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FULL PAPER

New co-ordination compounds derived from barium(II) and the anionic 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onate ligand (Q^-). Crystal and molecular structure of $[Ba_2Q_4(H_2O)_4]$, $[Ba_2Q_4(Him)_4]$, $[BaQ_2(tetraglyme)]$ (tetraglyme = 2,5,8,11,14-pentaoxapentadecane) and $[BaQ_2(phen)_2]$

Claudio Pettinari,[a] Fabio Marchetti,[a] Augusto Cingolani,[a] Dante Leonesi,[a] Sergei Troyanov[b] and Andrei Drozdov[b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, 62032 Camerino, Italy. E-mail: pettinar@camserv.unicam.it*
[b] *Moscow State University, Chemistry Department, Vorobjevy Gory, 119899 Moscow, Russia. E-mail: drozdov@inorg.chem.msu.ru*

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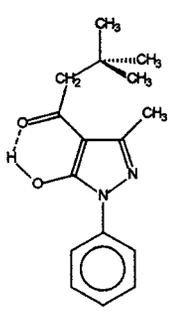
By reaction of 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-one (HQ) with metallic Ba in MeOH the dinuclear derivative $[\{BaQ_2(H_2O)_2\}_2]$ **1** has been synthesized. It contains two barium atoms each eight-co-ordinated by a terminal bidentate Q ligand, two bridging double chelating Q ligands and two molecules of water. When the reaction of HQ with Ba was carried out in the presence of mono-, bi- or poly-dentate *O*- or *N*-donor ligands, derivatives of formula $BaQ_2L_n(H_2O)_m$ have been obtained, depending on the nature of the ancillary ligand and reaction conditions employed [L = 2,5,8,11,14-pentaoxapentadecane (tetraglyme), 2,5,8,11-tetraoxadodecane (triglyme), 2,5,8-trioxanonane (diglyme), 2,2′:6′,2″-terpyridine (terpy), 2,3-bis(2-pyridyl)pyrazine (Pypy), $n = 1$, $m = 0$ or 1; L = imidazole (Him), 1-methylimidazole (1-MeIm), 2-methylimidazole (2-MeImH), 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy), 2,9-dimethyl-1,10-phenanthroline (Cupr) and triphenylphosphine oxide (PPh_3O), $n = 2$, $m = 0$ or 1]. In the nine-co-ordinated $[BaQ_2(tetraglyme)]$ the Ba atom is co-ordinated by all the five oxygen atoms of tetraglyme and by four oxygen atoms of two bidentate Q whereas the co-ordination number of barium in $[BaQ_2(phen)_2]$ is eight due to four oxygen atoms of the two Q ligands and four nitrogen atoms of the two 1,10-phenanthrolines. The derivative $[\{BaQ_2(Him)_2\}_2]$ is dinuclear with the Ba atoms linked by two double chelating Q ligands. The imidazoles complete the co-ordination number of Ba to 8. The compound $[(BaQ_2)_n]$ has been obtained by heating derivative **1** *in vacuo* at 100 °C, whereas the 1:1 adduct $[BaQ_2(phen)]$ was obtained only when $[(BaQ_2)_n]$ was treated in diethyl ether with an equimolar solution of phen. When a methanol solution of $[BaQ_2(Pypy)]$ reacts with an equimolar methanol solution of $CdCl_2$ scrambling of the ligand occurs and derivatives **1** and $[(CdCl_2)_2(Pypy)]$ are obtained. All the compounds obtained have been characterised by IR and far-IR data, conductivity and vaporimetric molecular weight measurements, ^1H NMR and in some cases also variable temperature ^1H NMR spectra. Comparison was made with structural and spectroscopic data reported for related barium(II) compounds.

