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Lanthanide acylpyrazolonates: synthesis, properties and structural features

Yu A Belousov, A A Drozdov

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Abstract. Data concerning synthesis and structural features of lanthanide acylpyrazolonates including tris-complexes, heteroligand complexes with aromatic N-heterocycles and phosphorus-containing ligands and anionic tetrakis-complexes are summarized. The effect of substituents in the acyl moiety on the structural and luminescence properties of the compounds is considered. The key features of acylpyrazolonate coordination polymers and bis(acylpyrazolonates) of rare earth elements are discussed. The bibliography includes 71 references.

I. Introduction

Classical reviews on the coordination chemistry of lanthanides [1–4] evade certain groups of compounds. Among them are complexes of acylpyrazolones, *i.e.*, of heterocyclic analogues of diketones. By now, several general reviews (see, *e.g.*, Refs 5 and 6) concerning metal acylpyrazolonates have been published, but although lanthanide complexes with these ligands are of particular interest and constitute nearly one third of the total number of acylpyrazolone complexes, there was no special review article devoted to them. The aim of the present review is to consider the coordination and structural chemistry and the key applications of lanthanide acylpyrazolonates. For diketonates, it is well known [6] that the stability constants increase and vacuum sublimation temperatures decrease on going from left to right along the lanthanide series. No similar investigations of the dependence of properties of acylpyrazolonate complexes of lanthanides on the central atom nature have been performed, while some general ideas were based on just a few studies.[7–10]

Acylpyrazolones, heterocyclic analogues of β-diketones, were first synthesized [11] at the end of the 19th century. Ligands of this type combine many of the advantages of classical β-diketones (chelating properties of the singly charged anion and complex and ligand solubility in many organic solvents) with the ease of synthesis and modification caused by easy introduction of various substituents in the acyl group. Acylpyrazolonates of various metals (first of all, barium and copper) attract attention as precursors for the chemical deposition of metal oxide films from vapours of volatile metal compounds (MOCVD);[12, 13] some titanium derivatives have antitumour activity.[14] Acylpyrazolones were proposed as heavy metal ion extractants,[15] as reagents for separation of actinides and other metals. Lanthanide acylpyrazolonates may be useful as luminescent materials,[16–19] certain gadolinium complexes have been tested as components of layers with electronic conductivity for organic light-emitting diodes;[20] and the catalytic activity of some cerium complexes was investigated.[21, 22]

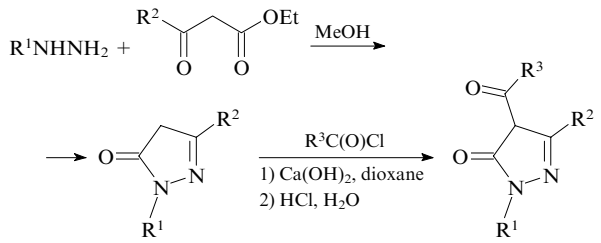
II. Brief description of the ligands

The traditional synthetic approach to 4-acylpyrazol-5-ones [5] includes two steps (Scheme 1). The first one is the formation of disubstituted (with substituents R^1 and R^2) pyrazolone upon condensation of the corresponding hydrazine (phenylhydrazine is the most common choice, so usually $R^1 = Ph$) and an ester (acetoacetic ester is generally used, so usually $R^2 = Me$). The reaction is performed in methanol or ethanol. The second step is acylation of the 4-position by a carboxylic acid chloride, $R^3C(O)Cl$, in the presence of calcium oxide or hydroxide in dioxane (calcium ion is proposed to function not only as a base but also as a template) followed by the decomposition of the calcium salt by the hydrochloric acid. In some cases the reaction is performed in pyridine serving not only as a solvent but as a base as well. To perform the synthesis in pyridine, the corresponding acid anhydride is taken as an acylating agent.

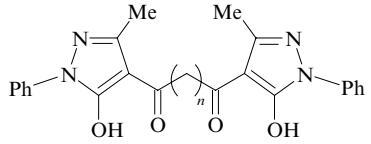
Yu A Belousov Department of Materials Science, M V Lomonosov Moscow State University
A A Drozdov Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory 1, 119991 Moscow, Russian Federation.
Fax (7-495) 939 09 98, tel. (7-495) 939 45 49,
e-mail: belousov@gmail.com (Yu A Belousov),
drozdov@inorg.chem.msu.ru (A A Drozdov)

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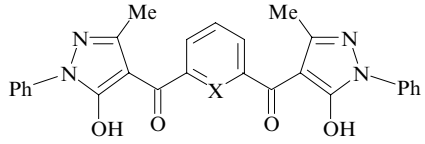
Scheme 1



To designate 4-acylpyrazol-5-ones in complexes, a simple pattern has been proposed:[5] if R^1 = Ph and R^2 = Me, the ligands are denoted as HQ^{R^3}, for example, HQ^{Et}, HQ^{Ph}. If $R^1 \neq$ Ph, R^2 = Me, the designation HQ^{R^1,R^3} is used. In the case of $R^2 \neq$ Me, the acronym comprises all the three substituents irespective of the nature of R^1 to give HQ^{R^1,R^2,R^3}. For bis(acylpyrazolones), *i.e.* ligands that have two 4-acylpyrazol-5-one moieties separated by a methylene chain $(CH_2)_n$ or a phenylene (or pyridine-2,6-diyl) moiety, designations $H_2Q(n)Q$ and $H_2Q(i,j\text{-Ar})Q$ (H_2QpyQ) are used, respectively. For example,



$H_2Q(n)Q$

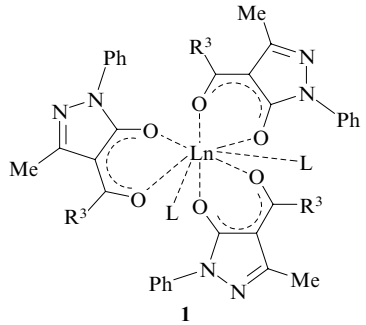


$H_2Q(1,3\text{-Ar})Q$ (X = CH),
H_2QpyQ (X = N)

Similarly the single currently known tris(acylpyrazolone) may be denoted as $H_3Q_3(1,3,5\text{-Ar})$ wherein 1,3,5-Ar is benzene-1,3,5-triyl.

Typical 4-acylpyrazol-5-one ligands forming complexes with lanthanide ions are given in Table 1.

In metal complexes, acylpyrazolone anions show different types of coordination: the ligand can act as a mono- or bidentate O-donor ligand, as N,O-donor ligand and there are examples of its coordination as a bridging ligand. Hovewer, in all presently known lathanide complexes, acylpyrazolones are bonded to the lanthanide atom as bidentate O,O′-donor ligands (except for the complex described in Ref. 23, which is considered in detail below).



1

Table 1. Typical acylpyrazolone ligands (R^1 = Ph).

Designation	R^2	R^3 or the central moiety	Typical lanthanide complexes [a]
HQ^{Me}	Me	Me	$[LnQ_3(solv)_n]$ (n = 1, 2) $[LnQ_3L_n]$ (n = 1, 2) $[LnQ_4]^-$
HQ^{Ph}	Me	Ph	
HQ^{cPe}	Me	cyclo-C_5H_9	
HQ^{nPe}	Me	neo-C_5H_{11}	
HQ^{Bn}	Me	Bn	
HQ^{cPeE}	Me	$CH_2CH_2C_5H_9$-cyclo	
HQ^{Ad}	Me	1-adamantyl	
HQ^{Th}	Me	2-thienyl	
HQ^{CF_3}	Me	CF_3	
HQ^{pCP}	Me	p-CNC_6H_4	
HQ^{PhPhBn}	Ph	Bn	
$H_2Q(2)Q$	Me	$(CH_2)_2$	$[Ln_2\{Q(X)Q\}_3L_m]$ (m = 2–4) $[Ln\{Q(8)Q\}_2]^-$
$H_2Q(3)Q$	Me	$(CH_2)_3$	
$H_2Q(8)Q$	Me	$(CH_2)_8$	
$H_2Q(1,3\text{-Ar})Q$	Me	m-phenylene	
$H_2Q(1,4\text{-Ar})Q$	Me	p-phenylene	
$H_3Q(1,3,5\text{-Ar})$	Me	benzene-1,3,5-triyl	$[Ln_8\{Q_3(1,3,5\text{-Ar})\}_8]$

[a] solv is solvent, L is neutral auxiliary ligand, X is the bridge in bis(acylpyrazolone).

