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A new family of ionic dinuclear strontium $(imH_2)_2[Sr_2(Q)_6]$ compounds (imH = imidazole; QH = 1-phenyl-3-methyl-4-acylpyrazol-5-one)

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New neutral $[Sr(Q)_2(L)_n]_m$ or ionic $(imH_2)_2[Sr_2(Q)_6]$ air stable complexes (QH = 1-phenyl-3-methyl-4-R(C=O)-pyrazol-5-one; in detail $Q = Q_T$ for $R = CH_2CMe_3$, $Q = Q_P$ for R = Ph and $Q = Q_F$ for $R = CF_3$; $n = m = 1$ for L = tetraglyme (2,5,8,11,14-pentaoxapentadecane); $n = m = 2$ for $L = H_2O$; $n = 2$ and $m = 1$ for moeH (2-methoxyethanol), dmaeH (*N,N*-dimethylaminoethanol) or phen (1,10-phenanthroline); imH = imidazole) have been synthesized and fully characterized. The X-ray crystal structures of $[Sr(Q_T)_2(moeH)_2]_2$ and of $(imH_2)_2[Sr_2(Q_T)_6]$ have been determined. The compound $[Sr(Q_T)_2(moeH)_2]_2$ contains an eight-co-ordinate Sr atom in a square antiprismatic environment, due two bidentate chelating Q donors and two bidentate 2-methoxyethanol ligands. The compound $(imH_2)_2[Sr_2(Q_T)_6]$ is composed of two imidazolium cations and a dianionic fragment $[Sr_2(Q_T)_6]^{2-}$, which is a centrosymmetric dimer containing four terminal and two bridging Q donor ligands.

Introduction

The co-ordination chemistry of alkaline-earth metals with β-diketonates has recently received increased attention due to their volatility at reduced pressure, a property which makes some derivatives suitable for application in CVD processes in the manufacture of thin films of oxide superconducting materials.[1,2] It has been shown that volatility depends on the nuclearity of compounds, which can be controlled by using additional ancillary donors as aromatic bidentate amines or polyethers.[2] In fact they are able to saturate the metal environment avoiding co-ordination of water or other solvent molecules, which are generally responsible for the formation of oligomeric or even polymeric low volatile species.[2–4]

In recent years new techniques, such as aerosol-assisted (AA) CVD,[5] spray pyrolysis,[6] spray MOCVD,[7] supercritical fluid transport (SFT) CVD[8] and atomic layer deposition (ALD)[9] are becoming attractive. In fact they overcome delivery problems caused by poor volatility and the attention is now directed on tailoring molecular precursors suitable for these new delivery methods.

Recently we started an investigation of the chemistry of alkaline-earth derivatives with a class of heterocyclic β-diketones named 4-acyl-5-pyrazolones (QH, Fig. 1).

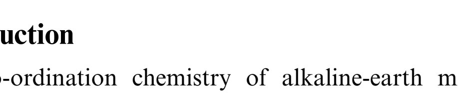

Fig. 1 Proligands QH used in this work.

This family of ligands, widely used as extractants for metal traces[10] and for dyes,[11] is markedly different with respect to the classical β-diketonates. They are low-cost molecules easily functionalizable in N1 or C3 or C4 of the pyrazole ring. Some of these molecules show good solubility not only in several organic solvents, but also in alcohols and water,[12] a very important property in view of the possible industrial and biological applications of their metal derivatives. Furthermore the 4-acylpyrazolone ligands possess an additional donor center, the pyridinic N atom, often involved in secondary bonding interactions which influence the structure of the metal derivatives.[13] We have recently reported the synthesis and full characterization of new main group and transition metal acylpyrazolonate derivatives and showed how it is possible to vary the structure in the solid state by careful choice of substituents in Q donors.[14] For example, Cu(I) and Cu(II) acylpyrazolonates have been shown to increase their volatility by using arylphosphines or aromatic diamines, respectively.[15] We have also synthesized and characterized several calcium and barium acylpyrazolonates in which nuclearity can be controlled by a combination of Q ligands and ancillary mono-, bi-, tri-, tetra- or pentadentate O- or N-donors.[16]

Now we extend our studies to the interaction of this family of β-diketones toward strontium. Here we report the synthesis and characterization of novel Sr(II) derivatives with three different acylpyrazolonates, having a neopentyl, a phenyl or a CF_3 group in the acyl fragment (Fig. 1), together with the crystal X-ray studies for two of these compounds, undertaken to provide structural information for different combinations of Q with Sr(II) and mono-, bi- and polydentate L ligands ($L = H_2O$, phenanthroline (phen), 2-methoxyethanol (moeH), *N,N*-dimethylaminoethanol (dmaeH) or 2,5,8,11,14-pentaoxapentadecane (tetraglyme). In particular, a new type of 2 : 1 ionic complex, which contains a dinuclear dinegative $Sr_2(Q)_6^{2-}$ anion has been obtained and fully characterized.

Experimental

General remarks

All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. Solvent evaporations were always carried

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out under vacuum using a rotary evaporator. The samples for microanalysis were dried *in vacuo* to constant weight (20 °C, *ca.* 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium; dichloromethane was distilled from calcium hydride. All solvents were degassed with dry nitrogen prior to use. Elemental analyses (C,H,N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a VXR-300 Varian instrument and on a Bruker AC 200 spectrometers operating at room temperature (respectively at 300 and 200 MHz for ^{1}H and 75, 50 MHz for ^{13}C, 282.2 MHz for ^{19}F). H and C chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ whereas F chemical shifts in ppm from $CFCl_3$ (^{1}H, ^{19}F and ^{13}C calibration by internal deuterium solvent lock). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_m, reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane or acetone solutions of complexes were taken with a Crison CDTM 522 conductimeter at room temperature. Molecular weight determinations (M.W.) were performed at 40 °C with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil. The solvent was Baker Analysed Spectrophotometric grade chloroform or acetone. The results were reproducible to ±2%. The donors Q_TH, Q_PH and Q_FH were synthesized with the procedure previously reported and purified by several recrystallizations from methanol.[15,16]

