Investigation on the Rare Earth Terpyridyl System

IV. Terpyridyl Complexes of Higher Lanthanides

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The preparation of terpyridyl chelates of heavier rare earths of the type $M(Terp)(NO_3)_3 \cdot n\,H_2O$ ($M = Tb - Yb$ and $n = 0 - 3$) is described. The infrared studies of the solid chelates show the coordinated nature of both terpyridyl and nitrate groups. A spectrochemical series based on the shift of the "breathing" vibration of terpyridyl in the complexes is proposed.

In earlier papers [1, 2] the preparation and spectral studies of the terpyridyl complexes of lighter lanthanides have been presented. The fluorescence properties of Dy^{3+} and Tm^{3+} terpyridyl complexes are also discussed [3]. This communication deals with the preparation and characterization of the terpyridyl complexes of heavier lanthanides (Tb – Yb) and their infrared spectra.

Results and Discussion

The rare earth-mono-terpyridyl nitrate complexes have been isolated and their infrared spectra have been studied. The representative spectra for anhydrous and hydrated complexes are given in Fig. 1, and the observed infrared bands between 4000 and 700 cm^{-1} are tabulated in Table 1 with possible assignment.

(a) Terpyridyl Vibrations

In these spectra, the terpyridyl vibrations show the same trend as before [1] on coordination. However, the presence of nitrate group has complicated the spectra and some mixing of vibrations is unavoidable.

A larger shift towards higher wavenumbers of the 1600 cm^{-1} (C = C and C = N) band group is ob-

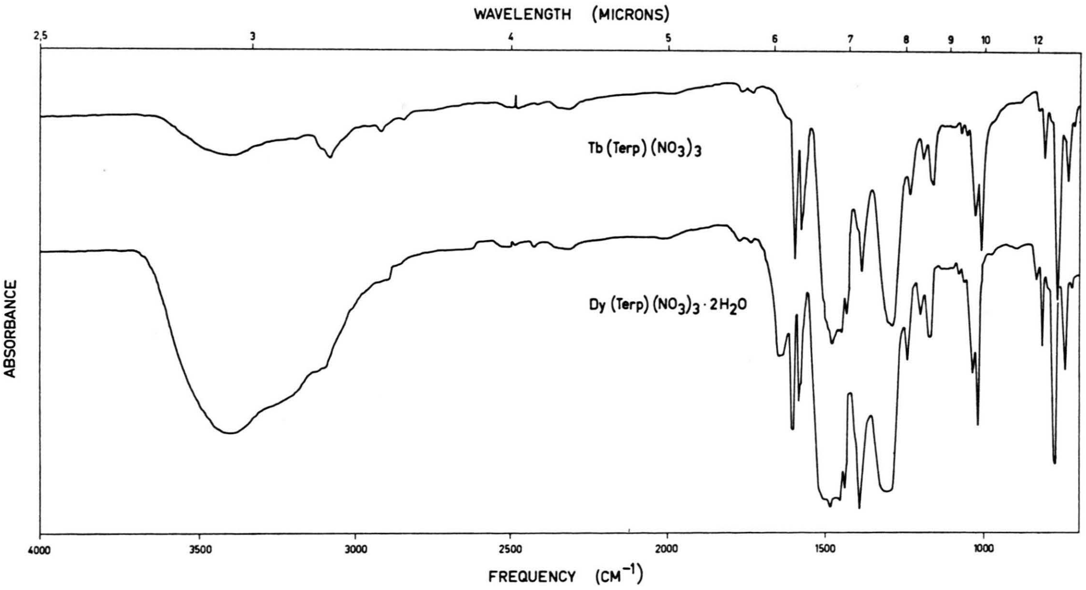

Fig. 1. Infrared absorption spectra of typical rare earth-mono-terpyridyl nitrate complexes.

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[1] S. P. SINHA, Z. Naturforschg. **20 a,** 552 [1965].
[2] S. P. SINHA, Z. Naturforschg. **20 a,** 164 [1965].
[3] S. P. SINHA, Z. Naturforschg. **20 a,** 835 [1965].