The structure of a typical mononuclear acylpyrazolonate corresponds to structure **1**.

Note that the two oxygen atoms in acylpyrazolone are non-equivalent. On the average, the Ln–O bond length with the oxygen atom bonded to the heterocycle is 2.32 Å, whereas the average Ln–O bond length with the oxygen atom of the acyl substituent is 2.41 Å. This is accounted for by the electron density shift from the pyrazolone oxygen atom towards the heterocycle under the effect of two nitrogen atoms.

Numerous lanthanide complexes with acylpyrazolones HQ, several mono- and binuclear bis(acylpyrazolone) complexes and the cluster $La_8(Q_3Ar)_8$ have been synthesized.

III. Lanthanide complexes with acylpyrazolones HQ

1. General characteristics

Presently, 56 crystal structures of lanthanide complexes with acylpyrazolones HQ have been reported; 24 of them comprise solvent molecules (water ot ethanol) as auxiliary ligands $[LnQ_3(solv)_n]$ (n = 1, 2). Known also are three crystal structures of adducts with aromatic N-heterocycles $[LnQ_3L]$ [L is 9,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bipy)], seven anionic tetrakis-complexes $[LnQ_4]^-$ and twelve structures of complexes with phosphorus-containing ligands, namely, triphenylphosphine oxide (TPPO), triisobutyl phosphate $(Bu^iO)_3PO$, bis(diphenylphosphino)methane dioxide ($dppmO_2$) and bis(diphenylphosphino)butane dioxide ($dppbO_2$). In most of these compounds, the lanthanide atom has a coordination number (C.N.) of 8 and a square antiprism coordination polyhedron. The possible ways of ligand arrangement around the central atom in the case of n = 2 and 0 are shown in Fig. 1.

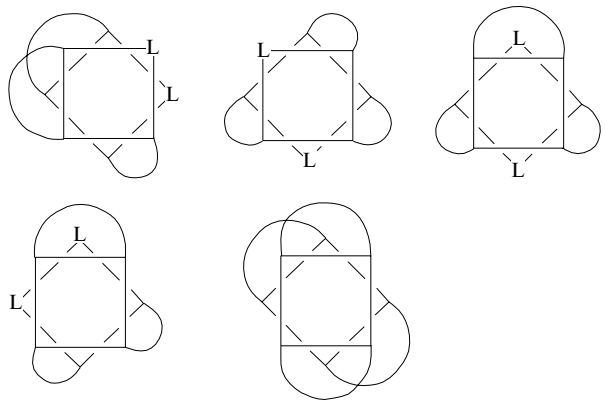


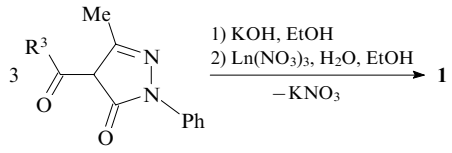
Figure 1. Coordination patterns of the chelating and two auxiliary ligands (L) in lanthanide diketonates having C.N. 8.

2. Main types of complexes

a. Synthesis of lanthanide pyrazolonates with neutral auxiliary ligands

Complexes of the type $[Ln(Q^R)_3L]_n$, where $n = 1, 2$; L is solvent (generally, water, ethanol or methanol) or a neutral ligand [mono- and bis(phosphine oxides), N-heteroaromatic compounds, *etc.*][7,24–39] are obtained according to the following procedure (Scheme 2): an alkali (preferably, KOH because of lower solubility of KNO_3) and the corresponding ligand taken in a 1 : 1 molar ratio are dissolved in alcohol (when the auxiliary ligand differs from the solvent, the former is dissolved in the same solvent). Then an aqueous-alcohol or alcohol solution of a lanthanide salt, usually nitrate (1 equiv.) is added dropwise to the solution. The solution is refluxed for several minutes followed by the addition of 1–2 volumes of chloroform. The formed precipitate of the potassium salt is filtered off and evaporation gives crystals of the complex. This method suits well for the synthesis of any lanthanide acylpyrazolonates soluble in the ethanol–chloroform mixture. When obtaining polymeric complexes, one should use triethylamine as a base and the complex should be isolated by diluting the solution by 4–5-fold volumes of distilled water.

Scheme 2



Single crystals of these complexes can be obtained, most often, by slow evaporation of the solvent (ethanol or chloroform) at room temperature in an open beaker or in an L-shaped sealed ampoule. Single crystals of polymeric complexes $[Eu(Q^{Th})_3(dppbO_2)]$ and $[Tb(Q^{cPe})_3(dppbO_2)]$ were obtained[40] by recrystallization from ethanol using the solvothermal method in a steel autoclave fitted with a Teflon insert upon slow cooling of the autoclave from 180 °C at a rate of 3 °C h^{-1}.

b. Complexes of the $[LnQ_3L_n]$ type with solvent molecules as auxiliary ligands

Lanthanide acylpyrazolonates with water and alcohol molecules as auxiliary ligands have been described most comprehensively (Table 2). Generally, the C.N. of lanthanide is 8, and only in two cases, for $[Tb(Q^{cPe})_3(H_2O)]$ (Ref. 32) and $[Tb(Q^{nPe})_3(H_2O)]$ (Ref. 36) it is 7. The latter circumstance is related to the fact that ligands in such a structure bear a bulky substituent impeding the coordination of the second solvent molecule. For the ligand HQ^{cPe}, the complex $[Tb(Q^{cPe})_3(dppbO_2)]$ is known[40] in which the C.N. of terbium atom is 8. For the ligand HQ^{nPe}, the complex $[Tb(Q^{nPe})_3(phen)]\cdot CHCl_3$ has been described[36] in which the C.N. of the central atom is also 8. This may result from the greater thermodynamic benefit due to the coordination of auxiliary ligands compared to the coordination of water molecule.

In lanthanide complexes with trifluoromethyl-substituted acylpyrazolone HQ^{CF_3}, the Ln–O(Q) bond lengths are distinctly less than the average values for alky- and aryl-substituted ligands, thus being consistent with the high electronegativity of the trifluoromethyl group.[31]

On the average, the Ln–O(H_2O) distance in such complexes is 2.439 Å, the bond length expectedly decreasing on going from La to Lu. In six complexes of known structure comprising ethanol as one of the auxiliary ligands, the Ln–O(EtOH) distance ranges from 2.368 to 2.529 Å (on the average, 2.452 Å), which exceeds slightly the analogous parameter for aqua-complexes. A somewhat greater distance is due to the lower polarity of the alcohol molecules.

There are two non-equivalent Gd atoms in the structure of the gadolinium complex $[Gd(Q^{Pr^i})_3(H_2O)(EtOH)\cdot Gd(Q^{Pr^i})_3(H_2O)_2]\cdot EtOH$.[35] The coordination environment of each central atom is a distorted square antiprism. A substantial role in the crystal package belongs to hydrogen bonding between the nitrogen atom N(2) of the pyrazolone ring and the oxygen atoms of inner- and outer-sphere water and ethanol molecules.

