Inorganica Chimica Acta, *82* (1984) 173–181

The Donor Properties of 2,2′-Biquinolyl-N,N′-dioxide. I. Lanthanide(III) and Dioxouranium(VI) Complexes

A. SEMINARA, A. MUSUMECI and A. CHISARI

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università, viale A. Doria 8, 95125 Catania, Italy

Received June 10, 1983

Several new complexes of lanthanide(III) nitrates, perchlorates, chlorides and trifluoromethanesulfonates with the ligand 2,2′-biquinolyl-N,N′-dioxide and the parent 2,2′-biquinolyl, have been prepared and characterized. Information on the electron-donating power of the ligands and the geometry of the complexes has been inferred from the absorption and emission f–f spectra. Uncommonly high values for the intensity of the hypersensitive transitions have been measured for the complexes with 2,2′-biquinolyl-N,N′-dioxide. A drop in symmetry has been observed with respect to the corresponding complexes with 2,2′-bipyridyl-N,N′-dioxide. Complexes of dioxouranium(VI) nitrate, perchlorate and trifluoromethanesulfonate with biquO$_2$ *and biqu have also been prepared and characterized.*

Introduction

The donor properties of heterocyclic aromatic amine-N-oxides in complexes with metal ions have been extensively studied in recent years. It has been established that seven-membered metal chelate rings form with appropriate ligands. With poly-oxygen donor molecules, stable complexes can be formed if the ligand assumes suitable conformation or yields polymeric species. Steric considerations suggest that when 2,2′-bipyridyl-N,N′-dioxide acts as a chelating ligand in metal complexes it must adopt a non-planar conformation. Chelation requires in fact that the plane of one of the pyridine-N-oxide rings is rotated with respect to the other, giving rise to a distorted (staggered) conformation. On the other hand, non-planar conformation has been suggested for this ligand in the solid state [1].

Several complexes of metal ions with the bidentate ligand 2,2′-bipyridyl-N,N′-dioxide (bipyO$_2$) have been reported in the past years. This ligand acts as a strong ligand towards lanthanide(III) cations [2]. Complexes also form in aqueous solutions. The synthesis and spectra of the complexes of lanthanide(III) and dioxouranium(VI) cations with the ligand 2,2′-biquinolyl-N,N′-dioxide (biquO$_2$) are reported in this paper. This molecule is remarkably bulkier than bipyO$_2$ and is expected to give rise to complexes less rich in ligand and/or to weaken the metal–oxygen bonds.

The synthesis and spectra of some complexes of lanthanide(III) and dioxouranium(VI) cations with the parent 2,2′-biquinolyl (biqu) are also reported.

Experimental

Complexes of biquO$_2$ and biqu with lanthanide(III) and dioxouranium(VI) nitrates, perchlorates, chlorides and trifluoromethanesulfonates were prepared.

Materials

Metal trifluoromethanesulfonates were prepared according to a previous procedure [3]. The salts were heated at 150 °C for 1 hr at reduced pressure (~10^{-2} mm Hg) and immediately dissolved in the appropriate anhydrous solvent. The ligand 2,2′-biquinolyl-N,N′-dioxide was prepared following the Nakano procedure [4] and recrystallized from ethanol. Required for $C_{18}H_{12}N_2O_2$: %C = 74.99; %H = 4.20; %N = 9.72; found: %C = 74.37; %H = 4.11; %N = 9.58.

Preparation of the Complexes

Complexes with biquO$_2$

Complexes of biquO$_2$ with lanthanide(III) and uranyl nitrates, perchlorates, chlorides and trifluoromethanesulfonates were easily obtained by mixing and stirring 1 mmol of the cation in 10 ml of hot anhydrous ethanol with 2.0 (nitrates) or 4.0 (perchlorates, trifluoromethanesulfonates, chlorides) mmol of the ligand dissolved in the minimum requir-

0020-1693/84/$3.00

TABLE I. Selected Analytical Data and Molar Conductivity of Uranyl and Lanthanide Complexes with 2,2'-Biquinolyl-N,N'-dioxide ($biquO_2$). In parentheses the calcd. values.