Synthesis of the complexes

$[Sr_2(Q_T)_4(H_2O)_4]$ (1). Compound **1** has been obtained by interaction of strontium metal (powder, 1 mmol) with the proligand Q^TH (2 mmol) in 30 ml of absolute ethanol. The solution obtained after the evolution of hydrogen was stirred for 1 hour, filtered to remove any unreacted metal residue, and then concentrated on a rotary evaporator. After the addition of diethyl ether (20 ml) a colourless precipitate afforded, which was filtered off, washed with diethyl ether and dried *in vacuo*. It is soluble in dmso, acetone and alcohols and slightly soluble in chlorinated solvents. Recrystallized from chloroform. Yield 93%, mp 310 °C dec. Calc. for $C_{64}H_{84}N_8O_{12}Sr_2$: C, 58.03; H, 5.78; N, 8.46. Found: C, 57.61; H, 6.64; N, 8.30%. F.W. 1333, M.W. (acetone): 1290 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (acetone, 298 K) 2.6 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 3000–3300vs (br) $\nu(H_2O)$, 1620vs (br) ν(C=O), 374m, 344s, 322m ν(Sr–O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.19 (s) (18H, $\mathrm{CH_2C(C}H_3)_3$), 2.49 (s) (6H, 3-CH_3), 2.65 (s) (4H, $\mathrm{C}H_2\mathrm{C(CH_3)_3}$), 3.13 (s br) (4H, H_2O), 7.12 (t), 7.38 (t), 8.32 (d) (10H, $H_{aromatic}$ of Q_T). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ, 19.4 (s, C3-$C\mathrm{H_3}$), 31.4 (s, $\mathrm{CH_2C(}C\mathrm{H_3)_3}$), 32.4 (s, $\mathrm{CH_2}C\mathrm{(CH_3)_3}$), 51.7 (s, $C\mathrm{H_2C(CH_3)_3}$), 107.7 (s, *C*4), 119.9, 123.8, 129.3, 142.1 (s, $C_{aromatic}$ of Q_T), 148.1 (s, *C*3), 166.9 (s, *C*5), 194.0 (s, *C*O).

$[Sr_2(Q^P)_4(H_2O)_4]$ (2). Compound **2** has been synthesized similarly to **1**. It is soluble in acetone, dmso and alcohols and slightly soluble in chlorinated solvents. Yield 82%, mp 225–227 °C. Calc. for $C_{68}H_{60}N_8O_{12}Sr_2$: C, 60.21; H, 4.46; N, 8.26. Found: C, 60.45; H, 4.48; N, 8.33%. F.W. 1356, M.W. (acetone): 1302 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (acetone, 298 K) 3.7 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 3000–3300vs (br) $\nu(H_2O)$, 1627vs (br) ν(C=O), 336m (br) ν(Sr–O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.62 (s) (6H, 3-CH_3), 3.10 (s br) (4H, H_2O), 6.99 (t), 7.23 (t), 7.41 (m), 8.19 (d) (20H, $H_{aromatic}$ of Q_P). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ, 17.1 (s, C3-$C\mathrm{H_3}$), 106.0 (s, *C*4), 119.6, 123.6, 128.5, 128.9, 130.2, 141.4, 143.6 (s, $C_{aromatic}$ of Q_P), 148.5 (s, *C*3), 166.7 (s, *C*5), 190.3 (s, *C*O).

$[Sr_2(Q_F)_4(H_2O)_4]$ (3). Compound **3** has been synthesized similarly to **1**. It is soluble in water, dmso, acetone, diethyl ether, alcohols and chlorinated solvents. Yield 89%, mp 300 °C dec. Calc. for $C_{48}H_{40}F_{12}N_8O_{12}Sr_2$: C, 43.54; H, 3.04; N, 8.46. Found: C, 43.25; H, 2.90; N, 8.27%. F.W. 1324, M.W. (acetone): 1245 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (acetone, 298 K) 6.5 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 3600s, 3000–3400vs br $\nu(H_2O)$, 1661vs br ν(C=O), 433m, 383m, 356vs, 297m ν(Sr–O). ^{1}H NMR ($CDCl_3$, 298 K): δ 1.93 (s, 6H, 3-CH_3); 2.23 (s, 4H, H_2O); 6.90–7.20, 7.45–7.60 (m, 10H, $H_{aromatic}$ of Q_F). ^{1}H NMR (acetone-d_6, 298 K): δ, 2.19 (q) (6H, $^6J(^1H–^{19}F)$: 2.2 Hz, 3-CH_3), 2.40 (q) (6H, $^6J(^1H–^{19}F)$: 2.2 Hz, 3-CH_3), 3.11 (br) (4H, H_2O), 7.14 (t), 7.21 (t), 7.37 (t), 7.43 (t), 8.23 (d), 8.26 (d) (10H, $H_{aromatic}$ of Q_F). ^{19}F{^{1}H} NMR (acetone-d_6, 298 K): δ, −72.4[20] (s) −76.3[1] (s).† ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ, 16.7 (q, $^5J(^{13}C–^{19}F)$: 5.3 Hz, C3-$C\mathrm{H_3}$), 101.8 (s, *C*4), 119.2 (q, $^1J(^{13}C–^{19}F)$: 286.0 Hz, $C\mathrm{F_3}$), 119.6, 124.3, 129.1, 140.8 (s, $C_{aromatic}$ of Q_F), 146.6 (s, *C*3), 168.1 (s, *C*5), 170.5 (q, $^2J(^{13}C–^{19}F)$: 34.1 Hz, $C\mathrm{OCF_3}$).

$[Sr(Q_T)_2(tetraglyme)]$ (4). Strontium metal (powder, 1 mmol) was added to a stirred solution of the proligand Q_TH (2 mmol) and of tetraglyme (1 mmol) in absolute ethanol (20 ml). The solution was stirred for 1 hour, filtered to remove any unreacted metal residue, and then the solvent was concentrated on a rotary evaporator. After the addition of benzene (20 ml) a colourless precipitate was formed, which was filtered off, recrystallized from ethanol–benzene, and dried *in vacuo*. It is soluble in acetone, dmso, diethyl ether, benzene, alcohols and chlorinated solvents. Yield 91%, mp 150–153 °C. Calc. for $C_{42}H_{60}N_4O_9Sr$: C, 59.13; H, 7.09; N, 6.57; Found: C, 58.43; H, 7.23; N, 6.57%. F.W. 853, M.W. ($CHCl_3$): 838 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.7 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 1636vs (br) ν(C=O), 343s, 319m ν(Sr–O). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.07 (s) (18H, $\mathrm{CH_2C(C}H_3)_3$), 2.46 (s) (6H, 3-CH_3), 2.51 (s) (4H, $\mathrm{C}H_2\mathrm{C(CH_3)_3}$), 3.19 (s), 3.38 (m), 3.55 (m), 3.76 (m) (22H, $H_{tetraglyme}$), 7.02 (t), 7.24 (t), 8.16 (d), (10H, $H_{aromatic}$ of Q_T). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ, 18.9 (s, C3-$C\mathrm{H_3}$), 30.4 (s, $\mathrm{CH_2C(}C\mathrm{H_3)_3}$), 31.7 (s, $\mathrm{CH_2}C\mathrm{(CH_3)_3}$), 51.1 (s, $C\mathrm{H_2C(CH_3)_3}$), 59.4 (s, OCH_3 of *tetraglyme*), 69.6, 69.9, 70.1, 71.0, (s, OCH_2-CH_2O of *tetraglyme*), 106.7 (s, *C*4), 119.4, 123.0, 128.2, 140.4 (s, $C_{aromatic}$ of Q_T), 147.8 (s, *C*3), 165.2 (s, *C*5), 192.9 (s, *C*O).