In a study[25] dealing with the hydrate composition of some lanthanide acylpyrazolonates, compounds of $Ln(Q^{Ph})_3\cdot n\,H_2O$ type ($n = 3$: Ln = Pr, Sm, Eu, Gd, Tb, Ho, Er, Y; $n = 1$, Ln = Yb) have been studied. Differential thermal analysis data for all trihydrates indicate the existence of two endothermal effects (in the ranges of 100–125 and 130–180 °C), the temperature of the first one successively increasing and that of the second one decreasing along the lanthanide series. Thus, dehydration of trihydrates proceeds in two steps, which has been attrubuted to the presence of water molecules in both the inner and outrer coordination spheres of the complexes. According to differential thermal analysis data, light lanthanide (Ln = Sm, Eu) complexes were found to lose one molecule of water at the first step, while the complexes of heavier lanthanides (Ln = Er, Ho) lose two H_2O molecules. Consequently, the number of water molecules in the inner coordination sphere decreases from 2 to 1 on going from light to heavy lanthanides (*i.e.*, the C.N. changes from 8 to 7). In the case of ytterbium monohydrate, a single water molecule is eliminated at 180 °C, thus confirming its inner-sphere location. The complexes $Ln(Q^{Ph})_3\cdot n\,H_2O$ with for cations of the middle and the end of the lanthanide series poorly crystallize, and this hampers their investigation by X-ray diffraction. For trihydrates of the first half of the lanthanide series, the existence of at least three different structural types was reliably established,[25] for 1) Ln = La, Pr, Nd; 2) Ln = Eu, Gd; and 3) Ln = Sm.

Table 2. Crystallographic data for complexes LnQ_3L_n (L = H_2O, EtOH; n = 1, 2).

Compound	Space group	Z	C.N.	CP	Distance /Å					Ref.
					Ln – O(Q) mean	Ln – O(Q) max	Ln – O(Q) min	Ln – O(L)	Ln – O(L′)	
$[Eu(Q^{CF_3})_3(H_2O)_2]\cdot H_2O$	$P2_1/a$	4	8	SA	2.383	2.454	2.311	2.479	2.396	31
$[Nd(Q^{CF_3})_3(H_2O)_2]\cdot H_2O$ [a]	$P2_1/a$	–	–	–	–	–	–	–	–	31
$[Nd(Q^{Bn})_3(EtOH)(H_2O)]$	$P\bar{1}$	2	8	SA	2.421	2.458	2.386	2.490 (EtOH)	2.475 (H_2O)	33
$[Dy(Q^{Bn})_3(EtOH)(H_2O)]\cdot EtOH$	$P\bar{1}$	2	8	SA	2.333	2.410	2.268	2.368 (EtOH)	2.411 (H_2O)	33
$[Er(Q^{Me})_3(H_2O)_2]$	$P2_1/c$	4	8	t-TP	2.328	2.376	2.266	2.421	2.383	24
$[Tb(Q^{cPe})_3(H_2O)]$	$P2_1/n$	4	7	PB	2.321	2.351	2.290	2.321		32
$[Nd(Q^{Et})_3(H_2O)_2]$	$P2_1/c$	4	8	SA	2.415	2.447	2.372	2.504	2.463	7
$[Sm(Q^{Et})_3(H_2O)_2]$	$P2_1/c$	4	8	SA	2.388	2.4248	2.349	2.478	2.4382	7
$[Gd(Q^{Et})_3(H_2O)_2]$	$P2_1/c$	4	8	SA	2.373	2.4056	2.337	2.449	2.411	7
$[Dy(Q^{Et})_3(H_2O)_2]$	$P2_1/c$	4	8	SA	2.343	2.363	2.306	2.432	2.395	7
$[Tb(Q^{Et})_3(H_2O)_2]\cdot EtOH$	$P2_1/c$	4	8	SA	2.338	2.372	2.304	2.487	2.412	34
$[Tb(Q^{cPeE})_3(H_2O)(EtOH)]\cdot 2\,EtOH$	$P\bar{1}$	2	8	SA	2.359	2.412	2.324	2.391 (EtOH)	2.470 (H_2O)	32
$[\{Gd(Q^{Pr^i})_3(H_2O)(EtOH)\}\cdot\{Gd(Q^{Pr^i})_3(H_2O)_2\}]\cdot EtOH$ [b]	$P\bar{1}$	2	8, 8	SA, SA	2.368 2.375	2.415 2.431	2.308 2.347	2.529 (EtOH) 2.451 (H_2O)	2.414 (H_2O) 2.474	35
$[Tb(Q^{nPe})_3H_2O]$	$P2_1/c$	4	7	m-TP	2.298	2.320	2.282	2.404		36
$[Yb(Q^{Ph})_3(H_2O)]$ [a]	see [c]	–	–	–	–	–	–	–		25
$[Eu(Q^{Ph})_3(H_2O)_2]$ [a]	$P2_1/n$	–	–	–	–	–	–	–	–	27
$[Yb(Q^{Ph})_3(H_2O)_2]$	$P2_1/n$	4	8	SA	2.308	2.370	2.257	2.366	2.340	28
$[Ho(Q^{Ph})_3(H_2O)_2]\cdot EtOH\cdot H_2O$	$P2_1/n$	4	8	SA	2.347	2.400	2.277	2.412	2.361	29
$[La(Q^{Ph})_3(H_2O)_2]$	$C2/c$	8	8	t-TP	2.470	2.518	2.431	2.617	2.530	30
$[Nd(Q^{Ph})_3(H_2O)_2]$	$C2/c$	4	8	SA	2.410	2.457	2.368	2.526	2.461	26
$[Tb(Q^{Ph,Ph,dBOP})_3(H_2O)_2]$ [d]	$P\bar{1}$	2	8	SA	2.347	2.378	2.301	2.492	2.411	37
$[Tb(Q^{Ph,Ph,Bn})_3(H_2O)(EtOH)]$	$P\bar{1}$	2	8	SA	2.343	2.363	2.300	2.455 (H_2O)	2.428 (EtOH)	37
$[Yb(Q^{Ph,Ph,Me})_3(H_2O)_2]\cdot 3\,EtOH$	$P2_1/n$	4	8	SA	2.307	2.360	2.255	2.388	2.341	38
$[Eu(Q^{Th})_3(H_2O)(EtOH)]$	$P2_1/n$	4	8	SA	2.377	2.41	2.35	2.51 (EtOH)	2.50 (H_2O)	33
$[Eu(Q^{Th})_3(H_2O)(EtOH)]$ [a]	$P2_1/n$	–	–	–	–	–	–	–	–	39

Note. Hereinafter, the following designations are used: Z is the number of formula units in the cell, C.N. is the coordination number, CP is the coordination polyhedron, SA is the square antiprism, t-TP is the two-capped trigonal prism, m-TP is the monocapped trigonal prism, PB is the pentagonal bipyramid.

[a] Atomic coordinates were not determined; [b] the structure comprises two molecules of the complex differing in composition; [c] the symmetry is no higher than monoclinic; [d] dBOP is 3,5-di(benzyloxy)phenyl.

The regularities of variation of the properties upon varying the central atom were studied [7] using the crystal structures of $[Ln(Q^{Et})_3(H_2O)_2]$ (Ln = Nd, Sm, Gd, Dy) as examples. Terbium and gadolinium tris-complexes with the HQ^{Et} ligand have been described;[34] for $[Tb(Q^{Et})_3(H_2O)_2]\cdot EtOH$, the crystal structure was determined.

Bombiery *et al.*[38] synthesized the complex $[Yb(Q^{Ph,Ph,Me})_3(H_2O)_2]$ and investigated its crystal structure.

Terbium complexes bearing ligands HQ^{cPe} and HQ^{cPeE} were reported.[32] For complexes with HQ^{cPe}, the existence of seven-coordinate central atom was established, possibly resulting from the steric hindrances due to the bulky cyclopentyl substituent.

Chlorine-containing acylpyrazolone $HQ^{Ph,Me,(Me),CH_2Cl}$ was used [23] to obtain the samarium complex $\left[Sm\left(Q^{Ph,Me,(Me),CH_2Cl}\right)(H_2O)_4\right](ClO_4)_3\cdot 4\,H_2O$ (Fig. 2). In this compound, the C.N. of the central atom is 9, which is a unique example among lanthanide acylpyrazolonates. Since proton abstraction is impossible for this ligand, metallocycles that form upon the coordination are non-planar and one of the three ligands is coordinated only through one oxygen atom.