Complex	Ln	n	%C	%H	%N	%M	Λ_M^{a}
$Ln(biquO_2)_4(ClO_4)_3 \cdot nH_2O$	La	1	53.11(53.76)	2.98(3.13)	7.05(6.97)	8.45(8.64)	285
(Ln = La–Ho)	Nd	1	52.63(53.58)	3.03(3.12)	6.76(6.94)	9.12(8.94)	280
	Eu	1	53.07(53.36)	3.18(3.11)	6.83(6.91)	9.52(9.37)	315
	Ho	2	51.90(52.33)	3.08(3.17)	6.55(6.78)	9.77(9.98)	320
$Ln(biquO_2)_3(ClO_4)_3 \cdot nH_2O$	Yb	2	48.37(47.26)	3.10(2.94)	6.25(6.12)	12.33(12.61)	290
(Ln = Tm–Lu)							
$Ln(biquO_2)_4(CF_3SO_3)_3 \cdot nH_2O$	La	1	52.09(51.26)	2.77(2.87)	6.05(6.38)	8.13(7.90)	287
(Ln = La–Ho)	Nd	1	51.63(51.10)	2.70(2.86)	5.98(6.36)	8.45(8.18)	275
	Eu	2	50.74(50.37)	3.12(2.93)	6.01(6.27)	8.20(8.50)	295
	Ho	2	49.84(50.01)	3.18(2.91)	5.86(6.22)	8.95(9.16)	320
$Ln(biquO_2)_2(NO_3)_3 \cdot nH_2O$	La	0	47.20(47.96)	2.90(2.68)	10.69(10.88)	15.18(15.41)	12
(Ln = La–Tm)	Nd	0	46.62(47.68)	2.48(2.67)	10.57(10.81)	15.74(15.91)	22
	Eu	0	46.44(47.27)	2.82(2.65)	10.39(10.72)	16.99(16.62)	16
	Ho	2	43.81(44.87)	3.15(2.93)	9.73(10.18)	17.80(17.12)	75
	Tm	2	45.07(44.68)	3.21(2.92)	9.82(10.13)	17.14(17.46)	98
$En(biquO_2)_4Cl_3 \cdot 2H_2O$ (Nd, Eu)	Eu	2	58.26(59.74)	3.55(3.62)	7.38(7.74)	10.93(10.50)	
$UO_2(biquO_2)_3(CF_3SO_3)_2$			46.02(46.93)	2.65(2.53)	5.54(5.87)	16.95(16.61)	178
$UO_2(biquO_2)(NO_3)_2$			31.89(31.68)	1.61(1.47)	7.69(8.21)	35.64(34.89)	10

^{a}Ohm^{-1} cm^2 M^{-1}, at 25 ± 0.1 °C, in solution of a mixture of acetonitrile and chloroform (3:1); c = 0.9–1.6 × 10^{-3} M. In the same mixture of solvents the molar conductivity or pyridinium salts is, as average value, 112 ohm^{-1} cm^2 M^{-1}, c = 1.8–2.0 × 10^{-3} M.

ed volume of hot ethanol. Microcrystalline products rapidly formed; they were immediately filtered off, washed with hot ethanol, and dried *in vacuo* at room temperature.

Complexes with biqu

A boiling solution of uranyl or lanthanide(III) nitrate or perchlorate (1 mmol) in anhydrous ethanol was mixed with a boiling solution containing 1.0 (nitrates) or 2.0 (perchlorates) mmol of biqu in benzene. The complexes precipitated slowly by stirring and reducing the volume of the solution. The precipitates were rapidly filtered off, washed with a mixture of hot ethanol and benzene (1:5) followed by benzene alone, and dried *in vacuo* at room temperature.

Measurements

IR spectra were obtained with a Perkin-Elmer 684 spectrophotometer on samples suspended in a KBr or CsBr matrix, or mulled with mineral oil. Electronic absorption spectra were recorded with a Perkin-Elmer 330 spectrophotometer on solutions of the complexes in methanol or mixtures of acetonitrile and chloroform. The diffuse reflectance spectra were determined with the same instrumet on solid compounds pasted with nujol and spread on a disk of filter paper. Other experimental procedures (electrolytic conductivity measurements, thermal analysis and fluorescence spectra) were as described previously [2].

Results and Discussion

The reaction between the bulky $biquO_2$ and lanthanide(III) chlorides, perchlorates and trifluoromethanesulfonates in ethanol yields powdered crystals of various complexes. The latter, in spite of the great steric hindrance of the ligand, can be formulated on the basis of their analyses, electrolytic conductivity, thermal analysis and IR data, as the chlorides, perchlorates and trifluoromethanesulfonates of the tetrakis(2,2'-biquinolyl-N,N'-dioxide)-lanthanide(III) cations: $[Ln(biquO_2)_4]X_3 \cdot nH_2O$, where X = Cl, ClO_4, CF_3SO_3; Ln = La–Ho; n = 0–2. Tris($biquO_2$) complexes formed with the heaviest cations (Table I). All complexes were yellow, soluble in mixtures of acetonitrile and chloroform, but insoluble in water and alcohols. Molar conductivity values indicate 1:3 electrolytic behaviour. These complexes generally contain one or two molecules of water which is retained up to relatively low temperature (70–90 °C). The dehydrated complexes remain unaltered up to 270–280 °C.

When the nitrate is used as the counter ion, only bis(2,2'-biquinolyl-N,N'-dioxide)lanthanide(III) complexes were obtained. In this case the cation coordinates, also with three or two bidentate nitrato groups.

TABLE II. Selected Analytical Data and Molar Conductivity of Lanthanide and Uranyl Complexes with 2,2′-Biquinolyl (biqu). In parentheses the calcd. values.