Tb(Terp)	Dy(Terp)	Ho(Terp)	Er(Terp)	Tm(Terp)	Yb(Terp)	Assignments
—	~ 3400	~ 3410	~ 3410	~ 3410	~ 3410	O–H stretching
— —	1650 1635	1654 1636	(1646) 1638	(1649) 1640	1640	H–O–H bending
1607 1586 (1579) (1567)	1608? 1602 1585 (1579) (1570)	1608 1586 (1570)	1608 1587 (1578) (1573)?	1610 1587 (1570)	1610 1588 (1575)	terpyridyl band (C=N, C=C)
1487[a]	1485	1488	1488	1518 1490	1520 1490	ν_4 nitrato group (asym. NO_2 stretching)
1467 1457 1439	1454 1439	1459 1441	1456 1440	1470 1460	1470 1460 1447	terpyridyl band
1395	1392	1395	1391	1395	1398	ν_3 nitrate ion[b]
(1309) 1297	(1315) 1299	1318 1301	(1320) 1293	(1320) 1300	(1315)? 1305	ν_1 nitrato group (sym. NO_2 stretching)
1242 1200 1168	1242 1202 1170	1244 1203 1170	1243 1201 1178 1170	1245 1202 1172	1249 1206 1174	ring vibration ortho substituted pyridine vibration
1037[a]	1035	1039	1036	1035	1040	ν_2 of nitrato group (NO stretching)
1017	1020	1021	1020	1025	1028	pyridine ring breathing
837	835	836	836	837	840	ring hydrogens
817	818	816	818	818	819	ν_6 nitrato group (out of plane rocking)
777	778	781	778	782	785	ring hydrogens
742	745	746	748	750	750	ν_3 nitrato group

[a] smaller peaks on high wavenumber side are present
[b] the nitrate ion absorption peak resulted due to anion exchange with the disk material.

Table 1. Infrared frequencies of rare earth-mono-terpyridyl nitrato complexes in cm^{-1}. Only the peak maximum and prominent shoulders in parenthesis are given.

served in the present case as compared to the complexes of lighter lanthanides. The band group between 1400 and 1500 cm^{-1} for terpyridyl is strongly influenced by the nitrate vibration frequency in this region. The author believes that the bands higher than 1490 cm^{-1} are due to nitrate vibration and below it are possibly the terpyridyl vibrations. However, one can identify the pyridine ring "breathing" vibration around 1020 cm^{-1} for the coordinated terpyridyl beside the nitrate vibration at ~1035 cm^{-1} (see below). It has been found that the "breathing" vibration is particularly sensitive to metal ions[4]. Taking the shift of the "breathing" vibration in the rare earth terpyridyl complexes with respect to the free ligand[1] (988 cm^{-1}) as a measure of metal-ligand interaction we can construct a spectrochemical series with increasing "interaction" as follows:

M^{3+}	Pr ≈ Nd ≈ Gd	< Sm	< Tb	< Eu	< Ho	< Ce ≈ Dy ≈ Er	< Tm	< Yb
$\Delta\nu$ (cm^{-1})	27	28	29	30	31	32	37	40

Although a general trend of increase in $\Delta\nu$ is observed with the increase in atomic numbers in the rare earth series (i. e. decrease in ionic size of the trivalent rare earths) one can easily see that certain discontinuity do exist. It is also quite interesting to see the break in the Eu–Gd–Tb region, compatible with the observations in the measurements of stability constants[5].

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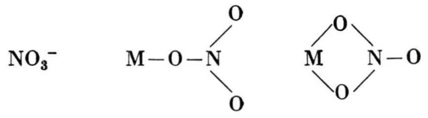
[4] S. P. Sinha, Spectrochim. Acta **20**, 879 [1964]; Z. Chem. **4**, 150 [1964].

[5] For a general discussion of the stability constants of various rare earth complexes see S. P. Sinha, Complexes of the Rare Earths, Pergamon Press, Oxford 1965.

(b) Nitrate Group Vibrations

The change of vibrational frequencies with the change of symmetry from nitrate ion (NO_3^-), belonging to D_{3h} point group, to the nitrato group in the coordinated nitrato complex (both unidentate and bidentate nitrato group possess C_{2v} symmetry) has been discussed by several authors [6–8]. In going from $D_{3h} \rightarrow C_{2v}$ and consequently a lowering of symmetry gives rise to the following change of infrared frequencies.