During the last years the chemistry of alkaline-earth metal β-diketonates has become an active area of research due to the volatility of these compounds at reduced pressure.[1–3] Some barium β-diketonates, such as $[Ba_4(thd)_8]$[4] (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) or $[\{Ba(hfa)_2\}_n]$[5–7] (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) are applied in CVD processes to prepare thin films of oxide superconducting materials. On the contrary, the chemistry of alkaline-earth metal derivatives of heterocyclic β-diketones has been poorly studied.[8,9] For example, the co-ordination ability of 4-acylpyrazolones towards tin(IV),[10] rhodium(I),[11] copper-(I)[12] and -(II)[13] acceptors has been explored but until now no barium compounds have been reported. This family of ligands, widely used as extractants for metal traces[14–17] and for dyes,[18] is markedly different with respect to the other β-diketonates. For example some of these compounds show good solubility not only in several organic solvents, but also in alcohols and water: a very important property in view of the possible industrial and biological applications of their metal derivatives. Furthermore, the 4-acylpyrazolones possess an additional donor centre, the N(1) atom, which is often involved in secondary bonding interactions and is able to influence the structure of the metal derivatives. For example, we recently reported the preparation, characterisation and crystal structure of the calcium complex with 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-one (HQ)[13] containing also an ethanol molecule co-ordinated to the central atom. It was found that the supramolecular structure is deeply influenced by a hydrogen-bond network involving the proton of EtOH and a nitrogen of the pyrazole moiety in the ligand Q. As often indicated by us[10–13] and also by other researchers,[19,20] the structural and spectroscopic features of metal acylpyrazolonates can be very different from those of analogous metal acetylacetonates.



Now we have decided to extend our study to the synthesis and full characterisation of new barium complexes containing the ligand 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onate (Q^-). The choice of this ligand is due to its similarity with dipivaloylmethanate (thd), which contains bulky *tert*-Bu groups providing weak intermolecular interactions and therefore could yield rather highly volatile chelates. An additional reason is the presence in Q^- of a peripheral *N*-donor atom suitable to coordinate metal centres and also capable of complementary hydrogen bonding: in fact it has been previously reported that this kind of ligand (besides two carbonyl groups) forms additional M–L bonds[21–23] and is employed as a building block in the supramolecular assembly of inorganic polymers directed by hydrogen-bonding interaction.[13]

It has been observed that, upon addition of neutral Lewis bases, polymeric or oligomeric β-diketonate species containing alkaline-earth metals are often cleaved to yield simpler molecular species having a greater volatility.[24] For this reason our strategy has been also the synthesis of mixed-ligand complexes containing different mono-, bi- or poly-dentate *O*- or *N*-donor ancillary ligands (L). We also report here room-temperature single crystal X-ray studies for four of these compounds, undertaken to provide structural information for different combinations of Q with Ba^{II} and L. The stability of these compounds in solution and in the solid state was also investigated.

Experimental

Solvents were used as supplied or distilled using standard methods. The reagents were obtained from Aldrich Chemical Company Ltd. or Fluka. Chemical analyses of the samples dried *in vacuo* to constant weight (20 °C, *ca*. 0.01 Torr) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. The IR spectra in the interval 4000–100 cm^{-1} were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer, 300 MHz ^1H and 121.4 MHz ^{31}P NMR spectra using a VXR-300 Varian spectrometer operating at room temperature. Proton chemical shifts are reported in ppm *vs.* Me_4Si while phosphorus chemical shifts are in ppm *vs.* 85% H_3PO_4. Melting points were determined on an IA 8100 Electrothermal instrument. Molecular weight determinations were performed at 40 °C with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to ±2%.

Synthesis

The proligand HQ was synthesized according to the procedure described in ref. 13. With the exception of derivatives **14** and **15** all the compounds have been obtained in air starting from the same amount (0.137 g, 0.001 mol) of barium metal.