Complex	Ln	n	%C	%H	%N	%M	Λ_M[a]
$Ln(biqu)(NO_3)_3 \cdot nH_2O$	La	3	34.90(34.03)	3.00(2.86)	10.78(11.03)	22.10(21.87)	10
(Ln = La–Tm)	Nd	3	32.83(33.75)	2.91(2.83)	10.60(10.93)	22.73(22.52)	13
	Eu	3	33.12(33.34)	3.07(2.80)	10.57(10.80)	23.31(23.44)	7
	Ho	2	32.97(33.61)	2.63(2.51)	10.92(10.89)	25.58(25.64)	9
$Ln(biqu)_2(ClO_4)_3 \cdot nH_2O$	La	3	43.56(43.07)	3.15(3.01)	5.41(5.58)	13.53(13.84)	85
(Ln = La–Er)	Nd	3	42.37(42.84)	2.98(3.00)	5.28(5.55)	14.70(14.29)	93
	Eu	3	41.88(42.52)	3.20(2.97)	5.23(5.51)	14.65(14.94)	102
	Ho	3	40.74(41.98)	3.07(2.94)	5.09(5.44)	15.48(16.01)	98
$UO_2(biqu)(NO_3)_2 \cdot 2H_2O$			31.15(31.50)	2.78(2.35)	7.79(8.16)	35.40(34.68)	8

[a] Ohm^{-1} cm^2 M^{-1}, at 25 ± 0.1 °C, in solution of a mixture of acetonitrile, chloroform and benzene (1:1:2); c = 0.8–1.3 × 10^{-3} *M*. In the same mixture of solvents the molar conductivity of pyridinium salts is, as average value, 64 ohm^{-1} cm^2 M^{-1}; c = 1.6 × 10^{-3} *M*.

Both bipyO$_2$ [2] and biquO$_2$ thus have difficulty in replacing coordinated anions, namely nitrate. These complexes lose their molecules of water between 60 and 90 °C and decompose thermally at 250–260 °C through an exothermic multistep process. Molar conductivity values indicate that the complexes of light cations behave as non-electrolytes, while values afforded by the complexes of heavy cations suggest ionization of one nitrate group.

Like its dioxide derivative, 2,2′-biquinolyl is very bulky; by contrast, it acts as a weak ligand towards lanthanide(III) cations. The prepared complexes are yellow, insoluble in non-polar solvents, and decompose by exposure to the air moisture or by dissolution in alcohols and acetonitrile. The nitrate complexes behave as non-electrolytes while conductivity values for the perchlorate complexes indicate that not all perchlorate groups are ionic (Table II).

IR Spectra

Ligand modes

The IR spectra of the complexes with biqu, in comparison with that of free ligand, show those enhancements that have been normally associated with N-coordination. The new and asymmetric band at 1380 cm^{-1} arises from an activated vibration due to a lowering in symmetry owing to the distortion away from coplanarity undergone by the ligand upon coordination.

To our knowledge, the IR spectrum of biquO$_2$ has never been reported. The rich spectrum shows in the range 1340–1120 cm^{-1}, where the NO stretching mode is expected, eight bands which, except for the two strong and asymmetric bands at 1333 and 1212 cm^{-1}, are also shown (though enhanced in intensity and position) by the parent 2,2′-biquinolyl.

It is known that electron-releasing substituents in heterocyclic aromatic amine-N-oxides increase the contribution of the NO single-bond canonical forms and thus shift the NO stretching mode to lower frequencies. Shindo [5] suggests that the NO stretching mode is not a pure vibration in quinoline-N-oxides but that it is coupled with aromatic ring vibrations, this amounting to a lowering of the energy of the π-system. Pyridine-N-oxide exhibits the ν(NO) mode at 1265 cm^{-1} while quinoline-N-oxide and isoquinoline-N-oxide exhibit these vibrations respectively at 1229 and 1182 cm^{-1}. We tentatively assign the band at 1212 cm^{-1} to the NO-stretching mode.

The band at 1333 cm^{-1} may be due to an activated vibration because of the distortion that 2,2′-biquinolyl undergoes upon dioxidation. Like bipyO$_2$ this molecule would not exist in coplanar conformation in the solid state. This band shifts at 1350–1355 cm^{-1} in the spectra of the complexes.

Similarly, the strong absorption shown by the uncoordinated ligand at 813 cm^{-1} can be attributed to the NO bending mode. The splitting or asymmetry of these bands agrees with a non-symmetrical (non-coplanar) conformation.

In the spectra of the complexes the band at 1212 cm^{-1} splits and shifts to lower frequencies (Table III) as a result of oxygen to metal coordination. The barycentre of this band lies between 1200 and 1195 cm^{-1}, thus representing a small shift. It is relatively smaller than the 30–40 cm^{-1} shifts observed for the corresponding bipyO$_2$ complexes [2]. Since biquO$_2$ is remarkably bulkier than bipyO$_2$, it is reasonable to expect that for the biquO$_2$ com-

TABLE III. Infrared Frequencies (cm^{-1}). L = 2,2′-biquinolyl-N,N′-dioxide ($biquO_2$): L_I = 2,2′-biquinolyl (biqu).