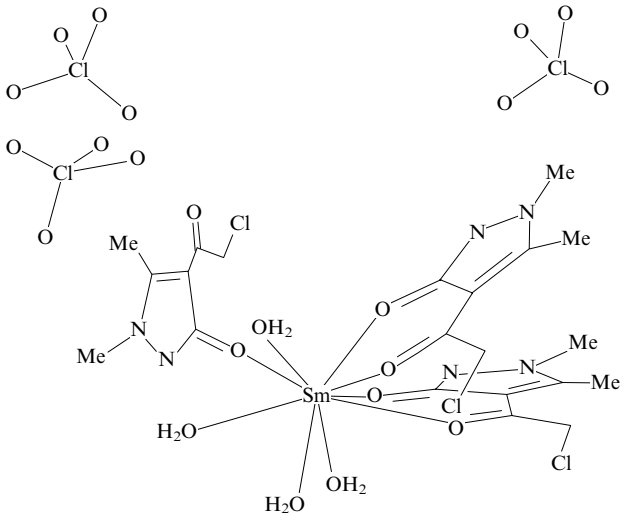
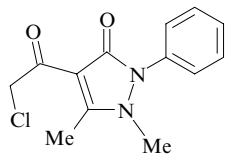


Figure 2. Structure of the complex $[SmQ_3(H_2O)_4](ClO_4)_3\cdot 4\,H_2O$ [$Q = Q^{Ph,Me,(Me),CH_2Cl}$].
The phenyl groups and the outer-sphere water molecules are omitted for clarity.



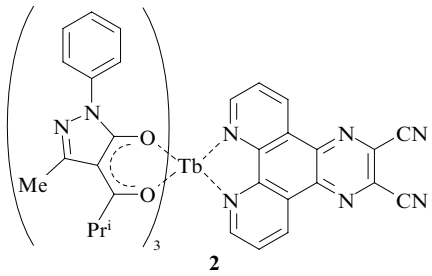
$HQ^{Ph,Me,(Me),CH_2Cl}$

The Sm—O distance for water molecules averages 2.470 Å, exceeding slightly the mean distance for common tris-acylpyrazolonates and fits well with the steric hindrances caused by coordination of nine donor atoms around one metal cation. The polyhedron is characterized by low symmetry and may be described as a highly distorted monocapped antiprism.

c. Complexes of the [LnQ_3L] type with N-heterocyclic ligands

Xin *et al.*[36] studied the influence of variuos auxiliary ligands on photo- and electroluminescence of terbium complexes of pyrazolone. As the auxiliary ligands, they used TPPO, H_2O and phenanthroline. In the last-mentioned case, the single crystals were obtained from a chloroform solution and the crystal structure included one $CHCl_3$ molecule per complex molecule. The chloroform molecules were involved in the weak interactions stabilizing the structure.

Terbium complex **2** with dicyano phenanthroline derivative has been studied[35] (the crystal structure was not determined). The compound was obtained by the reaction of HQ^{Pr^i}, $TbCl_3$ and an auxiliary N-donor ligand in the presence of Et_3N in ethanol; upon completion of the reaction, the mixture was evaporated to dryness, and the residue was washed with water and recrystallized from ethanol.



2

The luminescence properties of the complex were investigated, in particular, luminescence titration with n-butylammonium salts containing different anions was carried out. Data concerning the luminescence buildup in the presence of acetate and fluoride ions in acetonitrile solutions and strong luminescence quenching by fluoride ions in aqueous solutions are given. The authors suggested no explanation for these effects.

Also, compounds [LnQ_3L] (Ln = Eu, Tb; Q = Q^{cPe}, Q^{cPeE}; L = phen, bathophenanthroline)[41] and [$Eu(Q^{Ph,Ph,Me})_3$(phen)] were synthesized.[42]

Pettinari *et al.*[43] prepared the complexes [$Ln(Q^{Ad})_3L$] (Ln = Eu, Tb; L = bipy, phen, 4,4′-Me_2 bipy). For the compounds [$Tb(Q^{Ad})_3$(4,4′-Me_2bipy)], the crystal structure was determined. The complexes were obtained in an ethanol solution by the reaction of HQ^{Ad}, $Ln(NO_3)_3$ and the corresponding heteroaromatic compounds in the presence of KOH; after a short-term refluxing, chloroform was added to the solution and potassium nitrate was separated by filtration. The compounds were obtained by slow evaporation of the mother liquor.

The crystal structures were determined for three adducts of lanthanide acylpyrazolonates with N-heteroaromatic compounds (Table 3).

d. Acids and salts comprising the complex anions $[LnQ_4]^-$

Complexes of this type (Table 4) are characterized by a high symmetry of the coordination polyhedron, which is an Archimedean antiprism in all cases. Such complexes may be synthesized by the conventional reaction

$$Ln(NO_3)_3 + 4\,HQ + 4\,NR_3 \longrightarrow HR_3N^+[LnQ_4]^- + 3\,HR_3NNO_3$$

or by dissociation of the tris-complexes in solution

$$[LnQ_3(solv)_2] + H_2O \longrightarrow LnQ_2(OH) + [H_{2n+1}O_n]^+[LnQ_4]^-$$

This method was used to prepare the single crystals of the compound $[H_5O_2][Eu(Q^{Cy})_4]$ (Cy is cyclohexyl), containing the Zundel cation $H_5O_2^+$ (Ref. 44).

Europium and terbium complexes with the ligands HQ^{cPe} and HQ^{cPeE} were synthesized and investigated; in particular, the tetrabutylammonium salts of the corresponding tetrakis-acids were obtained (Scheme 3).

The complexes form ionic crystals with a very high (compared to other acylpyrazolonates) symmetry of the coordination environments of the central atom. This is also manifested in their luminescence spectra (Fig. 3). From the fine structure of lines corresponding to $^5D_0 - {}^7F_1$ and $^5D_0 - {}^7F_2$ transitions, it is evident that in the case of less symmetric complexes (see Fig. 3 *a*, *b*), more Stark components are observed. The spectrum of the symmetric anionic Eu acylpyrazolonate (see. Fig. 3 *c*) shows narrower lines and less Stark components. The anionic complexes $[LnQ_4]^-$ with known crystal structures are listed in Table 4.

Numerous investigations are devoted to Langmuir–Blodgett films (LB) based on salts comprising lanthanide

Table 3. Crystallographic data for complexes [LnQ_3L] (L is N-heterocycle).

Compound	Space group	*Z*	Distance /Å					Ref.
			Ln—O mean	Ln—O max	Ln—O min	Ln—N	Ln—N′	
[$Tb(Q^{Ad})_3$(4,4′-Me_2bipy)]	*C*2/*c*	8	2.320	2.346	2.293	2.558(3)	2.583(5)	43
[$Tb(Q^{nPe})_3$(phen)]·$CHCl_3$	$P\bar{1}$	2	2.3413	2.396	2.287	2.581	2.576	36
[$Eu(Q^{Ph,Ph,Me})_3$(phen)]	*C*2/*c*	8	2.372	2.449	2.308	2.621	2.616	42

Note. In all cases, C.N. = 8.

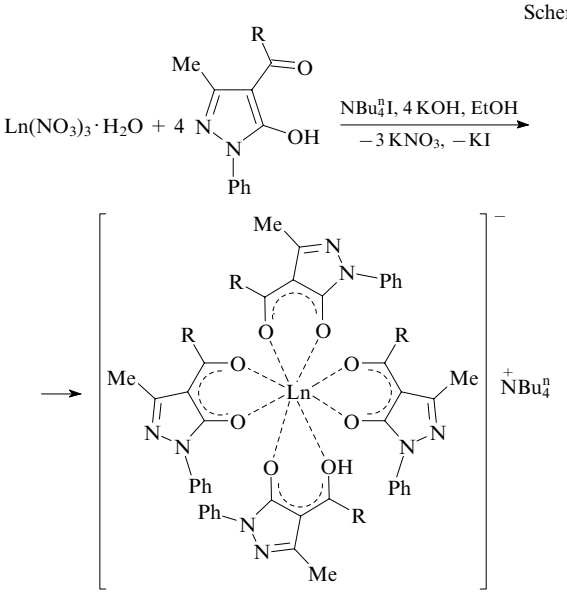
Table 4. Crystallographic data for complexes of the type $M^+[LnQ_4]^-$ ($M = R_4N^+$, H_3O^+, $H_5O_2^+$).