$[Ba_2Q_4(H_2O)_4]$ 1. Compound **1** was obtained by interaction of barium metal (0.137 g, 0.001 mol) with the proligand HQ (0.545 g, 0.002 mol) in 30 ml of methanol. The solution obtained after the evolution of hydrogen was concentrated on a rotary evaporator. After the addition of diethyl ether (20 ml) a colourless precipitate formed which was soluble in acetone, methanol, ethanol and chloroform, insoluble in hexane and poorly soluble in benzene and diethyl ether. Recrystallised from chloroform. Yield 90%, mp 202–204 °C (Found: C, 53.35; H, 6.21; N, 7.67. Calc. for $C_{32}H_{42}BaN_4O_6$: C, 53.68; H, 5.91; N, 7.82%). IR (Nujol): 3100br, $\nu(H_2O)$; 1685m, $\delta(H_2O)$; 1598vs (br), ν(C=O); 356m, 328m, ν(Ba–O). ^1H NMR (20 °C, CD_3OD): δ 1.07 (s) [18 H, $CH_2C(CH_3)_3$]; 2.37 (s) [4 H, $CH_2C(CH_3)_3$]; 2.72 (s) (6 H, 3-CH_3); 7.14 (t), 7.36 (t) and 7.76 (d) (10 H, NC_6H_5). ^1H NMR (20 °C, $CDCl_3$): δ 0.93 (s, br) [18 H, $CH_2C(CH_3)_3$]; 2.13 (br) (4 H, H_2O); 2.37 (s, br) [10 H, 3-CH_3, $CH_2C(CH_3)_3$]; 7.12 (t, br), 7.25 (t, br) and 7.56 (d, br) (10 H, NC_6H_5). ^1H NMR (−55 °C, $CDCl_3$): δ 0.42 (s, br), 0.83 (s, br), 0.98 (s, br), 1.01 (s, br) [18 H, $CH_2C(CH_3)_3$]; 2.02 (s, br), 2.33 (s, br), 2.48 (s, br), 2.54 (s, br), 2.97 (s, br) [10 H, $CH_2C(CH_3)_3$, 3-CH_3]; 4.00 (br) (4 H, H_2O); 6.80–7.40 (m, br), 7.58 (d, br) and 7.93 (d, br) (10 H, NC_6H_5). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 1338.

$[BaQ_2$(tetraglyme)] 2. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and of tetraglyme (2,5,8,11,14-pentaoxapentadecane) (0.222 g, 0.001 mol) in absolute ethanol (20 ml). The solution was stirred for 1 h and then the solvent was removed under reduced pressure. The colourless solid was recrystallised from ethanol–benzene, washed with benzene and dried *in vacuo*. Compound **2** is soluble in benzene, ethanol, acetone and chlorinated solvents. Yield 95%, mp 171–172 °C (Found: C, 55.70; H, 6.81; N, 6.27. Calc. for $C_{42}H_{60}BaN_4O_9$: C, 55.91; H, 6.70; N, 6.21%). IR (Nujol): 1633vs (br), ν(C=O); 341m, 325m, ν(Ba–O). ^1H NMR ($CDCl_3$): δ 1.10 (s) [18 H, $CH_2C(CH_3)_3$]; 2.47 (s) (6 H, 3-CH_3); 2.53 (s) [4 H, $CH_2C(CH_3)_3$]; 3.31 (s), 3.44 (m), 3.51 (m), 3.76 (m), 3.79 (m) (22 H, tetraglyme); 7.04 (t), 7.26 (t) and 8.21 (d) (10 H, NC_6H_5). ^1H NMR (CD_3OD): δ 1.08 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 2.74 (s) [4 H, $CH_2C(CH_3)_3$]; 3.36 (s), 3.57 (m), 3.64 (m) (22 H, tetraglyme); 7.06 (t), 7.36 (t) and 7.79 (d) (10 H, NC_6H_5). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 721.

$[BaQ_2$(triglyme)] 3. Complex **3** was synthesized with the same procedure as that for **2** by using triglyme (2,5,8,11-tetraoxadodecane) (0.178 g, 0.001 mol). Yield 95%, mp 139–140 °C (Found: C, 55.83; H, 6.68; N, 6.57. Calc. for $C_{40}H_{56}BaN_4O_8$: C, 55.98; H, 6.58; N, 6.53%). IR (Nujol): 1633vs (br), ν(C=O); 367m, 336vs (br), 324s, ν(Ba–O). ^1H NMR ($CDCl_3$): δ 1.06 (s) [18 H, $CH_2C(CH_3)_3$]; 2.45 (s) (6 H, 3-CH_3); 2.51 (s) [4 H, $CH_2C(CH_3)_3$]; 3.30 (s), 3.54 (m), 3.71 (m) (18 H, triglyme); 7.04 (t), 7.28 (t) and 8.06 (d) (10 H, NC_6H_5). ^1H NMR (CD_3OD): δ 1.06 (s) [18 H, $CH_2C(CH_3)_3$]; 2.38 (s) (6 H, 3-CH_3); 2.67 (s) [4 H, $CH_2C(CH_3)_3$]; 3.35 (s), 3.55 (m), 3.64 (m) (18 H, triglyme); 7.15 (t), 7.33 (t) and 7.80 (d) (10 H, NC_6H_5).

