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Review

Acylpyrazolone ligands: Synthesis, structures, metal coordination chemistry and applications

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Contents

Abbreviations: acacH, 2,4-pentanedione; bipy, 2,2′-bipyridine; Bnim, 1-benzylimidazole; Bn, benzyl; Bu, butyl; *i*Bu, *iso*-butyl; *t*Bu, *tert*-butyl; bzpy, 2-benzoylpyridine; cod, 1,5-cyclooctadiene; coe, cyclooctene; cot, cyclooctatetraene; Cp, cyclopentadienyl; cupr, 2,9-dimethyl-1,10-phenanthroline; Cy, cyclohexyl; dbzmH, dibenzoylmethane; Dd, dodecanoyl; diglyme, 2,5,8-trioxanonane; dmaeH, *N*,*N*-dimethylaminoethanol; dmf, dimethylformamide; dmso, dimethylsulphoxide; diphen, 4,7-dimethyl-1,10-phenanthroline; dppb, bis(diphenylphosphino)butane; dppe, bis(diphenylphosphino)ethane; dppf, 4,4′-bis(diphenylphosphino)ferrocene; dppm, bis(diphenylphosphino)methane; dppof, 4,4′-bis(diphenylphosphinooxide)ferrocene; dppp, bis(diphenylphosphino)propane; en, ethylene; Et, ethyl; etCp, ethylene-cyclopentadienyl; fur, furyl; $H_2C(tmpz)_2$, bis(3,4,5-trimethylpyrazol-l-yl)methane); haphH, 2-hydroxyacetophenone; (Hd, heptadecyl; He, hexyl; hex, 1,5-hexadiene; Hmimt, 1-methylimidazolin-2-thione; Hp, heptyl; imH, imidazole; Me, methyl; Meim, 1-methylimidazole; 2-MeimH, 2-methylimidazole; moeH, 2-methoxyethanol; nbd, 2,5-norbornadiene; OAc, CH3COO; Oc, octyl; pephen, 4,7-dipheyl-1,10-phenanthroline; Pd, pentadecyl; nPe, neo-pentyl; Ph, phenyl; phen, 1,10-phenanthroline; phencarz, 1-ethyl-2-(*N*-ethyl-carbazole-4-yl)imidazo[4,5-f]-1,10-phenanthroline; pmdien, *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine; Pr, propyl; *i*Pr, *iso*-propyl; py, pyridyl; pypr, 2,3-bis(2-pyridil)pyrazine; pzH, pyrazole; sm, succinimide; terpy, terpyridine; tetraglyme, 2,5,8,11,14-pentaoxapentadecane; tfb, tetrafluorobenzobarrelene; thf, tetrahydrofurane; thi, thienyl; tmeda, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; tmpzH, 3,4,5-trimethylpyrazole; triglyme, 2,5,8,11-tetraoxadodecane; trime, *N*,*N*,*N*′-trimethylethylenediamine; tppo, triphenylphosphine oxide; ttaH, thenoyltrifluoroacetone; Vy, vinyl; Xd, hexadecyl

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Abstract

This review summarizes the literature on 4-acyl-5-pyrazolone ligands, their synthesis, characterization and coordination chemistry toward main group, transition, lanthanide and actinide metals and relevant applications of their metal complexes.

Keywords: Acylpyrazolone ligands; Metal derivatives; Coordination chemistry

1. Introduction

Acylpyrazolones are an interesting class of β-diketones, containing a pyrazole fused to a chelating arm. The first synthesis of an acylpyrazolone appeared at the end of the XIX century [1]. However, it was only in 1959 that Jensen reported an advantageous method of preparation of 1-phenyl-3-methyl-4-acylpyrazol-5-ones [2]. We have recently reported a review on the coordination chemistry of β-diketones, a part of which was focused on relevant results in the field of acylpyrazolones [3]. Here, we report a more detailed description of acylpyrazolones coordination chemistry, which has greatly increased in the last decades. In this respect, acylpyrazolone ligands have also been used as advantageous metal extractants or chelating reagents in the spectroscopic determination of metals in traces [4] and a great number of studies have appeared in the literature on their ability to complex formation with metals. Such reactions are broadly used in analytical chemistry for determination and isolation of almost all metal ions, due to quite a number of valuable properties of these complexes such as hugh extracting ability, intense colour of the complex extracts and low-solubility of the complexes in some solvents. Moreover, the formation of the metal complexes with acylpyrazolones is applied for the separation of elements with similar properties, i.e. lanthanides, coinage metals, actinides, early transition metals, etc. [5]. However, these studies gave only selected data on acid dissociation constants of acylpyrazolones and metal complexes formation constants, without any other indication on the structure of metal derivatives, so here we give only references of some of the most relevant of these papers appeared in the last half century [6–21].

2. Ligands structure and substituents

There are many variations in this class of molecules, regarding mainly the donor atoms in the chelating ring, i.e. a sulphur or a nitrogen atom at the place of one or both oxygen atoms of chain and pyrazole carbonyls. However, in this review we will limit the discussion on the coordination chemistry of 1-R^1-3-R^2-4-R^3(C=O)-pyrazol-5-one ligands (Fig. 1), here indicated as HQ in general, where H is an enolizable proton.

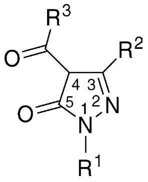


Fig. 1. Generic structure for acylpyrazolones.

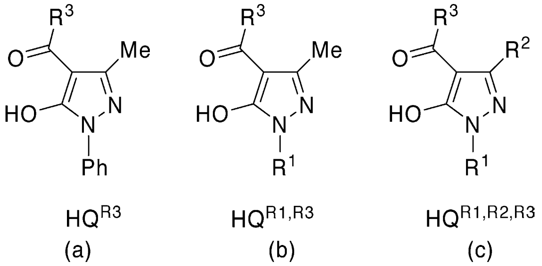


Fig. 2. Symbolism used in this review for the acylpyrazolones.

The following symbolism will be used: symbols up to right of Q indicate the substituents R^1, R^2 and R^3. However, due to the fact that generally $R^1 = Ph$, $R^2 = Me$, in this case only R^3 will be indicated, i.e. Q^{tBu} means $R^1 = Ph$, $R^2 = Me$, $R^3 = t$Bu (Fig. 2a). When $R^1 \neq Ph$, $R^2 = Me$, both R^1 and R^3 will be indicated up to right of Q, i.e. $Q^{Me,Ph}$ means $R^1 = Me$, $R^2 = Me$, $R^3 = Ph$ (Fig. 2b). Only when $R^1 =$ or $\neq$ Ph, $R^2 \neq Me$, all R^1, R^2, R^3 groups will be indicated, i.e. $Q^{Ph,Ph,Me}$ means $R^1 = Ph$, $R^2 = Ph$, $R^3 = Me$ (Fig. 2c).

3. Ligands synthesis

In the classical method of synthesis of HQ-type species, the reactants are the corresponding acyl chlorides and 1-phenyl-3-methylpyrazol-5-one, easily obtained from condensation between phenylhydrazine and ethyl acetoacetate. Acylation easily occurs at C-4 position of the pyrazole ring in basic (calcium hydroxide) dioxane or thf at reflux. Subsequent treatment with acid aqueous solution affords the HQ in high yield as a solid powder insoluble in water (Fig. 3) [2,22,23].

A variation in the synthesis was introduced when the acyl group was trifluoromethyl $-CF_3$ or heptafluoropropyl $-CF_2CF_2CF_3$: the reaction is performed at 0° in pyridine, which acts as solvent and base, and 1-phenyl-3-

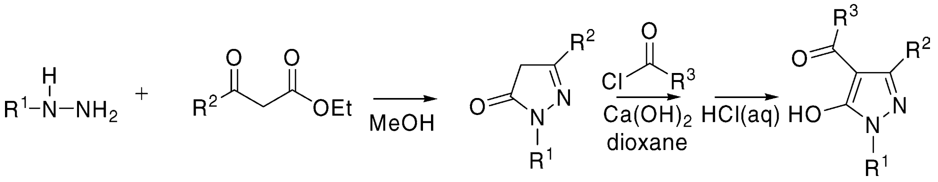
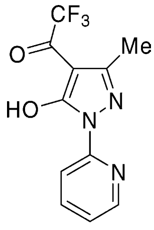


Fig. 3. Jensen's [2] and Okafor's [22,23] syntheses of the acylpyrazolones.

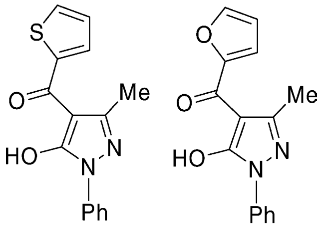
methylpyrazol-5-one reacts with fluorinated anhydrides. Addition of acqueous solution of HCl again provokes formation and precipitation of HQ [24,25]. The peripheral positions R^1, R^2 and R^3 can be easily changed in order to vary the electronic and steric features of HQ ligands. Other groups different to phenyl ring have been introduced in N^1 position, by using different starting hydrazines in the preparation of 1-R^1-3-methylpyrazol-5-one ($R^1 = –CH_3$, $–C_6H_4–NO_2$, $C_6H_4–CF_3$, $–C_5H_4N$) [26–29]. Among them it is worth mentioning the introduction of a pyridine ring, which increases the number of donor atoms in HQ^{py,CF_3}, a ligand potentially O_2,N_2-tetradentate, with two different chelating moieties placed in opposite faces of the pyrazole ring (Fig. 4) [29].

It is also possible to substitute the methyl in C-3 position, for example with a phenyl one, by using ethyl benzoylacetate in the preparation of the reactant 1-R^1-3-R^2-pyrazol-5-one [30,31]. Also, a vinyl group can be introduced in R^2, the corresponding HQ ligands ($Q = Q^{Ph,Vy,Me}$, $Q^{Ph,Vy,Et}$, $Q^{Ph,Vy,Ph}$) being only used in organic synthesis to form pyranopyrazolones and not in the interaction with metal acceptors [32]. However, acyl substitution has been much more explored, where a large number of groups, from alkyl to aryls, have been introduced by simply choosing different acyl chlorides. Heteroatoms in the acyl position have also been introduced, i.e. heteroaromatic rings such as thienyl and furyl groups in HQ^{thi} and HQ^{fur} (Fig. 5), but to date these ligands have not displayed any coordination through the additional O- and S-donor atoms [33,34].



$HQ^{py,CF3}$

Fig. 4. Structure of the proligand HQ^{py,CF_3}.



HQ^{thi} HQ^{fur}

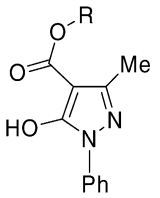
Fig. 5. Structures of the proligands HQ^{thi} and HQ^{fur}.

A recent work on lanthanide derivatives reported the use of Q ligands containing –OEt, $–NMe_2$ or $–NPh_2$ groups in the acyl position [25]. We have found that alkoxy groups OR can be introduced in the acyl moiety of Q^{CCl_3} by substitution of the CCl_3 with an OR group when the reactions were carried out in alcoholic ROH solvents (R = Me, Et, *i*Pr, Bn) (Fig. 6) [35,36].

Fusion of 5-pyrazolone with $AcNH_2$ followed by the alkaline hydrolysis affords 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, which undergoes condensation with RCHO (R = phenyl, furyl, *p*-$Me_2NC_6H_4$, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-HOC_6H_4, *p*-$O_2NC_6H_4$), affording Q ligands containing a C=C double bond in α-position to the chain C=O (Fig. 7) [37].

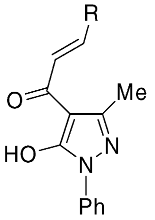
An alternative way to obtain HQ ligands containing a C=C double bond in α-position to chain C=O is the classical Jensen method, [2] by using 1-phenyl-3-methyl-5-pyrazolone and *trans*-cinnamoyl chloride [38]. However, the potentials of these Q ligands have been not yet tested.

An exotic variation in acyl moiety is represented by a $–CH_2C(=O)CH_3$ group, to form a 1-phenyl-3-methyl-4-acetoacetyl-5-pyrazolone [39] which has been characterized



R = Me, Et, *i*Pr, Bn

Fig. 6. Generic structure of the proligands HQ^{OR} derived by HQ^{CCl_3} by substitution of the CCl_3 with an OR group.



R = Ph, fur, Ph-p-NMe_2, Ph-p-Me,
Ph-p-OMe, Ph-p-OH, Ph-p-NO_2,

Fig. 7. Generic structure of the acylpyrazolones containing a C=C double bond in α-position to the chain carbonyl.

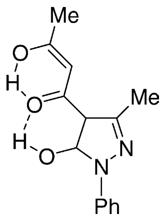
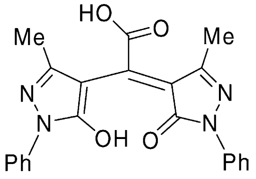


Fig. 8. Structure of 1-phenyl-3-methyl-4-acetoacetyl-5-pyrazolone.

also by X-ray studies (Fig. 8) showing the molecule to exist in a tautomeric form containing two intramolecular H-bonds [40].

Another interesting variation is represented by H_2QnQ ligands where two acylpyrazolone units are linked one to each other through a polymethylene chain of variable length ($n = 0$–8, 10, 20) (Fig. 9). They are potentially tetradentate bis-chelating donors that can be synthesized by using the appropriate diacyl chloride [41].

Similarly, a phenyl group can be introduced between the two acylpyrazolone moieties, by using the appropriate benzenedicarbonyl chlorides, as in the tetradentate donors $H_2Q(n, m)PhQ$ ligands ($n,m = 1,2$ or 1,3 or 1,4) (Fig. 10) [42].



H_2QBz

Fig. 11. Structure of the proligand H_2Q_2Bz.

We have recently reported that attempted synthesis of the hypothetical ligand $H_2Q(1,2)PhQ$, following Yoshikuni method from phthaloyl chloride and 1-phenyl-3-methylpyrazol-5-one in anhydrous dioxane, afforded a completely different species than bis(acylpyrazolone) [43]. The crystal structure shown it to be 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]-benzoic acid (H_2Q_2Bz) (Fig. 11). In fact, the use of phthaloyl chloride prevents the formation of bis(acylpyrazolone), due to the formation of the stable lactone intermediate, which hydrolyses in alkali media giving H_2QBz in high yield. Moreover, the spectral data of H_2QBz are in accordance with those reported by Yoshikuni [42].

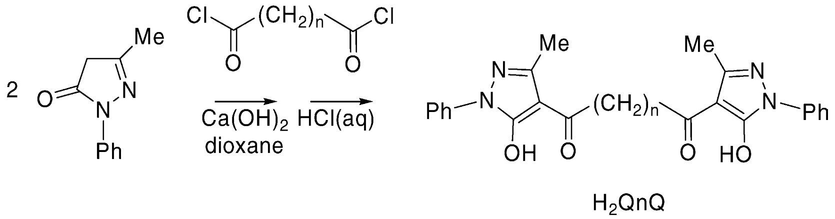


Fig. 9. Umetani's [41] synthesis of the proligands H_2QnQ (where n = number of methylene groups between the acylpyrazolone units).

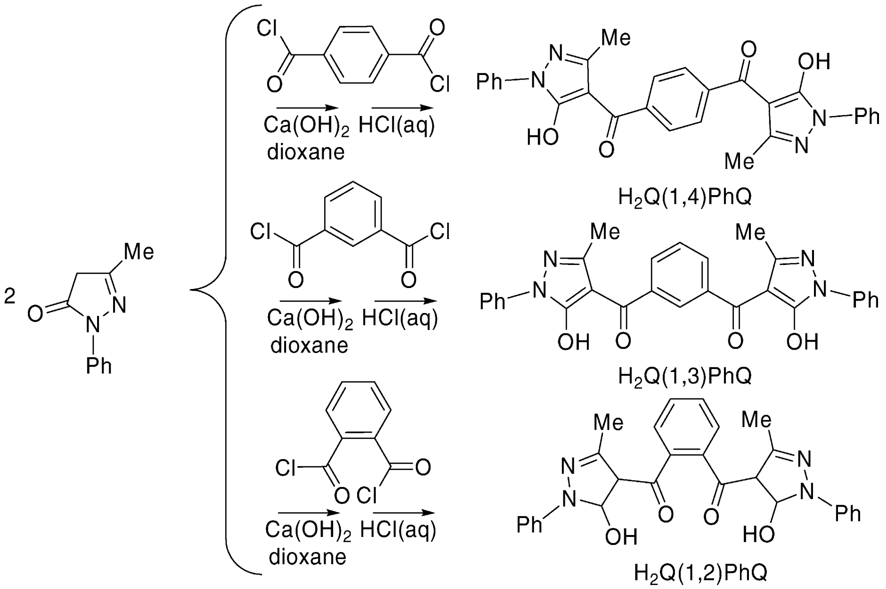


Fig. 10. Yoshikuni's [42] syntheses of the proligands $H_2Q(n,m)PhQ$ (where n,m = 1, 2 or 1, 3 or 1, 4).

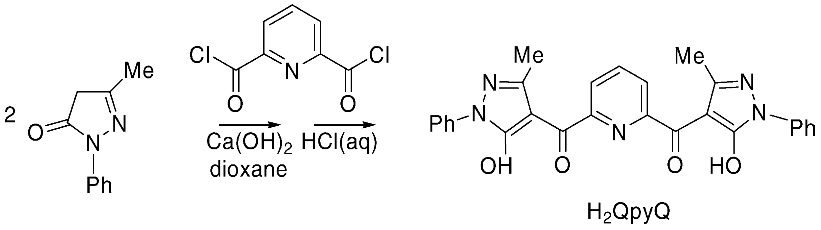


Fig. 12. Pettinari's [44] synthesis of the proligand H_2QpyQ.

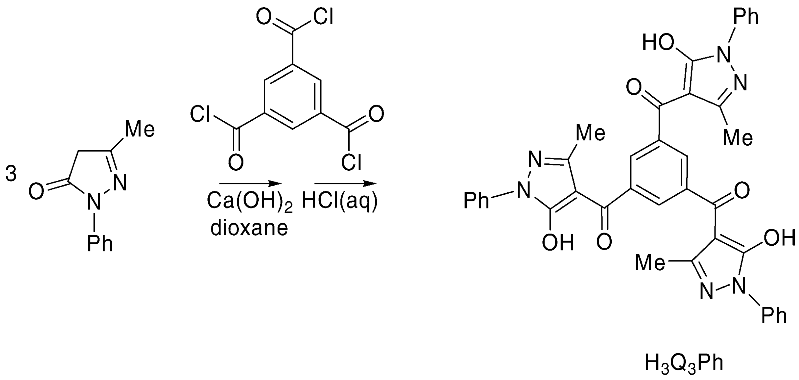


Fig. 13. Raymond's [45,46] synthesis of the proligand H_3Q_3Ph.

A polydentate O_4, N-donor ligand H_2QpyQ (Fig. 12), can be synthesized by using the corresponding pyridine-2,6-dicarbonyl chloride and 1-phenyl-3-methyl-5-pyrazolone [44].

A potentially hexadentate trischelating donor ligand H_3Q_3Ph has been synthesized (Fig. 13) starting from 1,3,5-benzene tricarbonyl trichloride and 1-phenyl-3-methylpyrazol-5-one [45,46].

The synthesis of 4-acylpyrazol-5-one-substituted crown ethers metal-chelating reagents has been recently described [47]: 4-acylpyrazol-5-one-substituted dibenzo-16-crown-5 (X = $CH_2CH_2OCH_2CH_2$), 4-acylpyrazol-5-one-substituted dibenzo-19-crown-6 (X = $CH_2CH_2OCH_2CH_2OCH_2CH_2$) and bis(4-acylpyrazol-5-one)-substituted diaza-18-crown-6 (Fig. 14) have been prepared by simple coupling reactions between α-chloro 4-acylpyrazol-5-one and the corresponding crown ethers. These ligands have been found effective as metal ion-selective extraction reagents, but no detailed studies on their coordination and structural chemistry have been reported till now [47].

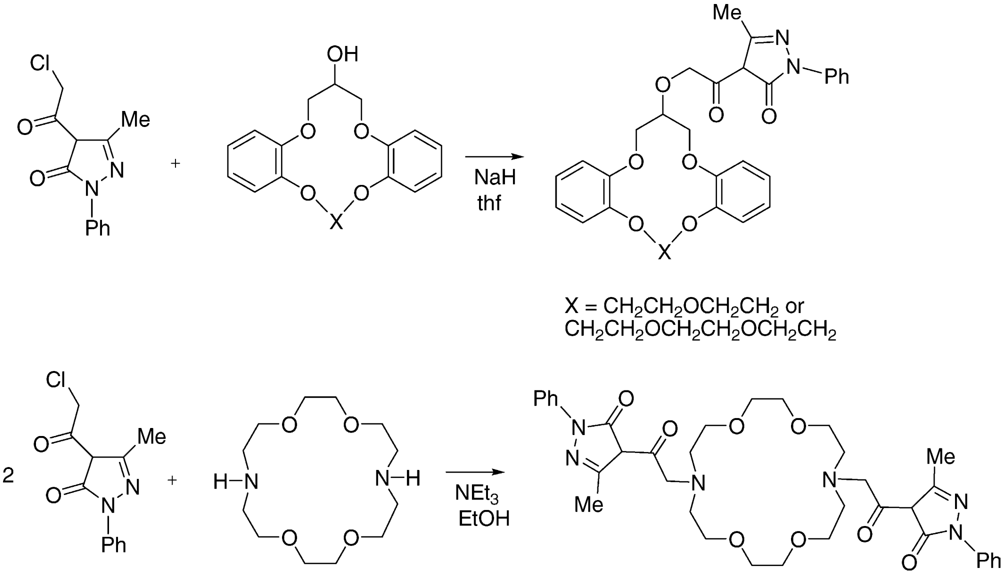


Fig. 14. Umetani's [47] syntheses of 4-acylpyrazol-5-one-substituted crown ethers.

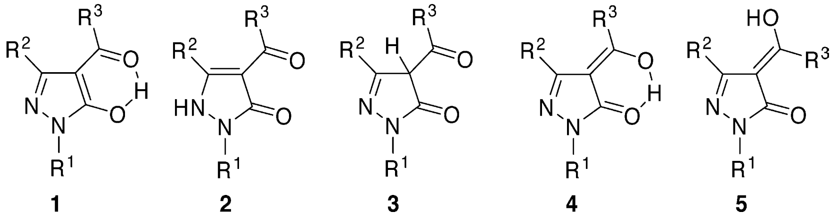


Fig. 15. Tautomeric forms of acylpyrazolones.

4. Ligands characterization

The neutral acylpyrazolones HQ can exist both in solution and in the solid state in several possible tautomeric forms as those reported in Fig. 15.

The spectroscopic characterization of many HQ ligands through IR, Raman, UV–vis, ^{1}H and ^{13}C NMR, mass spectra and ab initio calculations have been reported, factors influencing the equilibrium between the tautomeric forms being mainly explored [38,48–62]. The OH enol form 1 is generally preferred in non-polar solvents, however, a phenyl ring in R^2 position stabilizes the NH amino-diketo form 2 [31]. The same situation has also been observed with a Ph-*p*-CF$_3$ in R^1 [63]. Crystal structure X-ray analyses of some HQ ligand have been performed showing HQ ligands, crystallized from chloroform, in the enol form 1, and an intramolecular O–H···O system, as in the structure of HQ^{Ph} [64], HQ^{Pr} [65], HQ^{Me} [66], HQ^{fur} [67], HQ^{Et}, HQ$^{CH=CHPh}$ [38].

Whereas the amino diketonic form 2, stabilized by an extensive network of intermolecular N–H···O bonding, can be obtained from re-crystallization in polar solvents like methanol, as found in the ligand HQ^{Ph} [64,40], HQ^{Me} [68] and HQ^{thi} [38].

5. Coordination modes of acylpyrazolones

The acylpyrazolones have displayed some interesting coordination modes in the neutral HQ form (Fig. 16). The enol tautomer can coordinates to metal in a chelating bidentate O$_2$-form (Fig. 16a), as found in the crystal structure of [Ba(Q^{Ph})$_2$(HQ^{Ph})$_2$]H$_2$O, where the enolic H is bonded to an external water molecule [69], or also through the ring N^2 atom of the pyrazole (Fig. 16b), as observed in the crystal structure of [Rh(CO)$_2$Cl(HQ^{fur})] [67]. The neutral HQ can also coordinate in O$_2$-chelating bidentate keto amino tautomeric form (Fig. 16c), as found in [SnR$_n$Cl$_{4-n}$(HQ)] adducts (Q = Q^{Ph}, Q^{Me}, Q^{CF_3}, Q^{PhpNO_2}, Q^{PhpOMe}) [70], and in O$_2$-chelating bidentate diketo form (Fig. 16d), as observed in complexes [Cr^I(NO)(CN)$_2$(HQ)(H$_2$O)] (Q = Q^{Me}, Q^{Pr}, Q^{CH_2Cl}, Q^{PhpCl}) [71].