	Assignment				
	$\nu(NO)$	$\nu(M–X)$ (X = O, N)	$\nu_3(UO_2)$		Anion modes
$biquO_2$	1212s, 1200sh				
$Ln(L)_4(CF_3SO_3)_3 \cdot nH_2O$	1206–1204m 1196–1194s	352–348mbr		1280sbr, 1033s, 640s[a]	$\nu_4(E)$, $\nu_1(A_1)$ and $\nu_3(A_1)$ modes of $–SO_3$ group having C_{3v} symmetry
$UO_2(L)_3(CF_3SO_3)_2 \cdot 2H_2O$	1195sbr	358sbr	905s	1280sbr, 1033s, 640s[a]	
$Ln(L)_4(ClO_4)_3 \cdot nH_2O$	1206–1204m 1196–1194s	353–348mbr		1095vs, 624s	ν_3 and ν_4 modes of ClO_4 group having T_d symmetry
$UO_2(L)_3(ClO_4)_2$	1197s, 1193sh	355sbr	908s	1090vs, 624s	
$UO_2(L)(NO_3)_2$	1200m, 1195s	360sbr	928vs	1775w, 1730w, 1530vs[b] 1280s, 1020s, 805m	$\nu_2 + \nu_5$, $\nu_2 + \nu_6$, ν_1, ν_4, ν_2 and ν_3 modes of NO_3 group having C_{2v} symmetry and ν_3 mode in D_{3h} symmetry
$Ln(L)_2(NO_3)_3 \cdot nH_2O$	1207–1205m	354–350mbr		1775w, 1730w, 1480s [b]	
(Ln = La–Ho)	1195–1193s			1310s, 1040m, 818m	
(Ln = Tm–Lu)	1195–1193s	354–350mbr		*idem* + 1390s	
$UO_2(L_I)(NO_3)_2 \cdot 2H_2O$		c	930s	1775w, 1730w, 1530vs 1280s, 1020s, 803m, 740m	$\nu_2 + \nu_5$, $\nu_2 + \nu_6$, ν_1, ν_4, ν_2, ν_3 and ν_5 modes of NO_3 group having C_{2v} symmetry
$Ln(L_I)(NO_3)_3 \cdot nH_2O$		c		1775w, 1730w, 1480s, 1310s, 1035m, 812m, 745m	
$Ln(L_I)_2(ClO_4)_3 \cdot nH_2O$		c		1150s, 1110s, 1070m, 940w, 1095s, 625sbr	ν_1, ν_6, ν_8, ν_2 modes of ClO_4 group having C_{2v} symmetry and ν_3 and ν_4 modes in T_d symmetry

[a] $\nu_2(A_1)$, $\nu_5(E)$ and $\nu_6(E)$ bands are masked by ligand absorptions. [b] ν_5 and ν_6 bands are masked by ligand absorptions. [c] The attribution of the $\nu(M–N)$ is doubtful or not observed in these complexes. In the spectra of the complexes $M(biqu)(NO_3)_2$, where M = Co, Ni, Cu, this band appears respectively at 292, 295 and 320 cm^{-1} [7].

plexes the metal–oxygen bond becomes weaker by a steric interaction not only between the metal and the bulky ligand, but also by a ligand–ligand repulsion. The gap is, however, too large to be simply explained on this basis alone. This effect is the same as that observed for the complexes of d-transition metal ions with some pyridine- and quinoline-N-oxides. No shift, or shift to higher frequencies, of the NO stretching mode was observed for the complexes with quinoline-N-oxides. A reasonable explanation for this result is most likely to be connected with a lowering of the π-system energy and a more metal-to-ligand back-donation of electron density to replace the electron density on the oxygen atom lost by σ-donations [6].

The NO-bending mode is slightly affected upon complexation and generally appears as a doublet between 820 and 810 cm^{-1}. This effect is the same as that observed for the NO-stretching and for some skeletal and CH modes, and is largely due to the ligand *trans–cis* rearrangement that is necessary for chelation. A staggered conformation becomes, however, the only one possible in this case, as suggested by steric considerations.

In the CsBr region the spectrum of $biquO_2$ shows a number of absorptions which are attributed to the various skeletal modes. In the spectra of the complexes a new band appears between 400 and 300 cm^{-1} where the ligand has only two weak absorptions at 368 and 330 cm^{-1}. This band can be associated with metal–oxygen stretching vibration. This assignment is supported by the observation that the other bands remain essentially unchanged upon complexation, whilst the frequency of the new band depends on the metal ion following the series: $Cu^{2+} > Ni^{2+} > Co^{2+} > UO_2^{2+} > Ln^{3+}$ [7]. The measured frequency values are 5–10 cm^{-1} lower than those observed for the $bipyO_2$ complexes having the same stoichiometry, as expected from the greater steric hindrance of $biquO_2$.

Uranyl nitrate and lanthanide perchlorate complexes with biqu suspended in a matrix of CsBr do not show any absorption which can be associated reasonably with M–N stretching vibrations. On the other hand, the low thermodynamic stability of these complexes may arise from monodentation of the ligand; the other nitrogen atom could be involved in bonding *via* the hydrogen of water molecules.

Anion modes

Perchlorate ions have T_d symmetry and two active IR vibrations. Coordination through one or two oxygen atoms causes the symmetry to be lowered to C_{3v} or C_{2v}, respectively, and the IR active vibrations become six or nine. The $-SO_3$ group has C_{3v} symmetry and, thus, six IR active vibrations which become nine by coordination through one oxygen atom.

The complexes of lanthanide perchlorates with $biquO_2$ show two bands while the trifluoromethanesulfonate complexes show three bands between 1300 and 600 cm^{-1} (Table III). These spectral patterns are relatively simple and indicate the presence in these complexes of ionic groups only.