$[\{BaQ_2$(diglyme)$\}_2]\cdot 2H_2O$ 4. Compound **4** was prepared with the same procedure as that for **2** by using diglyme (2,5,8-trioxanonane) (0.134 g, 0.001 mol). Yield 88%, mp 156–158 °C (Found: C, 54.72; H, 6.64; N, 6.78. Calc. for $C_{38}H_{54}BaN_4O_8$: C, 54.85; H, 6.54; N, 6.73%). IR (Nujol): 3120br, $\nu(H_2O)$; 1675m, $\delta(H_2O)$; 1637vs (br), ν(C=O); 340m, 326m, ν(Ba–O). ^1H NMR ($CDCl_3$): δ 0.97 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 2.40 (br) (2 H, H_2O); 2.42 (s) [4 H, $CH_2C(CH_3)_3$]; 3.33 (s), 3.51 (m) (14 H, diglyme); 7.04 (t), 7.26 (t) and 7.85 (d) (10 H, NC_6H_5). ^1H NMR (CD_3OD): δ 1.06 (s) [18 H, $CH_2C(CH_3)_3$]; 2.38 (s) (6 H, 3-CH_3); 2.68 (s) [4 H, $CH_2C(CH_3)_3$]; 3.35 (s), 3.53 (m), 3.55 (m), 3.60 (m) (14 H, diglyme); 7.12 (t), 7.34 (t) and 7.78 (d) (10 H, NC_6H_5). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 1632.

$[BaQ_2$(phen)$_2]$ 5. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and of phen (0.365 g, 0.002 mol) in absolute ethanol (20 ml). The solution was stirred for an hour and then the solvent was removed under reduced pressure. The colourless solid residue was washed with benzene. Yield 90%. The product is soluble in ethanol, acetone and chlorinated solvents, insoluble in hexane and poorly soluble in diethyl ether and benzene. It was recrystallised from benzene as colourless plates which were used for crystal structure analysis, mp 165 °C (decomp.) (Found: C, 64.82; H, 5.38; N, 10.54. Calc. for $C_{56}H_{54}BaN_8O_4$: C, 64.65; H, 5.23; N, 10.77%). IR (Nujol): 1620vs (br), ν(C=O); 336m, 325m, ν(Ba–O); 280vs, 247vs, ν(Ba–N). ^1H NMR (20 °C, $CDCl_3$): δ 0.69 (s) [18 H, $CH_2C(CH_3)_3$]; 2.17 (s) (6 H, 3-CH_3); 2.20 (s) [4 H,

$CH_2C(CH_3)_3$]; 6.93 (t), 7.12 (t), 7.82 (d) (10 H, NC_6H_5); 7.42 (m), 7.71 (s), 8.16 (d) and 9.15 (d) (16 H, CH_{phen}). ^{1}H NMR (−55 °C, $CDCl_3$): δ 0.68 (s, br), 0.49 (s, br) [18 H, $CH_2C(CH_3)_3$]; 2.13 (s, br) (6 H, 3-CH_3); 2.24 (s, br) [18 H, $CH_2C(CH_3)_3$]; 6.90 (br), 7.10 (br), 7.88 (br) (10 H, NC_6H_5); 7.50 (br), 7.74 (br), 8.21 (br) and 9.19 (br) (16 H, CH_{phen}). ^{1}H NMR (CD_3OD): δ 0.97 (s) [18 H, $CH_2C(CH_3)_3$]; 2.33 (s) (6 H, 3-CH_3); 2.63 (s) [4 H, $CH_2C(CH_3)_3$]; 7.12 (t), 7.30 (t), 7.69 (d) (10 H, NC_6H_5); 7.72 (m), 7.91 (s), 8.44 (d) and 9.10 (d) (16 H, CH_{phen}). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 669.