By treatment with a base such as NR$_3$, or KOH, or NaOMe, the HQ ligand can be deprotonated (Fig. 16). In the anionic form the most observed coordination mode is the O$_2$-chelating bidentate (Fig. 16e). Two different M–O bond distances have been observed, due to intrinsically different donating power of the two carbonyl oxygen atoms, as found in diorganotin(IV) [26] and dioxo uranium(VI) derivatives [72]. A bridging tetradentate η^4-O$_2$-coordination mode (Fig. 16f) has been found in alkaline earth metal derivatives such [Ba(Q^{nPe})$_2$(L)$_2$]$_2$ (L = H$_2$O, imH) [73] and (imH$_2$)$_2$[Sr$_2$(Q)$_6$] [74]. The acylpyrazolonate have been found effective as monodentate O-donors to tin in [SnR$_3$(Q)(H$_2$O)] (R = alkyls) (Fig. 16g) where the chain carbonyl and ring N^2 are involved in H-bonding network with hydrogen atoms of water [75,76]. The acylpyrazolonates can also coordinate metals through N^2 atom of the pyrazole ring, as observed in silver [66] and lead spcies [77,78], where Q is bonded in a bridging ^{3}-O$_2$,N-mode (16h). The Q ligands bind in a bridging η^2-N,O-mode in some silver derivatives (Fig. 16i) [66]. In a lead derivative [Pb(Q^{nPe})$_2$], recently reported the Q^{nPe} ligand chelates a Pb in a O$_2$-chelating mode interacting with the Pb of a second molecule through a phenyl ring (Fig. 16j) [79]. When the substituent in 1-position is a pyridine ring as in Q^{py,CF_3}, the ligand binds one silver atom in the N$_2$-chelating mode (Fig. 16k), two silver atoms in the bridging η^3-O,N$_2$-mode (16l), and finally two silver atoms in the bridging η^4-O$_2$,N$_2$-bis-chelating ligand (16m) [29].

6. Metal derivatives of acylpyrazolones

6.1. Group IA: Na and K

The derivatives [Na(Q^{Ph})] and [K(Q^{Ph})] have been isolated and characterized by analytical and spectral techniques but no conclusive data were reported on the structure adopted in the solid state structure from both compounds. Their synthesis is very easy and they are likely ionic in the solid state [22].

6.2. Group IIA: Be, Mg, Ca, Sr and Ba

The first reports on alkaline earth metal Q derivatives have described the synthesis and characterization of a number of metal acylpyrazolonates having formula [M(Q)$_2$(H$_2$O)$_2$] (M = Be, Mg, Ca, Ba; Q = Q^{Me}, Q^{Ph}, Q^{CF_3}) [22–24,80]. Replacement of the Me group of the 4-acetyl moiety by the Ph group in the metal chelates of Q^{Me} decreases the C=O, C=C, M–O stretching frequencies of the chelate ring. Whereas, replacement of the Me group by CF$_3$ group in the acetyl moi-

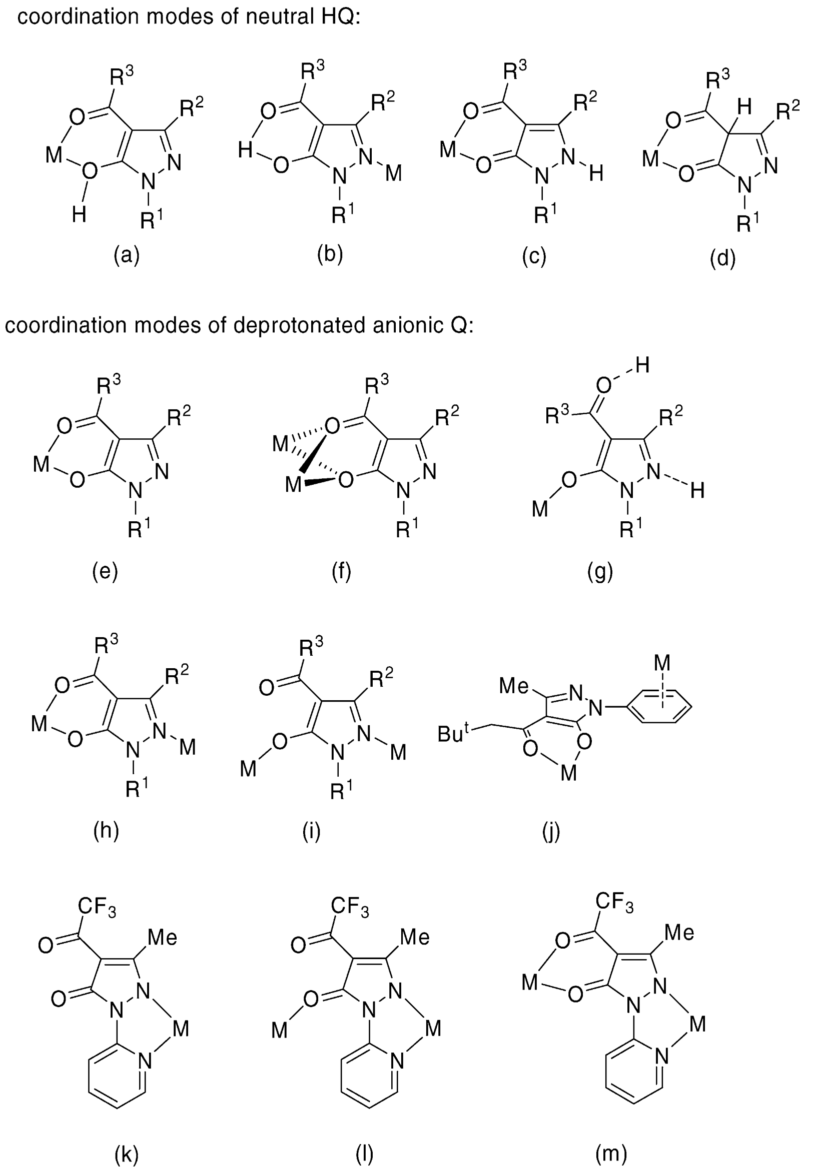


Fig. 16. Coordination modes of acylpyrazolones.

ety of Q^{Me} increases the C=O and C=C bond strengths and decreases that of the M–O bond [22–24,80]. Calcium derivatives $[Ca(Q)_2]\cdot xH_2O$ ($x = 0$, 1/2, 1, 2) ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}) have been synthesised from $Ca(OAc)_2$ and HQ in H_2O/EtOH. The spectral data are consistent with weak Ca–O bonds [81,82]. In 1995, the first X-ray crystal structures of Ca and Ba acylpyrazolonates have been described [69]. In $[Ca(Q^{Ph})_2(EtOH)_2]$, the Q^{Ph} ligands are in the equatorial plane coordinated in a O_2-bidentate fashion, arranged in an *anti* configuration to each other. The two EtOH molecules are in axial positions (Fig. 17) involved in an intermolecular extended H-bonding network with N atoms of pyrazole by neighbouring molecular units. In $[Ba(Q^{Ph})_2(HQ^{Ph})_2]\cdot H_2O$, the Ba atom shows an eight-coordination by two anionic O_2-bidentate Q^{Ph} and two neutral O_2-bidentate HQ^{Ph} with a water molecole H-bonded to the oxygen atom of a neutral HQ^{Ph} (Fig. 18) [69].

From the interaction of $CaCl_2$ with HQ^{nPe} in EtOH in the presence of KOH, the compound $[Ca(Q^{nPe})_2(EtOH)_2]$ has been obtained and structurally characterized [83], which is isostructural to previous mentioned $[Ca(Q^{Ph})_2(EtOH)_2]$

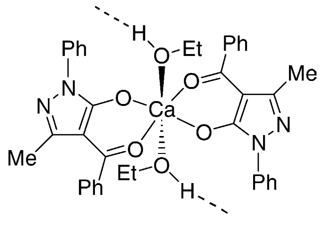


Fig. 17. Structure of the derivative $[Ca(Q^{Ph})_2(EtOH)_2]$.

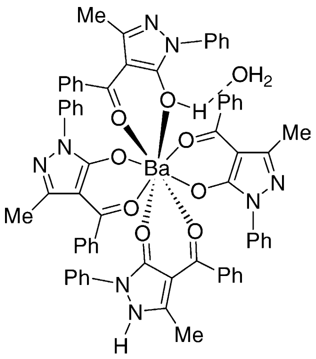


Fig. 18. Structure of the derivative $[Ba(Q^{Ph})_2(HQ^{Ph})_2]\cdot H_2O$.

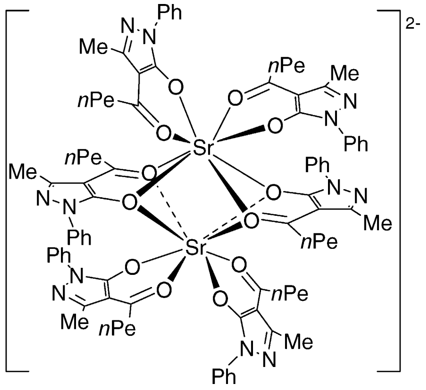


Fig. 21. Structure of the derivative $(imH_2)_2[Sr_2(Q^{nPe})_6]$.

[69]. The interaction between $[Ca(Q^{nPe})_2(EtOH)_2]$ and phen in chloroform afforded $[Ca(Q^{nPe})_2(phen)]$ (Fig. 19). $[Ca(Q^{nPe})_2(ROH)_2]$ were generally obtained in alcoholic ROH solvents when R = Me or Pr^i, whereas the compound $[Ca(Q^{nPe})_2(H_2O)_2]$ formed when R = *t*Bu, $-CH_2C\equiv CH$ or CH(*t*Bu)(*i*Pr) [83].

Neutral $[Sr(Q)_2(L)_n]$ or ionic $(imH_2)_2[Sr_2(Q)_6]$ complexes (QH = Q^{nPe}, Q^{Ph}, Q^{CF_3}; L = tetraglyme, moeH, dmaeH, phen, $n = 1$; L = H_2O, imH, $n = 2$) were recently synthesized with a one-pot reaction between metallic Sr, HQ and L or imH in EtOH [74]. $[Sr(Q^{nPe})_2(moeH)_2]$ (Fig. 20) contains an eight-coordinate Sr atom in a square antiprismatic environment from two bidentate chelating Q-donors and two bidentate moeH ligands [74]. The complex $(imH_2)_2[Sr_2(Q^{nPe})_6]$ (Fig. 21) is composed of two imidazolium cations and a dianionic fragment $[Sr_2(Q^{nPe})_6]^{2-}$, which is a centrosymmetric dimer containing four terminal and two bridging Q-donor ligands [74].

$[\{Ba(Q^{nPe})_2(H_2O)_2\}_2]$ [72] is a dinuclear compound in the solid state (Fig. 22), with η^2-terminal and η^4-bridging Q^{nPe} ligands, the H_2O being involved in a intermolecular H-bonding interactions. The reaction of HQ^{nPe} with metallic Ba in the presence of mono- , bi- or poly-dentate O- or N-donor ligands, afforded derivatives of formula $[Ba(Q^{nPe})_2(L)_n(H_2O)_m]$, depending on the nature of the ancillary ligand and reaction conditions employed (L = tetraglyme, triglyme, diglyme, terpy, pypr; $n = 1$, $m = 0$ or 1; L = imH, Meim, 2-MeimH, phen, bipy, cupr, tppo; $n = 2$, $m = 0$ or 1) [73]. In the nine-coordinated $[Ba(Q^{nPe})_2(tetraglyme)]$ (Fig. 23), the Ba atom is bonded to all the five oxygen atoms of tetraglyme and to four oxygen atoms of two bidentate Q^{nPe} whereas in $[Ba(Q^{nPe})_2(phen)_2]$ the coordination number of Ba is 8 (Fig. 24), due to four oxygen atoms of the two Q^{nPe} ligands and four nitrogen atoms of the two phen. The derivative $[\{Ba(Q^{nPe})_2(imH)_2\}_2]$ is dinuclear (Fig. 22) with the Ba atoms linked by two

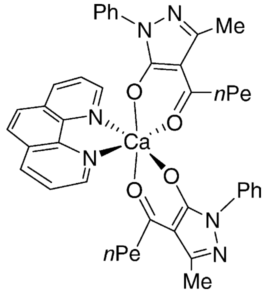


Fig. 19. Structure of the derivative $[Ca(Q^{nPe})_2(phen)]$.

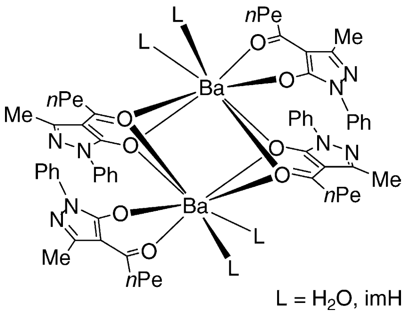


Fig. 22. Structure of the derivative $[\{Ba(Q^{nPe})_2(H_2O)_2\}_2]$.

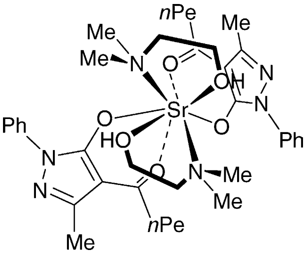


Fig. 20. Structure of the derivative $[Sr(Q^{nPe})_2(moeH)_2]$.

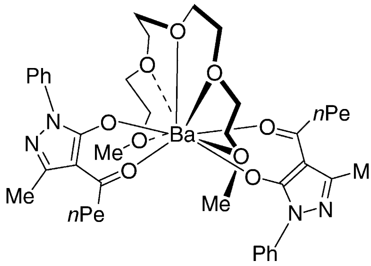


Fig. 23. Structure of the derivative $[Ba(Q^{nPe})_2(tetraglyme)]$.

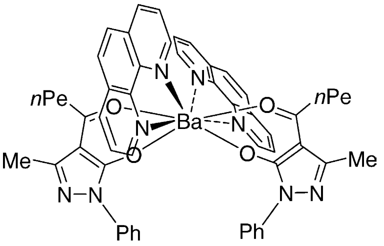


Fig. 24. Structure of the derivative [Ba($Q^{n\mathrm{Pe}}$)$_2$(phen)$_2$].

η^4-O_2-bridging double chelating $Q^{n\mathrm{Pe}}$ ligands [73]. The compound [{Ba($Q^{n\mathrm{Pe}}$)$_2$}$_n$] has been obtained by heating [{Ba($Q^{n\mathrm{Pe}}$)$_2$(H_2O)$_2$}$_2$] in vacuo at 100 °C, whereas the 1:1 adduct [Ba($Q^{n\mathrm{Pe}}$)$_2$(phen)] was obtained from a 1:1 diethyl ether solution of [{Ba($Q^{n\mathrm{Pe}}$)$_2$}$_n$] and phen [73]. By reaction between [Ba($Q^{n\mathrm{Pe}}$)$_2$(pypr)] and $CdCl_2$, scrambling of the ligand occurs. [{Ba($Q^{n\mathrm{Pe}}$)$_2$(H_2O)$_2$}$_2$] and [($CdCl_2$)$_2$(pypr)] being obtained [73].

The poorly volatile mononuclear Ba-$Q^{n\mathrm{Pe}}$ derivatives are not suitable molecular precursors for chemical vapour deposition (CVD) [84].

Barium acylpyrazolonate derivatives containing polydentate N-donor ligands, [Ba(Q)$_2$(tmeda)$_2$] (Fig. 25), [Ba(Q)$_2$(pmdien)(H_2O)] (Fig. 26) ($Q = Q^{n\mathrm{Pe}}$, $Q^{t\mathrm{Bu}}$) and [Ba(Q)$_2$(pmdien)(Meim)] ($Q = Q^{n\mathrm{Pe}}$, $Q^{t\mathrm{Bu}}$) have been synthesized and analytically and spectroscopically characterized [85]. They are air and solution stable compounds containing an eight-coordinated barium atom. The X-ray crystal structures of hydrated [Ba($Q^{n\mathrm{Pe}}$)$_2$(pmdien)(H_2O)] and [Ba($Q^{t\mathrm{Bu}}$)2(pmdien)(H_2O)] (Fig. 26) show the water molecule directly bonded to Ba and involved in intermolecular H-bonding network [85].

In [Ba(Q)$_2$(pmdien)(Meim)] ($Q = Q^{n\mathrm{Pe}}$, $Q^{t\mathrm{Bu}}$) (Fig. 27), one molecule of Meim takes the places of a molecule of water [85]. The derivative [Ba($Q^{t\mathrm{Bu}}$)$_2$(pmdien)(NEt_3)] (Fig. 28) has also been prepared from the interaction of [Ba($Q^{t\mathrm{Bu}}$)$_2$(pmdien)(H_2O)] with an excess of triethylamine in acetonitrile [85].

An alkaline earth metal derivative containing a 4-acylbis(pyrazol-5-onate) ligand, [Ca(Q8Q)], has been prepared and described as a monomeric compound with a four-coordinate Ca atom [86].

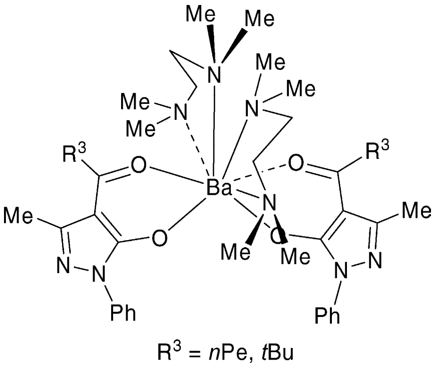


Fig. 25. Structure of the derivatives [Ba(Q)$_2$(tmeda)$_2$].

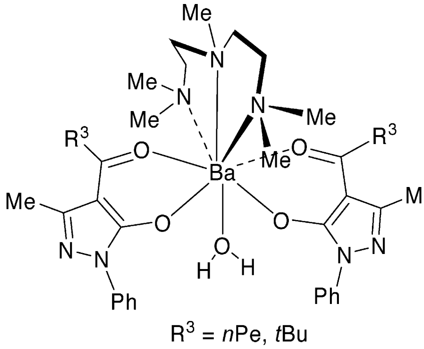


Fig. 26. Structure of the derivatives [Ba(Q)$_2$(pmdien)(H_2O)].

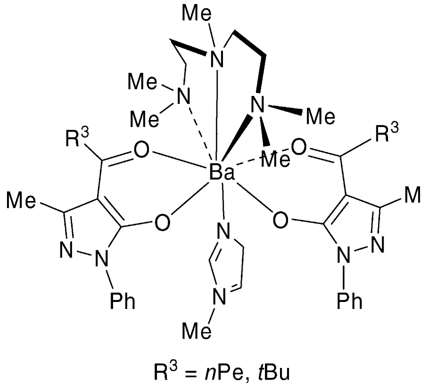


Fig. 27. Structure of the derivatives [Ba(Q)$_2$(pmdien)(Meim)].

6.3. Group IVB: Ti and Zr

A zirconium(IV) acylpyrazolone derivatives [Zr(Q^{Ph})$_4$], has been synthesized and characterized spectroscopically and magnetically in 1981 [87]. An analogous [Zr(Q^{CF_3})$_4$] derivatives has been reported in the same year (Fig. 29) [88,89].

The first Ti acylpyrazolonates, [Ti(OR)$_{4-n}$(Q)$_n$] and [$TiCl_{4-n}$(Q)$_n$] ($n = 1$, 2; R = Et, *i*Pr; $Q = Q^{\mathrm{Ph}}$, Q^{Me}, Q^{Et}, Q^{PhpCl}), were described in 1982 [90]. [Ti(OR)$_{4-n}$(Q)$_n$] react with *t*BuOH affording [Ti(O*t*Bu)$_{4-n}$(Q)$_n$] whereas [Ti(O*i*Pr)$_2$(Q)$_2$] react with PhNCO in benzene to give [Ti(NPhC(O)O*i*Pr)(O*i*Pr)$_2$(Q)$_2$] [90]. Analogous [Zr(O*i*Pr)$_{4-n}$(Q)$_n$] derivatives ($n = 1$–4) were obtained, and they react with *t*BuOH affording [Zr(O*t*Bu)$_{4-n}$(Q)$_n$] ($n = 1$–3) [91].

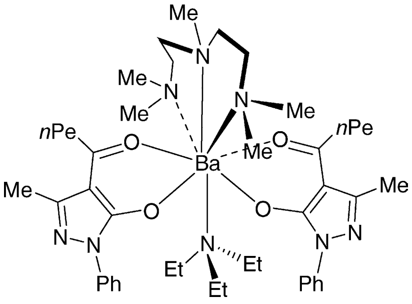


Fig. 28. Structure of the derivative [Ba($Q^{n\mathrm{Pe}}$)$_2$(pmdien)(NH_3)].

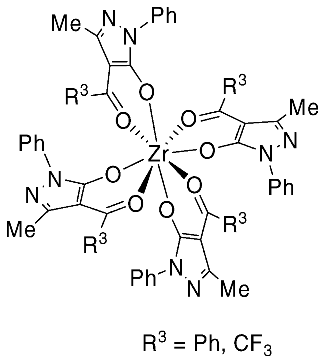


Fig. 29. Structure of the derivatives $[Zr(Q)_4]$.

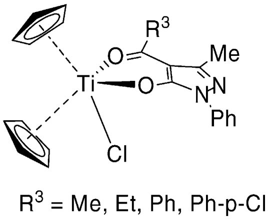


Fig. 30. Structure of the derivatives $[TiCp_2Cl(Q)]$.

Mononuclear $[TiCp_2Cl(Q)]$ (Fig. 30) and dinuclear $[(\eta^1:\eta^5\text{-}C_5H_4)Ti(Q)_2]_2$ (Fig. 31) can be obtained by treating Cp_2TiCl_2 with 1 or 2 equivalent HQ ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{PhpCl}) in the presence of NEt_3 [92]. The dinuclear species contain $\eta^1:\eta^5$-bridged cyclopentadienyl groups. Whereas $TiCpCl(Q^{Me})_2$ (Fig. 32) was obtained from interaction of $CpTiCl_3$ and HQ^{Me} [92]. Dinuclear $[(\eta^1:\eta^5\text{-}C_5H_4)Ti(Q)_2]_2$ were also prepared from reaction of $[TiCp_2Cl(Q)]$ with HQ and NEt_3 or by treating $[TiCpCl(Q^{Me})_2]$ with NEt_3 [92].

The insecticidal activity of some of these compounds against *Trogoderma granarium* was tested, and the following order found $Q^{PhpCl} > Q^{Me} > Q^{Ph}$ [93]. Isostructural $[ZrCp_2Cl(Q)]$, $[ZrCpCl(Q)_2]$ and dinuclear $[(\eta^1:\eta^5\text{-}C_5H_4)Zr(Q)_2]_2$ were also prepared [94].

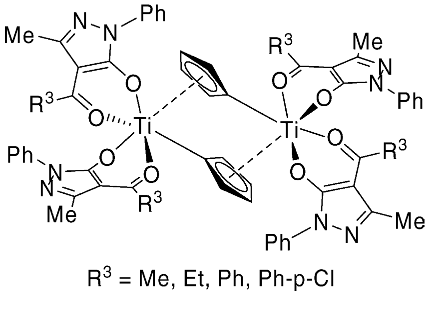


Fig. 31. Structure of the derivatives $[(\eta^1:\eta^5\text{-}C_5H_4)Ti(Q)_2]$.

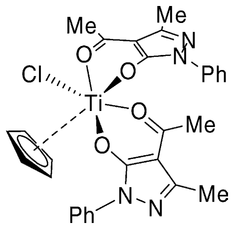


Fig. 32. Structure of the derivative $[TiCpCl(Q^{Me})_2]$.

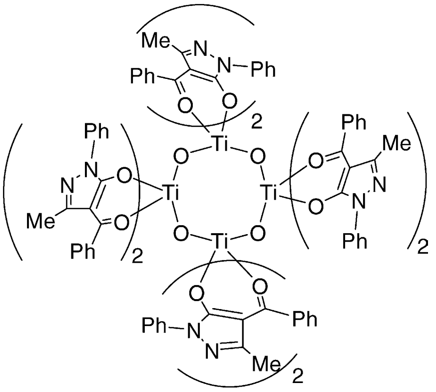


Fig. 33. Structure of the derivative $[Ti(\eta^2\text{-}O)(Q)_2]_4$.

Other studies on the insecticidal activity of dinuclear Ti and Zr acylpyrazolones toward *Periplaneta americana* (a household pest), *Trogoderma granarium* and *Tribolium castaneum* (stored product pests), and the larvae of *Aedes aegypti* (an insect pest of medical importance) have been reported, assessing their potentials with respect to Cp_2MCl_2 (M = Ti, Zr) or HQ alone [95].