Ionic nitrates have D_{3h} symmetry and three IR active vibrations. If coordination occurs through one or two oxygen atoms, the symmetry is lowered to C_{2v} in both instances and all six normal modes of vibration become IR active.

The spectra of the $biquO_2$ complexes with large lanthanide(III) nitrates only show bands which are expected from bidentate nitrato groups (Table III). The appearance of a strong band at 1390 cm^{-1} in the spectra of the complexes of heavy nitrates also indicates the presence of ionic nitrate groups. Ten-coordination is most likely stabilized for large cations by three bidentate nitrato groups and two bidentate $biquO_2$ molecules, while eight-coordination could be attained by the heaviest cations through two bidentate nitrato groups and two bidentate $biquO_2$ molecules.

The IR spectra of the perchlorate complexes with biqu indicate the presence of both coordinated and ionic perchlorate groups, while the spectra of the nitrate complexes do not show any band arising from D_{3h} symmetry (Table III).

Electronic Spectra

Two intense π–π^* transition bands can be observed in the UV spectrum of $biquO_2$ in $CHCl_3$ at 258 and 300 nm, both showing shoulders at higher and lower frequencies. The broad band appearing as a shoulder at 345 nm can be associated with n–π^* transitions.

It has been found that crystalline $bipyO_2$ exists in the *trans*-form although a doublet associable with the ν(NO) mode in the IR spectrum suggests non-coplanarity of the two aromatic rings. This molecule assumes a configuration which is close to that of the *cis*-form in the metal chelates. The band at 258 nm shifts on the whole to higher frequencies in the $biquO_2$ complexes, while the band at 300 nm suffers large splitting and globally shifts to lower frequencies. These effects are those observed for the $bipyO_2$ complexes with metal ions. The chelation of $bipyO_2$ has been expressed in terms of molecular *trans–cis* rearrangement. The same behaviour seems to characterize the $biquO_2$ complexes with d- and f-blocks cations. The overall UV evidence suggests that free ligand has a configuration which is close to the *trans*-form in the solid state and assumes in the metal chelates a configuration which is (of necessity) close to the *cis*-form, but involving non-coplanarity of the two quinoline rings.

A charge-transfer band appears between 420 and 460 nm in the spectra of the f-ions complexes. It

TABLE IV. Intensity, as Oscillator Strengths, of the Hypersensitive Transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ in Nd^{3+} ion and $^7F_0 \rightarrow {}^5D_2$ in Eu^{3+} Ion.

Complex	10^6 P	σ[a]
$Nd(biquO_2)_4(ClO_4)_3 \cdot H_2O$[b]	52.62	17090
$Nd(biquO_2)_4(CF_3SO_3)_3 \cdot H_2O$	53.84	17090
$Nd(biquO_2)_2(NO_3)_3$	47.34	17120
$Eu(biquO_2)_4(CF_3SO_3)_3 \cdot 2H_2O$	0.29	21488
$Eu(biquO_2)_2(NO_3)_3$	0.26	21537
$Nd(biqu)(NO_3)_3 \cdot 3H_2O$	[c]	17211[d]
$Nd(biqu)_2(ClO_4)_3 \cdot 3H_2O$	[c]	17235[e]

[a] Barycentre of the band (cm^{-1}) in acetonitrile–chloroform mixture (3:1). [b] The oscillator strength values for the $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$ and $^4I_{9/2} \rightarrow {}^2H_{9/2}$, $^4F_{5/2}$ transitions are respectively 5.15 and 5.90 for the perchlorate complex and 5.63 and 6.82 for the nitrate complex. [c] Not determined because of solvolysis. [d] For the solid. For crystalline $Nd(NO_3)_3 \cdot 5H_2O$ the σ value is 17211 cm^{-1}. [e] For the solid. For crystalline $Nd(ClO_4)_3 \cdot nH_2O$ the σ value is 17271 cm^{-1}.

also appears to be much more intense in the spectra of the complexes with divalent d-transition metal ions.

The UV spectrum of biqu is characterized along with the strong π–π^* absorption at 262 nm by another band below 300 nm, which has π–π^* benzene peaks at 314, 327 and 340 nm. Upon complexation this band shifts to lower frequencies as a result of N-coordination. All complexes reported here exhibit a charge-transfer band at 435 nm which decreases in intensity (perchlorates) or disappears totally (nitrates) by dissolution in polar solvents.

f–f spectra

The f–f bands upon complexation undergo weaker perturbations than do the d–d bands. Increase in the intensity of the hypersensitive transitions, splitting and shift of the bands with respect to the aquo-ions are effects normally observed on complex formation.

Indeed, the spectra of the complexes with $biquO_2$ reported here show remarkable and rather uncommon enhancements in the band shape and intensity of the hypersensitive transitions (Table IV and Fig. 1). The tetrakis(2,2′-biquinolyl-N,N′-dioxide) lanthanide perchlorate and trifluoromethanesulfonate complexes have 8-coordinated $[LnO_8]$ type environments and are characterized by the presence of uncoordinated anions and by f–f spectra which are practically unaffected by the anion present. The band splits into a great number of components while the intensity of the hypersensitive transitions increases remarkably, reaching values which are only a little smaller than those reported for the corresponding complexes with bipyO [2]. Thus, one must infer that this chelating ligand represents, like $bipyO_2$, an example of a strong ligand towards lanthanide(III) cations. Both ligands form, on chelation, seven-membered metal chelate rings, but the $biquO_2$ molecule is remarkably bulkier than $bipyO_2$ and is probably constrained to adopt a higher-distorted conformation and to lengthen the Ln–O bond distance.