	(D_{3h})	(C_{2v})	(C_{2v})
NO stretch	1050 (ν_1)	1000 (ν_2)	1630 (ν_1)
NO_2 stretch	1390 (ν_3)	1290 (ν_1) sym. 1550 – 1480 (ν_4) asym.	980 (ν_2) sym. 1250 (ν_4) asym.
NO_2 bend	720 (ν_4)	740 (ν_3) sym. 715 (ν_5) asym.	785 (ν_3) sym. 750 (ν_5) asym.
out of plane rocking	830 (ν_2)	800 (ν_6)	700 (ν_6)

Of the characteristic nitrate ion frequencies only ν_1 (1050 cm^{-1}) is infrared inactive and the other three are infrared active. In both unidentate and bidentate nitrato complex the former 1050 cm^{-1} frequency becomes infrared active and appears as a strong peak due to reduction of symmetry. There is also considerable difference in the higher frequency region (NO and NO_2 stretching bands) between unidentate and bidentate nitrato group. However, it is believed [8, 9] that the high frequency of terminal NO stretching at ~1630 cm^{-1} found in $Sn(NO_3)_4$ and $Ti(NO_3)_4$ is due to the influence of high metal oxidation states, Sn(IV) and Ti(IV). In some cases where the X-ray results point out the presence of bidentate nitrato group [10], the infrared spectrum cannot distinguish the uni or bidentate nature of the nitrato group and shows roughly the same frequencies as that of the unidentate one.

Except for the ~1400 cm^{-1} band, which is resulted due to the anion exchange with the pelleting material (KBr) giving nitrate ion, the infrared spectra of the complexes studied show the coordinated nature of the nitrato group. It is however difficult to judge from the recorded spectra whether the nitrate group is unidentate or bidentate in view of the above discussion. In Table 1 we have given the unidentate assignments of the nitrato group frequencies.

Katzin [11] has considered the splitting of the asymmetric (ν_4) and symmetric (ν_1) NO_2 stretching frequency of the nitrato group (unidentate) as a measure of the coordinated nature of this group. In case of ionic nitrate there is no *a priori* criteria of the splitting of the stretching frequency (ν_3), although in some cases [12], especially in TBP solutions [11], a maximum splitting of ~100 cm^{-1} was observed. The coordinated nitrato groups however show a separation of ~200 cm^{-1} for the symmetric and asymmetric NO_2 stretching. Thus he considered the boarder-line of the empirical division between essentially electrostatic splitting and splitting due to coordination is around 100 cm^{-1}. Another thought-provoking relation of examining the ratio ν_{sym}/ν_{asym} of the NO_2 stretching frequency arise. The author has examined a number of cases taking the values given in literature. It seems that the ν_{sym}/ν_{asym} ratio of NO_2 stretching frequency may be conveniently used for distinguishing the bonding character of the nitrate. The following classification is proposed:

nitrates	ν_{sym}/ν_{asym}
ionic	0.95 – 0.9
coordinated	~0.9 – 0.8
"purely" covalent	below 0.8

Methyl nitrate has a value of ~0.77 and that for bidentate $Sn(NO_3)_4$ is 0.78.

The rare earth-mono-terpyridyl nitrate complexes show a ν_{sym}/ν_{asym} value of ~0.86 eg. the coordinated nitrate group, allowing for the fact that the exact location of the ν_1 frequency is somewhat complicated due to the presence of terpyridyl bands.

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[6] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, J. Inorg. Nucl. Chem. **8**, 75 [1958].

[7] C. C. Addison and B. M. Gatehouse, J. Chem. Soc. **1960**, 613.

[8] C. C. Addison and W. B. Simpson, J. Chem. Soc. **1965**, 598.

[9] C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, Proc. Chem. Soc. **1964**, 367.

[10] For example $[Co(O_2NO)_4]^{2-}$ ion shows the presence of bidentate nitrato group (X-ray studies), F. A. Cotton and J. G. Bergman, J. Amer. Chem. Soc. **86**, 2941 [1965], whereas the infrared spectrum differs very little from that of unidentate nitrato group.

[11] L. I. Katzin, J. Inorg. Nucl. Chem. **24**, 245 [1962].

[12] S.-I. Mizushima and J. V. Quaglino, J. Amer. Chem. Soc. **75**, 4870 [1953].

Experimental

The complexes were prepared according to the previous method[1]. The results of microanalysis are presented below. For the hydrated complexes, the amount of water was at first determined and then the analysis was carried out on the anhydrous samples.