A decades later a cyclo-tetranuclear $[Ti(\eta^2\text{-}O)(Q)_2]_4$ (Fig. 33) derivative has been synthesised and fully characterized also by X-ray diffraction methods [96]. The antitumor activity of this compound, encapsulated in a dipalmitoylphosphatidylcholine liposome, has been studied in vitro using TA-3 (*mouse mammary adenocarcinoma*), HEP-2 (*human epithelial larynx carcinoma*) and VERO (*African green monkey kidney*) cell lines and in vivo in CF-1 and AJ female mice i.p. inoculated with TA-3 [96]. In vitro cytotoxicity is greater for TA-3 than for HEP-2 and null for VERO cell lines. In vivo results show a marked increase in survival time ($T/C = 293\%$ for AJ, 208% for CF-1), whereas tumor weight decrease was observed for CF-1-treated mice [96]. These results suggest the Ti complex–liposome system may be promising as an antitumor drug [96].

A number of Ti derivatives have been recently reported by interaction of $TiCl_4$ or $Ti(OR)_4$ with a variety of Q ($Q = Q^{Ph}$, Q^{PhpOMe}, Q^{PhpNO_2}, Q^{nPe}, Q^{Bn}, Q^{Cy}, Q^{He}, $Q^{Ph,Ph}$) [97]. When the reaction was carried out in aerobic conditions cyclo-tetranuclear $[Ti(\eta^2\text{-}O)(Q)_2]_4$, olygonuclear $[Ti(\eta^2\text{-}O)(H_2O)_x(Q)_2]_n$ $[Ti(OH)_3(H_2O)_x(Q)]_n$ or $[Ti(\eta^2\text{-}O)(OH)(Q)]_n$, and mononuclear $[Ti(OH)(OR)(Q)_2](H_2O)$ afforded, upon Ti–O(alkoxy) (or Ti–Cl) bonds cleavage due to hydrolysis [96]. Whereas, by carrying out the reactions in anhydrous conditions under N_2, monomeric compounds $[TiCl_2(Q)_2]$ and $[Ti(OR)_2(Q)_2]$ have been obtained [97]. DFT studies on the *cis* isomers of $[Ti(OMe)_2(Q^{nPe})_2]$ shown one of them less stable than the others. In the case of $[TiCl_2(Q^{nPe})_2]$ all *cis* isomers show similar stabilities [97]. Potential antitumor compounds water-soluble having a Ti/Q ratio of 1:1 do

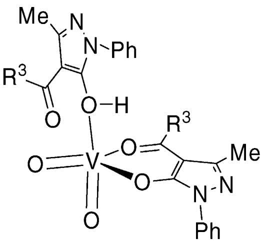

R^3 = Ph, Me, Et, Pr, Bu, Hp, CF_3, CCl_3

Fig. 34. Structure of the derivatives $[VO_2(Q)(HQ)]$.

not disproportionate, unlike the analogous acetylacetonato derivatives [97].

6.4. *Group VB: V and Nb*

The first report on vanadium(IV) acylpyrazolonate derivatives appeared in 1976, when an oxovanadium(IV) $[VO(Q^{Ph})_2]$ compound, synthesized from interaction between $VOSO_4{\cdot}5H_2O$ and HQ^{Ph} in the presence of NaOAc in EtOH, has been characterized spectroscopically and magnetically [98]. A series of dioxovanadium(V) derivatives $[VO_2(Q)(HQ)]$ ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}, Q^{CF_3}, Q^{CCl_3}) was synthesized from interaction of an ethanol solution of HQ and aqueous solution of NH_4VO_3 acidified with HCl. The acylpyrazolonates coordinate both in the anionic Q and neutral keto–enol monodentate HQ forms. IR studies show that O=V=O system is likely bent in a trigonal bipyramidal environment (Fig. 34) [99].

Square pyramidal oxovanadium(IV) compounds $[VO(Q)_2]$ ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}, Q^{CF_3}, Q^{CCl_3}), were prepared by mixing an ethanolic solution of HQ with a H_2O/EtOH solution of V_2O_5 acidified with HCl (Fig. 35) [100].

Mixed-ligand complexes of oxovanadium(IV), $[VO(Q)(L)(H_2O)]$ ($Q = Q^{Ph}$, Q^{Pr}; HL = acetoacetanilide, *o*-acetoacetotoluidide, *o*-acetoacetanisidide, methylacetoacetate, etylacetoacetate or dibenzoylmethane (dbzmH) have been synthesized by interaction of $VOSO_4{\cdot}5H_2O$ with HQ and HL in aqueous ethanol medium [101,102]. The three-dimensional molecular modelling and analysis on some of these compounds indicates an octahedral environment on V with a linear O=V–OH_2 moiety (Fig. 36) [101,102].

Similar mixed-ligand complexes $[VO(Q)(sm)(H_2O)]$ (sm = succinimide; $Q = Q^{Me}$, Q^{Pr}) have been obtained and characterized by magnetic measurements, ESR, electronic and IR spectral studies, indicating octahedral geometries for these derivatives (Fig. 37) [103].

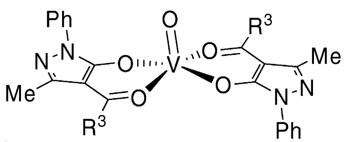

R^3 = Ph, Me, Et, Pr, Bu, Hp, CF_3, CCl_3

Fig. 35. Structure of the derivatives $[VO(Q)_2]$.

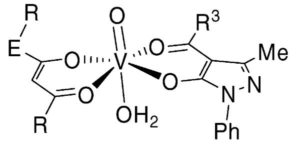

R^3 = Ph, Pr; E = O, NH; R = Me, Et, Ph, PhoMe

Fig. 36. Structure of the derivatives $[VO(Q)(L)(H_2O)]$.

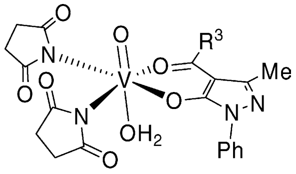

R^3 = Me, Pr

Fig. 37. Structure of the derivatives $[VO(Q)(sm)(H_2O)]$.

Monomeric derivatives $[VO_2(HQ4Q)]{\cdot}H_2O$ and $[VO_2(HQ8Q)]{\cdot}H_2O$, containing the bis(acylpyrazolone) ligands in the monoanionic HQnQ form and acting as η^3-tridentate O-donors, have been reported and characterized [104]. IR spectra showed that O=V=O species exist as the *cis* form in the complexes [104]. Some ionic oxoniobium(V) acylpyrazolone derivatives $(H_2Q^{Ph})[NbOX_n]$ (X = Cl, NO_3; $n = 4$; X = SO_4; $n = 2$) (Fig. 38), have been spectroscopically and magnetically characterized [87].

6.5. *Group VIB: Cr and Mo*

The complex $[Cr(Q^{PhmCl,Me})_3]{\cdot}H_2O$, containing an octahedrally six-coordinated chromium, has been reported. It is a paramagnetic compound with μ_{eff} 4.00 BM, typical of octahedral Cr complexes [105]. Some cyanonitrosyl chromium derivatives $[Cr^I(NO)(CN)_2(HQ)(H_2O)]$ ($Q = Q^{Me}$, Q^{Pr}, Q^{CH_2Cl}, Q^{PhpCl}) (with coordinated nitrosyl ligand as NO^+) were synthesized by mixing an aqueous acetic acid solution of HQ with an aqueous solution of $K_3[Cr(NO)(CN)_5]$. Analytical and spectral studies suggest a six-coordination on Cr atom, with CN ligands and O atoms of Q in equatorial plane and NO and H_2O *trans* to each other, in axial positions (Fig. 39). Two different ν(C=O) absorption bands have been detected in their IR spectra, the lower one for cyclic and higher one for exocyclic carbonyl groups

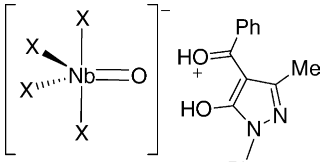
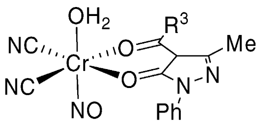

X = Cl, NO_3

Fig. 38. Structure of the derivatives $(H_2Q^{Ph})[NbOX_4]$.



R^3 = Me, Pr, CH_2Cl, Ph-p-Cl_3

Fig. 39. Structure of the derivatives $[Cr(NO)(CN)_2(HQ)(H_2O)]$.

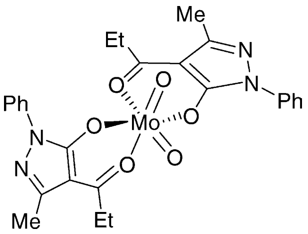


Fig. 40. Structure of the derivative $[MoO_2(Q^{Et})_2]$.

[71,106]. Magnetic ESR studies suggest they are low-spin d^5 complexes, with μ_{eff} 1.72–1.75 BM [71,106].

Thermal studies on derivative $[Cr(Q^{Ph})_3]$ were reported [107] together with the separation and identification of its two geometric isomers [108].

Octahedral diamagnetic molibdenum derivatives $[Mo^{II}(NO)(CN)_3(HQ^{Ph})(H_2O)]$ and $[Mo^0(NO)_2(Q^{Pr})_2]\cdot H_2O$ (with coordinated nitrosyl ligand as NO^+) have been synthesized and characterized [109,110]. Two different ν(C=O) absorption bands have been detected in the IR spectrum of derivative $[Mo^{II}(NO)(CN)_3(HQ^{Ph})(H_2O)]$, the lower one for cyclic and higher one for exocyclic carbonyl group [109].

The complexes $[MoO_2(Q^{Et})_2]$ (Fig. 40) and $[MoO_2(Q^{CCl_3})(Q^{CCl_3*})]$ (Fig. 41) have been synthesized by interaction between an ethanol solution of HQ and an aqueous solution of $(NH_4)_6Mo_7O_{24}$ acidified with HCl [111]. The X-ray structures of the derivatives show the two oxo groups in *cis* position, with Mo in a distorted octahedral geometry [111]. The peculiarity of the derivative $[MoO_2(Q^{CCl_3})(Q^{CCl_3*})]$ (Fig. 41) is to contain a Q^{CCl_3*} ligand in which an ethoxy moiety is introduced in the acyl moiety due to a deprotonation reaction between the complex and ethanol solvent[111].

The compound $[MoO_2(Q8Q)\cdot(1/2)H_2O]$ is a monomeric species with a tetradentate Q8Q and the oxo groups in *cis* position, whereas in $[(MoO_2)_2(Q4Q)(OH)(EtO)]$ the Q4Q ligand coordinates both MoO_2 moieties. One Mo environment is completed by an OH group, the other from an ethoxy group. The O=Mo=O moiety has always *cis* arrangement, as supported by IR data [104].

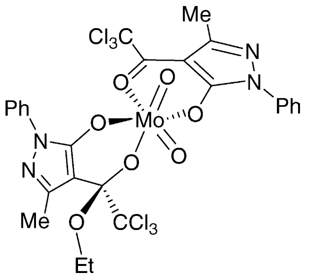
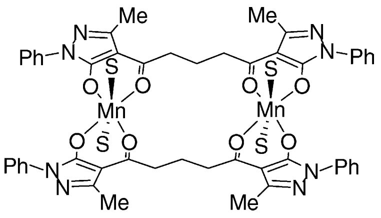


Fig. 41. Structure of the derivative $[MoO_2(Q^{CCl_3})(Q^{CCl_3*})]$.



S = dmf

Fig. 42. Structure of the derivative $[Mn\ (Q3Q)(dmf)_2]_2$.

6.6. Group VIIB: Mn

Mn acylpyrazolonates of formula $[Mn(Q)_2(H_2O)_2]$ ($Q = Q^{Me}$, Q^{Ph}, Q^{CF_3}) were synthesized by reaction of $Mn(OAc)_2$ and HQ. Replacement of a Me by a Ph group in the 4-acyl moiety decreases the C=O, C=C, and M–O stretching frequencies. Substitution of a Me group by CF_3 increases the C=O and C=C bond strengths and decreases M–O bond strength [22–24,80]. $[Mn(Q)_2(EtOH)_x(H_2O)_y]$ ($x = 0$–2; $y = 0$, 2; $Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}) are d^5 high-spin derivatives, μ_{eff} being in the range 5.30–5.60 BM [112]. Also some Mn(II) derivatives with Q*n*Q ligands have been reported: $[Mn(Q4Q)(H_2O)_{3/2}]$, $[Mn(Q3Q)(EtOH)_3(H_2O)_3]$ and $[Mn(Q3Q)(dmf)_{2.5}(H_2O)_{0.5}]$ were fully characterized and the crystal structure of the latter resolved (Fig. 42), which is a dimeric compound containing bridging tetradentate Q3Q ligands connecting two Mn atoms [113,114]. These compounds are in a distorted octahedral environment with dmf molecules in *trans* positions. They are high-spin paramagnetic d^5 derivatives. A variable temperature magnetic susceptibility study showed that a weak antiferromagnetic exchange interaction exists between the metal centres in the complexes [113,114].

6.7. Group VIIIB: Fe, Co, Rh, Ir and Ni

Derivatives $[M(Q)_2(H_2O)_2]$ (M = Co, Ni; $Q = Q^{Ph}$, Q^{Me}, Q^{CF_3}) have been hypothesized to exist in an octahedral geometry with *trans* H_2O ligands [22–24,115]. Trivalent $[M(Q^{CF_3})_3]$ (M = Fe, Co, Rh) complexes were reported [88,89] and spectroscopic [116] and thermal studies [107] of $[Fe(Q^{Ph})_3]$ have been reported. Several aspects of the triplet state ketone-sensitized photoreduction of $[Ni(Q^{Et,Me})_2]$ were studied. The sensitized reduction was much more efficient than direct photolysis in H-donating solvents, and the reaction products were identified as the metal in (0) oxidation state, the free protonated ligand, and oxidation products derived from the solvents [117]. The rate constant (k_q) for quenching of the benzophenone triplet state by the complex was detected and an overall mechanism for the sensitized photore-

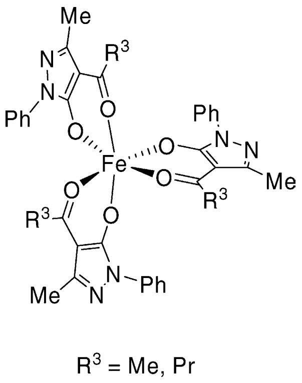


Fig. 43. Structure of the derivatives $[Fe(Q)_3]$.

duction proposed [117]. Derivatives $[Fe(Q)_3]$ ($Q = Q^{Me}$, Q^{Et}, Q^{Pr}, Q^{iPr}, Q^{Bu}, Q^{iBu}, Q^{Hp}, Q^{Pd}) were synthesized by reaction of $Fe(NO_3)_3$ with HQ in the presence of HCl. They were spectroscopically characterized by IR and electronic spectroscopy; the magnetic moment values μ_{eff} were found in the range 5.80–5.90 BM, thus indicating they are high-spin octahedral complexes [82,118]. Crystal structures of $[Fe(Q^{Me})_3]$ and $[Fe(Q^{Pr})_3]$ derivatives were reported, showing they crystallize as *fac*-isomeric octahedral species (Fig. 43) [65].

Cobalt(II) derivatives $[Co(Q)_2(H_2O)_2]$ ($Q = Q^{CCl_3}$, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}, Q^{Pd}) were synthesized and characterized by interaction of $Co(OAc)_2$ with HQ [119]. Several metal group VIIIB derivatives with H_2QnQ ligands have been reported. $[Fe_2(Q8Q)_3]$ has been characterized by spectral IR and electronic analysis and its magnetic moment μ_{eff} is 4.27 BM [86]. In derivatives $[Fe(QnQ)(H_2O)(EtOH)]$ ($n = 4$ or 8) the Q4Q ligand forms a dimeric species whereas Q8Q forms a monomeric compound [120]. The compounds $[M(QnQ)(H_2O)_2]$ (M = Co(II), Ni(II), $n = 4$ or 8) were synthesised and spectroscopically characterized, however, no conclusive proof was reported on the nuclearity of the complexes [114]. The anhydrous compounds [M(Q8Q)] (M = Co(II) or Ni(II)) have been prepared by an electrochemical method which generates the dianion $Q8Q^{2-}$ that can reacts with $M(SO_3CF_3)_2$ [121]. The derivatives $[Co(NO_3)(HQ3Q)(EtOH)]$, $[Co(Q3Q)(H_2O)_{2.5}]$ and $[Ni(Q3Q)(EtOH)(H_2O)_2]$ are dinuclear with bridging tetradentate Q3Q ligands [113].

The first report on organorhodium(I) and -iridium(I) acylpyrazolonates was on monomeric derivatives $[M(diene)(Q^{Ph})]$ (M = Rh, Ir; diene = cod, nbd, tfb) and $[M(olefin)_2(Q^{Ph})]$ (M = Rh, Ir; olefin = et, coe), having a square-planar geometry, obtained from interaction between $[Rh(cod)Cl]_2$ and HQ in the presence of Net_3 [122]. $[Rh(diene)(Q^{Ph})]$ reacts with dppb and *tert*-butylisocyanide ($CNBu^t$) affording $[Rh(dppb)(Q^{Ph})]$ and $[Rh(Q^{Ph})(CNBu^t)_3]$, respectively, whereas phen displaces Q^{Ph} from Rh coordination sphere to give the ionic $[Rh(dien)(phen)](Q^{Ph})$. Addition of I_2 to $[M(cod)(Q^{Ph})]$ (M = Rh, Ir) afforded octahedral Rh(III) and Ir(III) derivatives $[M(cod)(I)_2(Q^{Ph})]$ [122]. Direct reaction of HQ^{Ph} with $RhCl_3{\cdot}xH_2O$ resulted in the formation of $[Rh(Q^{Ph})(CO)_2]$, that can also be obtained from $[Rh(cod)(Q^{Ph})]$ and CO. Triphenylphosphine replaces a CO ligand affording $[Rh(CO)(PPh_3)(Q^{Ph})]$, which undergo oxidative addition with I_2 and MeI producing the Rh(III) complexes $[Rh(CO)(PPh_3)(I)_2(Q^{Ph})]$ and $[Rh(CO)(PPh_3)(I)(Me)(Q^{Ph})]$ [122]. Novel $[Rh(diene)(Q^{Me})]$ complexes (diene = cod, nbd, hex) have also been synthesized and characterized [123]. The crystal structure $[Rh(cod)(Q^{Me})]$ (Fig. 44) shows that the rhodium atom is in a square-planar configuration with two adjacent sites occupied by the Q^{Me} ligand in the O_2-bidentate form and the cod ring has a twisted boat conformation [123].

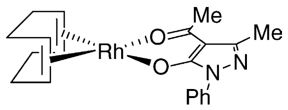


Fig. 44. Structure of the derivative $[Rh(cod)(Q^{Me})]$.

$[Rh(cod)(Q^{Me})]$ interacts with diphen and bipy yielding the cationic derivatives $[Rh(cod)(diphen)](Q^{Me})(H_2O)$, $[Rh(cod)(bipy)](Q^{Me})(H_2O)$ [123]. Whereas $[Rh(cod)(Q^{Me})]$ interacts with bzpy yielding the 1:1 adduct $[Rh(cod)(bzpy)(Q^{Me})]$ in which bzpy likely acts as N-monodentate donor. Monodentate P-donors as PPh_3, $P(OPh)_3$, PCy_3 and bidentate dppe displace the cod ligand from $[Rh(cod)(Q^{Me})]$ giving the neutral derivatives $[Rh(PR_3)_2(Q^{Me})]$ (R = Ph, OPh, Cy) and $[Rh(dppe)(Q^{Me})](H_2O)$ [123]. HQ^{Me} reacts with the dinuclear $[Rh(CO)_2Cl]_2$ yielding $[Rh(CO)_2Cl(HQ^{Me})]$ containing a likely monodentate HQ^{Me}. In presence of NEt_3, HQ^{Me} reacts with $[Rh(CO)_2Cl]_2$ yielding $[Rh(CO)_2(Q^{Me})]$. In this complex, 1 mol of CO can be replaced by 1 mol of diphen or bipy, or by 2 mol of PPh_3 or $AsPh_3$, yielding the derivatives $[Rh(CO)(L)_n(Q^{Me})]{\cdot}xH_2O$ (L = diphen or bipy, $n = 1$; L = PPh_3 or $AsPh_3$, $n = 2$). Whereas 1 mol of dppe displaces both the CO ligands, yielding $[Rh(dppe)(Q^{Me})]$ [123]. The tetradentate cot reacts with $[Rh(CO)_2(Q^{Me})]$ yielding the derivative $[Rh(cot)(Q^{Me})]$ where the olefin acts as η^2-bidentate [123]. The reactivity of [Rh(cod)(Q)] toward N_2-chelating has been explored, with expected formation of $[Rh(cod)(N_2\text{-donor})](Q)$ ($Q = Q^{thi}$, Q^{fur}, Q^{nPe}; N_2-donor = phen, bipy) [124,125]. The reaction under air of [Rh(cod)(Q)] with P_2-chelating dppe, dppf and monodentate P-donor ligands as PPh_3 afforded displacement of cod with oxidation of Rh(I) to Rh(III) and formation of peroxo species $[Rh(dppe)_2(O_2)](Q)$ and $[Rh(dppf)(O_2)(Q)]$ or Rh(I) species [Rh(dppof)(Q)] containing the diphosphine in the oxidized form [124]. Reaction between [Rh(cod)(Q)] and allyl bromide yielded the known $[Rh(cod)Br]_2$ [124]. The crystal structures of $[Rh(cod)(Q^{thi})]$ and $[Rh(cod)(phen)](Q^{thi})$ (Fig. 45), containing a Rh(I) atom in a square coordinate environment, have also been reported [124].

From reaction between [Rh(cod)(Q)] and PPh_3, dppe or dppp in anhydous solvents under N_2, $[Rh(Q)(PPh_3)_2]$,

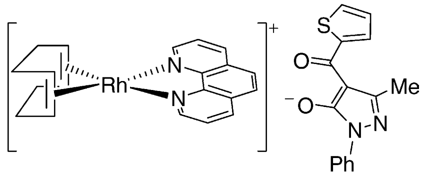


Fig. 45. Structure of the derivative [Rh(cod)(phen)](Q^{thi}).

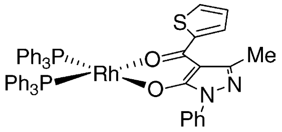


Fig. 46. Structure of the derivative [Rh(Q^{thi})$(PPh_3)_2$].

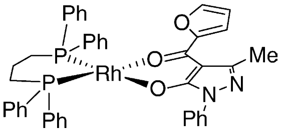


Fig. 47. Structure of the derivative [Rh(Q^{fur})$(dppp)_2$].

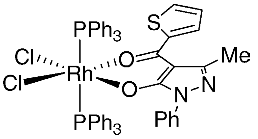


Fig. 48. Structure of the derivative [Rh(Q^{thi})$Cl_2(PPh_3)_2$].

$[Rh(dppe)_2](Q)$ and [Rh(dppp)(Q)] (Q = Q^{thi}, Q^{fur}) were obtained, respectively [34]. The reactions of [Rh(cod)(Q^{thi})] with MeI, I_2, HCl or C_3H_5Br in the presence of PPh_3 were also studied [34]. The X-ray crystal structures of [Rh(Q^{thi})$(PPh_3)_2$] (Fig. 46), $[Rh(dppe)_2]$(Q^{thi}), [Rh(Q^{fur})(dppp)] (Fig. 47) and [Rh(Q^{thi})$Cl_2(PPh_3)_2$] (Fig. 48) were reported, showing a Rh(I) in square-planar environments in the former derivatives and an octahedral Rh(II) in the latter compound, respectively [34].

Oxidation of $[Rh(Q)(PPh_3)_2]$ and [Rh(Q)(dppp)] occurs in the air, species containing a η^2-peroxo group being always identified by NMR as several five-coordinated Rh(I) isomers (Fig. 49) [34].

Reaction of $[Rh(CO)_2Cl]_2$ with enolic form of HQ^{fur} yields a new rhodium(I) dicarbonyl compound [Rh$(CO)_2$Cl(HQ^{fur})] containing the neutral 4-acylpyrazolone bonded in *N*-unidentate fashion (Fig. 50), as found in its crystal structure [67]. Both enolic and ketonic forms of HQ^{fur} are unreactive toward $[Rh(III)(Cp^*)Cl]_2$ in the absence of base, whereas in the presence of base the complex [Rh(III)(Cp*)Cl(Q^{fur})] has been obtained [67].

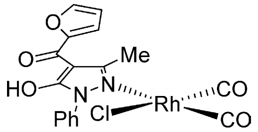


Fig. 50. Structure of the derivative [Rh$(CO)_2$Cl(HQ^{fur})].

Reaction of the polydentate O_4,N-donor ligand $H_2QpyQ{\cdot}3HCl$ with $[Rh(cod)Cl]_2$ affords the dinuclear compound $[Rh_2(cod)_2(QpyQ)]{\cdot}3HCl$, which reacts with PPh_3 forming $[Rh(PPh_3)_2Cl_2(HQpyQ)]$, able to interact with $SnMe_2Br_2$ yielding the heterobimetallic adduct $[Rh(PPh_3)_2Cl_2(HQpyQ)SnMe_2Br_2]$ (Fig. 51) [44]. The X-ray structure of $[Rh(PPh_3)_2Cl_2(HQpyQ)]$ shows the Rh(III) centre in a slightly distorted octahedral environment with Cl atoms situated in *cis* position and two PPh_3 in *trans* [44].