Compound	Space group	Z	Distance /Å			Ref.
			Ln–O mean	Ln–O min	Ln–O max	
$H_3O[Tb(Q^{Ad})_4]$	$P2/n$	4	2.37	2.434	2.317	43
$NBu^n_4[Eu(Q^{CF_3})_4]$	$C2/c$	8	2.398	2.474(3)	2.315(3)	33
$[H_5O_2][Eu(Q^{Cy})_4]$	$C2/c$	4	2.400	2.448	2.361	44
$NBu^n_4[Eu(Q^{cPeE})_4]\cdot H_2O$	Cc	4	2.380	2.450	2.319	41
[4-$Me_2NC_6H_4CH{=}CHC_5H_4N(C_{12}H_{25}$-n)Me][$La(Q^{Ph})_4$] [a]	$P\bar{1}$	4	2.4888	2.507	2.447	45
			2.4853	2.525	2.530	45
$H_3O[Eu(Q^{Th})_4]$	$P\bar{1}$	2	–	–	–	46
$H_3O[Tb(Q^{Th})_4]$	$P\bar{1}$	2	2.365(4)	2.429(5)	2.318(3)	46

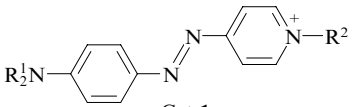
Note. In all cases, C.N. = 8. [a] In the structure, there are two non-equivalent $[LaQ_4]^-$ ions.

acylpyrazolonate complex anions and cationic chromophores, *e.g.*, Cat-**1**, Cat-**2**.[47–53]

Scheme 3

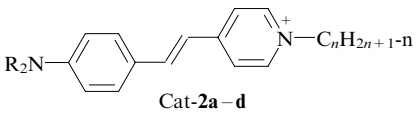


Li *et al.*[47] used cation Cat-**1a** salts with various anionic europium diketonates including a symmetric tetrakis-anion $[Eu(Q^{Ph})_4]^-$ and heteroligand anions $[Eu(Q^{Ph})_3Q^{C_{15}H_{31}}]^-$ and $[Eu(dbm)_3Q^{C_{15}H_{31}}]^-$ (Hdbm is dibenzoylmethane) to obtain LB films. It was shown that to form a uniform monolayer film and to provide its functional properties (the second-harmonic generation SHG), heteroligand anions having a long-chain alkyl substituent are preferred. A



Cat-**1a**–**c**

R^2 = n-$C_{18}H_{37}$: R^1 = Me (**a**), Et (**b**); R^1 = n-$C_{16}H_{33}$, R^2 = Me (**c**)



Cat-**2a**–**d**

R = Me: n = 14 (**a**), 16 (**b**), 18 (**c**); R = Et, n = 16 (**d**)

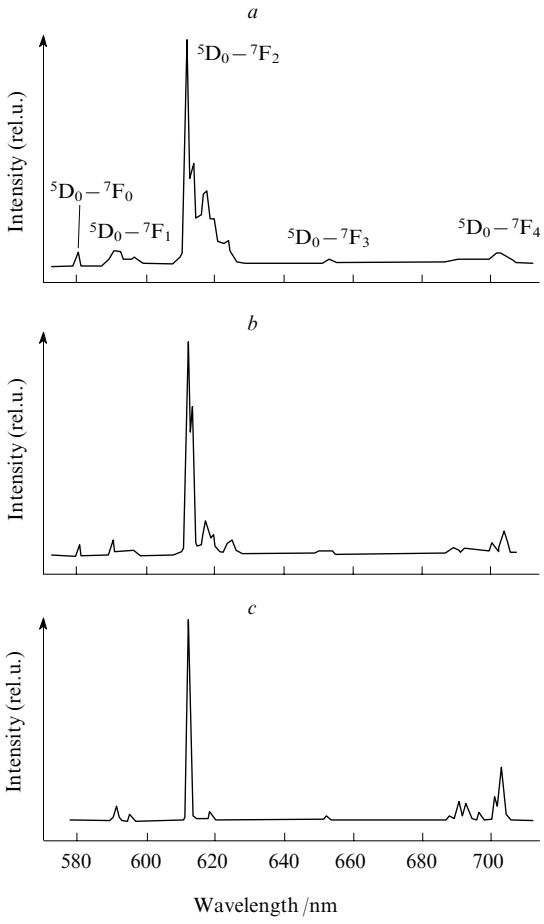


Figure 3. Luminiscence spectra of europium compounds.[41] (*a*) $[Eu(Q^{cPe})_3(H_2O)(EtOH)]$, (*b*) $[Eu(Q^{cPe})_3(phen)]$ and (*c*) $NBu^n_4[Eu(Q^{cPe})_4]$.

similar study[48] considers salts comprising cation Cat-**1b** and the dysprosium-containing anions $[Dy(Q^{Ph})_4]^-$ and $[Dy(Q^{Ph})_3Q^{C_{11}H_{23}}]^-$. The authors of this study point out an enhancement of the SHG effect upon replacement of the commonly used iodide anion by the complex anion. Also, similarly to Ref. 47, it was found that it is preferable to use a heteroligand anion with a long-chain alkyl substituent.

Electrical and optical properties of the films having composition Cat[Ln(Q^{Ph})$_4$] (Cat = Cat-**2a**–**c**; Ln = La–Nd, Sm–Lu) have been investigated;[49] however, in terms of the lanthanide effect, only melting points were analyzed, increasing uniformly on going from lanthanum to lutetium. The influence of the alkyl substituent length in the pyridinium cation on the film morphology was shown and also a solvatochromism was found — a shift of the absorption peak depending on the solvent polarity. The complex Cat-**1c**[La(Q^{Ph})$_4$] was studied [51] in terms of its application in non-linear optics. Complex monolayers were deposited from a chloroform solution onto the surface of quartz or calcium fluoride. The complex was found to form a stable monolayer film. High value of second order hyperpolarizability was discovered: 1.4×10^{-47} cm^3 V^{-2}. This is one of the highest values for non-linear-optical materials based on azo-compounds.

The complex Cat-**2b**[Yb(Q^{Ph})$_4$] was used [52] as a doping agent to obtain a photoelectroactive membrane. The replacement of the iodide anion by the complex anion [Yb(Q^{Ph})$_4$]$^-$ was found to induce a considerable enhancement of the doped film photoresponse. Presumably, the complex anion provides the charge transfer through the membrane.

For LB films based on dysprosium complexes Cat-**1a**[Dy(Q^{Ph})$_4$], Cat-**1a**[Dy(Q^{Ph})$_3$$Q^{C_{15}H_{31}}$] (Ref. 50) and Cat-**2d**[Dy(Q^{Ph})$_4$], Cat-**2d**[Dy(Q^{Ph})$_3$$Q^{C_{11}H_{23}}$] (Ref. 53), reversible quenching of SHG effect in the presence of various gases and vapours (HCl, Et_3N, H_2O, $CHCl_3$, HOAc, Pr^iOH) was observed. The results of both studies attest that long-chain alkyl substituents in ligands Q have a beneficial effect on the film stability and the magnitude of the SHG effect.

e. Complexes of type [LnQ$_3$L$_n$] with phosphorus-containing ligands

Phosphorus-containing ligands, namely, phosphine oxides and organic phosphates, occupy a special place in the chemistry of lanthanide complexes. Phosphine oxides, primarily triphenylphosphine oxide, form stable complexes with lanthanide ions. Organic phosphates, mainly tributyl phosphate (TBP), are used in extraction methods of lanthanide recovery and separation.