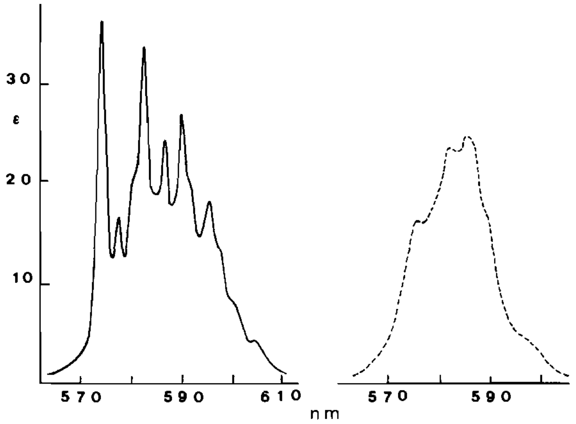

Fig. 1. $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions in Nd^{3+} ion. (——) $Nd(biquO_2)_4(ClO_4)_3 \cdot H_2O$; (------) $Nd(biquO_2)_2(NO_3)_3$.

Small enhancements in both band shape and intensity of the hypersensitive transitions can be observed, with respect to the crystalline hydrated salts, in the spectra of the solid complexes with biqu. Only the perchlorate complexes clearly show a relative increase, though small, in both intensity and number of components. There is thus evidence for ligand coordination, but also reasonable connection with a weak electron-donating power of this ligand towards lanthanide(III) cations.

The number of components which appear in the region of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ hypersensitive transitions in neodymium complexes with $biquO_2$ is higher than that predicted for the splitting for the half-integral J values in cubic symmetries and thus indicates lower symmetry (Fig. 1). In this regard, the splitting that undergoes the $^7F_0 \rightarrow {}^5D_2$ transition in the europium(III) perchlorate and trifluoromethanesulfonate complexes with $biquO_2$ is meaningful. Three peaks appear at 21512, 21471 and 21458 cm^{-1}, which indicate not only lower than cubic symmetries but also D_4 symmetry. This symmetry has been suggested by spectral data [2] for the tetrakis(2,2′-bipyridyl-N,N′-dioxide)europium(III) perchlorate and trifluoromethanesulfonate complexes. In this case this transition consists of a unique, though slightly asymmetric, band centered at 21530 cm^{-1}.

TABLE V. Partial Energy Level Scheme for Europium(III) Complexes with 2,2'-Biquinolyl-N,N'-dioxide (biquO_2) and 2,2'-Biquinolyl (biqu). The values refer to the barycentre of the band (cm^{-1}).

Complex	Level								η^c
	$^5D_2$	$^5D_1$	$^5D_0$	$^7F_4$	$^7F_3$	$^7F_2$	$^7F_1$	$^7F_0$	
Eu(biquO_2)$_4$(CF_3SO_3)$_3$·2H_2O^{a}	21489	18961	17235	2840^b	1916	947	384	0	4.8
Eu(biquO_2)$_4$(ClO_4)$_3$·H_2O	21492	18961	17241	2838^b	1923	947	380	0	5.2
Eu(biquO_2)$_4$$Cl_3$·2$H_2O$	21497	18965	17253	2869^b	1939	942	367	0	5.4
Eu(biquO_2)$_2$(NO_3)$_3$	21527	^{b}	17247	2811	1905	1022	388	0	4.1
Eu(biqu)(NO_3)$_3$·3H_2O			17259	^{b}	1915	1041	364	0	2.9

[a] The $^5D_1 \rightarrow {}^7F_{1,2}$ bands have been not observed because of their weakness. The barycentre of the $^5D_1 \rightarrow {}^7F_3$ band is located at 17038 cm^{-1}. [b] Very weak. [c] η = (intensity ratio) $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$.

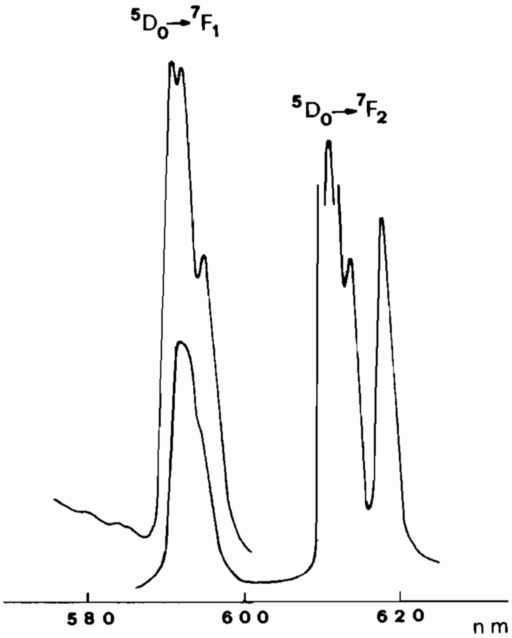

Fig. 2. Emission spectrum, from solid at 77 K, of Eu(biquO_2)$_4$(ClO_4)$_3$·H_2O; excitation with 365 nm radiation.