6.8. Group IB: Cu and Ag

The first report on copper acylpyrazolonates was on the [Cu$(Q^{Ph})_2$] compound, synthesized by mixing $Cu(OAc)_2{\cdot}H_2O$ and HQ^{Ph} [97]. The derivatives $[Cu(Q)_2(H_2O)_2]$ (Q = Q^{Me}, Q^{Ph}, Q^{CF_3}) were prepared similarly and a detailed IR study was performed [22–24,89,115]. Electronic and infrared studies of several Cu(II) derivatives of acylpyrazolonates, containing a 4-acyl moiety of variable chain length (Q = Q^{Ph}, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}), show bathochromic shift of the Q absorptions upon coordination [126]. The stability of the C=O bond of the CO–Cu bonding system decreases while that of the Cu–O bond in the same system increases as the carbon chain of the 4-acyl substituent in Q increases [126]. The complexes have μ_{eff} values within the range of 1.75–1.82 BM [126]. The triplet state ketone-sensitized photoreduction of [Cu$(Q^{Me})_2$] was investigated and shown to be much more efficient than direct photolysis in H-donating solvents [117]. The reaction products were identified as the metal in 0 oxidation state, the free

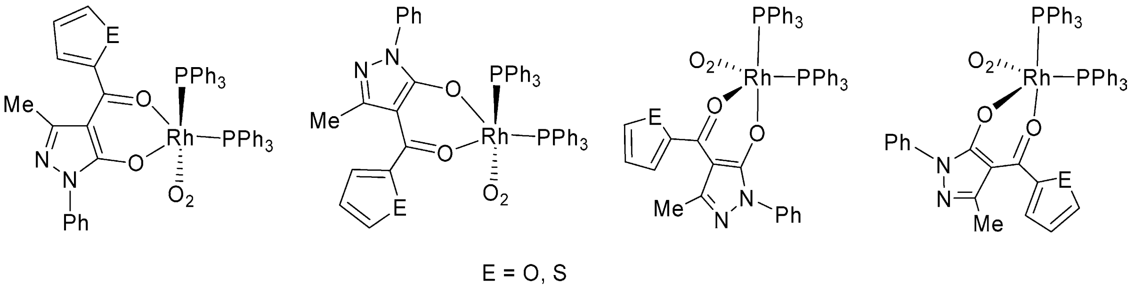


Fig. 49. Rh(I) isomers derived from oxidation of [Rh(Q)(PPh_3)] identified by NMR.

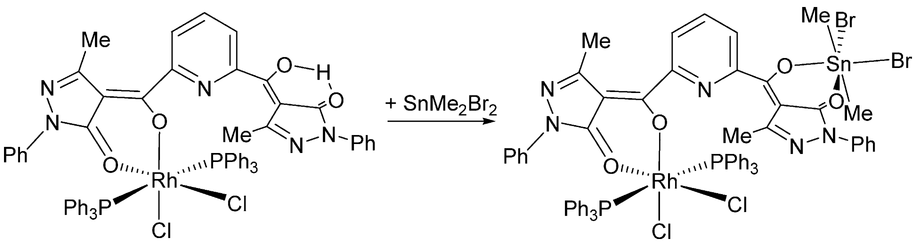


Fig. 51. Synthesis of the heterobimetallic adduct $[Rh(PPh_3)_2Cl_2(HQpyQ)SnMe_2Br_2]$.

protonated ligands and oxidation products derived from the solvents [117].

Derivatives $[Cu(Q^{Ph})_2]$ (Fig. 52) and $[Cu(Q^{Ph})_2(MeOH)_2]$ (Fig. 53) have been also structurally investigated [127]. The coordination geometry around Cu(II) in the former is slightly distorted square-planar, while the geometry around Cu(II) in the latter is distorted octahedral with four oxygen atoms of two Q^{Ph} ligand occupying the equatorial positions and two methanol molecules occupying the axial positions [127].

A number of $[Cu(Q)_2]$ and $[Cu(Q)_2(L)]$ derivatives ($Q = Q^{Ph}$, Q^{Me}, Q^{CF_3}, Q^{CCl_3}, Q^{PhpBr}, Q^{PhpOMe}, Q^{He}, $Q^{Me,Ph}$, $Q^{Me,Me}$, Q^{Cy}, Q^{Bn}, Q^{CHPh_2}, Q^{thi}; L = bipy or phen) were reported [125,128,129]. In $[Cu(Q^{thi})_2(EtOH)]$ and $[Cu(Q^{fur})_2(EtOH)]$ the additional donor atoms of heterocycles in 4-acyl moiety has virtually no effect on the structure and composition of the complexes formed, and coordination happens through always both carbonyl arms of Q ligands [125]. When $[Cu(Q)_2]$ interact with an excess of PR_3, reduction from Cu(II) to Cu(I) was observed and $[Cu(Q)(PR_3)_2]$ (R = Ph, Cy, Bn, Ph-*p*-Me) complexes were synthesized (Fig. 54) [128]. These Cu(I) derivatives can also be prepared from $CuNO_3(PR_3)_2$, HQ and NaOMe [128,129]. The X-ray crystal structures of $[Cu(Q^{CF_3})(PPh_3)_2]$ [128], $[Cu(Q^{Bn})(PPh_3)_2]$, $[Cu(Q^{CHPh_2})(PPh_3)_2]$ and $[Cu(Q^{Ph})(PCy_3)_2]$ [129] shows a strongly distorted tetrahedral coordination environment of Cu, where distortion increases as steric hindrance in 4-acyl moiety of Q and, mainly, in phosphine substituents increase. The P–Cu–P bond angles vary from 127° to 140° [128,129].

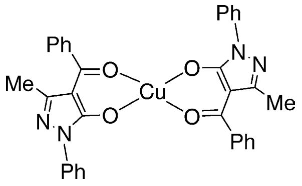


Fig. 52. Structure of the derivative $[Cu(Q^{Ph})_2]$.

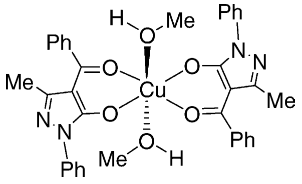
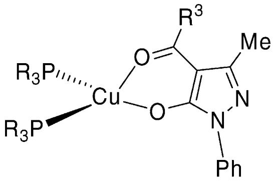


Fig. 53. Structure of the derivative $[Cu(Q^{Ph})_2(MeOH)_2]$.



R = Ph, Cy; $R^3 = CF_3$, Ph, Bn, $CHPh_2$

Fig. 54. Structure of the derivatives $[Cu(Q)(PR_3)_2]$.

$[Cu(Q)(PR_3)_2]$ undergo partial dissociation in solution through breaking of Cu–P and, when R = Cy, also of Cu–O bonds [129], whereas $[Cu(Q^{CF_3})(PPh_3)_2]$ exist in solution as a mixture of species containing a CuO_2P_2 and a $CuOP_2$ central core, in equilibrium with each other [128]. $[Cu(Q^{Cy})(PPh_3)_2]$ reacts with 1-methylimidazoline-2-thione (Hmimt), with 1,10-phenanthroline (phen), with 2,9-dimethyl-1,10-phenanthroline (cupr) and with bis(diphenylphosphino)propane (dppp), yielding the mixed-ligand compounds $[Cu(PPh_3)(Hmimt)_3](Q^{Cy})$ (Fig. 55), $[Cu(Q^{Cy})(PPh_3)(phen)]$ (Fig. 56), $[Cu(cupr)_2](Q^{Cy})$ (Fig. 57) and $[Cu(dppp)_2](Q^{Cy})$ (Fig. 58), respectively [129].

The crystal structures of $[Cu(Q^{Ph})_2(bipy)]\cdot 1.5(acetone)$ and $[Cu(Q^{CF_3})_2(phen)]\cdot EtOH$ (Fig. 59) were detected, showing the Cu atom in a tetragonally distorted octahedral arrangement of the four O-atoms of Q with N_2-donor ligand in

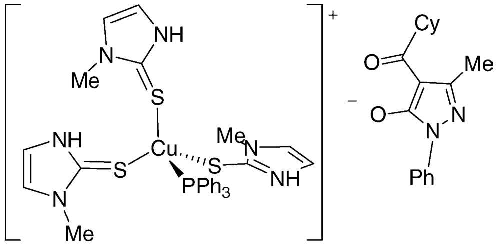


Fig. 55. Structure of the derivative $[Cu(PPh_3)(Hmimt)_3](Q^{Cy})$.

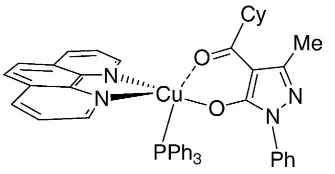


Fig. 56. Structure of the derivative $[Cu(Q^{Cy})(PPh_3)(phen)]$.

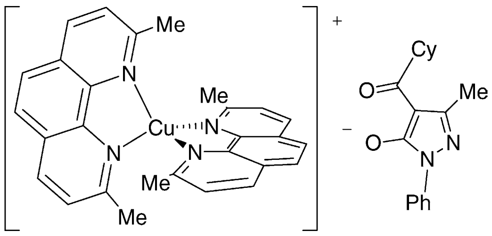


Fig. 57. Structure of the derivative $[Cu(cupr)_2](Q^{Cy})$.

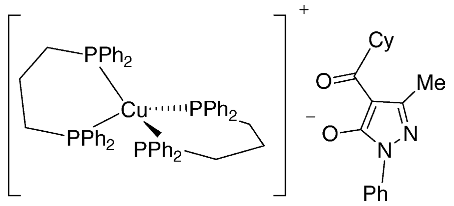


Fig. 58. Structure of the derivative $[Cu(dppp)_2](Q^{Cy})$.

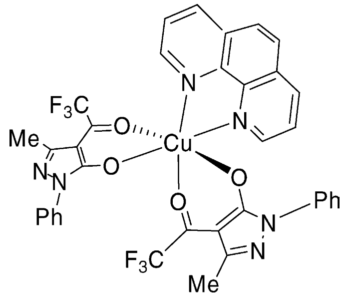


Fig. 59. Structure of the derivative $[Cu(Q^{CF3})_2(phen)]\cdot EtOH$.

equatorial position [130]. Two sets of Cu–O distances, the longer being in axial positions, were found [130].

Volatility studies, electrospray mass spectra and IR in vapour phase were carried out for Cu(I) and Cu(II) Q complexes. These compounds show volatility in a narrow range of temperature and their use as molecular precursors in CVD explored [84,130]. Studies on thermal decomposition of a number of $[Cu(Q)_2]$ compounds show the melting points decreasing linearly by increasing the molecular weight of the complexes [131]. The crystal structure of $[Cu(Q^{n\mathrm{Pe}})_2(H_2O)]$ (Fig. 60) shows a square-pyramidal structure with $Q^{n\mathrm{Pe}}$ ligands arranged in an *anti* configuration to each other and with H_2O at the apex of polyhedron [83]. Both hydrogen atoms of H_2O are involved in an intermolecular H-bonding network with pyridinic nitrogen atoms of $Q^{n\mathrm{Pe}}$-donors belonging to two neighbouring complexes [83].

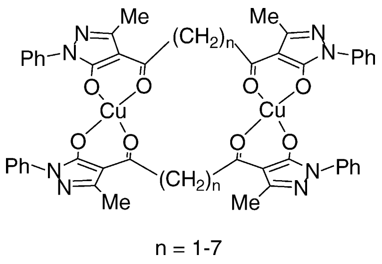


Fig. 61. Structure of the derivatives $[Cu(QnQ)]_2$ (n = 1, 7).

Derivative $[Cu(Q^{n\mathrm{Pe}})_2(H_2O)]$ reacts with substituted phenanthrolines such as cupr and pephen to give $[Cu(Q^{n\mathrm{Pe}})_2(cupr)]$ and $[Cu(Q^{n\mathrm{Pe}})_2(pephen)]$ [83]. An excess of cupr provokes reduction of Cu(II) to Cu(I) with formation of the ionic diamagnetic $[Cu(cupr)_2](Q^{n\mathrm{Pe}})$ [83]. $[Cu(Q^{n\mathrm{Pe}})_2(H_2O)]$ reacts with ethylendiamine (en) to give the ionic complex $[Cu(en)_3](Q^{n\mathrm{Pe}})_2\cdot 2H_2O$ [83]. By interaction of $[Cu(Q^{n\mathrm{Pe}})_2(H_2O)]$ with Meim the compound $[Cu(Q^{n\mathrm{Pe}})_2(Meim)_2]$ was isolated [83]. The PR_3-donors (R = Ph or Cy) reduce copper(II) affording the copper(I) derivatives $[Cu(Q^{n\mathrm{Pe}})(PR_3)_2]$ [83].

Dinuclear mixed-ligand complexes $[Cu(haph)_2(HQ)]_2$ containing 2-hydroxyacetophenonato (haph) and neutral HQ have been synthesized by reaction between $[Cu(haph)_2(H_2O)]$ and HQ (HQ = HQ^{Ph}, HQ^{Me}, HQ^{Et}, HQ^{Pr}) [132]. Octahedral geometries on copper atoms have been proposed, based on magnetic measurements, EPR, electronic and IR studies, and HQ likely act as bridging bidentate neutral donor ligands [132].

The complexation of Cu(II) with potentially tetradentate ligands H_2QnQ (n = 0–8, 10, 20) was investigated. Complex structure and stoichiometry are affected by the polymethylene chain length, through a steric effect [41,114]. $[Cu(HQnQ)_2]$ and $[Cu_2(QnQ)_2]$ (n = 1–7) are dimeric species (Fig. 61) whereas $[Cu(QnQ)]$ (n = 8, 10, 20) are monomers (Fig. 62) [41,114].

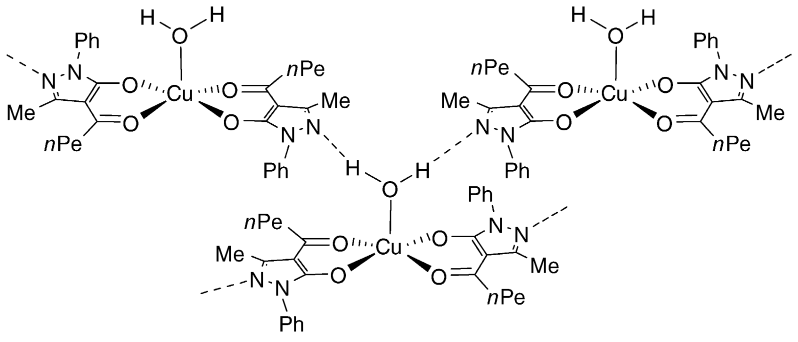


Fig. 60. Structure and intermolecular H-bonding network of the derivative $[Cu(Q^{n\mathrm{Pe}})_2(H_2O)]$.

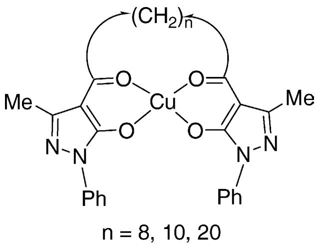


Fig. 62. Structure of the derivatives [Cu(QnQ)] (n = 8, 10, 20).

The compound [Cu(Q8Q)] has also been prepared by an electrochemical method which generates the dianion $Q8Q^{2-}$ that reacts with $Cu(SO_3CF_3)_2$ [121]. The crystal structure of [Cu(Q8Q)] consists of two types of mononuclear units, characterized by different conformations of the polymethylene chain [133]. Both molecules contain a Cu atom in an almost square-planar environment of O atoms and all Q moieties are planar [133]. The compound $[Cu_2(Q2Q)_2]\cdot 2H_2O$ has been prepared and its thermal and electrochemical properties investigated by TG-DTG techniques and cyclic voltammetry [134].

Silver derivatives of Q ($Q = Q^{Ph}$, Q^{Me}, Q^{CF_3}) and PR_3-donors (R = Ph, Cy, Ph-*o*-Me) have been recently synthesized [66]. The mononuclear $[Ag(Q)(PR_3)_2]$ species, with a distorted tetrahedral central AgO_2P_2 core (Fig. 63), are prepared by HQ, NaOMe, $AgNO_3$ and PR_3 in 1:1:1:2 ratio. Dinuclear $[Ag(Q)(PR_3)]_2$ species (Fig. 64), with a distorted tetrahedral central AgO_2PN core, where Q act as η^3-N,O_2-bridging ligands, are obtained by a 1:1:1:1 ratio [66]. The $[Ag(Q)(PR_3)_2]$ are fluxional in chloroform when PR_3 is sterically hindered (R = Cy or Ph-*o*-Me), and dissociate partially to the $[Ag(Q)(PR_3)]$ fragment and free PR_3 [66].

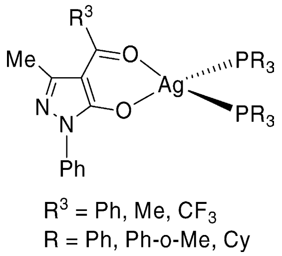


Fig. 63. Structure of the derivatives $[Ag(Q)(PR_3)_2]$.

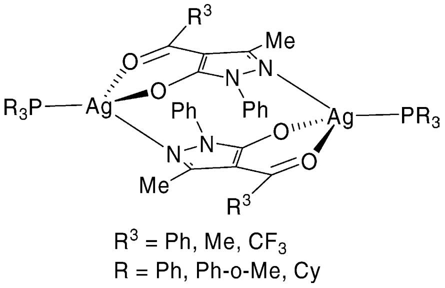


Fig. 64. Structure of the derivatives $[Ag(Q)(PR_3)]_2$.

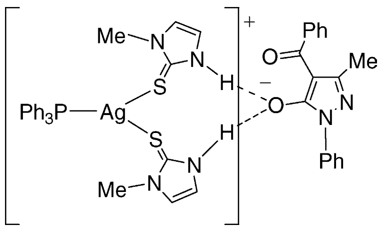


Fig. 65. Structure of the derivative $[Ag(Hmimt)_2(PR_3)](Q^{Ph})$.

$[Ag(Q^{Ph})(PPh_3)_2]$ reacts with Hmimt affording $[Ag(Hmimt)_2(PPh_3)](Q^{Ph})$ (Fig. 65), a ionic species also in the solid state, where Ag is tri-coordinated by PPh_3 and two Hmimt and Q^{Ph} is in anionic no-bonded form [66]. $[Ag(Q)(PPh_3)_2]$ react with dppe in 1:1 or 1:2 ratios affording [Ag(Q)(dppe)] and $[Ag(dppe)_2](Q)$, respectively, the latter being ionic species [66]. From interaction of $AgNO_3$ with HQ and trime derivatives $[Ag(Q)(trime)]_\infty$ formed ($Q = Q^{Ph}$, Q^{CF_3}) (Fig. 66) [66]. They are polynuclear species with η^2-N,O-bridging Q ligands coordinated through the O ring-carbonyl and the N-donor atom of pyrazole ring [66].

Additional S- or O-donor atoms in acyl moiety of Q^{thi} and Q^{fur}, respectively, do not affect the structure and stoichiometry of monomeric $[Ag(Q)(PR_3)_2]$ and dimeric $[Ag(Q)(PR_3)]_2$ derivatives, the thienyl and furyl moieties being always non bonded [33]. $[Ag(Q^{thi})(PPh_3)_2]_2$ reacts with Hmimt affording $[Ag(Hmimt)(PPh_3)(Q^{thi})]$ and $[Ag(Q^{fur})(PPh_3)]_2$ reacts with Meim affording $[Ag(Meim)(PPh_3)(Q^{fur})]$ [33]. $[Ag(Q^{thi})(PPh_3)]_2$ reacts with phen affording $[Ag(phen)(PPh_3)](Q^{thi})$, whereas $[Ag(Q^{thi})(PPh_3)_2]$ reacts with phen producing the ionic species $[Ag(phen)(PPh_3)_2](Q^{thi})$ (Fig. 67), structurally characterized [33].

The new *Janus*-type ligand Q^{py,CF_3} has been recently synthesized and its coordination chemistry toward silver explored [29]. HQ^{py,CF_3} reacts with $AgNO_3$ and NaOMe af-

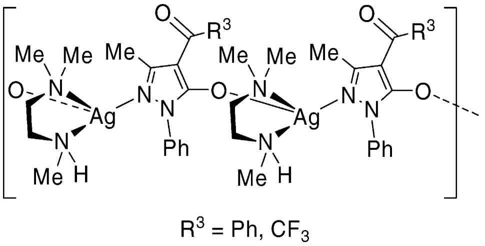


Fig. 66. Structure of the derivative $[Ag(Q)(trime)]_\infty$.

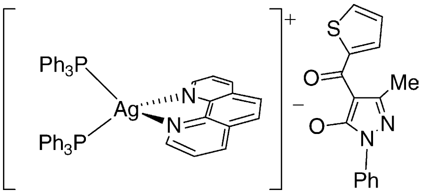


Fig. 67. Structure of the derivative $[Ag(phen)(PPh_3)_2](Q^{thi})$.

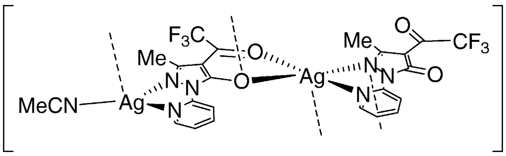
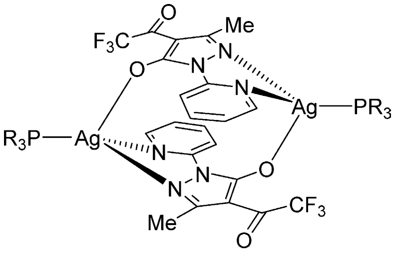


Fig. 68. Structure of the derivative $[Ag(Q^{py,CF_3})]_\infty$.



R = Ph;Ph-o-Me, Ph-o-F, Cy, Bu^i)

Fig. 69. Structure of the derivatives $[Ag(Q^{py,CF_3})(PR_3)]_2$.

fording $[Ag(Q^{py,CF_3})]_\infty$ (Fig. 68), which is a polynuclear species composed of dinuclear building blocks containing two different Ag environments and two Q^{py,CF_3}-donors differently connected: a terminal η^2-N_2-donor Q^{py,CF_3} and a bridging η^4-N_2,O_2-donor Q^{py,CF_3} [29].

By adding neutral ligands such as PR_3 (R = Ph, Cy, Ph-*o*-Me, Ph-*p*-F, Bu^i) to $[Ag(Q^{py,CF_3})]$, dinuclear $[Ag(Q^{py,CF_3})(PR_3)]_2$ derivatives are isolated (Fig. 69), containing bridging η^3-N_2,O-exotridentate Q^{py,CF_3}-donors spanning a pair of $AgPR_3$ moieties [29]. Reaction of $[Ag(Q^{py,CF_3})(PPh_3)]_2$ with an excess PPh_3 produces the mononuclear $[Ag(Q^{py,CF_3})(PPh_3)_2]$ compounds (Fig. 70) which contains the Q^{py,CF_3} coordinated to silver in a N_2-chelating mode [29]. Reaction between $[Ag(Q^{py,CF_3})]$ and dppe yields $[Ag(Q^{py,CF_3})(dppe)]$, having a polynuclear structure in the solid state. In solution the formation of two new species has been observed, the mononuclear neutral $[Ag(Q^{py,CF_3})(dppe)]$ and the dinuclear ionic $[Ag_2(dppe)_2](Q^{py,CF_3})_2$ [29]. $[Ag(Q^{py,CF_3})]$ reacts also with N-donors L (L = imH, Meim, Hmimt, phen) and new mononuclear species $[Ag(Q^{py,CF_3})(L)]$ are isolated (Fig. 71) [29].

$[Ag(Q^{py,CF_3})(PPh_3)_2]$ reacts with $SnRCl_3$ (R = Ph, Bu) affording heterotrimetallic $[\{(Ph_3P)_2AgCl\}_2SnRCl_3]$ derivatives [29].

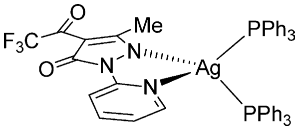
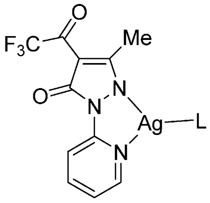


Fig. 70. Structure of the derivative $[Ag(Q^{py,CF_3})(PPh_3)_2]$.



L = Meim, imH, Hmimt

Fig. 71. Structure of the derivatives $[Ag(Q^{py,CF_3})(L)]$.

6.9. Group IIB: Zn, Cd and Hg

The compounds $[M(Q)_2(H_2O)_2]$ (M = Zn, Hg; Q = Q^{Me}, Q^{Ph}, Q^{CF_3}) were synthesized by reaction of $M(OAc)_2$ and HQ [22–24,89]. They were hypothesized to be six-coordinate by O_2-bidentate chelating Q-donors and two water molecules in the metal coordination sphere [22–24,88]. Compounds $[Zn(Q)_2(EtOH)_x(H_2O)_y]$ ($x = 0$–2; $y = 0$, 2; Q = Q^{Ph}, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}) were reported together with a detailed analytical and spectroscopic characterization a decades later [112].