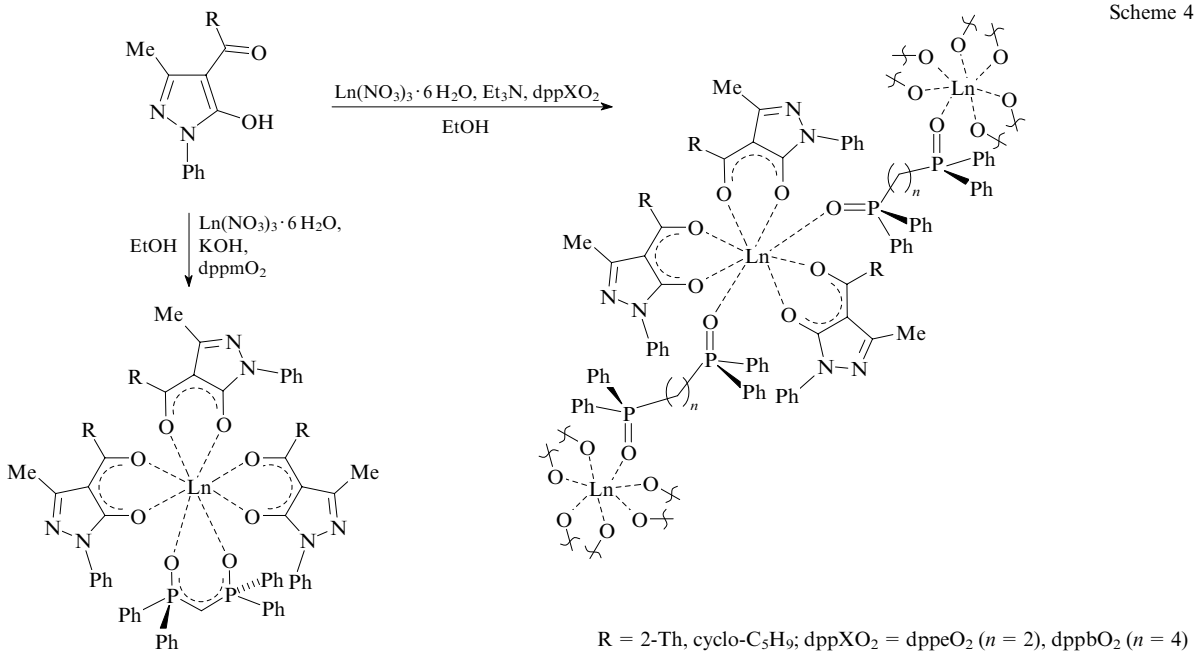
Twelve crystal structures of heteroligand lanthanide complexes comprising the acylpyrazolonate anion and phosphorus-containing ligand have been described.

The complexes [Tb(Q^{nPe})$_3$TPPO] (Ref. 36) and [Tb($Q^{Pe\text{-}3}$)$_3$TPPO] (Pe-3 is pent-3-yl),[54] differing only in the aliphatic moiety in the carbonyl group of the ligand, have been synthesized and investigated. In both cases, the C.N. of the central atom is 7 and the coordination geometry is a monocapped octahedron. Both complexes show more intense photo- and electroluminescence compared to the similar complex with H_2O instead of TPPO. The increase in photoluminescence results from the fact that the position of the first excited singlet level of the TPPO ligand is such that the energy absorbed by it is effectively transferred to the acylpyrazolone ligand or terbium ion.

The isostructural complexes [Ln(Q^{Pr^i})$_3$(TPPO)$_2$] (Ln = Dy, Eu, Lu) are described.[55–57] In these structures, the Ln^{3+} coordination polyhedron, square antiprism, is somewhat more distorted than usual due to the bulky phenyl groups of TPPO. The complex [Eu(Q^{pCP})$_3$.(TPPO)(H_2O)] is of interest as a unique example of combining H_2O and TPPO as auxiliary ligands at the central europium atom.[58] The water molecule was shown to eliminate readily upon heating of this complex.

A study [40] concerns the synthesis of coordination polymers of a predetermined structure based on extensively investigated LnQ_3 moieties (Q = Q^{Th}, Q^{cPe}) through their cross-linking by bis(phosphine oxides) $Ph_2P(O)(CH_2)_n$-$P(O)Ph_2$ (n = 1, 2, 4). When n = 1, monomeric molecular complexes were shown to form, whereas when n = 2 and 4, coordination polymers may be formed (Scheme 4). In particular, the crystal structures of [Eu(Q^{Th})$_3$(dppmO$_2$)], [Eu(Q^{Th})$_3$(dppbO$_2$)]$_n$ and [Tb(Q^{cPe})$_3$(dppbO$_2$)]$_n$ have been determined. The polymer complexes are poorly soluble only in DMSO and DMF and are insoluble in ethanol and acetone; the mononuclear complexes are readily soluble in the said solvents. The polymeric structure for complexes [LnQ$_3$(dppeO$_2$)]$_n$ [dppeO$_2$ is bis(diphenylphosphino)ethane

Scheme 4



R = 2-Th, cyclo-C_5H_9; dppXO$_2$ = dppeO$_2$ (n = 2), dppbO$_2$ (n = 4)

Table 5. Crystallographic data for complexes of the type $[LnQ_3L_n]$ (L is phosphorus-containing ligand, $n = 1, 2$).

Complex	Space group	Z	C.N.	CP	Distance /Å					Ref.
					Ln–O(Q) mean	Ln–O(Q) max	Ln–O(Q) min	Ln–O(L)	Ln–O(L′)	
$[Tb(Q^{Pe\text{-}3})_3TPPO]$	$P2_1$	2	7	m-TP	2.308	2.372	2.260	2.288		54
$[Tb(Q^{cPe})_3dppbO_2]$	$C2/c$	4	8	SA	2.377	2.506	2.240	2.324	2.324	40
$[Dy(Q^{Pr^i})_3(TPPO)_2]$	$P2_1/n$	4	8	t-TP	2.373	2.499	2.276	2.364	2.325	55
$[Eu(Q^{Pr^i})_3(TPPO)_2]$	$P2_1/n$	4	8	TD	2.391	2.513(3)	2.296(3)	2.391(3)	2.358(3)	56
$[Lu(Q^{Pr^i})_3(TPPO)_2]$	$P2_1/n$	4	8	t-TP	2.318	2.453	2.211	2.248	2.283	57
$[Tb(Q^{nPe})_3TPPO]$	$P\bar{1}$	4	7	m-TP	2.327	2.399	2.281	2.302		36
$[Eu(Q^{Ph})_3\{(Bu^iO)_3PO_2\}]$ [a]	see [b]	—	—	—	—	—	—	—	—	59
$[Eu(Q^{Ph})_3\{(Bu^iO)_3PO_2\}]$	Bb	4	8	SA	2.38	2.51(3)	2.29(2)	2.35(3)	2.35(3)	60
$[La(Q^{Ph})_3\{(Bu^iO)_3PO_2\}]$	see [b]	—	—	—	—	—	—	—	—	59
$[Eu(Q^{pCP})_3TPPO]\cdot H_2O$	$P\bar{1}$	2	8	t-TP	2.386	2.472	2.344	2.363 (TPPO)	2.490(H_2O)	58
$[Eu(Q^{Th})_3(dppmO_2)]$	$P2_1/c$	4	8	SA	2.391	2.473	2.339	2.396	2.396	40
$[Eu(Q^{Th})_3(dppbO_2)]$	$C2/c$	4	8	SA	2.390	2.432	2.337	2.319	2.319	40

Note. The following designations are accepted: L and L′ are two monodentate or one bidentate ligand, TD is trigonal dodecahedron. [a] The coordinates were not determined, [b] $C2/c$ or Cc.

P,*P*′-dioxide] was proposed based on the solubility data, IR and ^{1}H NMR spectroscopy data and luminescence spectra.

Single crystals of the adducts of lanthanide acylpyrazolonates with triisobutyl phosphate have been obtained,[59, 60] though the quality of the experiment gave no way to determine the atomic coordinates. In particular, these compounds are formed during the recovery and separation of lanthanides by extraction (see, *e.g.* Ref. 15).

The crystal structures of lanthanide acylpyrazolonates with phosphorus-containing auxiliary ligands are presented in Table 5.