$[Sr(Q_P)_2(tetraglyme)]$ (5). Compound **5** has been synthesized similarly to **4**. It is soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 87%, mp 106–109 °C. Calc. for $C_{44}H_{48}N_4O_9Sr$: C, 61.13; H, 5.60; N, 6.48. Found: C, 60.67; H, 5.78; N, 6.15%. F.W. 864, M.W. ($CHCl_3$): 848 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.5 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 1633vs (br) ν(C=O), 338s, 325sh ν(Sr–O). ^{1}H NMR ($CDCl_3$, 298 K): δ 1.73 (s) (6H, 3-CH_3), 3.25 (s), 3.40 (m), 3.52 (m), 3.73 (m) (22H, $H_{tetraglyme}$), 7.03 (t), 7.26 (t), 7.38 (m), 7.48 (m), 8.16 (d) (20H, $H_{aromatic}$ of Q_P). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ, 16.9 (s, C3-$C\mathrm{H_3}$), 59.5 (s, OCH_3 of *tetraglyme*), 69.3, 70.1, 70.4, 71.0 (s, OCH_2CH_2O of *tetraglyme*), 105.3(s, *C*4), 119.5, 123.2, 127.7, 127.8, 128.2, 128.6, 129.5, 140.2, 142.9 (s, $C_{aromatic}$ of Q_P), 148.8 (s, *C*3), 165.7 (s, *C*5), 189.8 (s, *C*O).

$[Sr(Q_F)_2(tetraglyme)]$ (6). Compound **6** has been synthesized similarly to **4**. It is soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 65%, mp 175–176 °C. Calc. for $C_{34}H_{38}F_6N_4O_9Sr$: C, 48.14; H, 4.52; N, 6.60. Found: C, 48.45; H, 4.42; N, 6.71%. F.W. 848, M.W. ($CHCl_3$): 851 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.2 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): δ 1661vs (br) ν(C=O), 386m, 357vs ν(Sr–O). ^{1}H NMR ($CDCl_3$, 298 K): δ, 2.37 (q) (6 H, $^6J(^1H–^{19}F)$: 2.1 Hz, 3-CH_3), 3.25 (s), 3.40 (m), 3.52 (m), 3.73 (m), 3.82 (m) (22H, $H_{tetraglyme}$), 7.08 (t), 7.29 (t), 8.08 (d) (10 H, $H_{aromatic}$ of Q_F). ^{19}F{^{1}H} NMR ($CDCl_3$,

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† Ratio of relative intensities in square brackets.

298 K): *δ*, −71.8 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *δ*, 16.4 (q, $^{5}J(^{13}C–^{19}F)$: 4.9 Hz, C3-*C*H$_3$), 59.4 (s, O*C*H$_3$ of *tetraglyme*), 68.9, 70.1, 70.6, 70.7 (s, O*C*H$_2$*C*H$_2$O of *tetraglyme*), 101.3 (s, *C*4), 118.2 (q,$^{1}J(^{13}C–^{19}F)$: 285.9 Hz, *C*F$_3$), 119.6, 123.9, 128.3, 139.5 (s, $C_{aromatic}$ of Q_F), 147.0 (s, *C*3), 167.1 (s, *C*5), 170.5 (q, $^{2}J(^{13}C–^{19}F)$: 34.6 Hz, *C*OCF$_3$).

$[Sr(Q_T)_2(phen)_2]$ (7). Compound **7** has been synthesized similarly to **4**. It is soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 79%, mp 246–250 °C. Calc. for $C_{56}H_{54}N_8O_4Sr$: C, 66.68; H, 5.60; N, 11.11. Found: C, 66.79; H, 5.59; N, 11.37%. F.W. 991, M.W. ($CHCl_3$): 970 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.6 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): *δ* 1633vs (br) *ν*(C=O), 369m, 341m, 320s*ν*(Sr–O), 252m, 237m *ν*(Sr–N). ^{1}H NMR ($CDCl_3$, 298 K): *δ*, 0.61 (s) (18H, CH$_2$C(C*H*$_3$)$_3$), 2.16 (s) (4H, C*H*$_2$C(CH$_3$)$_3$), 2.21 (s) (6H, 3-C*H*$_3$), 6.98 (t), 7.15 (t), 7.89 (d), (10H, $H_{aromatic}$ of Q_T), 7.41 (dd), 7.64 (s), 8.11 (dd), 9.20 (dd) (16H, H_{phen}). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *δ*, 18.6 (s, C3-*C*H$_3$), 29.8 (s, CH$_2$C(*C*H$_3$)$_3$), 31.1 (s, CH$_2$*C*(CH$_3$)$_3$), 50.7 (s, *C*H$_2$C(CH$_3$)$_3$), 106.7 (s, *C*4), 119.9, 123.2, 128.0, 140.2 (s, $C_{aromatic}$ of Q_T), 123.0, 126.3, 128.6, 136.5, 145.7, 150.7 (s, C_{phen}), 147.7 (s, *C*3), 165.2 (s, *C*5), 193.4 (s,*C*O).

$[Sr(Q_P)_2(phen)_2]$ (8). Compound **8** has been synthesized similarly to **4**. It is soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 75%, mp 258–261 °C. Calc. for $C_{58}H_{32}N_8O_4Sr$: C, 69.48; H, 4.22; N, 11.18. Found: C, 69.34; H, 4.39; N, 11.32%. F.W. 993, M.W. ($CHCl_3$): 976 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.7 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): *δ* 1623vs (br) *ν*(C=O), 336m, 322s *ν*(Sr–O), 259m, 248m *ν*(Sr–N). ^{1}H NMR ($CDCl_3$, 298 K): *δ*, 1.50 (s) (6H, 3-C*H*$_3$), 6.96 (t), 7.14 (t), 7.25 (m) 7.87 (d), (10H, $H_{aromatic}$ of Q_P), 7.36 (dd), 7.53 (s), 8.03 (dd), 9.20 (dd) (16H, H_{phen}). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *δ*, 16.3 (s, C3-*C*H$_3$), 105.3 (s, *C*4), 119.4, 123.1, 126.2, 127.3, 127.5, 127.8, 128.3, 129.3, 139.6, 142.2 (s, $C_{aromatic}$ of Q_P), 122.9, 126.1, 129.1, 136.2, 145.4, 150.3 (s, C_{phen}), 148.4 (s, *C*3), 165.2 (s, *C*5), 189.8 (s,*C*O).