The crystal structure of $[Zn(Q^{Hp})_2(H_2O)]$ (Fig. 72) shows a five-coordinate Zn, in a square-pyramidal environment, which is realized by the coordination of one molecule of H_2O in the apical position and two O_2-chelating Q ligands in the equatorial plane [135]. The coordination polyhedron is significantly distorted towards a trigonal-bipyramidal arrangement [135]. The compound $[Cd(Q^{Hd})_2(EtOH)_2]$ (Fig. 73) contains two coordinated EtOH molecules and is octahedral [135].

The compound $[Zn(Q^{Ph})_2(dmf)_2]$ has been prepared and fully characterized [136]. The Q ligand is bidentate with coordination through the two oxygen atoms, and the zinc atom displays an octahedral coordination geometry with *trans* dmf molecules [136]. The crystal structure of $[Zn(Q^{Ph})_2]$ shows a

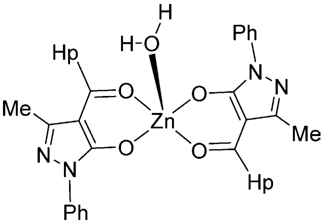


Fig. 72. Structure of the derivative $[Zn(Q^{Hp})_2(H_2O)]$.

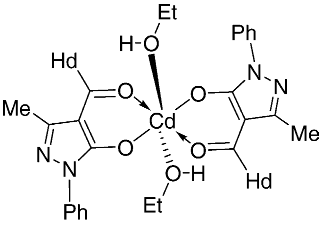


Fig. 73. Structure of the derivative $[Cd(Q^{Hd})_2(EtOH)_2]$.

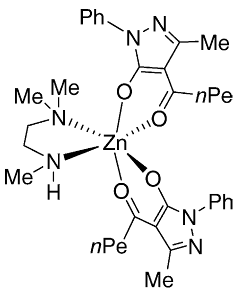


Fig. 74. Structure of the derivative $[Zn(Q^{nPe})_2(trime)]$.

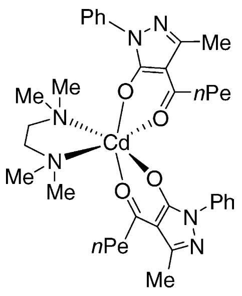


Fig. 77. Structure of the derivative $[Cd(Q^{nPe})_2(tmeda)]$.

slightly distorted square-planar geometry around zinc [127]. The crystal structure of $[Cd(Q^{Ph})_2(EtOH)_2]$ consists of a centrosymmetrical complex with a distorted octahedral geometry on Cd and the ethanol molecules in *trans* position to each other [137]. Zinc derivatives $[Zn(Q)_2(S)_n]$ ($Q = Q^{nPe}$, Q^{Cy}; $S = H_2O$, $n = 1$; S = MeOH, $n = 2$) react with N-donors L (L = phen, bipy, trime, tmeda) yielding $[Zn(Q)_2(L)]$ [138]. The X-ray structure of derivative $[Zn(Q^{nPe})_2(trime)]$ (Fig. 74) shows a six-coordinate zinc in a slightly distorted octahedral environment [138]. Reaction of $[Zn(Q^{nPe})_2(MeOH)_2]$ with L' (L' = imH, Meim, $NHEt_2$) affords monomeric derivatives $[Zn(Q^{nPe})_2(L')]$, whereas by interaction with Hmimt the dinuclear compound $[Zn(Q^{nPe})_2(Hmimt)]_2$ has been obtained, containing bridging η^2-sulphur donor Hmimt (Fig. 75) [138].

Cadmium derivatives $[Cd(Q)_2(EtOH)_2]$ ($Q = Q^{nPe}$, Q^{Cy}) were reported and the crystal structure of $[Cd(Q^{nPe})_2(EtOH)_2]$ resolved (Fig. 76), which contains a six-coordinate Cd with *anti* Q-donors and *trans* EtOH molecules, involved in intermolecular H-bonding network [139]. Interaction with N_2-bidentate donors L afforded $[Cd(Q)_2(L)]$ (L = phen, bipy, trime, tmeda) [139]. The X-ray structures of derivatives $[Cd(Q^{nPe})_2(tmeda)]$ (Fig. 77) and $[Cd(Q^{Cy})_2(phen)]$ (Fig. 78) show Cd atoms in strongly distorted octahedral environments due to steric requirements of the N_2-donors [139]. Multinuclear NMR studies, as ^{113}Cd, were also reported [139].

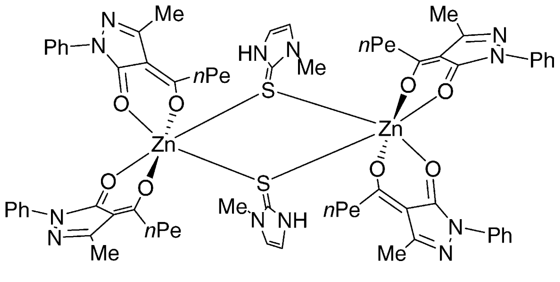


Fig. 75. Structure of the derivative $[Zn(Q^{nPe})_2(Hmimt)]_2$.

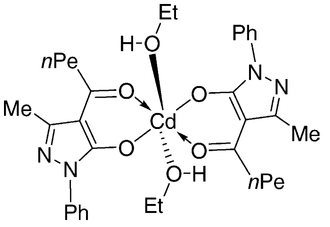


Fig. 76. Structure of the derivative $[Cd(Q^{nPe})_2(EtOH)_2]$.

Zinc and Cadmium derivatives of other Q-donor ligands ($Q = Q^{Me,Me}$, Q^{CHPh_2}, Q^{CF_3}) have been reported and their reactivity toward N_2-donor ligands, as phen and bipy, explored [140]. $[M(Q)_2(trime)]$ and $[M(Q)_2(tmeda)]$ (M = Zn, Cd) were synthesised and characterized in the solid state and in solution, also with ^{113}Cd NMR spectroscopy [140]. $[M(Q)_2(Bnim)]$ and $[M(Q)_2(Meim)_2]$ derivatives (M = Zn, Cd; $Q = Q^{Ph}$, Q^{Me}, $Q^{Me,Ph}$), show square-pyramidal and *trans*-octahedral environment respectively. The different ligand to metal ratio has been attributed to steric hindrance of Bnim with respect to Meim [141].) Derivative $[ZnCl_2\{H_2C(tmpz)_2\}]$ reacts with HQ^{Ph} in the presence of a base, to yield $[Zn\{H_2C(tmpz)_2\}(Q^{Ph})_2]$, whereas $[Cd(Q^{Ph})_2(H_2O)]$ and $[Hg(Q^{Ph})_2(Et_2O)]$ were obtained when a similar reaction was carried out with $[CdCl_2\{H_2C(tmpz)_2\}]$ and $[HgCl_2\{H_2C(tmpz)_2\}]$, respectively [142].

$[M(Q)_2(solvent)]$ derivatives (M = Zn, Cd or Hg; $Q = Q^{Ph}$, Q^{nPe}, Q^{CHPh_2}; solvent = EtOH or H_2O) were synthesized by reaction between $M(OAc)_2$ and HQ [143]. These compounds undergo a condensation reaction with diamines, affording novel Schiff-base metal derivatives $[M(L)(H_2O)_2]$ (L = bis(1-phenyl-3-methyl-4-R(C=N)-pyrazolone)$(CH_2)_n$diimine, where R = Ph, $n = 2$, 3 or 4; R = nPe, $n = 2$, 3 or 4; R = $CHPh_2$, $n = 2$ or 3; M = Zn, Cd or Hg) [143]. These compounds possess a six-coordinate metal environment [143]. $[Zn(L)(H_2O)_2]$ reacts with $CuCl_2$ and $Cu(ClO_4)_2$ affording $[Cu(Q)_2]$ and $[Cu(en)_2](ClO_4)_2$, respectively, upon breaking of the C=N bond in the Schiff-base donor [143]. $[Zn(L)(H_2O)_2]$ reacts with phen to yield

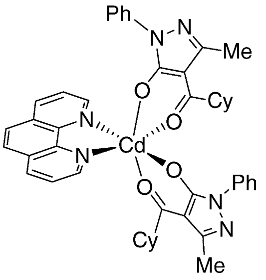


Fig. 78. Structure of the derivative $[Cd(Q^{Cy})_2(phen)]$.

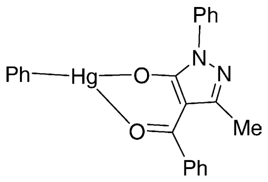


Fig. 79. Structure of the derivative [HgPh(Q^{Ph})].

[Zn(Q)$_2$(phen)], whereas the reaction with $CdCl_2$ affords [Cd(L)(H_2O)$_2$], due to exchange of the metal centre [143]. The compound [Zn(L)(Hmimt)], likely containing a five-coordinate ZnN_2O_2S central core, has been obtained from the exchange reaction between [Zn(L)(H_2O)$_2$] and Hmimt [143].

The synthesis of organomercury(II) derivatives [HgR(Q)] (R = Me, Ph; Q = Q^{Ph}, Q^{Me}) have been performed from interaction between MeHgI and HQ in the presence of NaOMe, and between PhHgOAc and HQ [144]. The derivatives have been characterized by spectral data (IR and ^{1}H, ^{13}C and ^{199}Hg NMR) [144]. The X-ray structure of [HgPh(Q^{Ph})] (Fig. 79) shows the Q-donor chelating through both oxygen atoms to soft metal Hg, affording a T-shaped three coordinated compound [144]. ^{199}Hg NMR analysis has been also reported [144].

Zinc derivatives with 4-acylbis(pyrazol-5-one) ligands were reported: [Zn(Q4Q)]$_2$·(3/2)H_2O is a dimeric species whereas [Zn(Q8Q)]·(3/2)H_2O is a monomer, due to steric requirements of polymethylene chain between pyrazolone units in the ligands [114].

6.10. Group IIIA: B, Al, Ga, In and Tl

The interaction of 2-isopropoxy-1,3,2-benzodioxaborole or 2-isopropyl-5,5-dimethyl-1,1,3,2-dioxaborinane with HQ (Q = Q^{Ph}, Q^{Me}, Q^{Et}, Q^{PhpCl}) gives boron derivatives [(ORO)B(Q)] (R = C_6H_4, $C_6H_4CH_2$, $CH_2C(CH_3)_2CH_2$) (Fig. 80) [145]. The tetracoordination of the boron atom in these complexes has been proposed on the basis of IR and ^{1}H NMR spectra [145].

The reaction of H_3BO_3 with HQ (Q = Q^{Ph}, Q^{Me}, Q^{Et}, Q^{PhpCl}) in acetic anhydride has been reported to give [(AcO)$_2$B(Q)] [146]. The OAc-groups in [(AcO)$_2$B(Q)] are substituted during reaction with *i*PrOH, 1,2-ethanediol, 2,3-dimethyl-2,3-butanediol, catechol, 1,2-ethanedithiol, *o*-aminophenol and *o*-aminothiophenol, and the corresponding boron complexes have been characterized by IR, ^{1}H and ^{11}B NMR spectra [146].

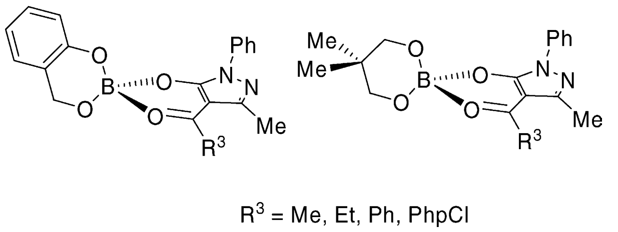


Fig. 80. Structure of the derivatives [(ORO)B(Q)] (where R = $C_6H_4CH_2$, $CH_2C(CH_3)_2CH_2$).

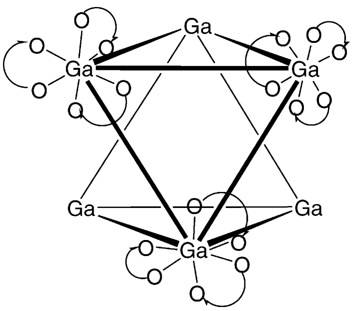


Fig. 81. Gallium backbone with the metal coordination environment in the structure of the derivative [Ga(Q_3Ph)].

Group IIIA metal complexes of Q^{CF_3} ligand were reported having the composition [M(Q^{CF_3})$_3$] (M = Al, In) [88,89]. The compound [Ga(Q^{Ph})$_3$] was reported together with its spectral features [116]. Thermal studies on [M(Q^{Ph})$_3$] (M = Al, Ga, In) derivatives have been reported, showing the thermal stabilities following the sequence Ga < In < Al [107]. For Al, Ga and In, a linear relation was obtained between the melting point of the complexes and the ionic radii of the central metals [107]. Two diphenylthallium(III) derivatives [$TlPh_2$(Q)] (Q = Q^{Ph}, Q^{Me}), containing O_2-bidentate chelating Q ligands, have been synthesised by interaction of Ph_2TlOH and HQ in EtOH [144].

The potentially O_6-hexadentate donor ligand H_3Q_3Ph reacts with Ga(acac)$_3$ affording an high-symmetry, three-dimensional metal–ligand cluster [Ga_6(Q_3Ph)$_6$], which possesses a cylindrical geometry [45]. Each Ga is coordinated by six O atoms from three chelating arms of three different Q_3Ph ligands (Fig. 81) [45]. The gallium atoms define a distorted trigonal antiprism in which six Q_3Ph ligands make up the equatorial faces of the cylinder with a hole at the top and the bottom (Fig. 82) [45]. The pseudo-three-fold faces of the “holes” are larger than those occupied by the (equatorial) ligands [45]. The molecule exists as a racemic mixture of homochiral, hexanuclear clusters (ΔΔΔΔΔΔ or ΛΛΛΛΛΛ) in the solid state and in solution [45]. There is no interconversion of the various possible isomers on the NMR time scale between 40 and 120 °C [45].

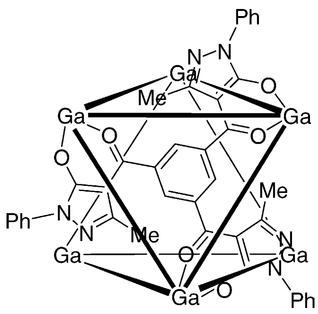


Fig. 82. Gallium backbone where it is showed one of the six bridging Q_3Ph ligands in the structure of the derivative [Ga_6(Q_3Ph)$_6$].

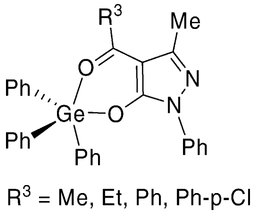


Fig. 83. Structure of the derivatives [$GePh_3$(Q)].

The ionic derivative ($Me_3NC_{16}H_{33}$)[Al(Q4Q)$_2$] has been reported to show enhanced fluorescence with respect to that of Q4Q ligand, thus a new fluorescence method has been put forward for determining Al^{3+} [147].

6.11. Group IVA: Ge, Sn and Pb

The halogermanium derivatives [$GeCl_2(Q)_2$] ($Q = Q^{Me}$, Q^{Ph}) were obtained from direct interaction between $GeCl_4$ and HQ [70]. They were hypothesized octahedral from analytical and spectral studies [70]. Some triphenylgermanium compounds [$GePh_3$(Q)] ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{PhpCl}) have recently been reported and shown to be monomeric with trigonal bipyramidal geometry from the phenyl groups and the O_2-bidentate Q ligand on Ge (Fig. 83) [148].

The tin chemistry with acylpyrazolones has been widely developed. Tin(II) derivatives [$Sn(Q)_2$] ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{PhpCl}) were synthesized from the reaction of $SnCl_2$ with HQ and NaOMe [149]. A distorted trigonal bipyramidal geometry was hypothesized, but uncorrect ^{119}Sn NMR assignments were made [149]. A number of [$Sn(Q)_2$] ($Q = Q^{Ph}$, Q^{Me}, Q^{CF_3}, Q^{He}, Q^{PhpF}, Q^{PhpCl}, Q^{PhpBr}, Q^{PhpI}, Q^{PhpOMe}, Q^{PhpNO_2}) compounds were prepared by interaction between $SnCl_2$, HQ and KOH, and a pseudo-trygonal bipyramidal structure was found for [$Sn(Q^{Me})_2$], in which the stereochemical active lone pair, occupies an equatorial position of the bipyramid (Fig. 84) [150].

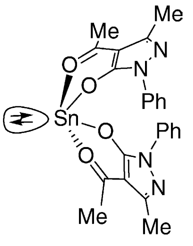


Fig. 84. Structure of the derivative [$Sn(Q^{Me})_2$].

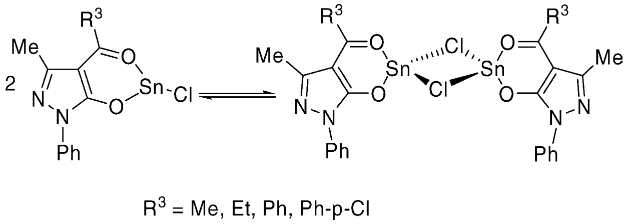


Fig. 85. Equilibrium between monomeric and dimeric species in solution proposed [152] for the derivatives [SnCl(Q)] on the basis of osmometric molecular weight measurements.

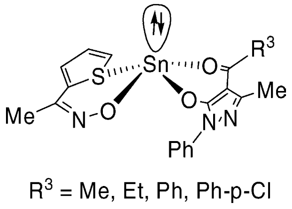


Fig. 86. Structure of the derivatives [Sn(Q)(acetylthiophene oxime)].

Correct ^{119}Sn NMR data were reported and a relationship between $\delta(^{119}Sn)$ and electronegativity of acyl substituents in Q ligands has been found [150]. Oxidative addition of iodomethane or dihalogens Br_2 or I_2 toward [$Sn(Q)_2$] provides a route to new tin(IV) compounds [$SnR_nX_{2-n}(Q)_2$] (X = Br or I; R = Me or X, $n = 1$ or 0) [150]. The crystal structure of the hydrate [$Sn(Q^{Me})_2$]·H_2O was also reported [151]. Derivatives [$Sn(Q)_2$] ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{PhpCl}) react with anhydrous $SnCl_2$ to give the redistribution products [SnCl(Q)] [152]. These should be dimeric in the solid state with η^2-bridging chloride, in fact an equilibrium between monomeric and dimeric species in solution have been proposed on the basis of osmometric molecular weight measurements (Fig. 85) [152].

Mixed-ligand tin(II) complexes have also been reported to form by interaction of [SnCl(Q)] with the sodium salt NaL of the S,O-bidentate donor ligand HL (HL = acetylthiophene oxime) [152]. They possess a four-coordinate tin(II) in a pseudo-trigonal bipyramidal geometry, with both Q and L chelating in a bidentate form (Fig. 86) [152].

New [$Sn(Q)_2$] derivatives with sterically congested Q-donors ($Q = Q^{Cy}$, Q^{CHPh_2}, Q^{Bn}, Q^{nPe}, Q^{Et}, Q^{tBu}, Q^{PhptBu}, Q^{PhpHe}, $Q^{PhpNO_2,Ph}$, $Q^{Me,Ph}$, $Q^{Me,Me}$, $Q^{Ph,Ph,Ph}$, $Q^{Ph,Ph,Me}$, $Q^{PhpCF_3,Ph}$, $Q^{PhpCF_3,Me}$) have been recently synthesized and characterized by multinuclear NMR, ESI-Mass and ^{119}Sn Mössbauer [79]. The crystal structure of [$Sn(Q^{Bn})_2$] has been reported and the reactivity of [$Sn(Q^{nPe})_2$] toward RI (R = Me or Et) and $Cr(CO)_6$ explored: tin(IV) derivatives [$SnRI(Q^{nPe})_2$] and heterobimetallic [$(CO)_5CrSn(Q^{nPe})_2$] afforded, respectively (Fig. 87) [79].

The interaction in chlorinated solvents of tetrahalotin(IV) or organotrihalotin(IV) acceptors with neutral HQ ($Q = Q^{Ph}$, Q^{Me}, Q^{CF_3}, Q^{PhpNO_2}, Q^{PhpOMe}, Q^{PhpF}, Q^{PhpCl}, Q^{PhpBr}, Q^{PhpI}) in the absence of base yields 1:1 adducts of general formula

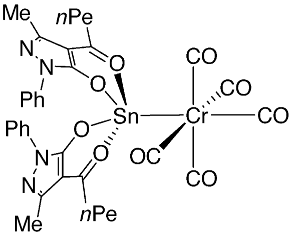
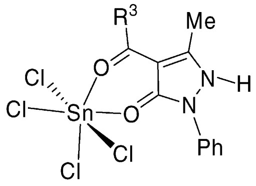


Fig. 87. Structure of the derivative [$(CO)_5CrSn(Q^{nPe})_2$].



R^3 = Ph, Me, CF3, Ph-p-NO_2,
Ph-p-OMe, Ph-p-F, Ph-p-Cl,
Ph-p-Br, Ph-p-I

Fig. 88. Structure of the derivatives [$SnCl_4$(HQ)].

[SnR_nX_{4-n}(HQ)] ($n = 0$ or 1; R = Me, Bu or Ph; X = Cl, Br or I) for which a six-coordinate octahedral geometry, with the donor acting as bidentate through both carbonyls in the neutral aminodiketonic form, has been hypothesized (Fig. 88) [70,153].

HQ in the neutral form are not able to coordinate the metal of triorganotin(IV) and also diorganotin(IV) acceptors, in accordance with the lower acceptor strength of these Lewis acids, the only exception being the compounds [$SnPh_2Cl_2$(HQ)], due to higher electron withdrawing power of phenyls on tin [70,153]. NMR studies of [$SnRX_3$(HQ)] in CD_3CN indicate the existence of geometrical isomers in solution [70,153]. When the synthesis was carried out in diethyl ether, solvated 1:1 adducts of general formula [SnR_nX_{4-n}(HQ)(Et_2O)] were isolated, where Et_2O is likely coordinated to Sn and HQ behaves as monodentate O-donor [70]. By prolonged heating [$SnCl_4$(HQ)] at 90 °C under low-pressure, decomposition occurs with formation of [$SnCl_2(Q)_2$] and elimination of HCl and $SnCl_4$ [70,153].

Mono(acylpyrazolonate)tin(IV) derivatives [$SnRCl_2$(Q)] can be synthesized in thf by interaction between R_nSnX_{4-n} (X = Cl, R = Me, Bu, Ph) and HQ in 1:1 molar ratio in the presence of NEt_3 [36,154,155]. Based on spectroscopic (IR and NMR) and analytical (osmometric molecular weight) data, they are supposed to possess five-coordinate tin centres [36,154,155].

Dibutylmonoalkoxytin(IV) complexes were synthesised in a similar manner starting from $SnBu_2(OPr^i)_2$ [156]. They were supposed to be five-coordinate tin species [156].

Tris(acylpyrazolonate)monobutyltin(IV) complexes [$SnBu(Q)_3$] (Q^{Me}, Q^{Et}, Q^{Ph}, Q^{PhpCl}) have been obtained by reaction of $BuSnCl_3$ and HQ in benzene in the presence of NaOMe [155]. A seven-coordinated tin was proposed on the basis of spectral characterization [155].

Diorganotin(IV) bis(acylpyrazolonate) derivatives can be synthesized in several ways. $R_2Sn(OPr^i)_2$ react directly with HQ in benzene, whereas R_2SnCl_2 react with HQ in chloroform with HQ in the presence of NEt_3, or in MeOH in the presence of KOH. Also, R_2SnO can be used with HQ in refluxing benzene [26,154,156,157]. Several [$SnR_2(Q)_2$] (R = Me, Et, *i*Pr, Bu, *t*Bu, Cy, Bn, Ph; Q = Q^{Ph}, Q^{Me}, Q^{CF_3}, Q^{PhpNO_2},Q^{PhpOMe}, Q^{PhpF}, Q^{PhpCl}, Q^{PhpBr}, Q^{PhpI}, Q^{Cy}, Q^{CHPh_2}, Q^{Bn}, Q^{nPe}, Q^{Et}, Q^{tBu}, Q^{PhptBu}, Q^{PhpHe}, $Q^{PhpNO_2,Ph}$, $Q^{Me,Ph}$, $Q^{Me,Me}$, $Q^{Ph,Ph,Ph}$, $Q^{Ph,Ph,Me}$) have been obtained and characterized by IR, far-IR, and multinuclear (^{1}H, ^{19}F, ^{13}C, ^{119}Sn) NMR studies in solution [26,154,156,157]. A wide number of crystal structures of [$SnR_2(Q)_2$] derivatives has been reported till now [26,27,153,157–160]. These derivatives exist in the solid state as skewed trapezoidal six-coordinate tin compounds, where O_2-bidentate Q-donors chelate Sn in the equatorial plane in a *syn* arrangement and R groups are *trans* to each other. The distortion of the octahedron, quantified by evaluation of the C–Sn–C angles, which range from 154° to 174° (Fig. 89), and by the difference in the Sn–O bond distances has been related to the nature of the R groups bonded to tin [26,27,153,157–160]. In fact, on going from alkyl to aryl groups on tin, a lesser distortion, together with an increase of the ligand bite, can be observed, likely due to electronic effects of the organic group (Bn and Ph are more electronegative than Me, Et, Bu, *t*Bu, Cy). Whereas steric hindrance of R groups shows almost no influence [26,27,153,157–160].