IV. Lanthanide bis(acylpyrazolonates)

Depending on the bridging group size and nature, bis(acylpyrazolones) may form mono-, bi- and polynuclear metal complexes. For lanthanides, the structures of one ionic complex (see below) and several binuclear complexes including the polymer $[Tb_2\{Q(2)Q\}_3(dppeO_2)]_n$, comprising binuclear repeated moiety, have been determined by the X-ray diffraction analysis (Table 6). The polymeric character of complexes with ligands $H_2Q(1,3\text{-Ar})Q$ and $H_2Q(1,4\text{-Ar})Q$ was suggested on the basis of indirect data, poor solubility and the lack of crystallinity.

The crystal structure of a bis(acylpyrazolonate) complex was first described[61] for $[Tb_2\{Q(3)Q\}_3(DMF)_4]\cdot DMF$ (Fig. 4). Later, the same authors determined the structures of samarium[62] and dysprosium[63] complexes. The molecules of these compounds exist as slightly twisted triple helices. In these three isostructural complexes, a minor but regular change in the distance between the Ln atoms in one complex is followed. Moreover, somewhat greater deviations from the mean Sm–O distances compared to that of Tb–O and Dy–O may be noted, indicating the slightly lower stability of the samarium complex structure.

Semenov *et al.*[64] studied the structural assembly $[Tb_2\{Q(2)Q\}_3]$ existing in the form of a triple helix. Owing to its stability, it was possible to obtain complexes with different terminal substituents at the terbium atom (H_2O or DMF) and then to cross-link these fragments into a polymer chain $[Tb_2(Q(2)Q)_3(dppeO_2)]_n$ by bis(diphenylphosphino)ethane *P*,*P*′-dioxide (Scheme 5).

Although this polymer complex may be synthesized by direct mixing of all reactants and long-term reflux of the alcohol solution (this was confirmed by elemental analysis data, luminescence spectra and IR spectra), obtaining of a single crystal required performing slow replacement of dimethylformamide molecule by $dppeO_2$ in the solution.

Table 6. Crystallographic data for lanthanide bis(acylpyrazolonates).

Compound	Space group	Z	C.N.	CP	Distance /Å						Ref.
					Ln–O(Q) mean	Ln–O(Q) max	Ln–O(Q) min	Ln–O(L) min	Ln–O(L) max	Ln–Ln min	
$[Dy_2\{Q(3)Q\}_3(DMF)_4]\cdot DMF$	$P\bar{1}$	2	8	SA	2.328	2.408	2.280	2.484	2.475	8.021	61
$[Sm_2\{Q(3)Q\}_3(DMF)_4]\cdot DMF$	$P\bar{1}$	2	8	SA	2.354	2.421	2.220	2.544	2.410	7.975	62
$[Tb_2\{Q(3)Q\}_3(DMF)_4]\cdot DMF$	$P\bar{1}$	2	8	SA	2.336	2.412	2.284	2.482	2.366	7.988	63
$[Tb_2\{Q(2)Q\}_3(H_2O)_2]\cdot H_2O\cdot EtOH$	$P\bar{1}$	6	7	m-O	2.315	2.352	2.271	2.353	2.318	6.108	64
$[Tb_2\{Q(2)Q\}_3(DMF)_2]$	$P\bar{1}$	2	7	m-O	2.310	2.363	2.259	2.328	2.328	6.224	64
$[Tb_2\{Q(2)Q\}_3(dppeO_2)]$	$P\bar{1}$	2	7	m-O	2.315	2.350	2.285	2.332	2.324	6.333	64
$[Na(DB\text{-}18\text{-}C\text{-}6)H_2O][Tb\{Q(8)Q\}_2]$ [a]	$C2/c$	4	8	SA	2.37	2.430	2.309				65

Note. The designations accepted: m-O is monocapped octahedron. [a] DB-18-C-6 is dibenzo-18-crown-6 ether.

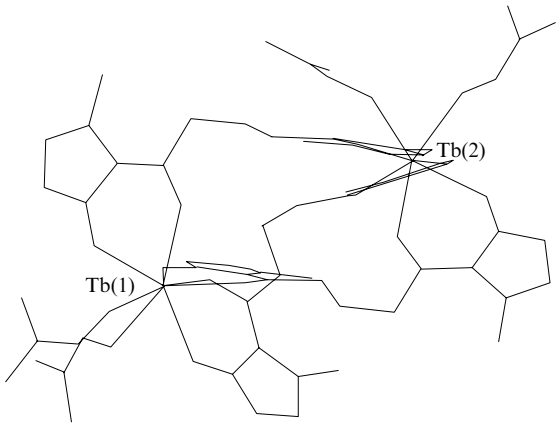


Figure 4. Structure of the complex $[Tb_2\{Q(3)Q\}_3(DMF)_4]$.[61] View along the axis *b*; the phenyl groups are omitted for clarity.

The observed high stability of the binuclear moiety of the helix complex fits well with quantum chemical calculations performed in the same work.

Remya *et al.*[65] synthesized the complexes $[Tb_2\{Q(8)Q\}_3 \cdot (H_2O)_2]$ and $[Gd_2\{Q(8)Q\}_3(H_2O)_2]$ and the ionic salt $[Na(DB\text{-}18\text{-}C\text{-}6)H_2O][Tb\{Q(8)Q\}_2]$; for the salt, the crystal structure was determined. Neutral complexes were obtained in aqueous ethanol in the presence of NaOH as a base. The ionic complex was also prepared in aqueous ethanol according to the reaction

$$4\,NaOH + 2\,H_2Q(8)Q + Tb(NO_3)_3 \cdot 6\,H_2O + DB\text{-}18\text{-}C\text{-}6 \rightleftharpoons$$
$$\rightleftharpoons 3\,NaNO_3 + [Na(DB\text{-}18\text{-}C\text{-}6)H_2O][Tb\{Q(8)Q\}_2] + 9\,H_2O$$

Single crystals were formed upon slow evaporation of the solvent within a week.

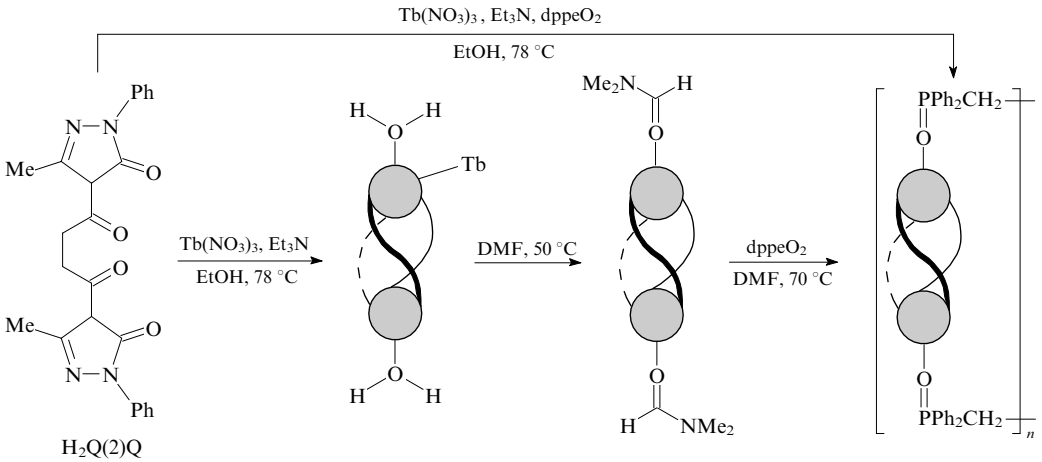
In the study of luminescence properties, it was found that the luminescence quantum yield grows considerably on going from the neutral complex ($\varphi = 4.82 \pm 0.01\%$) to the ionic complex ($\varphi = 18.13 \pm 0.82\%$). The authors explain this by a specific mechanism of luminescence involving a crown-ether moiety acting as an antenna.