Calc. for $Tb(C_{15}H_{11}N_3)(NO_3)$: C, 31,2; H, 1.9; N, 14.5. Found C, 31.7; H, 1.7; N, 14.9. — Calc. for $Dy(C_{15}H_{11}N_3)(NO_3)_3 \cdot 2\,H_2O$: H_2O, 5,8; C, 30.9; H, 1.9; N, 14.4. Found H_2O, 5.3; C, 30.2; H, 1.9; N, 13.9. — Calc. for $Ho(C_{15}H_{11}N_3)(NO_3)_3 \cdot 2\,H_2O$: H_2O, 5.8; C, 30.8; H, 1.9; N, 14.4. Found H_2O, 5.2; C, 30.8; H, 2.0; N, 14.1. — Calc. for $Er(C_{15}H_{11}N_3)(NO_3)_3 \cdot 3\,H_2O$: H_2O, 8.4; C, 30.7; H, 1.8; N, 14.3. Found H_2O, 8.2; C, 30.4; H, 1.6; N, 14.1. — Calc. for $Tm(C_{15}H_{11}N_3)(NO_3)_3 \cdot H_2O$: H_2O, 2.9; C, 30.7; H, 1.8; N, 14.2. Found H_2O, 3.0; C, 30.4; H, 2.0; N, 13.9. — Calc. for $Yb(C_{15}H_{11}N_3)(NO_3)_3 \cdot H_2O$: H_2O, 2.9; C, 30.4; H, 1.8; N, 14.2. Found H_2O, 2.9; C, 30.7; H, 1.4; N, 14.2.

The infrared spectra were measured with a Perkin Elmer 221 Spectrophotometer using KBr pellet technique. Anion exchange has taken place during the process as expected and peak due to nitrate ion vibration has been observed in these spectra.

Acknowledgement

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Schwingungsspektroskopische Untersuchungen anorganischer Festkörper IX[1]

Infrarotspektren von $Ni(NH_3)_3CS_3$ und $Zn(NH_3)_2CS_3$

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The infrared absorption frequencies of crystalline $Ni(NH_3)_3CS_3$, $Ni(ND_3)_3CS_3$, $Zn(NH_3)_2CS_3$, and $Zn(ND_3)_2CS_3$ between 4000 and 300 cm^{-1} are tabulated. The absorption bands corresponding to the fundamental vibrations are assigned. The positions of the bands are discussed in comparison with spectra of other ammine complexes and of non-complex trithiocarbonates.

Über schwingungsspektroskopische Untersuchungen an Trithiocarbonaten der Übergangsmetalle liegen bisher keine Angaben in der Literatur vor[2]. Da derartige Messungen wahrscheinlich Aussagen über die Art der Bindung der CS_3-Gruppe am Metallion zulassen, haben wir Infrarot-Festkörperspektren von $Ni(NH_3)_3CS_3$ und $Zn(NH_3)_2CS_3$ sowie von den perdeuterierten Derivaten dieser Verbindungen gemessen.

In Tab. 1 sind die im Bereich zwischen 4000 und 300 cm^{-1} ermittelten Absorptionsmaxima (Grundschwingungen) für alle vier dargestellten Verbindungen zusammengefaßt.

Aus der Untersuchung zahlreicher Komplexverbindungen der Übergangsmetalle geht hervor[3], daß sich die Kraftkonstanten innerhalb der Liganden beim Einbau in einen Komplex im allgemeinen nicht stark ändern und daß keine starke Kopplung der Schwingungen eines Liganden mit anderen Schwingungen erfolgt. Die relativ schwache Kopplung verhindert in den meisten Fällen eine im Spektrum deutlich sichtbare Aufhebung von Entartungen innerhalb der Liganden. Die Schwingungen des Komplexes lassen sich somit in guter Näherung in Ligandenschwingungen und Gerüstschwingungen aufteilen.

Im vorliegenden Fall ist es sicher sinnvoll, die Schwingungen einem Modell zuzuordnen, das aus einer $Me-NH_3$-Gruppierung[4] und einer

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[1] VIII. Mitteilung: B. KREBS u. A. MÜLLER, Z. Naturforschg. **20 a**, 1124 [1965]; zugleich XIX. Mitteilung über Chalkogenocarbonate; XVIII. Mitteilung dieser Reihe ist die oben als erste angegebene Arbeit.

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[3] R. G. WILKINS, The Infrared Spectra of Transition Metal Complexes, in Modern Coordination Chemistry, Interscience Publ., New York 1960.

[4] Vgl. hierzu K. NAKAMOTO, Infrared Spectra of Inorganic and Coordination Compounds, Wiley & Sons, New York und London 1963.