The ^{119}Sn Mössbauer data of several [$SnR_2(Q)_2$] compounds further confirm the six-coordination on tin with *trans* R groups in the solid state, severe distortion from ideal octahedral geometry being always observed [160].

The coordination chemistry of Q^{CCl_3} toward tin(IV) has been widely explored [35,36]. This ligand, containing a CCl_3 group in the 4-acyl moiety, undergoes a substitution reaction of the CCl_3 by a OR group in alcoholic ROH solvents (R = Me, Et, *i*Pr, Bn) in the presence of KOH and of the tin(IV) acceptor (Fig. 90) [35,36]. In the C–CCl_3 bond cleavage, the tin acceptor seems to play a key role [35,36].

The X-ray crystal structures of [$SnMe_2(Q^{OPr})_2$] and [$SnBn_2(Q^{OMe})_2$] were determined, thus confirming the substitution of CCl_3 moiety with OPr and OMe [35,36]. Whereas, in different reaction conditions, i.e. chloroform as solvent

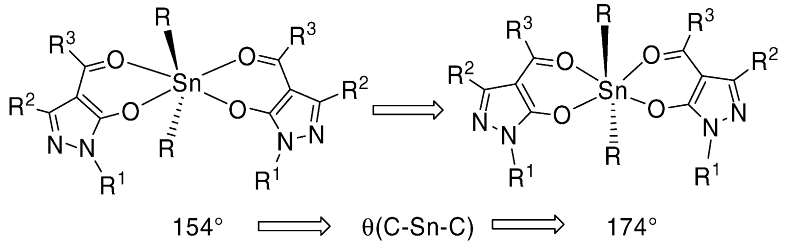


Fig. 89. Effect of the nature of the R groups bonded to tin in the distortion of the octahedral geometry: on going from alkyl to aryl groups, the C-Sn-C angle increases and the difference in the Sn-O distances decreases.

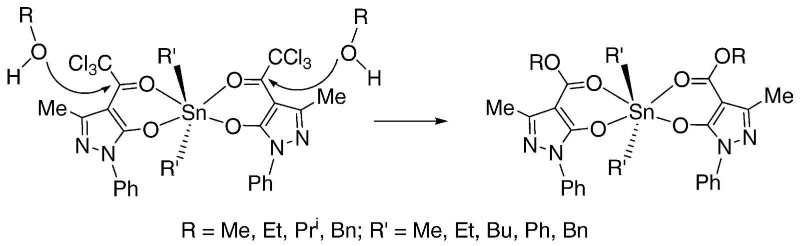


Fig. 90. Substitution reaction of the CCl_3 by a OR group during the formation of tin derivatives by using HQ^{CCl_3}, KOH and organotin(IV) acceptors, when the reaction has been carried out in alcoholic ROH solvents [35,36].

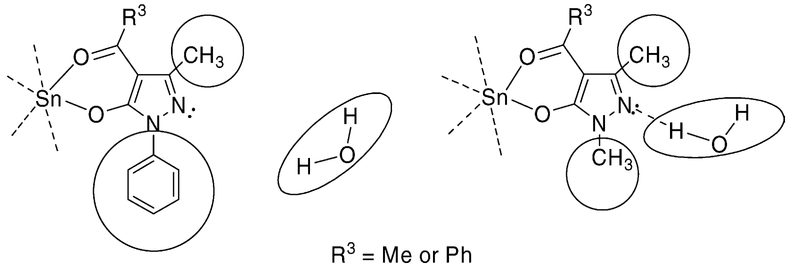


Fig. 91. The solubility in water of $[SnR_2(Q^{Me,Me})_2]$ and $[SnR_2(Q^{Me,Ph})_2]$ can be explained by the less steric hindrance of the methyl group with respect to phenyl in R^1 position of the acylpyrazolones, which allows the H-interaction with the solvent molecules.

and NEt_3 as base, tin(IV) derivatives $[SnR_2(Q^{CCl_3})_2]$ were obtained [35,36]. For the derivative $[SnMe_2(Q^{CCl_3})_2]$ the solid state structure has been determined [161]. Also, monoacylpyrazolonatotin(IV) complexes $[SnRCl_2(Q)]$ of Q^{CCl_3} and Q^{OR} have been isolated [36]. They exist in chlorinated solvents as a mixture of five-coordinate isomers interconverting one to another [36]. From the interaction of monorganotin(IV) halides with HQ^{CCl_3} in 1:1 molar ratio, anionic six-coordinate tin(IV) derivatives $[NHEt_3]^+[RSnCl_3(Q^{CCl_3})]^-$ have been obtained [36].

Diorganotin(IV) bis(acylpyrazolonate) derivatives $[SnR_2(Q)_2]$ of $Q^{Me,Me}$ showed solubility in water and alcohols: the solvent molecules interact with the ring N^2 atom of pyrazole through H-bonding interactions (Fig. 91) [26].

Monoorganotin(IV) bis(acylpyrazolonate) derivatives $[SnRCl(Q)_2]$ exist in solution as a mixture of *cis* and *trans* octahedral isomers, but no X-ray data exist for the solid state [26,27,153,155,157,160,162].

Dihalotin(IV) derivatives $[SnX_2(Q)_2]$ (X = F, Cl, Br, I) have been reported to exist in the solid state as *cis* octahedral isomers and in solution as a mixture of *cis* and *trans* isomers [26]. ^{119}Sn NMR solution data are discussed and related to electronic and steric properties of the Q-donor, and also to the nature of the halo groups bound to Sn [26]. The X-ray structure of the derivative $[SnCl_2(Q^{Et})_2]$ (Fig. 92) and [163] and ^{119}Sn Mössbauer data of $[SnCl_2(Q)_2]$ ($Q = Q^{Ph}$, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}, Q^{Pd}) confirm the *cis* octahedral geometry [164]. The molecular structure of $[SnCl_2(Q^{Me})_2]$ has also been detected using the molecular modelling HyperChem program [164].

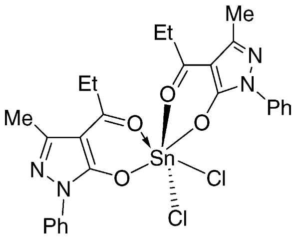


Fig. 92. Structure of the derivative $[SnCl_2(Q^{Et})_2]$.

Unexpected novel structural features have been observed in the derivatives $[SnR_2(Q)_2]$ with acylpyrazolone ligands containing a *para*-CF_3-Ph group bonded to N^1 of pyrazole ($Q^{PhpCF_3,Ph}$, $Q^{PhpCF_3,Me}$, Q^{PhpCF_3,CF_3}) [28,165]. The crystal structures of $[SnPh_2(Q^{PhpCF_3,Ph})_2]$ and $[SnMe_2(Q^{PhpCF_3,Ph})_2]$ (Fig. 93) show that it is possible to obtain both *syn* and *anti* isomeric skewed trapezoidal bipyramidal geometries on tin, by varying the solvent of crystallization [28,165]. This particular feature can be explained by a small difference in the energy content of both isomers, due

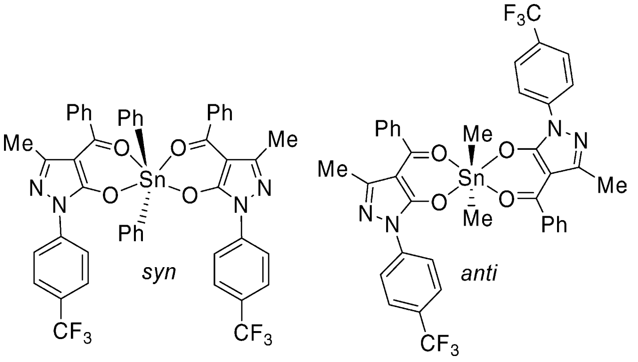


Fig. 93. *Syn* and *anti* geometries in the structures of the derivatives $[SnPh_2(Q^{PhpCF_3,Ph})_2]$ and $[SnMe_2(Q^{PhpCF_3,Ph})_2]$, respectively.

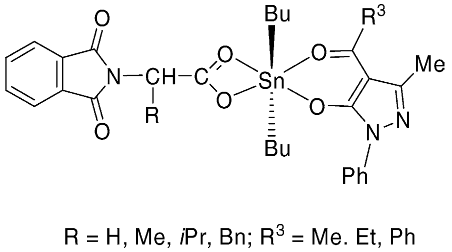


Fig. 94. Structure of the derivatives [$SnBu_2$(Q)(N-protected aminoacid)].

to lowering in the donating ability of pyrazole ring carbonyl caused by the presence of the electronwithdrawing CF_3 in the R^1 group [28,165]. The isomers can undergo interconversion in solution through a five-coordinate intermediate and/or a ionic monoacylpyrazolonate tin(IV) species [28,165].

A series of mixed-ligand diorganotin(IV) complexes containing N-protected aminoacid ligands [$SnBu_2$(Q)(L)] [Q = Q^{Me}, Q^{Et}, Q^{Ph}; HL = $C(O)C_6H_4C(O)NCHRCOOH$; R = H, Me, *i*Pr, Bn) has been recently synthesized by the interaction of Bu_2SnCl_2 with the corresponding ligands HQ and HA in the presence of NEt_3 in 1:1:1:2 molar ratios [166]. The central tin atom is six-coordinated in a *trans* octahedral environment by two butyl groups, a Q ligand and a N-protected amino acid ligands L (Fig. 94) [166].

Triorganotin(IV) derivatives have been reported by several authors and a clear picture now is emerged [31,63,74,75]. [$SnPh_3$(Q)] derivatives are five-coodinate in the solid state, with *cis* trigonal bipyramidal geometry on tin and an O_2-chelating ligand [31,63,75,76]. The crystal structures of the derivatives [$SnPh_3(Q^{PhpCF_3,Me})$] [63] and [$SnPh_3(Q^{Ph,Ph,Ph})$] confirmed this hypothesis (Fig. 95) [31].

These compounds are quite stable as anhydrous species due to the electron-withdrawing phenyl groups, which strengthen the Sn–O bonds of both arms of Q ligand [31,63,75,76]. Whereas [SnR_3(Q)] (R = alkyl as Me, Bu, Cy) rapidly absorb water from atmosphere and a composition as [$SnR_3(Q)(H_2O)$] has been observed [31,63,75,76]. This is due to the electron-releasing character of alkyl groups on tin, which weakens one Sn–O bond to a greater extent, so that Q behaves as monodentate O-donor and a water molecule is easily absorbed from atmosphere in order to complete the tin coordination environment [31,63,75,76]. In the crystal structures of [$SnBu_3(Q^{Ph})(H_2O)$] [75] and [$SnMe_3(Q^{PhpOMe})(H_2O)$] [76] a trigonal bipyramidal geometry has been found, with water and the oxygen of Q in *trans* position, and the alkyl groups in the equatorial plane (Fig. 96). Intermolecular H-bonding networks involving H of water, the chain carbonyl and the ring N^2 atom of the Q ligands of two different molecular units are found [75,76].

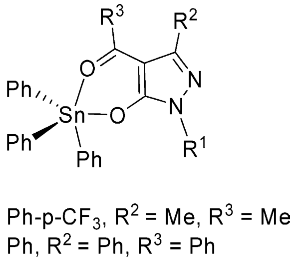


Fig. 95. Structure of the derivatives [$SnPh_3$(Q)].

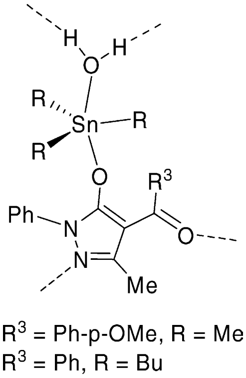
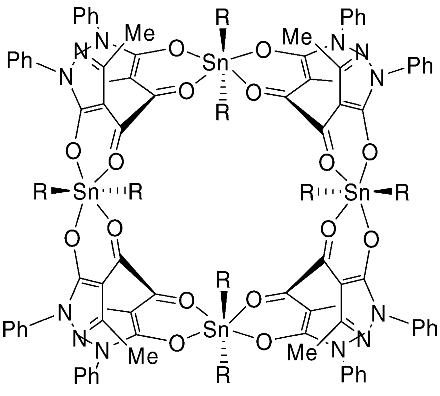


Fig. 96. Structure of the derivatives [$SnR_3(Q)(H_2O)$] (where R = Me or Bu).

Triorganotin derivatives [$SnR_3(Q)(H_2O)$] show a slow tendency to decomposition in solution, with formation of [$SnR_2(Q)_2$] and SnR_4 species [75,76].

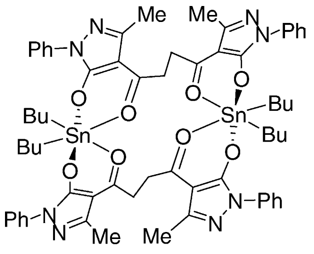
Many studies on the biological activity of tin acylpyrazolonates have appeared. [$SnBu_2(Q^{Ph})_2$] was shown to be toxic (by contact) against *Tribolium castaneum* and *Trogoderma granarium* and it affected the nervous system and behaviour of these insects [167]. The insecticidal activity of organotin(IV) derivatives [$SnBu_2(OPr^i)(Q)$] and [$SnBu_2(Q)_2$] (Q = Q^{Me}, Q^{Et}, Q^{Ph}, Q^{PhpCl}) was evaluated against *Rhizopertha dominica*, and attributed to the presence of $SnBu_2$ moiety. Both types of derivatives shown comparable activity [168]. The substituent in the acyl moiety plays a role in the activity, which decreases as follows: Ph-*p*-Cl, Ph, Me [168]. The fungicidal and insecticidal activities of HQ^{Me}, HQ^{Ph} and their diorganotin(IV) [$SnR_2(Q)_2$] (Q = Q^{Me}, Q^{Ph}, R = Bu, Ph) and triorganotin(IV) complexes [$SnR_3(Q)(H_2O)_n$] (Q = Q^{Me}, Q^{Ph}, R = Bu, Ph, *n* = 0, 1) have been evaluated and their E_D50 (fungicidal activity) and L_C50 (insecticidal activity) values are reported [169]. An attempt has been made to correlate the type of coordination geometry around the tin atom and the relative stabilities with the observed bioactivities [169]. The diorganotin(IV) complexes are more effective than the triorganotin(IV) as insecticides, and the effect of disproportionation of [SnR_3(Q)] to give [$SnR_2(Q)_2$] and SnR_4 is discussed with respect to insecticidal activity [169]. The stability constants of the diorganotin compounds are reported, suggesting they are sufficiently stable to prevent ligand exchange before their assimilation into the living tissues of the insects [169]. Triorganotin(IV) complexes [$SnR_3(Q)(H_2O)$] (Q = Q^{Me}, Q^{Et}, Q^{Ph}, Q^{PhpCl}; R = Bu, Ph) were screened for their toxicity against *Aedes aegypti larvae* and shown to be more active than the tin(II) [$Sn(Q^{PhpCl})_2$] derivative [170].

Tin(IV) derivatives of Q*n*Q tetradentate donor ligands have been also reported [171–173]. Stable



$[SnR_2(Q0Q)]_4$ (R = Me, Et, Bu, Ph)

Fig. 97. Structure of the derivatives $[SnR_2(Q0Q)]_4$ (where R = Me, Et, Bu, Ph).

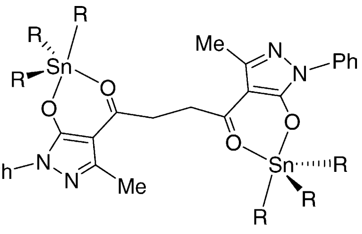


$[SnBu_2(Q2Q)]$

Fig. 98. Structure of the derivative $[SnBu_2(Q2Q)]_2$.

$[(QnQ)SnR_mCl_{2-m}]$ derivatives ($n = 0$, 2–8, 10; $m = 0$–2; R = Me, Et, Bu, Bu^i, Bu^t, Bn, Ph, Cy, vinyl, octyl, dodecyl) have been obtained and fully characterized [171,172]. The spectral data indicate that the Q*n*Q-donors coordinate through the four O atoms as dianionic tetradentate ligands [171–173]. Some of the Q2Q and Q3Q derivatives have been shown to be dimeric in solution, whereas the Q0Q derivatives are tetramers (Fig. 97) [171].

The X-ray crystal structure of $[SnBu_2(Q2Q)]_2$ shows the compound to be a dinuclear species (Fig. 98) with the tin atoms in a distorted octahedral Sn-*cis*-C_2O_4 environment (skewed trapezoidal bipyramidal), the C–Sn–C angles ranging from 107.28(14)° to 112.4(2)° [173].



R = Ph, Bu

Fig. 100. Structure of the derivatives $[(SnR_3)_2(Q2Q)]$ (where R = Bu, Ph).

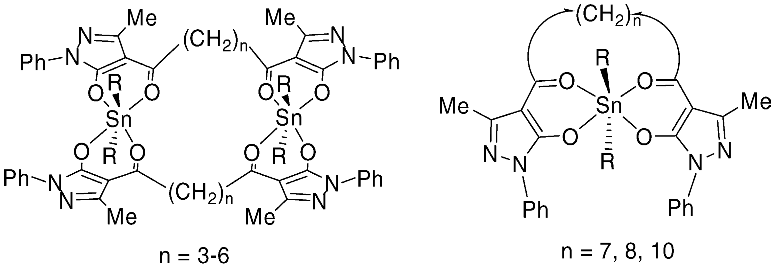
The dinuclear species containing Q3Q contain the tin atoms in a distorted octahedral Sn-*trans*-C_2O_4 environment, as deduced from $J_{(Sn-H)}$ and $J_{(Sn-C)}$ in ^1H and ^{13}C NMR spectra [171]. The length of the polymethylene chain, which links the two 3-methyl-1-phenylpyrazol-5-onato sub-units, affects the formation and the structure of the complexes [171–173]. The Q4Q, Q5Q and Q6Q derivatives are dinuclear or oligonuclear or at least polynuclear species, whereas Q7Q, Q8Q and Q10Q derivatives are monomers, the polymethylene chain being sufficiently long to allow coordination of the same metal atom from both chelating moieties of Q*n*Q (Fig. 99) [171–173].

Triorganotin(IV) derivatives of Q2Q ligand have been also reported [173]. The reaction between H_2Q2Q and $(R_3Sn)_2O$ in anhydrous conditions produces the derivatives $[(SnR_3)_2(Q2Q)]$ (R = Bu, Ph) [173]. $[(SnBu_3)_2(Q2Q)]$ reacts with water from atmosphere yielding the aqua complex $[(SnBu_3)_2(Q2Q)(H_2O)]$ [173]. The crystal structures of $[(SnBu_3)_2(Q2Q)]$ and $[(SnPh_3)_2(Q2Q)]$ have been reported (Fig. 100) [173]. They contain a dianionic ligand Q2Q bridged to two triorganotin(IV) fragments with the tin atoms in a strongly distorted trigonal bipyramidal environment [173].

Triorganotin(IV) derivatives are not indefinitely stable in solution and slowly undergo disproportionation reaction, affording SnR_4 and $[SnR_2(Q2Q)]_2$ [173].

The derivatives $[Pb(Q)_2(H_2O)_x]$ ($Q = Q^{Me}$, $x = 0$; $Q = Q^{Ph}$, $x = 2$; $Q = Q^{CF_3}$, $x = 0$) were synthesized by interaction between $Pb(OAc)_2$ and HQ in EtOH, and spectroscopically characterized [22–24,88].

Derivatives $[Pb(Q)_2]$ with different Q ligands ($Q = Q^{iPr}$, Q^{iBu}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{Hp}, Q^{Pd}, Q^{Ph}, Q^{Bn}, Q^{PhpCl}) were



n = 3-6

n = 7, 8, 10

(R = Me, Et, Bu, Ph)

Fig. 99. Structures of the derivatives $[SnR_2(QnQ)]$: dimeric derivatives when n = 3–6 and monomeric when n = 7, 8 and 10.

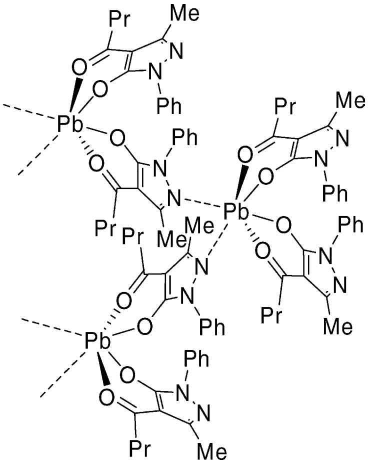


Fig. 101. Structure of the derivative $[Pb(Q^{Pr})_2]$ showing intermolecular N→Pb interactions.

reported [77,78,82,174,175] and the crystal structures of $[Pb(Q^{Me})_2]$ and $[Pb(Q^{Pr})_2]$ (Fig. 101) resolved [78], in which Pb is six-coordinated by two O_2-bidentate Q and by two additional pyrazole N atoms of Q ligands from two neighbouring molecular units. In each case the Pb atom makes four strong bonds to oxygen and two weaker bonds to either oxygen or nitrogen in adjacent molecules, Q ligands behaving as η^3-N,O_2-bridging donors [77,78,82,174,175].

Both Pb–O and Pb–N stretching modes were identified in the far-IR spectra, where the frequency of the Pb–O vibrations decrease with increasing of the length of 4-acyl substituent [175]. The compounds $[Pb(Q)_2]$ ($Q = Q^{tBu}$, Q^{nPe},$Q^{Php\,tBu}$, $Q^{Me,Me}$) were recently synthesized by interaction between $Pb(NO_3)_2$ and HQ in MeOH in the presence of KOH, and the X-ray structures of $[Pb(Q^{tBu})_2]$ and $[Pb(Q^{nPe})_2]$ in the solid state detected [79]. In the former a PbO_2N_2 core has been found, where Pb–N interactions involve N atoms of Q from the neighbouring molecules to produce polymeric forms [79]. $[Pb(Q^{nPe})_2]$ is unusual in having the Pb–O(pyrazolonato) bond longer than the Pb–O(acyl) one, probably due to a Pb–arene interaction with a neighbouring Ph ring (Fig. 102) [79]. The sterically less hindered $[Pb(Q^{Me,Me})_2]$ reacts with phen in benzene yielding the mixed-ligand complex $[Pb(Q^{Me,Me})_2(phen)]$ (Fig. 103) [79].

The synthesis of monomeric and dimeric $[Pb(QnQ)]$ ($n = 4$, 8) complexes has also been reported [114].

6.12. Group VA: As, Sb and Bi

Phenylarsenic(III) derivatives of Q ($Q = Q^{Me}$, Q^{Et}, Q^{Ph}, Q^{PhpCl}) having formula $[AsPh(Q)_nCl_{2-n}]$ ($n = 1$, 2) can be synthesised by the reactions of $PhAsCl_2$ with Q in the presence of NEt_3 in 1:1 and 1:2 molar ratios in benzene [176]. Analytical and spectral data indicate that they contain O_2-chelated Q in the solid state, whereas in solution Q ligands act in a O-monodentate fashion [176].

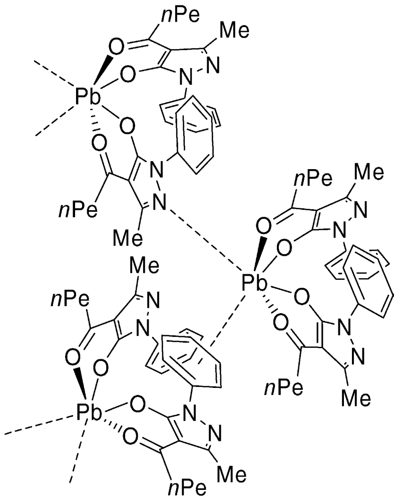


Fig. 102. Structure of the derivative $[Pb(Q^{nPe})_2]$ showing intermolecular N→Pb and arene→Pb interactions.

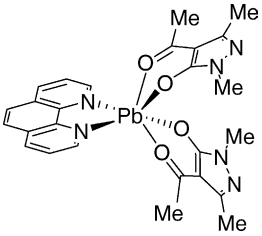


Fig. 103. Structure of the derivative $[Pb(Q^{Me,Me})_2(phen)]$.

Diphenylantimony(III) Q compounds $[SbPh_2(Q)]$ ($Q = Q^{Me}$, Q^{Et}, Q^{Ph}, Q^{PhpCl}) were reported containing O_2-chelated Q ligands, both in solution and in the solid state [177]. Oxo-bridged dinuclear tripenylantimony(V) derivatives $[\{SbPh_3(Q)\}_2O]$ ($Q = Q^{Me}$, Q^{Ph}) have been synthesized and the crystal structure of $[\{SbPh_3(Q^{Ph})\}_2O]$ reported, in which terminal Q^{Ph} chelate through both O atoms and each Sb is six-coordinated in a *mer*-arrangement of the ligand sets (Fig. 104) [178].