The synthesis and luminescence properties of a series of complexes $[Ln_2\{Q(2)Q\}_3(phen)_2]$ (Ln = La, Pr, Sm–Lu, Y) were described.[66] Basing on the spectroscopy data, the authors proposed these complexes to exist as triple helices. These data contradict to an extent the recent publication[64] where for all complexes having a $Tb_2\{Q(2)Q\}_3$ moiety, including dihydrate, the lanthanide atom was found to have C.N. of 7. In the next paper of the same authors,[67] various lanthanide and yttrium complexes with the $H_2Q(1)Q$ ligand, $[Ln_2\{Q(1)Q\}_3(phen)_2] \cdot n\,H_2O$ (Ln = La, Pr, Nd, Sm–Yb, Y; $n = 3-6$), were investigated. Basing on the IR and ^1H NMR spectroscopy data, a binuclear molecular structure of these complexes was suggested. The luminescence spectra of Pr, Sm, Eu, Tb, Dy, Tm complexes are discussed in the paper cited. Li *et al.*[68] reported the corresponding data for $[Ln_2\{Q(3)Q\}_3(bipy)_2] \cdot n\,H_2O$ ($n = 2$, Ln = Y; $n = 4$: Ln = Eu, Gd, Dy, Ho, Er, Tm, Yb; $n = 10$: Ln = La, Pr, Nd, Sm; $n = 3$, Ln = Tb).

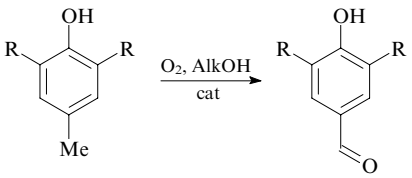
The cerium complexes $[(AcO)_2Ce\{Q(X)Q\}Ce(OAc)_2]$, $[Ce(OAc)\{Q(X)Q\}]$ and $[Ce_2\{Q(X)Q\}_3]$ [Q(X)Q = Q(1,2-Ar)Q, Q(1,3-Ar)Q, Q(1,4-Ar)Q] have been synthesized and their catalytic activity in the oxidation of 2,6-dilakoxy- and 2,6-dialkyl-4-methylphenols to the corresponding 4-hydroxybenzaldehydes by air oxygen in methanol was studied (Scheme 6).[21] The complex $[Ce(OAc)\{Q(1,2\text{-}Ar)Q\}]$ was found to be the most active as a catalyst in this process, providing 4-hydroxy-3,5-dimethoxybenzaldehyde in 84% yield in anhydrous methanol and in 55% yield in aqueous methanol. This circumstance is of special interest since performing the reaction in question in the presence of cerium triacetate requires absolutely anhydrous solvents, and this is disadvantageous from the economical and environmental viewpoints. Later, the same author[22] described the complexes $[Ce(OAc)\{Q^{Me}(X)Q^{Me}\}]$, where the ligand comprised two 1,3-dimethyl pyrazolone moieties (instead of 3-methyl-1-phenyl pyrazolone). These complexes showed even higher catalytic activity in the oxidation of disubstituted *p*-cresols, the yield of 4-hydroxy-3,5-dimethoxybenzaldehyde in a $MeOH-H_2O$ mixture exceeded 90%. On the average, the product yield decreased in the series 1,2-Ar > 1,4-Ar > $(CH_2)_2$ > 1,3-Ar depending on the nature of the central fragment X in the ligand.

Hovewer, there are doubts concerning the very existence of the ligand $H_2Q(1,2\text{-}Ar)Q$. Indeed, its synthesis was first reported in 1999[21] but an attempt[69] to reproduce this procedure resulted in a different product, namely, $H_2Q(CBZ)Q$. It should be noted that the ligands

Scheme 5

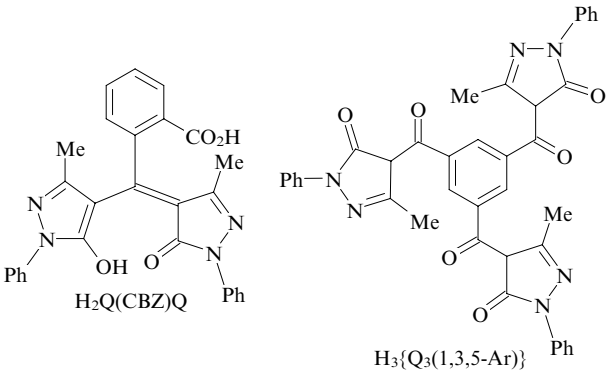


Scheme 6



R = OMe, OEt, OPr^n, OPh, Me, Et, Pr^i; Alk = Me, Pr^n

H_2Q(1,2-Ar)Q and H_2Q(CBZ)Q are indistinguishable by ^{1}H NMR spectra.



The unique octameric cluster [La_8{Q_3(1,3,5-Ar)}$_8$] of a molecular structure was prepared by targeted synthesis.[70] Earlier, the same researchers described the clusters [Ga_6{Q_3(1,3,5-Ar)}$_6$] and similar compounds of iron and vanadium.[71] The structure contains 8 lanthanum atoms forming practically an ideal square antiprism (the La—La distance is 10.30 Å in one base and 10.08 Å in the other base), and the vacant coordination sites are occupied by the dimethyl sulfoxide solvent molecules (Fig. 5). Unfortunately, the high value of the *R*-factor for this structure prevented it from being included into the Cambridge Crystallographic Database. The disorder is apparently connected with a variable amount of solvent molecules.

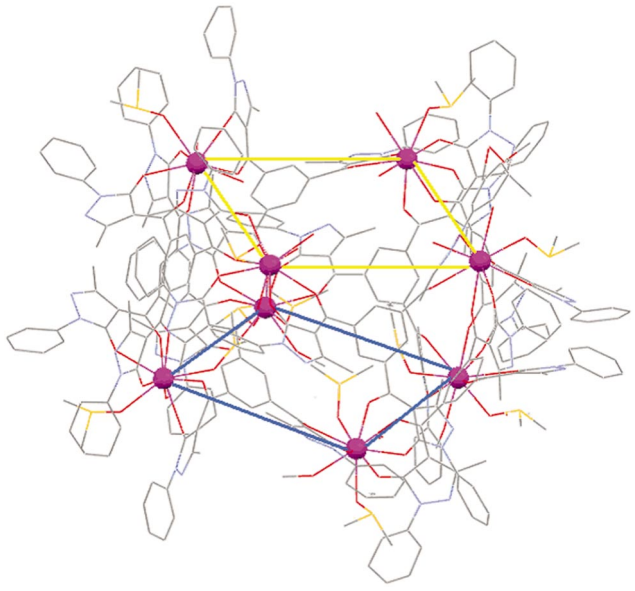


Figure 5. Structure of the cluster [La_8{Q_3(1,3,5-Ar)}$_8$].

* * *

Presently, the crystal structures are known for 56 lanthanide complexes with acylpyrazolones HQ, although the number of compounds that have been synthesized and characterized by indirect methods is several times larger. Generally, the tris-complexes obtained from aqueous alcohol solutions have a square-antiprism environment of the central atom except for ligands with very bulky substituents; for the latter, stabilization with C.N. = 7 is possible. Mononuclear LnQ_3 assemblies may be connected in a coordination polymer by phosphine oxide type ligands. These polymers may be used to obtain materials and molecular devices having luminescence properties. To increase the luminescence intensity, it is convenient to change the substituent in the acyl moiety: for terbium cations, aliphatic substituents providing an elevated triplet energy level of the ligand are preferred; to enhance the luminescence of europium and samarium complexes, the optimal choice is to use aromatic and conjugated unsaturated systems. High-symmetry square antiprismatic environment of the central atom is characteristic of complex tetrakis anions primarily with proton (H_3O^+, $H_5O_2^+$) cations.

Lanthanide bis(acylpyrazolonates) may have both mononuclear and binuclear structure. Varying the size and the nature of the bridge in bis(acylpyrazolones) provides a way to modify the complex geometry including obtaining of mono- and binuclear complexes and complex clusters.

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[a] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[b] — *Russ. J. Coord. Chem. (Engl. Transl.)*