$[Sr(Q_F)_2(phen)_2]$ (9). Compound **9** has been synthesized similarly to **4**. It is soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 88%, mp 248–250 °C. Calc. for $C_{48}H_{32}F_6N_8O_4Sr$: C, 58.45; H, 3.27; N, 11.36. Found: C, 58.66; H, 3.34; N, 11.10%. F.W. 986, M.W. ($CHCl_3$): 968 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.9 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): *δ* 1659vs (br) *ν*(C=O), 384m, 351s *ν*(Sr–O), 255m, 239m *ν*(Sr–N). ^{1}H NMR ($CDCl_3$, 298 K): *δ*, 2.14 (q) (6 H, $^{6}J(^{1}H–^{19}F)$: 2.4 Hz, 3-C*H*$_3$), 6.98 (t), 7.15 (t), 7.68 (d) (10 H, $H_{aromatic}$ of Q_F), 7.48 (dd), 7.61 (s), 8.12 (dd), 9.19 (dd) (16H, H_{phen}). ^{19}F{^{1}H} NMR ($CDCl_3$, 298 K): *δ*, −72.0 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *δ*, 16.1 (q, $^{5}J(^{13}C–^{19}F)$: 4.8 Hz, C3-*C*H$_3$), 101.5 (s, *C*4), 118.1 (q, $^{1}J(^{13}C–^{19}F)$: 286.4 Hz, *C*F$_3$), 119.5, 123.4, 128.1, 139.2 (s, $C_{aromatic}$ of Q_F), 123.6, 126.5, 128.8, 136.9, 145.4, 150.4 (s, C_{phen}), 146.8 (s, *C*3), 166.9 (s, *C*5), *C*OCF$_3$ not observed.

$(imH_2)_2[Sr_2(Q_T)_6]$ (10). Strontium metal (powder, 2 mmol) was added to a stirred solution of the proligand Q^TH (6 mmol) and of imH (2 mmol) in absolute ethanol (20 ml). The solution was stirred for 4 hours, filtered to remove any unreacted metal residue, and then the solvent was concentrated on a rotary evaporator. After the addition of MeCN (20 ml) a colourless precipitate was formed, which was filtered off, recrystallized from ethanol–benzene, and dried *in vacuo*. Compound **10** is soluble in acetone, dmso and alcohols. Yield 84%, mp 232–233 °C. Calc. for $C_{102}H_{124}N_{16}O_{12}Sr_2$: C, 63.10; H, 6.44; N, 11.54; Found: C, 62.86; H, 6.53; N, 11.58%. F.W. 1941, M.W. (acetone): 1818 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (acetone, 298 K) 9.4 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3136w, 3101w *ν*(N–H), 1615vs (br) *ν*(C=O), 399s, 381m, 372m, 337m, 321m *ν*(Sr–O). ^{1}H NMR (acetone-d$_6$, 298 K): *δ*, 1.07 (s) (27H, CH$_2$C(C*H*$_3$)$_3$), 2.39 (s) (9H, 3-C*H*$_3$), 2.57 (s) (6H, C*H*$_2$C(CH$_3$)$_3$), 7.06 (t), 7.29 (t), 8.11 (d) (15H, $H_{aromatic}$ of Q_T), 3.90 (br), 7.12 (s), 7.88 (s) (5H, *H* of imH$_2$). ^{1}H NMR (acetone-d$_6$, 193 K): *δ*, 0.97 (s, br) (27H, CH$_2$C(C*H*$_3$)$_3$), 2.27 (s, br) (9H, 3-C*H*$_3$), 2.40 (s, br) (6H, C*H*$_2$C(CH$_3$)$_3$), 6.97 (s, br), 7.15 (s, br), 8.04 (s, br) (15H, $H_{aromatic}$ of Q_T), 4.00 (br), 8.12 (s, br), 8.38 (s, br) (5H, *H* of imH$_2$). ^{13}C{^{1}H} NMR (acetone-d$_6$, 298 K): *δ*, 18.3 (s, C3-*C*H$_3$), 30.5 (s, CH$_2$C(*C*H$_3$)$_3$), 32.1 (s, CH$_2$*C*(CH$_3$)$_3$), 51.9 (s, *C*H$_2$C(CH$_3$)$_3$), 106.8 (s, *C*4), 119.9, 124.2, 129.0, 140.4 (s, $C_{aromatic}$ of Q_T), 122.1, 135.9 (s, *C* of imH$_2$), 147.9 (s, *C*3), 165.8 (s, *C*5), 194.0 (s,*CO*).

$(imH_2)_2[Sr_2(Q_P)_6]$ (11). Compound **11** has been synthesized similarly to **10**. Compound **11** is soluble in acetone, dmso and alcohols. Yield 90%, mp 135–138 °C. Calc. for $C_{108}H_{88}N_{16}O_{12}Sr_2$: C, 65.61; H, 4.49; N, 11.33; Found: C, 65.26; H, 4.50; N, 11.68%. F.W. 1977, M.W. (acetone): 1832 (c = 10^{-2} m). Λ_M (acetone, 298 K) 13.6 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3140w, 3103w *ν*(N–H), 1620vs (br) *ν*(C=O), 402m, 371m, 338s *ν*(Sr–O). ^{1}H NMR (acetone-d$_6$, 298 K): *δ*, 1.75 (s) (9H, 3-C*H*$_3$), 7.12 (t), 7.35 (t), 7.52 (m), 8.31 (d) (30H, $H_{aromatic}$ of Q_P), 4.30 (br), 7.22 (s, br), 8.15 (s, br) (5H, *H* of imH$_2$). ^{13}C{^{1}H} NMR (acetone-d$_6$, 298 K): *δ*, 17.1 (s, C3-*C*H$_3$), 105.9 (s, *C*4), 120.0, 123.8, 128.3, 128.6, 128.9, 130.0, 141.3, 143.7 (s, $C_{aromatic}$ of Q_P), 123.4, 134.9 (s, *C* of imH$_2$), 148.8 (s, *C*3), 166.6 (s, *C*5), 190.3 (s, *C*O).