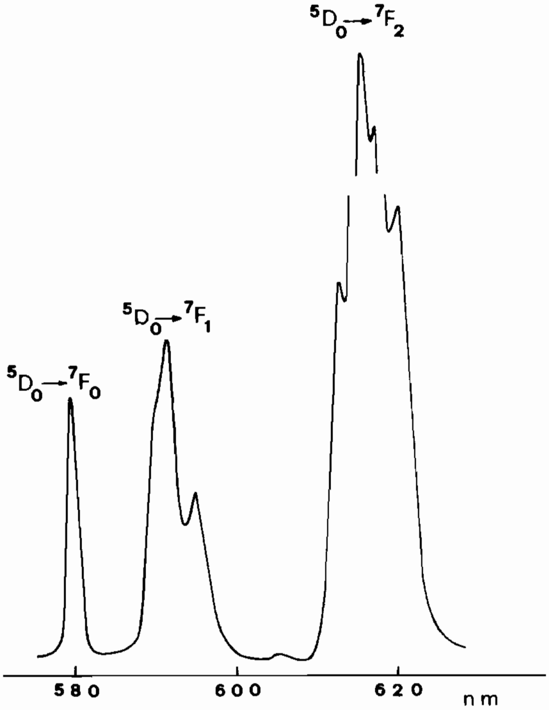

Fig. 3. Emission spectrum, from solid at 77 K, of Eu(biquO_2)$_2$(NO_3)$_3$; excitation with 355 nm radiation.

The spectral patterns of the nitrate complexes with biquO_2 differ from those of the perchlorate and trifluoromethanesulfonate complexes, as expected from different environments. The red shift is smaller and the intensity of the hypersensitive transitions is lower. However, these complexes were formed with the contribution of three or two nitrato groups and only two molecules of the more basic biquO_2 ligand. Because of solvolytic effects the solution spectra are different from the reflectance ones.

It is known that useful information concerning the nature of the chromophore and geometry of the complexes can be obtained by the study of the emission f–f spectra. Among the lanthanide(III) complexes in which strong emission has been observed, the europium complexes have been the subject of very extensive studies since the low J-values give rise to a smaller number of closely spaced energy levels.

The emission spectra of the europium(III) complexes with biquO_2 are reported in Figs. 2, 3 and Table V.

Both europium(III) perchlorate and trifluoromethanesulfonate complexes exhibit strong emissions when excited with 365 nm radiation at liquid nitrogen temperature. Emission originates almost totally at the $^5D_0$ excited state. Bands associated with $^5D_{1,2} \rightarrow {}^7F_{0,1,2}$ transitions are very weak.

There is little doubt, both from synthetic and spectroscopic data, that these complexes consist of the octacoordinated [Eu(biquO_2)$_4$]$^{3+}$ ion surrounded by the three perchlorate and trifluoromethanesulfonate ions. Both complexes show a line at 580.2 nm due to the $^5D_0 \rightarrow {}^7F_0$ transition. Its intensity is, however, less than 0.1% of the most intense $^5D_0 \rightarrow {}^7F_2$ transition and it can be taken as forbidden. The magnetic-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition consists of two almost equal intensity lines at 592.5 and 593.2 nm, which can be associated with an E-component. A peak at 594.8 nm arises also from this transition, indicating that two principal components lie under the overall envelope. An intense line at 612.6 nm and a weaker one at 618.8 nm arise from the electric-dipole allowed $^5D_0 \rightarrow {}^7F_2$ transition. A weak line at 614.0 nm arises also from this transition. Although the splitting of the lines at 612.6 and 614.0 nm is rather large (37 cm^{-1}) they could originate from an E-component. Unfortunately, both $^5D_0 \rightarrow {}^7F_{3,4}$ transitions are very weak and two poorly resolved bands appear in the relative regions.

The dominant geometries for eight-coordination are the square-antiprism (D_{4d} symmetry), the tetragonal dodecahedron (D_{2d} symmetry) and the bicapped trigonal prism (C_{2v} symmetry). Lack of bands in the region of the $^5D_0 \rightarrow {}^7F_0$ transition excludes C_{2v} site symmetry. On the other hand, when an europium(III) ion is located at a site that is a centre of inversion, the only purely electronic transitions which can occur are those for which the magnetic dipole selection rule $\Delta J = 0, \pm 1$ (except $J = 0 \rightarrow J' = 0$) is obeyed. At last, for the cation having D_{2d} site symmetry only two components of the $^5D_0 \rightarrow {}^7F_1$ transition and two components of the $^5D_0 \rightarrow {}^7F_2$ transition are allowed and should be, of course, observed in the spectra. Both $^5D_0 \rightarrow {}^7F_{1,2}$ transitions consist, in the spectra of these complexes, of two components each and agree well with dodecahedral geometry and D_{2d} site symmetry for the europium(III) ion.

