ν_5 absorption of the tris-napy complexes. Therefore, the fine structure observed in the combination bands of the bis-napy compounds is due at least in part to the split ν_5 absorption.

Lever, *et. al.*[32] have concluded that the combination band separation for the monodentate nitrate group is 5-26 cm^{-1}, and is 20-66 cm^{-1} for bidentate nitrate. In a series of tri-*n*-butyl phosphate complexes of rare earth nitrates in which all nitrate groups were shown to be bidentate by Raman spectroscopy, the separation range is 29-54 cm^{-1}.[34] As seen in Table IV, our $M(napy)_n(NO_3)_3$ complexes show a range of 30-44 cm^{-1} indicative of bidentate nitrate groups.

The values for the separation between the two combination modes (Table IV) are essentially the same for the observed and calculated values. Thus the difference in magnitude between the observed and calculated values for each combination mode is ascribed to error in the value reported for ν_2. Some error is expected for ν_2 since a ligand mode occurs at the same or similar energy. The agreement between observed and calculated combination values is quite good when compared with data reported for other nitrate complexes.[31]

Two bands in the range 700-750 cm^{-1}, one at 710-725 cm^{-1} (ν_3) and a stronger one at 735-750 cm^{-1} (ν_5) have been found in a series of uranyl complexes which are known to contain bidentate nitrate groups.[40] We also observe these modes in the infrared spectra of uor complexes in the regions 704-708 cm^{-1} and 736-752 cm^{-1}. The latter band occurs as a doublet in the bis-napy complexes. The ν_5 mode has been observed as a multiplet in numerous other nine– and ten-coordinate rare earth complexes[17,37,41] No ligand bands ocur in this region of the spectrum.

The ν_1 mode of coordinated nitrate has been observed over a wide range, even as low as 1430 cm^{-1} in some ethylenediamine complexes of lanthanide nitrates.[42] The position of this band is directly related to the amount of O-N-O angle distortion from D_{3h} symmetry experienced by the nitrate group, and thus to the coordination environment around the metal.[41] Steric hindrance caused by the size and/or number of ligands involved in coordination can force the nitrate groups away from the metal, weakening their coordinating ability and lowering the ν_1 frequency. Thus

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due to the steric crowding of the additional ligand molecule, the ν_1 absorption of the $M(napy)_3(NO_3)_3$ complexes is at a lower frequency than in the $M(napy)_2(NO_3)_3$ complexes The ν_1 band is broad in all the compounds due to the occurrance of ligand bands in this region.

The difference between the ν_1 and ν_4 frequencies, designated as Δ, is a measure of the dissymetry arising in the nitrate group.[33] For a covalent nitrate such as CH_3NO_3 $\Delta = 385$ cm^{-1}, whereas for an ionic nitrate such as $NaNO_3$ $\Delta = 0$. In our $M(napy)_3(NO_3)_3$ complexes Δ is 139-137 cm^{-1}. The $M(napy)_2(NO_3)_3$ complexes exhibit Δ values in the range 173-148 cm^{-1} indicating stronger bonded nitrate groups which is again consistent with steric considerations.

The vibrational modes of uncomplexed napy have been assigned.[43] Skeletal modes which undergo significant change, indicating ligand coordination, are those at 403, 600, 760, 1026, 1045, 1128 and 1556 cm^{-1}. For all the complexes reported herein these modes are observed at 417 $\pm$ 3, 622 $\pm$ 4, 781 $\pm$ 4, 1035 $\pm$ 4, 1054 $\pm$ 2, 1135 $\pm$ 2, and 1581 $\pm$ 5 cm^{-1}. The band positions for the $Fe(napy)_4(ClO_4)_2$ complex wherein napy is unequivocally bidentate are 419, 618, 780, 1032, 1055, 1138 and 1580 cm^{-1}.[44] As in the spectrum of $M(2,7\text{-dmnapy})_2(NO_3)_3$, M = La-Yb, and $M(napy)_2(ClO_4)_2$, M = Ca, Sr, Ba,[45] no frequencies assignable to νM-O or νM-N were observed for the $M(napy)_n(NO_3)_3$, M = La-Yb complexes. For $Y(napy)_2(NO_3)_3$ a band at 228 cm^{-1}, similar to the 229 cm^{-1}, band for $Y(2,7\text{-dmnapy})_2(NO_3)_3$[17] was assigned to νM-O. In anhydrous rare earth nitrates νM-O is observed from 270-180 cm^{-1}.[46]

Further evidence that napy is bidentate in these complexes is derived from the pmr spectra (to be completely treated in a separate paper) of the Y, La, and Sm complexes[1a] The 2– and 7– protons yield a sharp resonance pattern typical of equivalent protons, thus suggesting bidentate instead of monodentate coordination. Similar spectra have been observed for the $M(CO)_3napyX$, M = Mn, Re and X = Cl, Br, NO_3, series of complexes wherein napy is bidentate in nature.[47]

Conclusions

The crystal structures of the compounds $La(bipy)_2(NO_3)_3$[13] and $Tb(bipy)_2(NO_3)_3$[14] have shown that these species are ten-coordinate with all nitrate groups bound in a bidentate manner. Other lanthanide nitrate species also display ten-coordinate geometry as verified by crystallographic investigations.[15,16] The complexes $M(2,7\text{-dmnapy})_2(NO_3)_3$ synthesized in this laboratory also appear to be ten-coordinate.[17] Considering the data presented herein and the physical similarity between the napy compounds and the analogous phen, bipy, and 2,7-dmnapy complexes, we believe the bis-napy species to be ten-coordinate.

The nitrate group has been known to produce coordinate species such as $Co(NO_3)_4^{2-}$,[20] $Mn(NO_3)_4^{2-}$[21] and $Zn(NO_3)_4^{2-}$[21] which possess the high coordination number of eight. It has also been shown that napy displays this same tendency to yield eight-coordinate species with the first row transition metals as evidenced by the complexes $M(napy)_4(ClO_4)_2$ where M = Mn, Fe, Co, Ni, Cu and Zn.[22-25] Although coordination numbers higher than ten for the lanthanide ions are uncommon, the crystal structures of the compounds $Ce_2Mg_3(NO_3)_{12} \cdot 24M_2O$[18] and $(NH_4)_2Ce(NO_3)_6$[19] verify that in each compound the cerium atoms are twelve-coordinate, *i.e.*, surrounded by six bidentate nitrate groups. The salts of $Nd(NO_3)_6^{3-}$ and $Sm(NO_3)_6^{3-}$ are claimed to exist, and from infrared studies in the 1700-1800 cm^{-1} region are assumed to be twelve-coordinate.[32] In light of the data we have accumulated, and considering the ability of both the nitrate group and napy to form complexes of high coordination number, we believe the complexes $M(napy)_3(NO_3)_3$ are twelve-coordinate.

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