The derivative $[Bi(Q^{Ph})_3]$ has been spectroscopically and thermally characterized [107].

6.13. Group VIA: Te

A triphenyl telluronium derivative $[TePh_3(Q^{Me})]$ has been synthesised by reaction between Ph_3TeCl and HQ in hot water

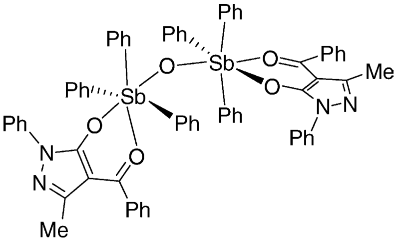


Fig. 104. Structure of the derivative $[\{SbPh_3(Q^{Ph})\}_2O]$.

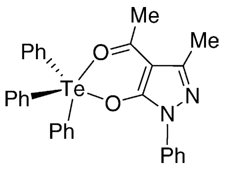


Fig. 105. Structure of the derivative [$TePh_3(Q^{Me})$].

in presence of NaOH [179]. It is a stable pentacoordinated Te derivative with Q^{Me} acting in O_2-chelating form (Fig. 105). It is effective against *Aspergillus niger* and *Curvularia lunata*, organisms able to degrade cellulose and related materials such as wood, paper, leather, etc. [179].

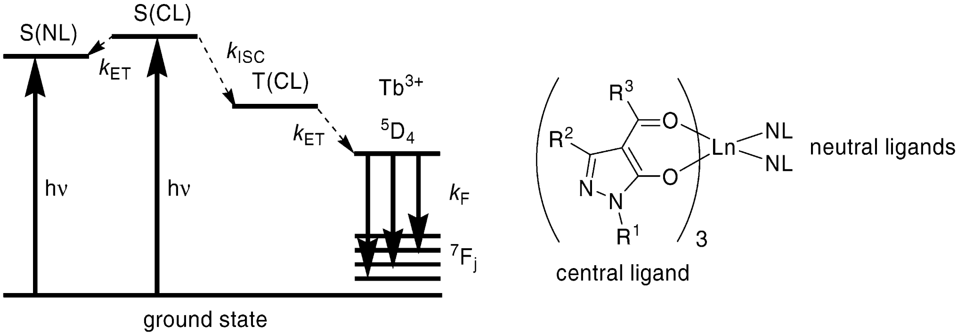
6.14. Lanthanides

The field of lanthanide acylpyrazolone coordination chemistry has received increased attention in the last decades, due to luminescence properties of these derivatives. A review on organic electroluminescent devices, containing lanthanide metal ion complexes and classical β-diketones and/or acylpyrazolones as the emitting layer, has been published in 2002 [180], but it is not properly focused on acylpyrazolone lanthanide compounds and does not cover all the field of lanthanide–acylpyrazolone coordination chemistry [180]. The basic principles related to the luminescence process of lanthanide ions have been extensively investigated. A commonly accepted energy diagram, showing how the energy is absorbed by the β-diketonate ligand, called "central ligand", transferred to the metal ion and finally converted to luminescence, is reported in Fig. 106 [181].

The central ligand absorbs energy and is excited to its singlet state, through intersystem crossing, then transits to its triplet state and the energy is intramolecularly transferred to the energy levels of the Ln ion. Luminescence is emitted when transition to the ground state occurs [181]. The central β-diketonate ligand plays a key role in the luminescence process. Its first absorption band is related to the singlet–singlet $n \rightarrow \pi^*$ transition involving the non-bonding electrons of the oxygen atom [181]. Substituents of the central ligand with different electron withdrawing of electronreleasing features in the structure of the ligand can affect the energy of this band and change any of these processes [181]. In addition to the negatively charged β-diketonate ligand, Ln ion also needs a zero-charged ligand, called "neutral ligand", to coordinate for structural stability [181]. This neutral ligand also influences the luminance of the complex. The left of the Fig. 106 indicates that luminescence quenching may occur when the energy is partially transferred to the singlet state of the neutral ligand by the excited singlet state of the central ligand [181]. So that three key factors related to this process are contributed to the luminescence intensity: (1) the efficiency of the absorption, (2) the efficiency of the ligand-to-metal energy transfer and (3) the efficiency of the metal luminescence [181].

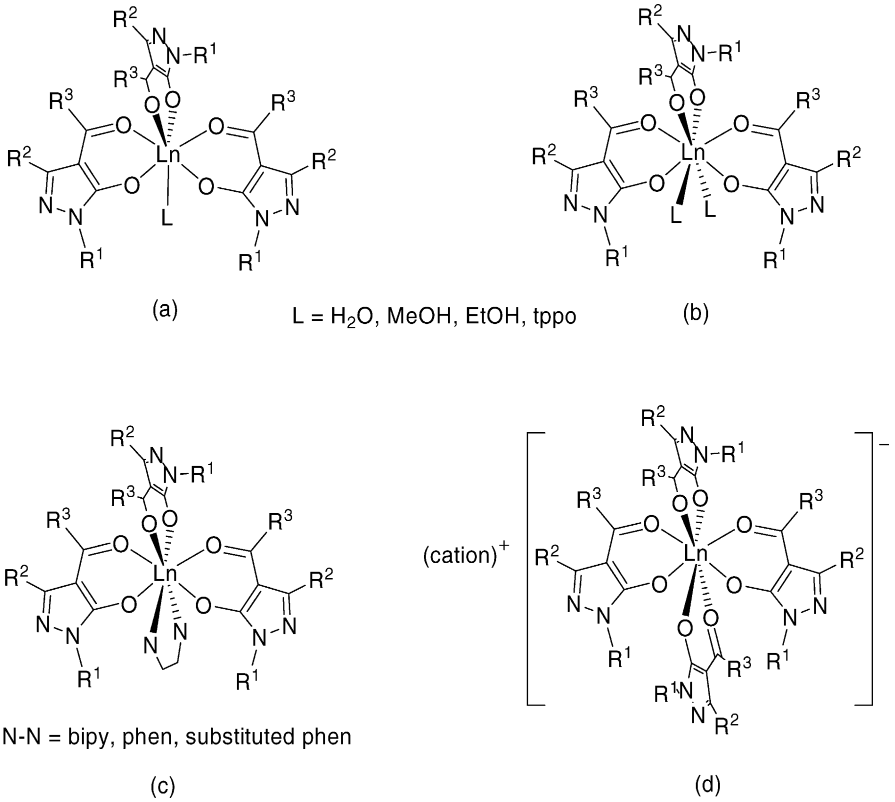
Lanthanide acylpyrazolonate derivatives can be synthesized from reaction in basic (for NaOH) ethanol/water solution between HQ and LnX_3 salts ($X = NO_3$, ClO_4, Cl). They conform to some general structurally well-defined type-complexes (Fig. 107). The Ln(III) have been mainly explored, where neutral hepta-coordinate [$Ln(Q)_3(L)$] (Fig. 107a) or octa-coordinated [$Ln(Q)_3(L)_2$] (Fig. 107b) or [$Ln(Q)_3(L_2)$] derivatives (Fig. 107c), or ionic octa-coordinated (cation)[$Ln(Q)_4$] (Fig. 107d) have been synthesized.

Derivatives [$Ln(Q^{Ph})_3 \cdot nH_2O$] ($n = 4$ for La–Sm, and $n = 1$ for Eu–Yb and Y), [$Ln(Q^{Ph})_3(py)_2 \cdot 2H_2O$], [$Ln(Q^{Ph})_3(L) \cdot EtOH$] (L = bipy, phen), [$NH_4$][$Ln(Q^{Ph})_4$]·EtOH and (cation)[$Ln(Q^{Ph})_4$]·EtOH (cation = quaternary ammonium cation of piperidine, pyrrolidine or morpholine) were firstly reported in 1978 [182]. The electronic spectra of the Nd(III) complexes were studied in detail to investigate the phenomenon of hypersensitivity with respect to the coordination environment and solvent medium [182]. The solvent does not play a significant role in causing variation in hypersensitivity [182]. Later, the synthesis and characterization of mixed-ligand tetrakis chelates Na[$M(acac)_3(Q)$] (M = La, Ce, Pr, Ne, Gd, $Q = Q^{Me}$, Q^{Ph}), that are ionic in solution



Representative energy level diagram for a typical Tb complex, where CL = central ligand, NL = neutral ligand, S(CL) = singlet excited state of CL, T(CL) = triplet esxcited state of CL, S(NL) = singlet ecited state of NL, k_{ET} = rate constant of intramolecular energy transfer, k_{ISC} = rate constant of intersystem crossing, k_F = rate constant of fluorescence decay.

Fig. 106. Diagram showing the mechanism of the luminescence process in lanthanide acylpyrazolonate derivatives.



(a) L = H_2O, MeOH, EtOH, tppo (b)

N-N = bipy, phen, substituted phen

(c)

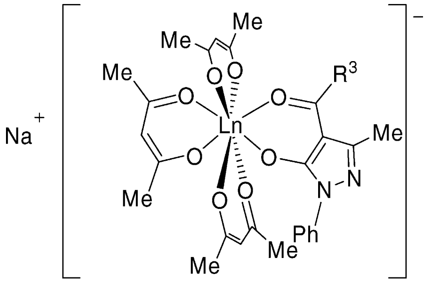
(d)

Fig. 107. Typical structures of $[Ln(Q)_3(L)]$ (a), $[Ln(Q)_3(L)_2]$ (b), $[Ln(Q)_3(N\text{-}N)]$ (c) and $(cation)[Ln(Q)_4]$ (d).

and Ln are eight-coordinated (Fig. 108), were reported [183].

Anhydrous six-coordinate derivatives $[Ln(Q^{Ph})_3]$ (Ln = Y, La, Nd, Eu, Gd, Dy, Er, Lu) were prepared and studied by UV, IR, and NMR spectroscopy [184]. The NMR results are consistent with a rapid *cis*–*trans* isomerization equilibrium [184]. The synthesis of anhydrous $[La(Q^{Bn})_3]$ and its characterization by UV, IR and ^1H, ^{13}C NMR spectral studies has also been reported [174].

Derivatives containing different Q ligands, with empirical formula $[Ln(Q^{CF_3})_3{\cdot}xH_2O{\cdot}y\text{EtOH}]$ (Ln = La, Nd, Eu, Dy, Er, Pr, Lu, $x = 2$ and $y = 0$; Ln = Y, Gd, $x = 2$ and $y = 0.5$) [185] and $[Ln(Q^{Me})_3(H_2O)_2]$ (Ln = Y, La, Ce, Nd, Eu, Gd, Dy, Er, Lu) were synthesised, characterized and compared with those of Q^{Ph} [186].



R^3 = Me, Ph

Fig. 108. Structure of the derivative $Na[Ln(acac)_3(Q)]$.

The synthesis and X-ray structure of the compound $[Yb(Q^{Ph,Ph,Ph})_3(H_2O)_2]{\cdot}3EtOH$ (Fig. 109) has been reported [187]. The three Q ligands are coordinated to the central metal ion in an O_2-bidentate form. Two water molecules are also coordinated, giving an eight-coordinated Yb atom [187].

Several $[Ln(Q)_3(H_2O)_2]$ have been reported with different Q ligands (Ln = La, Gd, Tb; Q = Q^{Me}, Q^{Et}, Q^{iPr}, Q^{iBu}, Q^{tBu}, Q^{Ph}) [82,188]. Time-resolved emission spectra and lifetimes were obtained for the complexes: the triplet states of the ligands were observed at room temperature [188]. In the phosphorescence spectra of Gd complexes the groups Me, Et or *i*Pr in acyl moiety of Q ligands seem to not affect emission properties of the complexes, whereas their substitution with *t*Bu or Ph causes a red shift of the Q ligand triplet state absorption and a decrease in Ln emission intensity [188]. Intramolecular energy transfer rate is proportional to the overlap of the phosphorescence spectrum of the Q ligand and the excitation

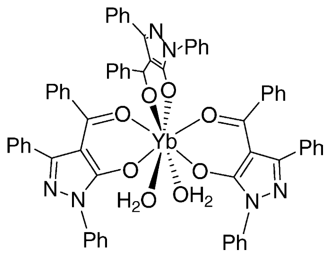


Fig. 109. Structure of the derivative $[Yb(Q^{Ph,Ph,Ph})_3(H_2O)_2]{\cdot}3EtOH$.

spectrum of the rare earth ion [188]. The energy level of the triplet state is one of the key parameters to the intramolecular energy transfer. Other properties of the excited singlet and triplet states such as the singlet and triplet lifetimes are also important [188].

The fluorescence and phosphorescence of $[\mathrm{Ln(Q)_3(H_2O)_2}]$ (Ln = Tb, Gd; Q = $\mathrm{Q^{Me}}$, $\mathrm{Q^{Et}}$, $\mathrm{Q^{Pr}}$, $\mathrm{Q^{Bu}}$, $\mathrm{Q^{Ph}}$) were described [189]. Ln derivatives of $\mathrm{Q^{Ph}}$ ligand show fluorescence emission spectra of low-intensity; this is attributed to the relatively low triplet energy level of $\mathrm{Q^{Ph}}$ ligand, which cannot efficiently transfer UV excitation energy to the lowest excited state of the Tb ion to obtain the characteristic emission of $\mathrm{Tb^{3+}}$ [189]. The substitution of Ph with an alkyl group in the acyl moiety of Q ligands decrease the electron conjugate system to yield a ligand with a higher triplet energy level, so that the ligand-to-metal energy transfer may proceed much more easily [189]. The molecular structure of derivative $[\mathrm{Tb(Q^{Et})_3(H_2O)_2}]$ shows a Tb in a square-antiprism coordination by eight O atoms, six from the three bidentate Q ligands and two from coordinated water molecules [189].

The complex $[\mathrm{Tb(Q^{Xd})_3(EtOH)}]$ has been used as Langmuir Blodgett (LB) film for the fabrication of a new microcavity, due to its fluorescence intensity and lifetime [190]. The use of microcavities as optical resonators was developed as a potential high-density light source for optical communications and colour displays [190]. Derivatives $[\mathrm{Ln(Q^{Bu})_3(H_2O)(EtOH)}]$ (Ln = La, Ce, Nd, Sm, Gd, Dy, Er) were synthesized and characterized by IR spectra and thermograms, showing that the complexes accept solvent molecules and become eight-coordinated [191].

A series of derivatives $[\mathrm{Tb(Q)_3(L)_2}]$ and $[\mathrm{Tb(Q)_3(N_2\text{-}donor)}]$ (Q = $\mathrm{Q^{Me}}$, $\mathrm{Q^{Et}}$, $\mathrm{Q^{Pr}}$, $\mathrm{Q}^{i\mathrm{Pr}}$, $\mathrm{Q^{OEt}}$, $\mathrm{Q^{NMe_2}}$, $\mathrm{Q^{NPh_2}}$, $\mathrm{Q^{PhpMe}}$, $\mathrm{Q^{Np}}$, $\mathrm{Q^{C_3F_7}}$; L = tppo, $\mathrm{H_2O}$; $\mathrm{N_2}$-donor = bipy, phen) were synthesized and their photoluminescence (PL) and electroluminescence (EL) analysed [25]. The first absorption band of the Q ligands gradually shifts toward the shorter wavelength region as the 4-acyl group changes from an electron acceptor to an electron donor [25]. Correspondingly, the photoluminescence quantum efficiency of the Tb complexes increases [25]. The neutral ligands L- and $\mathrm{N_2}$-donor also affect the photoluminescence and electroluminescence of the Tb complexes [25]. A photochemical explanation for the influence of the R group and neutral ligand on the photoluminescence is proposed in relation to ligand-to-metal energy transfer [25]. The EL of the Tb complexes having a neutral ligand comes from both the light-emitting layer and the hole-transport layer while the EL of the Tb complex without a neutral ligand is pure green, coming solely from the light-emitting layer. It therefore demonstrates that the former have higher electron-transport ability than the latter [25]. The mixed-ligand complex $[\mathrm{Eu(tta)_2(Q^{Php\mathit{t}Bu})(phen)}]$ (Fig. 110) has been reported to show photoluminescent and electroluminescent properties [192].

Derivatives $[\mathrm{Eu(Q)_3(H_2O)_2}]\cdot 2\mathrm{H_2O}$, $[\mathrm{Eu(Q)_3(phen)}]\cdot 2\mathrm{H_2O}$ (Q = $\mathrm{Q^{Ph}}$, $\mathrm{Q^{CH_2Cl}}$) and the ionic $[\mathrm{Bu_4N}][\mathrm{Eu(Q^{Ph})_4}]\cdot 2\mathrm{H_2O}$ have been synthesized and their fluorescence properties investigated [193].

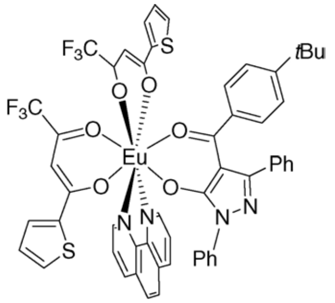


Fig. 110. Structure of the derivative $[\mathrm{Eu(tta)_2(Q^{Php\mathit{t}Bu})(phen)}]$.

Several derivatives of formula $[\mathrm{Ln(Q^{Bn})_3(EtOH)(H_2O)}]$, (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) $[\mathrm{Ln(Q^{Bn})_3(H_2O)_2}]$ (L = La or Lu), $[\mathrm{Ln(Q^{thi})_3(EtOH)(H_2O)}]$ (Ln = Tb or Eu) $[\mathrm{Tb(Q^{fur})_3(EtOH)(H_2O)}]$ $[\mathrm{Tb(Q^{CF_3})_3(H_2O)_2}]$, $[\mathrm{NBu_4}][\mathrm{Ln(Q)_4}]$ (Ln = Eu or Tb, Q = $\mathrm{Q^{CF_3}}$ or $\mathrm{Q^{Bn}}$) have been reported and characterized [194]. The crystal structures of $[\mathrm{Nd(Q^{Bn})_3(EtOH)(H_2O)}]$, $[\mathrm{Dy(Q^{Bn})_3(EtOH)(H_2O)}]\cdot\mathrm{EtOH}$ and $[\mathrm{Eu(Q^{thi})_3(H_2O)(EtOH)}]$, containing eight-coordinate lanthanide ions in a square-antiprismatic environment, have been also determined [194]. The coordination environment in the tetrakis complex $[\mathrm{NBu_4}][\mathrm{Eu(Q^{CF_3})_4}]$ is also close to the square-antiprismatic one [194]. Photoluminescence and phosphorescence of these compounds have been investigated, showing that the substituent in the acyl moiety of Q ligands does not affect the structure and composition of Ln derivatives but has a large effect on the luminescence properties [194].

Lanthanide complexes $[\mathrm{Ln(Q)_3(H_2O)(EtOH)}]$ (Ln = La, Eu; Q = $\mathrm{Q^{thi}}$, $\mathrm{Q^{fur}}$) have been synthesized and characterized by spectral IR and NMR and X-ray [125]. The presence of additional heteroatoms in Q ligands has virtually no effect on the structure and composition of the complexes formed. These Q ligands coordinate the metal atoms through O atoms similarly to other β-diketones, whereas the remaining heteroatoms only participate in the formation of a H-bonding system with additional Q ligands or coordinated solvent molecules [125]. The complexes $(\mathrm{H_3O})[\mathrm{Ln(Q^{thi})_4}]$ (Ln = Tb, Eu, Lu) have also been prepared and characterized [195]. The presence of the cation $\mathrm{H_3O^+}$ stabilized by H-bonding to the pyridinic N atom of $\mathrm{Q^{thi}}$ has been confirmed by X-ray (Fig. 111) and spectroscopic (NMR, IR) studies [195].

The compound $[\mathrm{Tb(Q^{\mathit{t}Bu})_3(tppo)}]$ as been shown to be a suitable emitter for the construction of an high-efficiency electroluminescent devices as organic light-emitting diode (OLED) with reduced reflectivity [196,197] and has also been used to prepare single layer devices with light emission and current-transporting properties [198]. The electroluminescent terbium complex of formula $[\mathrm{Tb(Q^{\mathit{t}Bu})_3(tppo)_2}]$ has been reported and investigated [199]. It has been shown that its EL efficiency overtakes tris(8-hydroxyquinolinate)

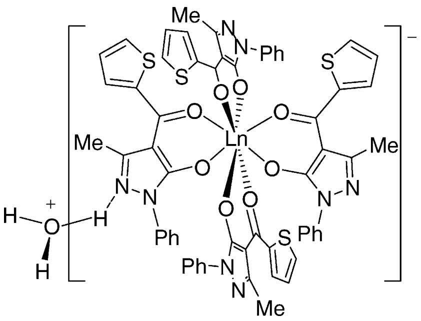


Fig. 111. Structure of the derivatives $(H_3O)[Ln(Q^{thi})_4]$ (Ln = Tb, Eu, Lu).

aluminium, the commonly used green light emitter [199]. Anhydrous six-coordinated derivatives $[Tb(Q^{tBu})_3]$ and $[Gd(Q^{tBu})_3]$ and $[Tb(Q^{tBu})_3(bipy)]$ and $[Gd(Q^{tBu})_3(bipy)]$ have been synthesized and the excitation transfer rates between their excited states described [200].

A bilayer organic light-emitting diode, using a blue-fluorescent $[Y(Q^{iPr})_3(bipy)]$ complex as an emitting material and poly(*N*-vinylcarbazole) (PVK) as a hole-transporting material, emitts bright green light instead of blue light [201]. It is attributed to the exciplex formation at the solid interface between the PVK and $[Y(Q^{iPr})_3(bipy)]$ layers, which was demonstrated by the measurement of the absorption, photoluminescence and photoluminescence excitation spectra of the mixture of PVK and $[Y(Q^{iPr})_3(bipy)]$ (molar ratio, 1:1) [201]. The compound $[Gd(Q^{iPr})_3(phen)]$ has been synthesized and used as a light-emitting material in the organic electroluminescent devices [202].

The compound $[Gd(Q^{iPr})_3(tppo)_2]$ has been synthesized and used as electron-transport layer, together with $[Eu(dbzm)_3(phencarz)]$, to prepare an electroluminescent device [203]. The compound $[Y(Q^{iPr})_3(phen)]$ exhibits photoluminescence and electroluminescence [204]. The complex has carrier-transporting and emitting properties, and it was applied to prepare a bilayer device, which exhibited green emission with good power efficiency [204]. A study of the EL spectra of double- and triple-layered devices based on a rare earth complex $[Tb(Q^{iPr})_3(tppo)_2]$ has been reported, proving that this compound possesses high electron mobility [205]. The PL and EL of the exciplex formed between the compound $[Tb(Q^{iPr})_3(phen)]$ and the hole-transporting material *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine were studied [206].

The Lu complexes $[Lu(Q^{iPr})_3(tppo)_2]$, $[Lu(Q^{iPr})_3(bipy)]$ and $[Lu(Q^{iPr})_3(phen)]$ were synthesized and the X-ray crystal structure of $[Lu(Q^{iPr})_3(tppo)_2]$ analysed [207]. When these complexes were used to prepare light-emitting devices, that with complex $[Lu(Q^{iPr})_3(tppo)_2]$ gave a blue light, originating from this complex, while the same configuration devices using the other two complexes exhibited green light [207].

The derivatives $[Tb(Q^{iPr})_3(tppo)_2]$, $[Tb(Q^{iPr})_3(EtOH)(H_2O)]$ and $[Tb(Q^{CHEt_2})_3(tppo)]$ have been synthesized and studies have revealed different carrier-transport and photo-physical properties [208]. $[Tb(Q^{iPr})_3(tppo)_2]$ has overly strong electron-transport properties, whereas $[Tb(Q^{iPr})_3(EtOH)(H_2O)]$ mainly revealed hole-transport properties, and $[Tb(Q^{CHEt_2})_3(tppo)]$ showed both electron- and hole-transport properties [208]. The crystal structure of the Tb complex $[Tb(Q^{CHEt_2})_3(tppo)]$ has been resolved [209]. Devices using this complex as emitter present good performance, better than what was reported previously with analogous derivatives. This result originated from the Tb complex's well-balanced charge-transport properties [209].

The terbium complexes $[Tb(Q^{nPe})_3(tppo)]$, $[Tb(Q^{nPe})_3(H_2O)]$ and $[Tb(Q^{nPe})_3(phen)]$ were synthesized and characterized, also by X-ray studies. The mechanism through which the neutral ligands affect photoluminescence and electroluminescence properties of terbium complexes has been investigated [210]: the neutral ligands tppo and phen strongly affect the terbium complex PL intensity, tppo enhances the PL intensity of complex $[Tb(Q^{nPe})_3(tppo)]$, while phen reduces the PL intensity of complex $[Tb(Q^{nPe})_3(phen)]$, compared to that of complex $[Tb(Q^{nPe})_3(H_2O)]$ [210]. This is caused by the different excited energy levels between Q, tppo and phen, which were obtained from their phosphorescence spectra measured with their corresponding gadolinium complexes $[Gd(Q^{nPe})_3(H_2O)(EOH)]$, $[Gd(NO_3)_3(tppo)_2]$ and $[Gd(NO_3)_3(phen)_2]$ [210].