Synthetic and spectroscopic data suggest that the complex $Eu(biquO_2)_2(NO_3)_3$ consists, like $Eu(bipyO_2)_2(NO_3)_3$ [2], of the $[EuO_{10}]$ entity formed by three bidentate nitrato groups and two bidentate $biquO_2$ molecules. The almost exclusive geometries for ten-coordination are the bicapped square-antiprism with D_{4d} symmetry and the bicapped dodecahedron with D_2 or C_{2v} symmetry. The bis(2,2′-bipyridyl-N,N′-dioxide) europium(III) nitrate complex has been described in terms of bicapped dodecahedron and D_2 site symmetry for the europium(III) ion [2]. The emission spectrum of the $biquO_2$ complex by excitation of the solid with 355 nm radiation at liquid nitrogen temperature shows an intense line at 579.8 nm associated with the $^5D_0 \rightarrow {}^7F_0$ transition. The activation of this transition excludes both D_{4d} and D_2 symmetries for the europium(III) ion, while it agrees with the following ones: C_n, C_s, $C_{n'v}$ ($n = 2, 3, 4, 6; n' = 1, 2, 3, 4, 6$) [8]. The $^5D_0 \rightarrow {}^7F_1$ transition consists of a broad band centered at 592.1 nm which has a shoulder at 590.2 nm. A weaker component of this transition appears at 595.6 nm. In the region of the $^5D_0 \rightarrow {}^7F_2$ transition, the spectrum shows a weak line at 613.8 nm and a strong one centered at 615.7 nm. Weaker components of this transition appear at 618.7 and 619.8 nm. An unique though broad band associated with the $^5D_0 \rightarrow {}^7F_3$ and two broad components of the $^5D_0 \rightarrow {}^7F_4$ transition appear in the relative regions. Both are very weak and are of no help. Nevertheless, this emission spectrum can be interpreted in terms of bicapped dodecahedral geometry having C_{2v} site symmetry.

The emission spectrum of the complex $Eu(biquO_2)_4Cl_3 \cdot H_2O$ is the same as that of the perchlorate complex, showing only small differences in the energy, relative intensity and magnitude of splitting of the bands associated with the various transitions. A reasonable conclusion is that this complex consists of the cation $[Eu(biquO_2)_4]^{3+}$ surrounded by the three anions. Dodecahedral geometry and D_{2d} site symmetry for the europium(III) ion are suggested by this spectrum.

Ten-coordination attained by three bidentate nitrato groups and four water molecules in bicapped dodecahedral geometry has been established for hydrated lanthanide(III) nitrates [9]. The emission spectrum of the complex $Eu(biqu)(NO_3)_3 \cdot 3H_2O$ from the solid excited with 395 nm radiation is similar to that of the crystalline europium(III) nitrate pentahydrate, showing only small enhancements in the intensity of the forbidden $^5D_0 \rightarrow {}^7F_0$ transition and splitting of the $^5D_0 \rightarrow {}^7F_{1,2}$ bands. These effects may arise from distortion of the original polyhedron because of replacement of water molecules by the bulkier biqu molecule.

Uranyl Complexes

All complexes of uranyl with $biquO_2$ and biqu are yellow. The perchlorate and trifluoromethanesulfonate complexes act as 1:2 electrolytes, while the nitrate complexes are non-electrolytes. These data agree with IR spectra which indicate the presence in these complexes of only ionic perchlorate and trifluoromethanesulfonate groups or bidentate nitrato groups (Table III).

In addition to the ligand and anion absorptions, the IR spectra of these complexes show a strong band between 930 and 900 cm^{-1}, associated with the ν_3 mode of the UO_2 group. The frequency of this vibration is lower, the greater the number of ligand molecules in the complex. The assignment of the ν_1 frequency is doubtful because of the ligand modes that appear in the relative region (850–800 cm^{-1}). On the other hand, this vibration is not IR active for a linear OUO entity.

Since $biquO_2$ and biqu act as bidentate ligands (chelating or bridging), the perchlorate and trifluoromethanesulfonate complexes with $biquO_2$ may be considered to have 8-coordinated environments. Eight-coordination is probably attained by uranyl ion in both nitrate complexes with biqu and biquO_2 through four oxygen atoms of two bidentate nitrato groups and two nitrogen or oxygen atoms of one bidentate ligand molecule.

References

1 A. Vinciguerra, P. G. Simpson, Y. Kakiuti and J. V. Quagliano, *Inorg. Chem.*, *2,* 287 (1963).
2 A. Musumeci, R. P. Bonomo, V. Cucinotta and A. Seminara, *Inorg. Chim. Acta, 59,* 133 (1982).
3 A. Seminara and E. Rizzarelli, *Inorg. Chim. Acta, 40,* 249 (1980).
4 S. Nakano, *Yakugaku Zasshi, 82,* 486 (1962); *C.A., 58,* 3390e (1963).
5 H. Shindo, *Chem. Pharm. Bull. (Tokyo), 8,* 845 (1960).
6 J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *Inorg. Chem., 7,* 1840 (1968).
7 To be published.
8 P. Porcher and P. Caro, *Séminaires de Chimie de l'Etat Solide, 5,* 141 (1972).
9 I. M. Rumanova, G. F. Volodina and N. V. Belov, *Crystallography (Soviet. Phys.), 9,* 545 (1965).