[BaQ_2(Cupr)$_2$] 6. Derivative **6** was synthesized following the same procedure as for **5** by using 0.416 g (0.002 mol) of 2,9-dimethyl-1,10-phenanthroline hydrate (Cupr). Its solubility is similar to that of **5**. Yield 93%, mp 200 °C (decomp.) (Found: C, 65.52; H, 5.85; N, 10.20. Calc. for $C_{60}H_{62}BaN_8O_4$: C, 65.72; H, 5.70; N, 10.22%). IR (Nujol): 1622vs (br), ν(C=O); 339s, 309m, ν(Ba–O); 279s, ν(Ba–N). ^{1}H NMR ($CDCl_3$): δ 0.71 (s) [18 H, $CH_2C(CH_3)_3$]; 1.98 (s) [4 H, $CH_2C(CH_3)_3$]; 2.07 (s) (6 H, 3-CH_3); 2.87 (s) (12 H, $CH_{3\ Cupr}$); 7.34 (d), 7.64 (s), 8.05 (d) (12 H, CH_{Cupr}); 6.97 (t), 7.15 (t) and 7.78 (d) (10 H, NC_6H_5). ^{1}H NMR (CD_3OD): δ 1.07 (s) [18 H, $CH_2C(CH_3)_3$]; 2.38 (s) (6 H, 3-CH_3); 2.69 (s) [4 H, $CH_2C(CH_3)_3$]; 2.86 (s) (12 H, $CH_{3\ Cupr}$); 7.12 (t), 7.34 (t), 7.80 (d) (10 H, NC_6H_5); 7.58 (m), 7.78 (s) and 8.25 (d) (12 H, CH_{Cupr}).

[BaQ_2(bipy)$_2$] 7. Compound **7** was obtained as a colourless solid following the same procedure as for **5** by using 0.132 g (0.002 mol) of 2,2′-bipyridine (bipy). Its solubility is similar to that of **6**. Yield 98%, mp 186–188 °C (decomp.) (Found: C, 62.70; H, 5.58; N, 11.22. Calc. for $C_{52}H_{64}BaN_8O_4$: C, 62.94; H, 5.48; N, 11.29%). IR (Nujol): 1631vs (br), ν(C=O); 404s, 321m, ν(Ba–O); 247m, ν(Ba–N). ^{1}H NMR ($CDCl_3$): δ 0.80 (s) [18 H, $CH_2C(CH_3)_3$]; 2.23 (s) (6 H, 3-CH_3); 2.25 (s) [4 H, $CH_2C(CH_3)_3$]; 6.95 (t), 7.15 (t), 7.75 (d) (10 H, NC_6H_5); 7.19 (t), 7.73 (t), 8.10 (d) and 8.60 (d) (16 H, CH_{bipy}). ^{1}H NMR (CD_3OD): δ 1.06 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 2.68 (s) [4 H, $CH_2C(CH_3)_3$]; 7.12 (t), 7.34 (t), 7.82 (d) (10 H, NC_6H_5); 7.46 (t), 7.94 (t), 8.30 (d) and 8.66 (d) (16 H, CH_{bipy}).

[BaQ_2(terpy)]·H_2O 8. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and terpy (0.233 g, 0.001 mol) in absolute ethanol (20 ml). The red solution formed was stirred for 1 h until it changed to pale yellow and then the solvent was removed under reduced pressure. The oil formed was crystallised in a refrigerator at −18 °C after the addition of 20 ml of *n*-hexane and then washed with benzene. Recrystallised from a chloroform–benzene mixture. Yield 93%. Compound **8** is soluble in acetone and chlorinated solvents, poorly soluble in benzene and ethanol, insoluble in diethyl ether and hexane, mp 210 °C (decomp.) (Found: C, 60.88; H, 5.57; N, 10.74. Calc. for $C_{47}H_{51}BaN_7O_5$: C, 60.62; H, 5.52; N, 10.53%). IR (Nujol): 3150br, ν(H_2O); 1680m, δ(H_2O); 1626vs (br), ν(C=O); 419m, 341m, ν(Ba–O); 303s, 247s, ν(Ba–N). ^{1}H NMR ($CDCl_3$): δ 0.84 (s) [18 H, $CH_2C(CH_3)_3$]; 2.10 (br) (2 H, H_2O); 2.29 (s) (6 H, 3-CH_3); 2.31 (s) [4 H, $CH_2C(CH_3)_3$]; 6.93 (t), 7.15 (t), 7.79 (d) (10 H, NC_6H_5); 7.23 (t), 7.83 (m), 7.95 (t), 8.03 (t) and 8.90 (d) (11 H, CH_{terpy}). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 744.