$(imH_2)_2[Sr_2(Q_F)_6]$ (12). Strontium metal (powder, 2 mmol) was added to a stirred solution of the proligand Q^FH (6 mmol) and of imH (2 mmol) in absolute ethanol (20 ml). The solution was stirred for 4 hours, filtered to remove any unreacted metal residue, and then the solvent was removed on a rotary evaporator. After the addition of n-hexane (20 ml) a colourless precipitate slowly formed at −20 °C, which was filtered off and dried *in vacuo*. Compound **12** is very soluble in acetone, dmso, alcohols, THF, diethyl ether, chlorinated and aromatic solvents, and quite soluble also in hydrocarbons. Yield 83%, mp 205–209 °C. Calc. for $C_{108}H_{88}F_{12}N_{16}O_8Sr_2$: C, 48.58; H, 3.03; N, 11.62; Found: C, 48.22; H, 3.08; N, 11.48%. F.W. 1928, M.W. (acetone): 1762 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (acetone, 298 K) 15.9 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3126w (br) *ν*(N–H), 1649vs (br) *ν*(C=O), 380m, 352s *ν*(Sr–O). ^{1}H NMR (acetone-d$_6$, 298 K): *δ*, 2.26 (q) (9H, $^{6}J(^{1}H–^{19}F)$: 2.2 Hz, 3-C*H*$_3$), 7.04 (t), 7.26 (t), 8.11 (d) (15H, $H_{aromatic}$ of Q_F), 4.20 (br), 7.09 (s), 7.74 (s) (5H, *H* of imH$_2$). ^{1}H NMR (acetone-d$_6$, 193 K): *δ*, 2.26 (br) (9H, 3-C*H*$_3$), 7.04[1] (t), 7.08[10] (t), 7.22[1] (t), 7.27[10] (t), 8.13[10] (d), 8.17[1] (d) (15H, $H_{aromatic}$ of Q_F), 3.60 (br), 7.23 (s), 8.02 (s), (5H, *H* of imH$_2$). ^{19}F{^{1}H} NMR (acetone-d$_6$, 298 K): *δ*, −72.5[10] (s), −76.5[1] (s). ^{19}F{^{1}H} NMR (acetone-d$_6$, 193 K): *δ*, −72.0[10] (s), −75.8[1] (s). ^{13}C{^{1}H} NMR (acetone-d$_6$, 298 K): *δ*, 16.5 (q, $^{5}J(^{13}C–^{19}F)$: 5.5 Hz, C3-*C*H$_3$), 101.5 (s, *C*4), 119.1 (q, $^{1}J(^{13}C–^{19}F)$: 285.9 Hz, *C*F$_3$), 122.4, 136.1 (s, *C* of imH$_2$), 119.5, 124.2, 129.0, 140.7 (s, $C_{aromatic}$ of Q_F), 146.7 (s, *C*3), 168.1 (s, *C*5), *C*OCF$_3$ not observed.

$[Sr(Q_T)_2(moeH)_2]$ (13). Compound **13** has been synthesized similarly to **4**. Soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 74%, mp 142–143 °C. Calc. for $C_{35}H_{46}N_4O_8Sr$: C, 58.33; H, 6.96; N, 7.16. Found: C, 57.96; H, 6.93; N, 7.15%. F.W. 738, M.W. ($CHCl_3$): 728 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.5 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3000–3400br *ν*(O–H), 1627vs (br) *ν*(C=O), 410m, 373m, 346s, 322w *ν*(Sr–O). ^{1}H NMR ($CDCl_3$): *δ*, 0.90 (s) (18H, CH$_2$C(C*H*$_3$)$_3$), 2.34 (s) (6H, 3-C*H*$_3$), 2.36 (s) (4H, C*H*$_2$C(CH$_3$)$_3$), 3.23 (s), 3.29 (t), 3.42 (t) 3.90 (s, br) (16 H, H_{moeH}), 7.02 (t), 7.20 (t), 7.69 (d), (10H, $H_{aromatic}$ of Q_T). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ*, 18.4 (s, C3-*C*H$_3$), 30.2 (s, CH$_2$C(*C*H$_3$)$_3$), 31.7 (s, CH$_2$*C*(CH$_3$)$_3$), 50.8 (s, *C*H$_2$C(CH$_3$)$_3$), 59.1, 60.9, 73.2 (s, C_{moeH}), 106.9 (s, *C*4), 121.2, 124.8, 128.6, 139.1 (s, $C_{aromatic}$ of Q_T), 148.0 (s, *C*3), 164.0 (s, *C*5), 195.0 (s, *C*O).

Table 1 Crystallographic data and some details of data collection and refinement for Sr complexes **10**·(H_2O) and **13**

	$(ImH_2)_2[Sr_2(Q_T)_6]\cdot H_2O$	$Sr(Q_T)_2(moeH)_2$
Molecular formula	$C_{102}H_{126}N_{16}O_{13}Sr_2$	$C_{38}H_{53}N_4O_8Sr$
M	1959.43	781.46
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	14.593(3)	10.412(3)
b/Å	14.646(3)	12.660(3)
c/Å	15.159(3)	17.005(5)
α/°	106.15(3)	69.43(3)
β/°	102.99(3)	80.05(3)
γ/°	114.62(3)	74.83(3)
V/Å^3	2605(1)	2017(1)
Z	1	2
D_{calc}/g cm^{-1}	1.249	1.286
μ/mm^{-1}	1.090	1.389
Crystal size/mm	0.5 × 0.4 × 0.3	0.6 × 0.4 × 0.4
T/K	293	293
Data collection range, θ/deg	2.5–27.0	2.5–27.0
Reflections collected	16129	11488
Independent reflections (R_{int})	10967 (0.082)	8093 (0.075)
Data/parameters in refinement	6502/611	4958/477
wR_2 (on F^2)	0.2189	0.0925
R_1 [$I \geq 2\sigma(I)$]	0.0816	0.0502
Largest diff. peak and hole/e Å $^{-3}$	2.214; −0.865	0.459; −0.628

$[Sr(Q_T)_2(dmaeH)_2]$ (14). Compound **14** has been synthesized similarly to **4**. Soluble in acetone, dmso, benzene, alcohols and chlorinated solvents. Yield 86%, mp 119–121 °C. Calc. for $C_{36}H_{49}N_6O_6Sr$: C, 59.42; H, 7.48; N, 10.39. Found: C, 59.78; H, 7.55; N, 10.15%. F.W. 749, M.W. ($CHCl_3$): 755 ($c = 10^{-2}$ mol kg^{-1}). Λ_M (CH_2Cl_2, 298 K) 0.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3000–3400br ν(O–H), 1627vs (br) ν(C=O), 409m, 373m, 342s, 320m ν(Sr–O), 275m ν(Sr–N). ^{1}H ^{1}H NMR ($CDCl_3$): δ, 0.96 (s) (18H, $CH_2C(CH_3)_3$), 2.41 (s) (6H, 3-CH_3), 2.45 (s) (4H, $CH_2C(CH_3)_3$), 3.42 (t), 3.46 (s br), 3.65 (t) 6.05 (s, br) (22 H, H_{dmaeH}), 7.04 (t), 7.22 (t), 7.81 (d), (10H, $H_{aromatic}$ of Q_T). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ, 18.4 (s, C3-CH_3), 30.2 (s, $CH_2C(CH_3)_3$), 31.6 (s, $CH_2C(CH_3)_3$), 50.9 (s, $CH_2C(CH_3)_3$), 43.3, 56.5, 59.5 (s, C_{dmaeH}), 106.8 (s, C4), 121.2, 124.5, 128.5, 139.3 (s, $C_{aromatic}$ of Q_T), 148.2 (s, C3), 164.2 (s, C5), 194.9 (s, CO).

X-Ray crystallographic studies

The data for complexes **10**·(H_2O) and **13** were collected on an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Numerical absorption correction was not applied. The structures were solved by direct methods (SHELXS-97)[17] and refined anisotropically for all non-hydrogen atoms using SHELXL-93.[18] Hydrogen atoms were included in the calculated positions and refined in a riding mode. The water molecule in structure **10**·(H_2O) was found to have a partial occupancy, which was finally fixed at sof = 0.5. The higher R values for this structure are apparently due to the poor crystal quality caused by partial loss of the water.