$[Tb(Q)_3(H_2O)]$ and $[Tb(Q)_3(H_2O)(EtOH)]$ derivatives ($Q = Q^{Cp}$, Q^{etCp}) have been prepared and characterized by elemental analyses, IR, NMR and X-ray [211]. They are seven- and eight-coordinate, respectively. The role of the reaction medium on the coordination number of Tb has been investigated [211].

$[Ln(Q)_3(H_2O)(EtOH)]$, $[Ln(Q)_3(N_2\text{-donor})]$ and $(NBu_4)[Ln(Q)_4]$ (Ln = Eu, Tb; $Q = Q^{Cp}$, Q^{etCp}; N_2-donor = phen, batophen) have been recently reported by our group [212]. Their spectral and fluorescence properties have been correlated to the ancillary donors and substituents in phenanthroline and Q ligands [212]. Quantum yield of Eu^{3+} luminescence of Q^{etCp} derivatives si somewhat lower than that of Q^{Cp} derivatives, due to quenching caused by high-frequency ethylene group vibrations in the acyl moiety of the Q^{etCp} [212]. The X-ray crystal structure of $(NBu_4)[Eu(Q^{etCp})_4]$ resolved [212].

Many efforts have been devoted to find appropriate precursors for Langmuir–Blodgett (LB) films with suitable optical properties. The compound ((*E*)–Me_2N–Ph–CH=CH–py–$C_{16}H_{33}$)$[Dy(Q^{Ph})_4]$ was synthesized and used to prepare Langmuir–Blodgett films that were characterized by UV–vis, IR, X-ray photoelectron spectroscopy, and low-angle X-ray diffraction (Fig. 112) [213]. High-quality LB films up to 50 layers on the hydrophilic substrates of quartz, calcium fluoride, and glass were obtained [213].

The same compound was also used to dope a highly photoactive bilayer lipid membrane [214]. A similar complex (py-$C_{16}H_{33}$)$[Eu(Q^{Ph})_4]$ was synthesized and used to form a stable floating Langmuir–Blodgett film at air–water interface that could be deposited onto various hydrophilic substrates of fused quartz, single crystal calcium fluoride and transparent

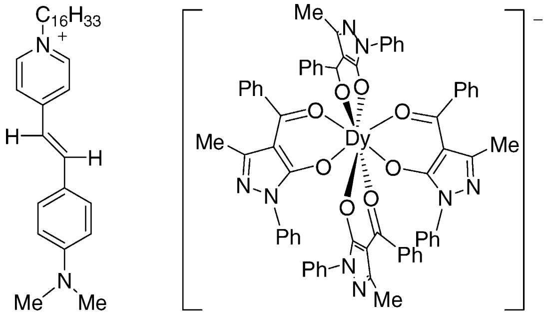


Fig. 112. Structure of the derivative ((*E*)-Me_2N-Ph-CH=CH-py-$C_{16}H_{33}$)[Dy(Q^{Ph})$_4$].

indium tin oxide (ITO) glass [215]. LB films were characterized and electrical and optical properties investigated [215].

The influence in monolayer-morphology of long-chain substituents in quaternary ammonium cation of derivatives ($Me_2N(C_nH_{2n+1})_2$)[Eu(Q^{Ph})$_4$] ($n = 14$, 16, 18) has been investigated and directly observed at the air–water interface by Brewster angle microscopy [216]. Other compounds ((*E*)–Me_2N–Ph–CH=CH–py–$C_{16}H_{33}$)[Ln(Q^{Ph})$_4$] (Ln = La, Nd, Dy, Yb) have been reported and their liquid crystal behaviours studied by using DSC, thermogravimetric and DTA and polarized optical microscopy [217]. Except for the La complex, the other three complexes display mesogenic behaviour with typical smectic mosaic textures [217].

The ionic amphiphilic derivatives (Et_2N–Ph–N=N–py–Me)[Dy(Q^{Ph})$_4$] (Fig. 113) and (Et_2N-Ph-N=N-py-Me)[Dy(Q^{Ph})$_3$(Q^{Xd})] have been synthesized and their LB film-forming properties evaluated [218].

A series of amphiphilic lanthanide complexes of general formula ((*E*)–Me_2N–Ph–CH=CH–py–C_nH_{2n+1})[Ln(Q)$_4$] ($n = 4$, 12 16; Ln = La, Nd, Dy, Yb; Q = Q^{Ph}, Q^{CF_3}; Q_2 = Q4Q) were designed and synthesized, in which the lanthanide complex anions act both as the counterions of hemicyanine and as the spacer within a LB film [219]. Ionic derivatives ((*E*)–Et_2N–Ph–CH=CH–py–$C_{16}H_{33}$)[Ln(Q^{Ph})$_4$] (Ln = Nd, Dy) and their electroluminescence from LB films has been developed for nonlinear optics applications [220]. LB films of the complexes produced on glass/InSn oxide substrates produce broad electroluminescence in the visible region of the spectrum, which is considerably red shifted relative to their photoluminescence [220]. The electroluminescent devices can operate in vacuo and at room temperature [220].

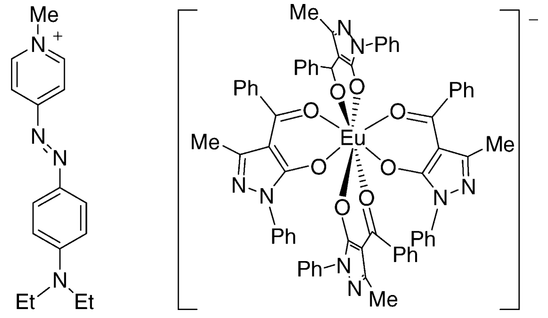


Fig. 113. Structure of the derivative (Et_2N-Ph-N=M-py-Me)[Dy(Q^{Ph})$_4$].

The ionic (($C_{16}H_{33}$)$_2$N–Ph–N=N–py–Me)[La(Q^{Ph})$_4$] forms a stable Langmuir monolayer film on a pure waste subphase when spread from a chloroform solution [221]. LB films were prepared by transferring the monolayers onto hydrophilic substrate of quartz and calcium fluoride [221]. The second-order hyperpolarizability of the complex was estimated, and the IR and variable-temperature UV spectra of the film were also reported [221]. The ionic ((*E*)–Me_2N–Ph–CH=CH–py–$C_{18}H_{37}$)[Dy(Q^{Pd})$_4$] has been used as a doping material in the construction of a highly photobilayer lipid membrane (BLM) [222]. Tautomerization of the azo-pyridinium compound takes place under irradiation [222]. The mechanism for photoelectric effect of this BLM system has also been proposed [222]. The ionic ((*E*)–Et_2N–Ph–CH=CH–py–$C_{16}H_{33}$)[Yb(Q^{Ph})$_4$] has been synthesized and applied to form LB films [223]. The luminescence of the films has also been investigated [223]. The complexes ((*E*)–Et_2N–Ph–CH=CH–py–$C_{16}H_{33}$)[Ln(Q^{Ph})$_4$] (Ln = La, Gd, Lu) exhibit solvatochromism from yellow to orange red in different solvents, due to dipolar interactions between the solvent and the complex [224]. The synthesis, thermal and spectroscopic properties of several ((*E*)–Me_2N–Ph–CH=CH–py–C_nH_{2n+1})[Ln(Q^{Ph})$_4$] dyes ($n = 14$, 16, 18; Ln = Eu, Gd, Tb, La, Ce, Pr, Nd, Sm, Dy, Ho, Er, Tm, Yb, Lu) have been reported [225]. All the complexes melt directly to an isotropic liquid, without passing through a mesophase [225]. The melting point increases sharply in the beginning of the lanthanide series, and remains constant over the second half of the series [225]. These complexes dissolved in organic solvents show strong solvatochromism (yellow to orange colour) [225].

A large number of lanthanum derivatives with polydentate Q*n*Q ligands has been synthesized and investigated for their luminescence properties. The syntheses of [Ln_2(Q2Q)$_3$(phen)$_2$]·nH_2O (Ln = Y, La, Pr, Sm-Lu; $n = 4$, 5) were reported by Yang et al. and the complexes were shown to exist as binuclear derivatives [226]. Derivatives [Ln_2(Q1Q)$_3$(phen)$_2$]·nH_2O (Ln = Y, La, Pr, Nd, Sm–Yb; $n = 3$–6) were prepared and a binuclear structure of the complexes was proposed on the basis of analytical and spectral (IR and NMR) investigations [227]. The UV spectra and TG-DTA were also reported. Fluorescence spectra show that Pr, Sm, Eu, Tb, Dy and Tm complexes have line emissions of metal ions [227]. The complexes [Tb_2(Q3Q)$_3$(H_2O)$_4$]·$2H_2O$ and [Tb_2(Q3Q)$_3$(dmf)$_4$]·dmf were synthesized [228]. The crystal structure of [Tb_2(Q3Q)$_3$(dmf)$_4$]·dmf was detected by X-ray diffraction methods [228]. In this complex Q3Q acts as a bridging ligand towards two Tb atoms. Each Tb is also coordinated by two dmf solvent molecules (Fig. 114) [228]. The coordination number of Tb is eight. The eight O atoms around the Tb make a distorted square antiprismatic coordination polyhedron [228].

Dinuclear complexes of the types [Ln_2(Q3Q)$_3$(bipy)$_2$]·nH_2O ($n = 2$ for Y, $n = 4$ for Eu, Gd, Dy, Ho, Er, Tm,

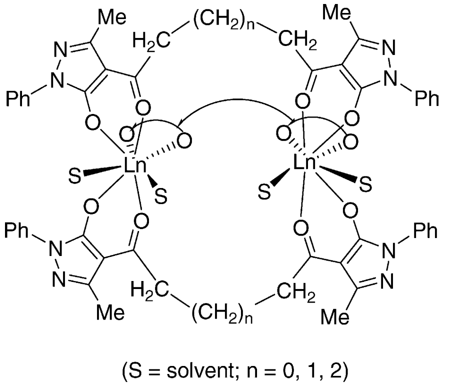


Fig. 114. Typical structure of the derivatives $[Ln_2(QnQ)_3(solvent)_4]$ (where *n* = 0, 1, 2).

Yb) and $[Ln_2(Q3Q)_3(bipy)]\cdot nH_2O$ ($n = 10$ for La, $n = 3$ for Pr, Nd, Sm, Tb) were synthesized and their fluorescence spectra investigated [229]. The dinuclear complexes $[Sm_2(Q3Q)_3(H_2O)_4]\cdot 3H_2O$ and $[Sm_2(Q3Q)_3(dmf)_4]\cdot dmf$ were prepared and the X-ray crystal structure of $[Sm_2(Q3Q)_3(dmf)_4]\cdot dmf$ detected [230]: each Q3Q acts as a bridging ligand toward two Sm atoms, two dmf molecules being also bonded to each Sm atom. The coordination number of the two Sm atoms is eight, in a distorted square antiprism configuration [230]. Two Dy derivatives of formula $[Dy_2(Q3Q)_3(H_2O)_2]$ and $[Dy_2(Q3Q)_3(dmf)_4]\cdot dmf$ have been synthesized and the crystal structure of the latter show each Q3Q ligand bridging both Dy atoms [231]. Two dmf solvent molecules bond to each Dy so that the C.N. is eight. The eight O atoms around each Dy make up a distorted square-antiprism coordination polyhedron [231]. Derivatives $[Y_2(Q4Q)_3EtOH)(H_2O)_4]\cdot H_2O$, $[La_2(Q4Q)_3(H_2O)_4]\cdot 0.5H_2O$ and $[La(Q8Q)(HQ8Q)(H_2O)]$ have been reported [120]. The former complexes consist of dinuclear molecules with bridging Q4Q tetradentate ligands, whereas the latter is likely a monomeric compound [120].

A number of work are in literature on the synthesis and potential applications of ionic Ln compounds with tetradentate acylpyrazonolates Q*n*Q. Derivatives $(Me_3NC_{16}H_{33})[Ln(Q3Q)_2]$ (Ln = Y, La, Pr, Nd, Sm–Yb) were reported and analysed with IR, ^1H NMR, UV, fluorescence spectra and thermogravimetric data [232]. A ionic monomeric structure for these species suggested (Fig. 115) [232].

The ionic species $(Me_3NC_{16}H_{33})[Sm(Q4Q)_2]$ shows a strong fluorescence intensity [233]. In this system some rare earth ions, such as Lu^{3+}, Y^{3+}, Gd^{3+} and Tb^{3+}, exert an evident fluorescence enhancement effect [233]. The formation conditions of the systems and the factors affecting the co-luminescence effect were studied in detail in order to detect trace amounts of Sm^{3+} [233]. The ionic $(Me_3NC_{16}H_{33})[Y(Q4Q)_2]$ has been reported and its natural fluorescence investigated [234]. Its fluorescence quenching by nucleic acids has also been reported [235]. It is considered that this complex can form a large complex with nucleic acid through the electrostatic attraction in the pH range of 4.2–6.8 [235]. Under optimal conditions, the difference of fluorescence intensity between the system without and with nucleic acids is proportional to the concentration of nucleic acids, and the method is applied for the detection of nucleic acids in actual sample [235]. The ionic species $(Me_3NC_{16}H_{33})[Tb(Q4Q)_2]$ (Fig. 115) shows a strong fluorescence intensity [236]. In this system some rare earth ions, such as Lu^{3+}, Y^{3+}, Gd^{3+} and Tb^{3+}, exert an evident fluorescence enhancement effect, and this co-luminescence effect can be used to detect trace amounts of Tb^{3+} [236,237]. Other co-luminescence systems are formed from $(Me_3NC_{16}H_{33})[Dy(Q4Q)_2]$ and trace amounts of Gd^{3+}, Y^{3+} and La^{3+}, than exert a fluorescence enhancement effect [238]. A rapid, simple and sensitive method has been developed for the determination of trace amounts of Dy^{3+} [238]. The fluorescence behaviour of the ionic compound $(Me_3NC_{16}H_{33})[Tm(Q4Q)_2]$ and the factors affecting the fluorescence were investigated [239]. The ionic compound ((*E*)–Et_2N–Ph–CH=CH–py–$C_{16}H_{33}$)$[Nd(Q4Q)_2]$ has been used as a deposited LB film to construct an organic light-emitting diodes (LED) [240]. Two terbium complexes $(Me_2N(C_{18}H_{37})_2)[Tb(Q4Q)_2]$ and $[Tb(Q^{Pd})_3(EtOH)]$ show strong fluorescence properties [241].

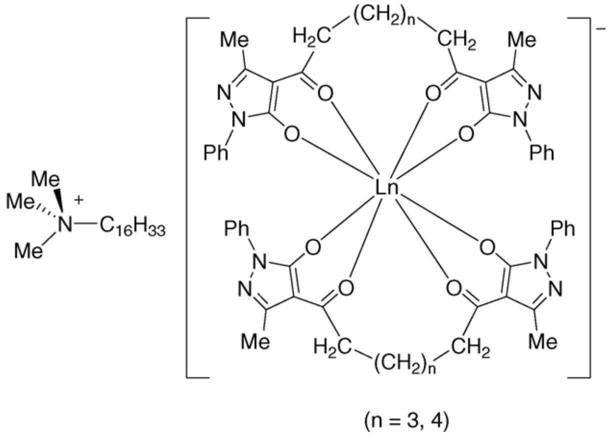
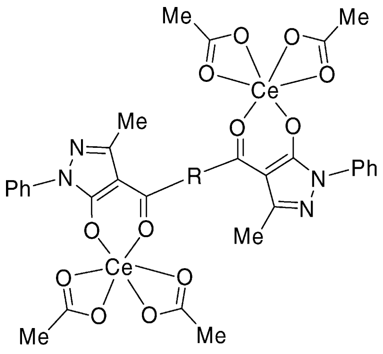


Fig. 115. Typical structure of the derivatives $(Me_3NC_{16}H_{33})[Ln(QnQ)_2]$ (where *n* = 3, 4).

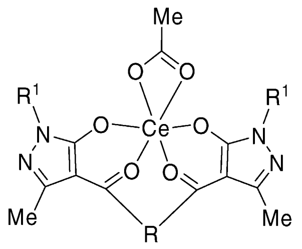
The cerium complexes $[(AcO)_2Ce(Q(n,m)PhQ)Ce(OAc)_2]$ (Fig. 116), $[Ce(OAc)(Q(n,m)PhQ)]$ and $[Ce_2(Q(n,m)PhQ)_3]$ (*n*,*m* = 1,2 or 1,3 or 1,4) were synthesized and their catalytic activity tested in the oxidation of 2,6-dialkoxy-4-methylphenols to 4-hydroxy-3,5-dialkoxybenzaldehydes with O_2 [42]. $[Ce(OAc)(Q(n,m)PhQ)]$ (1:1), containing the benzenedicarbonyl *ortho*-isomer, giving an 84% yield of 4-hydroxy-3,5-dimethoxybenzaldehyde, is the best catalyst among the positional isomers in anhydrous methanol [42].

The catalytic use of the complex $[Ce(OAc)(QRQ)]$ ($R = CH_2CH_2$, 1,2-C_6H_4) (Fig. 117) has been also reported. High yields of 3,5-dimethoxy-4-hydroxybenzaldehyde in the oxidation of 3,5-dimethoxy-*p*-cresol with molecular oxygen



(R = 1,2-C_6H_4, 1,3-C_6H_4, 1,4-C_6H_4)

Fig. 116. Structure of the derivatives $[(AcO)_2Ce(QRQ)Ce(OAc)_2]$.



(R^1 = H, Me, Ph; R = CH_2CH_2, 1,2-C_6H_4)

Fig. 117. Structure of the derivatives [Ce(OAc)(QRQ)].

in 25% methanolic aqueous solution [242] have been observed. The desired compound was obtained up to a 94% yield by increasing the concentration of the substrate or using a 1-propanol aqueous solution [242].

The O_6-hexadentate donor ligand H_3Q_3Ph reacts with $La(acac)_3$ in dmso affording an high-symmetry, three-dimensional metal–ligand cluster $[La_8(Q_3Ph)_8]$ [46]. The X-ray crystal study of the complex shows a unique square antiprismatic, 3-dimensional ring structure (Fig. 118) [46]. Each La atom is coordinated by three Q_3Ph ligands and each ligand coordinates to three La atoms. In this cluster nine-coordinate La atoms are linked by six-coordinate chelate ligands. The residual coordination sites of the La atoms are occupied by solvent molecules [46].

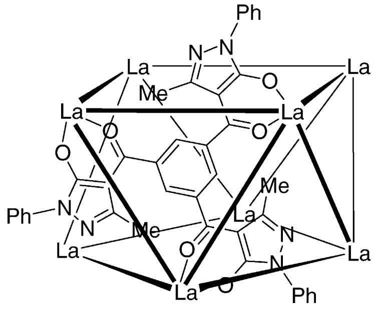
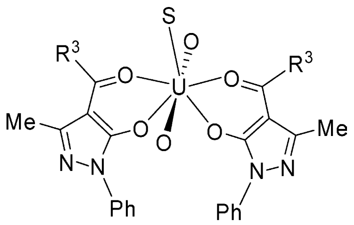


Fig. 118. Lanthanum backbone where it is showed one of the eight bridging Q_3Ph ligands in the structure of the derivative $[La_8(Q_3Ph)_8]$.



R^3 = Me, Ph
S = H_2O, PrOH

Fig. 119. Structure of the derivatives $[UO_2(S)(Q)_2]$ (where S = solvent).

6.15. Actinides

The crystal structure of $[UO_2(dmso)(Q^{Ph})_2]$ is composed of discrete molecules, containing a linear uranyl ion equatorially coordinated by two O_2-bidentate Q ligands and an O-bonded dmso molecule [243]. The U–O bond lengths for the O atoms on the pyrazolone rings are significantly shorter than those for the acyl O atoms [243]. Derivatives $[UO_2(solvent)(Q)_2]$ (Q = Q^{Me}, Q^{Ph}; solvent = H_2O, PrOH) were synthesised and characterized [72]. The X-ray crystal structures of $[UO_2(PrOH)(Q^{Ph})_2]$ and $[UO_2(H_2O)(Q^{Me})_2]$ were reported (Fig. 119) [72]. In each case, the coordination at U is pentagonal bipyramidal with short U–O bonds at axial positions. Four of the equatorial positions are occupied by O atoms from the Q ligands and the fifth by an O atom from the solvent [72].

The derivative $[Th(NO_3)_2(Q^{Ph})_2(tppo)_2]$ has been synthesized and its crystal structure is composed of discrete molecules containing a Th atom coordinated to 10 O atoms from two O_2-bidentate Q ligands, two bidentate NO_3 and two Ph_3PO ligands (Fig. 120) [244].

Stable $[M(Q)_4]$ [M = Pu, U, Th; Q^{Ph}, Q^{Me}, Q^{Et}, Q^{Pr}, Q^{Bu}, Q^{CF_3}, Q^{iPr}, Q^{iBu}, Q^{Bn}, Q^{Hp}, Q^{Pd}) were prepared and characterized (Fig. 121) [82,174,245,246]. The ^1H NMR spectra indicate they exist as a mixture of stereoisomers in solution and also reveal the presence of contact shift interactions for paramagnetic U chelates [82,174,245,246].

IR spectral data showed a stereochemical difference of the C=O–Th bonding systems present in some of the complexes [246]. The structures of some of the Th(IV) complexes such as that of the Q^{Et} were square antiprisms and others such as that of the Q^{Me} were bicapped trigonal antiprisms [246]. The complexes $[Th(HQ^{Ph})_2(AA)_2]$, $[Th(HQ^{Ph})_2(A)_4]$,

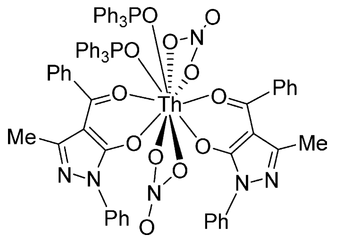


Fig. 120. Structure of the derivative $[Th(NO_3)_2(Q^{Ph})_2(tppo)_2]$.

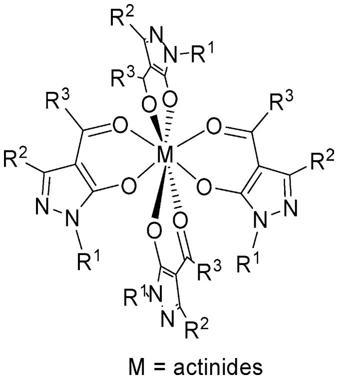


Fig. 121. Structure of the derivatives $[M(Q)_4]$ (where M = Pu, U, Th).

$[UO_2(HQ^{Ph})_2(AA)]$ and $[UO_2(HQ^{Ph})_2(A)_2]$ ($AA = SO_4{}^{2-}$, $S_2O_3{}^{2-}$, $C_2O_4{}^{2-}$, malonate; $A = NO_3{}^{-}$, SCN^{-}, OAc^{-}, $EtCOO^{-}$), containing HQ^{Ph} acting as neutral O_2-bidentate chelating donors, have been synthesized and analytically and spectroscopically characterized [247].

The uranyl derivative $[UO_2(Q8Q)(H_2O)]$ has been reported and characterized by analytical and spectral techniques, showing it a monomeric species [86,103].

7. Concluding remarks

The acylpyrazolones ligands have offered us a powerful tool in the extraction-separation methods and in the spectroscopic determination of a great number of metal ions, due to their superior chelating ability with respect to classical β-diketones. Further, the presence of the pyrazole stabilizes the metal derivatives by creating an extensive π-conjugate system, when the heterocyclic ring is directly bonded to an aromatic substituent. Particularly in the coordination chemistry of lanthanides many efforts have been made to design Q ligands with well suited substituents in order to control the electronic information flow from the ligand to the metal ion and to modulate the optical properties of the metal derivatives. In tin and titanium chemistry many contributions have been directed in designing Q ligands with different steric requirements, useful in tuning the structural features of the metal complexes and hence, also, their biological applications. Attempts in alkaline earth metals, copper, silver and rhodium chemistry have given interesting results. The asymmetrical chelating moiety of the acylpyrazolones, due to the different donating ability of the two CO(chain) and CO(pyrazole) arms, could play a key role in the catalytic properties of new organometal acylpyrazolonates, a vast area of coordination chemistry that is waiting to be further explored and developed, particularly in the case of group VIIIB metals, which are known to be potential catalysts in a variety of applications. Also, Q-donors with additional functionalities, for example, with other donor atoms in R^1, R^2 or R^3 positions, could afford interesting results in the synthesis of heteropolymetallic derivatives with new optical and electronic properties, as useful starting compounds in the field of material chemistry.

Acknowledgements

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