[BaQ_2(Pypy)]·$2H_2O$ 9. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and 2,3-bis(2-pyridyl)pyrazine (Pypy) (0.234 g, 0.001 mol) in absolute ethanol (20 ml). The solution was stirred for 1 h. The complex was then precipitated as a colourless solid upon addition of 10 ml of *n*-hexane, filtered off and washed with diethyl ether. Yield 90%. The compound is soluble in benzene, ethanol and acetone, poorly soluble in dichloromethane and insoluble in diethyl ether and hexane, mp 208–210 °C (decomp.) (Found: C, 58.06; H, 5.57; N, 11.18. Calc. for $C_{46}H_{52}BaN_8O_6$: C, 58.14; H, 5.52; N, 11.79%). IR (Nujol): 3100br, ν(H_2O); 1670m, δ(H_2O); 1620vs (br), ν(C=O); 418s, 326m, ν(Ba–O); 278s, 247s, ν(Ba–N). ^{1}H NMR ($CDCl_3$): δ 0.90 (s) [18 H, $CH_2C(CH_3)_3$]; 1.70 (br) (4 H, $2H_2O$); 2.35 (s) (6 H, 3-CH_3); 2.38 (s) [18 H, $CH_2C(CH_3)_3$]; 7.08 (t), 7.22 (t), 7.74 (d) (10 H, NC_6H_5); 7.28 (m), 7.62 (m), 8.41 (d) and 8.69 (s) (8 H, Pypy). ^{1}H NMR (CD_3OD): δ 1.08 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 2.72 (s) [18 H, $CH_2C(CH_3)_3$]; 7.13 (t), 7.34 (t), 7.77 (d) (10 H, NC_6H_5); 7.86 (m), 8.32 (d) and 8.77 (s) (8 H, CH_{Pypy}). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 710.

[BaQ_2(PPh_3O)$_2$]·H_2O 10. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and of PPh_3O (0.556 g, 0.002 mol) in absolute ethanol (20 ml) and stirred for 1 h. The complex was then precipitated as a colourless solid upon the addition of 10 ml of *n*-hexane, filtered off and washed with diethyl ether. Yield 86%, mp 185 °C (decomp.) (Found: C, 65.30; H, 5.73; N, 4.52. Calc. for $C_{70}H_{70}BaN_4O_7$: C, 65.10; H, 5.62; N, 4.47%). IR (Nujol): 3100 (br), ν(H_2O); 1668m, δ(H_2O); 1631vs (br), ν(C=O); 542vs, 512s, ν(PPh_3O). ^{1}H NMR ($CDCl_3$): δ 0.84 (s) [18 H, $CH_2C(CH_3)_3$]; 2.28 (s) [4 H, $CH_2C(CH_3)_3$]; 2.33 (s) (6 H, 3-CH_3); 6.91 (t), 7.25–7.60 (m) [30 H, $OP(C_6H_5)_3$]; 7.10 (t), 7.25–7.60 (m), 7.77 (d) (10 H, NC_6H_5); and 2.15 (br) (2 H, H_2O). ^{1}H NMR (CD_3OD): δ 1.08 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 2.74 (s) [4 H, $CH_2C(CH_3)_3$]; 7.10 (t), 7.50–7.70 (m) [30 H, $OP(C_6H_5)_3$]; 7.35 (t), 7.50–7.70 (m) and 7.97 (d) (10 H, NC_6H_5). ^{31}P NMR ($CDCl_3$, 20 °C): δ 30.45; ($CDCl_3$, −50 °C): 32.00. Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 569.

[Ba_2Q_4(Him)$_4$] 11. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and imidazole (0.136 g, 0.002 mol) in absolute ethanol (20 ml). The solution was stirred for 1 h and then compound **11** was precipitated as a colourless solid upon the addition of 10 ml of *n*-hexane, filtered off and washed with diethyl ether. Yield 78%, mp 205–210 °C (Found: C, 55.65; H, 5.75; N, 13.83. Calc. for $C_{38}H_{46}BaN_8O_4$: C, 55.92; H, 5.68; N, 13.73%). IR (Nujol): 1631vs (br), ν(C=O). ^{1}H NMR ($CDCl_3$): δ 0.92 (s) [18 H, $CH_2C(CH_3)_3$]; 2.33 (s) [4 H, $CH_2C(CH_3)_3$]; 2.35 (s) (6 H, 3-CH_3); 5.88 (s, br), 6.88 (s, br), 7.45 (s, br) (4 H, CH_{Him}); 7.61 (d), 7.19 (m), 7.04 (t) (10 H, NC_6H_5). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 814.