Crystallographic data and some details of data collection and structure refinement are found in Table 1. The interatomic distances and some selected angles for the Sr environments are listed in Table 2.

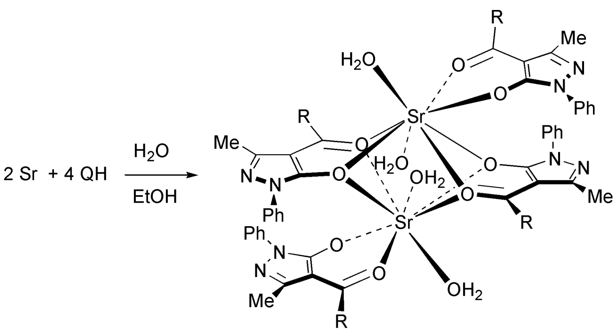
CCDC reference numbers 177244 and 177245.

See http://www.rsc.org/suppdata/dt/b2/b200189f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of the complexes

By interaction of metallic strontium powder with the proligands QH in absolute ethanol the hydrate derivatives **1**–**3** have been synthesized in high yields (Scheme 1).

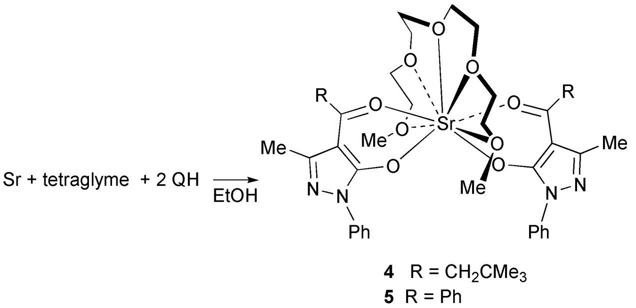


1 R = CH_2CMe_3
2 R = Ph
3 R = CF_3

Scheme 1

Derivatives **1**–**3** are air stable species soluble in acetone, dmso and alcohols but slightly soluble in chlorinated solvents. Molecular weight determinations carried out in acetone indicate a dinuclear nature. The conductivity values are typical of non-ionic compounds in acetone, as previously observed for a similar $Ba_2(Q)_4(H_2O)_4$ derivative.[16b]

By a synthetic procedure similar to that for **1**–**3**, in the presence of ancillary donors tetraglyme or phen, the compounds **4**–**9** have been obtained (Schemes 2 and 3).



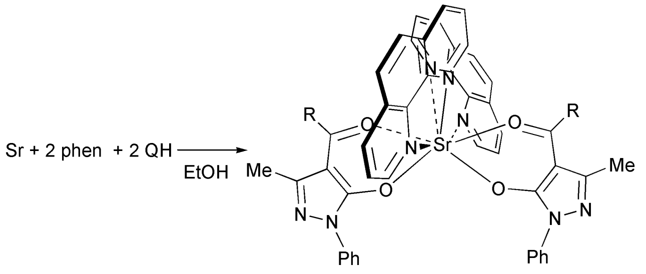
4 R = CH_2CMe_3
5 R = Ph
6 R = CF_3

Scheme 2

Derivatives **4**–**9** are air stable species which are very soluble in most organic solvents, apart from in ethers and hydrocarbons. Molecular weight determinations carried out in chloroform

Table 2 Co-ordination of the Sr atoms (distances in Å and angles in deg) in the crystal structures **10**·(H_2O) and **13**

10·(H_2O)		**13**	
Sr–O(1)	2.681(6)	Sr–O(1)	2.506(3)
Sr–O(1′)	2.645(6)	Sr–O(2)	2.470(4)
Sr–O(2)	2.646(5)	Sr–O(3)	2.489(4)
Sr–O(2′)	2.699(6)	Sr–O(4)	2.499(4)
Sr–O(3)	2.534(6)	Sr–O(5)	2.729(4)
Sr–O(4)	2.514(6)	Sr–O(6)	2.693(4)
Sr–O(5)	2.579(6)	Sr–O(7)	2.651(4)
Sr–O(6)	2.538(5)	Sr–O(8)	2.733(4)
O(1)–Sr–O(2)	65.8(2)	O(1)–Sr–O(2)	70.43(12)
O(3)–Sr–O(4)	68.9(2)	O(3)–Sr–O(4)	70.69(12)
O(5)–Sr–O(6)	68.1(2)	O(5)–Sr–O(6)	60.54(13)
		O(7)–Sr–O(8)	61.81(15)



7 R = CH_2CMe_3
8 R = Ph
9 R = CF_3

Scheme 3

give values typical of mononuclear derivatives. The stoichiometry of derivatives **4**–**9** is strongly dependent on the nature of the neutral ancillary ligand, for example derivatives **4**–**6** contain only one potentially η^5-tetraglyme while **7**–**9** contain two bidentate phen donors, in order to reach the co-ordination number 8 or 9 for Sr. Analogous stoichiometries have been previously found for barium species.[16b]

In contrast, the reaction of metallic Sr powder with QH and imH in EtOH afforded the ionic compounds **10**–**12**, independently by the ratio Sr : QH : imH employed (Scheme 4).

Derivatives **10** and **11** are quite soluble in alcohols, acetone and dmso, whereas derivative **12**, in addition to being very soluble in these solvents, is very soluble in acetonitrile, THF, diethyl ether, chlorinated and aromatic solvents, and slightly soluble even in aliphatic hydrocarbons. The excellent solubility properties of this complex are most likely to be due to the fluorinated side-groups of the Q_F ligands which reduce van der Waals interactions.

Derivatives **10**–**12** exist in the solid state as 2 : 1 ionic dinuclear compounds, as further confirmed by X-ray studies carried out for **10** (see below). The conductivity values indicate the existence of ionic pairs in acetone solution, also in accordance with the molecular weight values determined in same solvent.

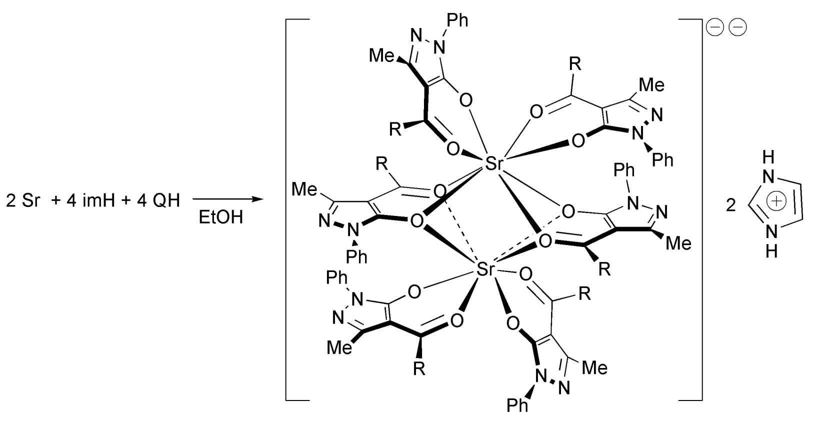
Finally the interaction between metal Sr and Q_TH in the presence of moeH or dmaeH in EtOH yielded compounds **13** and **14** (Scheme 5) which are air stable species very soluble in most organic solvents, such as acetone, dmso, alcohols and chlorinated solvents where they are non-electrolytes and mononuclear.

Spectroscopic characterization

The IR spectra of derivatives **1**–**14** show the typical shift of the band due to ν(C=O) at lower frequencies and the disappearance of the broad absorption between 2300 and 3000 cm^{-1} (OH ··· O of the QH in the keto-enol form) upon co-ordination of the anionic Q^- ligand to metal through both O atoms.[12–16] Additionally, in the case of **1**–**3** and **12**–**14**, broad absorptions over 3000 cm^{-1} confirm that the protic ancillary donors L (L = H_2O, imH_2^+, moeH or dmaeH) are involved in extensive intermolecular H-bonding. Strong bands in the far-IR region (300–500 cm^{-1}) appear upon co-ordination, which have been tentatively assigned to ν(Sr–O) and in the case of **7**–**9** also to ν(Sr–N) stretching modes.[16]

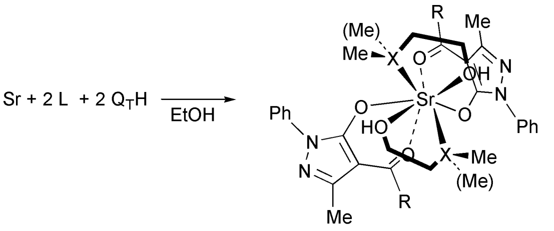
The ^1H, $^{19}F\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded in acetone-d_6 or $CDCl_3$, the choice of the solvent being dictated by the solubility of the derivatives. The number and integration of resonances are in accordance with the formulation proposed on the basis of previous analytical and infrared data. One set of resonances has been generally detected in the room temperature ^1H spectra, even for dinuclear derivatives **1**–**2** and **10**–**12**, thus indicating fluxionality around the co-ordination center in solution. Only in the ^1H NMR of derivative **3** an additional set of resonances for C3-CH_3 and for aromatic N-C_5H_5, of very low intensity, has been observed, in accordance with partial dissociation of Q_F ligands, further confirmed by the ^{19}F NMR spectrum. The resonances due to Q ligands are always displaced toward lower field, with respect to the same signals in the uncomplexed proligand QH, apart from those of C3-CH_3 in Q_P derivatives which experience a through-space ring-current anisotropy effect of the nearby aryl group.[19] The observed lower field shift is additional evidence in favour of the existence of the complexes in solution. In the case of **10**–**12**, we can exclude the occurrence of an equilibrium such as:

$$(imH_2)_2[Sr_2(Q)_6] \rightleftharpoons [Sr_2(Q)_4(imH)_2] + 2QH \qquad (1)$$



10 R = CH_2CMe_3
11 R = Ph
12 R = CF_3

Scheme 4



13 R = CH_2CMe_3, L = moeH, X = O
14 R = CH_2CMe_3, L = dmaeH, X = N

Scheme 5

on the basis of low temperature ^{1}H NMR study. In fact also at 193 K two resonances, typical of imidazolium, have been recognised. Analogous to **3**, the low temperature ^{1}H spectrum of derivative **12** shows an additional set of signals for Q_F, with very low intensity, likely due to partial dissociation of acylpyrazolonate. The $^{19}F\{^1H\}$ spectrum of **12** shows two signals of the CF_3 group, in a 1 : 10 ratio to each other, not only at low but also at room temperature.

The $^{13}C\{^1H\}$ spectra show in all cases only one set of resonances for either Q and ancillary L donors, further confirming fluxionality at room temperature for dinuclear derivatives **1**–**3** and **10**–**12**. The C3-*C*H$_3$, *C*3, *C*5 and *C*O signals of Q donors show a lower field shift upon co-ordination, in accordance with transfer of electron density from the ligand to the metal. In the room temperature $^{13}C\{^1H\}$ spectra of **11** and **12**, *C*4 and *C*5 of imH give one resonance, in accordance with previous observations in their proton spectra. The $^nJ(^{13}C–^{19}F)$ values detected in the spectra of Q_F derivatives are of the same order of magnitude as those found for neutral Q_FH and also tin or zinc or cadmium Q_F derivatives previously reported.[20,21] This seems to indicate that the acyl moiety in the ligand Q_F is not able to discriminate between hard and soft Lewis acids, likely because of its low donating ability due to the presence of the strongly electron-withdrawing CF_3. This further supports the partial dissociation observed for **3** and **12** in acetone, but not for analogous Q_P or Q_T derivatives.

Crystal structure description of $(imH_2)_2[Sr_2(Q_T)_6]$ (10) and $[Sr(Q_T)_2(moeH)_2]$ (13)

The crystal structure of derivative **10** is composed of a cationic part (two imidazolium ions), an anionic one (the anionic dinuclear strontium complex, Fig. 2), and a water molecule (with a partial occupancy).

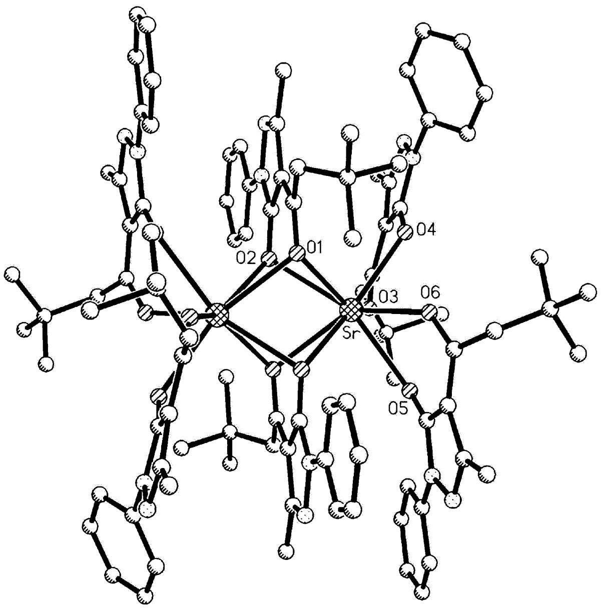
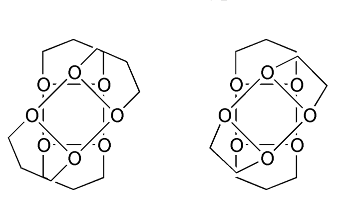


Fig. 2 Structure of the anionic complex part of **10**.

Structurally characterized anionic type compounds like this were not previously known for Sr with β-diketonate like donors, although some structural characterizations of such compounds were reported for Mg and Ba on an anionic derivative, for example, $[naph(NMe_2)_2H][Mg(hfac)_3]$,[22] (tmedaH)-$[Sr(tfac)_4]_2$[2b,23] and $(enH_2)_{1.5}[Ba(hfac)_5]·EtOH$[24] (hfacH = 1,1,1,5,5,5-hexafluoropentane-2,4-dione; tfacH = 1,1,1-trifluoropentane-2,4-dione; $naph(NMe_2)_2H$ = 1,8-bis(dimethylamino)naphthalene; tmeda = tetramethylethylenediamine; en = ethylenediamine).

The anion $[Sr_2(Q_T)_6]^{2-}$ is a centrosymmetric dimer, with four terminal and two bridging Q_T. For Sr β-diketonate derivatives structurally characterized the nuclearity ranges from monomeric to tetrameric, and three dimeric Sr derivatives have been reported up to now, but a different kind of dimerization and bridging mode was found. In **10**, the bridging mode of Q_T with two O_2-μ_4-acylpyrazolonate ligands was not known for Sr, but very well documented for Ba (see for example $Ba_2(thd)_4(bipy)_2$[25]).

The arrangement of oxygen atoms around each Sr is square antiprismatic (Scheme 6), with two types of Sr–O bond distance,



10 **13**

Scheme 6

one terminal Sr–O_t (from O3 to O6) ranging from 2.514 to 2.579 Å (av. 2.541 Å), which are shorter than bridging Sr–O_b (O1 and O2, from 2.645 to 2.699 Å, respectively, with av. 2.663 Å), the difference between av. Sr–O_t and Sr–O_b being ≈0.1 Å. The O–Sr–O bite angle of bridging Q_T is 65.8(2)° whereas those of terminal Q_T are a little bit higher, 68.1(2) and 68.9(2)°. All these values fall in the range typical for O–Sr–O bite angles of strontium β-diketonate.[26]

The imidazolium cation, imH_2^+, has been encountered in some previous crystal structures.[27] Both protonated N atoms of imidazolium cations are weakly hydrogen bonded to the dimeric anion with N7 ··· N4 2.777 and N8 ··· O5 2.683 Å. The distances from the partially occupied oxygen, O7, of the water of solvation to two N atoms, O7 ··· N2 2.946 and O7 ··· N6′ 2.864 Å, indicate the additional weak hydrogen bonds between dimers.

The crystal structure of **13** shows a monomeric derivative where the Sr co-ordination number is 8 (Fig. 3), and

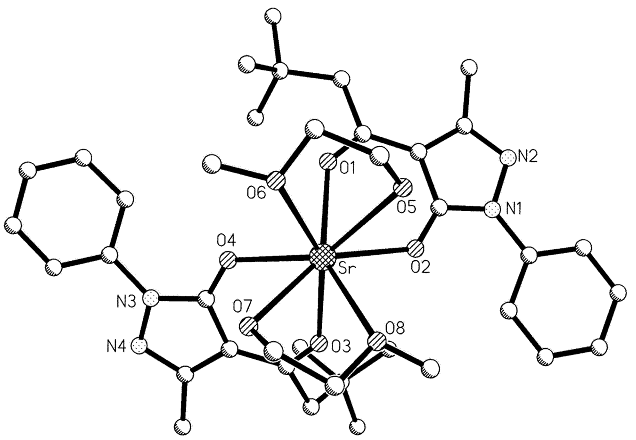


Fig. 3 Structure of a single molecule of **13**.

arrangement around the metal is again square antiprismatic, both Q_T being in one square plane and both L in the second square plane of the antiprism (Scheme 6).

Due to an absence of a chelating effect for the neutral moeH donor, the oxygen atoms are involved in weaker Sr–O bonds, the distances vary from 2.651 to 2.733 Å (av. 2.702 Å); they are longer than those of oxygen atoms of chelating anionic Q_T (2.470–2.506 Å, av 2.493 Å), the difference being about 0.2 Å. However it can be noticed that the av. Sr–O for neutral complex **13** (2.596 Å) is very close to that for anionic **10** (2.602 Å). The O–Sr–O bite angles of Q_T are 70.43(12) and 70.69(12)° whereas those of moeH are much lower, 60.54(13) and 61.81(15)°.

By comparing the structure of **13** with that of two other analogous monomeric diketonate-containing Sr structures, $Sr(hfac)_2(triglyme)$[28,2b] (**a**) and $Sr(thd)_2(triglyme)$[29] (**b**), both with $CN_{Sr} = 8$, we can observe the same trend in Sr–O bond distances, $Sr–O_{dike}$ (av. 2.521 Å in **a** and 2.495 Å in **b**) being shorter that $Sr–O_{glyme}$ (av. 2.651 Å in **a** and 2.674 Å in **b**), but, due to the presence of triglyme with four O atoms connected to each other, diketonate donors are in the *trans*-position to each other and the arrangement is not square antiprismatic as in **13**. Apparently, due to the different co-ordination mode the average Sr–O distances in **a** and **b**, 2.586 and 2.585 Å respectively, are slightly shorter than those in **10** and **13**.

In spite of its co-ordination number 8, this compound is very stable to air and moisture, thus denying the statement of Rees[2b] about the need for a co-ordination number of 9 to have stable Sr derivatives. This great stability could arise from the bulky Q_T donors which, compared to classical dike donors, possess a pyrazole fused to the chelating moiety, likely responsible for the greater delocalization of the charge of the metal ion.

Conclusions

We have synthesized for the first time strontium acylpyrazolonate derivatives containing several different ancillary donors. Direct interaction of metallic (powder) Sr with QH afforded hydrated dinuclear compounds, the solid state structure of which is stabilized by extensive H-bonding involving H atoms of water and N of the pyrazole ring. In the presence of one equivalent of pentadentate tetraglyme or two equivalents of bidentate phen or moeH or dmaeH, air and moisture stable mononuclear derivatives have been obtained.

Preliminary studies of volatility under reduced pressure for derivatives **3** and **6** were performed. They showed that in both cases the complexes decompose at *ca.* 200 °C (0,01 Torr) to strontium fluoride with sublimation of a minor quantity of anhydrous $[Sr(Q_F)_2]$. This precludes their application in classical CVD, but makes it possible to recommend them as precursors for injection CVD methods.

In the presence of imH donors, 2 : 1 ionic dinuclear species were afforded which contain the first example of a strontium β-diketonate dinegative anion such as $Sr_2(Q)_6^{2-}$. As these species are stable in solution, they should have potential applications for the SFTCVD process; particularly derivative **12** containing fluorinated substituents on the Q_F ligands bound to the metals, which confers greater solubility in most organic solvents compared with non-fluorinated analogues[30] and, due to its ionic nature, probably also in supercritical carbon dioxide. In fact, several reports of the solubilisation/extraction of metals in supercritical fluids using chelating agents such as fluorinated β-diketonate ligands have previously been published.[31] We will further investigate this point.

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