[Ba_2Q_4(N-MeIm)$_4$] 12. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and 1-methylimidazole (1-MeIm) (0.164 g, 0.002 mol) in absolute ethanol (20 ml). The solution was stirred for 1 h and then compound **12** was precipitated as a colourless solid upon the addition of 10 ml of *n*-hexane, filtered off and washed with diethyl ether. Yield 88%, mp 264–266 °C (decomp.) (Found: C, 56.72; H, 6.10; N, 13.45. Calc. for $C_{40}H_{50}BaN_8O_4$: C, 56.91; H, 5.97; N, 13.27%). IR (Nujol): 1625vs (br), ν(C=O). ^{1}H NMR ($CDCl_3$): δ 1.04 (s) [18 H, $CH_2C(CH_3)_3$]; 2.43 (s) (6 H, 3-CH_3); 251 (s) [4 H, $CH_2C(CH_3)_3$]; 3.64 (s, br) (3 H, $CH_{3\ 1\text{-}MeIm}$); 6.82 (s, br), 6.95 (s, br) (3 H, $CH_{1\text{-}MeIm}$); 7.18 (t), 7.30–7.60 (m) and 7.75 (d, br) (10 H, NC_6H_5).

[Ba_2Q_4(2-MeImH)$_4$] 13. Barium metal was added to a stirred solution of the proligand HQ (0.545 g, 0.002 mol) and 2-methylimidazole (0.164 g, 0.002 mol) in absolute ethanol (20 ml). The solution was stirred for an hour and then the complex was precipitated as a colourless solid upon the addition of 10 ml of *n*-hexane, filtered off and washed with diethyl ether. Yield 70%, mp 180 °C (decomp.) (Found: C, 56.48; H, 6.06; N, 13.48. Calc. for $C_{40}H_{50}BaN_8O_4$: C, 56.91; H, 5.97; N, 13.27%). IR (Nujol): 1635s (br), ν(C=O). ^{1}H NMR ($CDCl_3$): δ 0.94 (s, br) [18 H, $CH_2C(CH_3)_3$]; 2.25 (s, br) [4 H, $CH_2C(CH_3)_3$]; 2.32 (s, br) (6 H, 3-CH_3); 2.37 (s, br) (3 H, $CH_{3\ 2\text{-}MeImH}$); 5.10 (s, br), 6.77 (s, br) (3 H, $CH_{2\text{-}MeImH}$); 7.04 (m, br), 7.18 (m, br) and 7.72 (d, br) (10 H, NC_6H_5).

[$(BaQ_2)_n$] 14. Compound **14** was prepared by heating **1** *in vacuo* at 100 °C. The compound is hygroscopic. Yield 90%, mp 186 °C (decomp.). Soluble in benzene, methanol, ethanol, acetone and chlorinated solvents (Found: C, 56.35; H, 5.81; N, 8.05. Calc. for $C_{32}H_{38}BaN_4O_4$: C, 56.52; H, 5.63; N, 8.20%). IR (Nujol): 1620s, 1615s, ν(C=O); 371m, 352s, 344m, ν(Ba–O). ^{1}H NMR (20 °C, $CDCl_3$): δ 1.09 (s) [18 H, $CH_2C(CH_3)_3$]; 2.39 (s) [4 H, $CH_2C(CH_3)_3$]; 2.39 (s) (6 H, 3-CH_3); 7.10 (t), 7.26 (t) and 7.53 (d) (10 H, NC_6H_5). ^{1}H NMR (−55 °C, $CDCl_3$): δ 0.85 (s, br), 0.50 (s, br) [18 H, $CH_2C(CH_3)_3$]; 0.98 (s, br), 1.01 (s, br), 2.10 (s, br), 2.34 (s, br), 2.57 (s, br), 2.68 (s, br) [10 H, 3-CH_3, $CH_2C(CH_3)_3$]; 6.80–7.85 (m, br) and 7.98 (d, br) (10 H, NC_6H_5). ^{1}H NMR (CD_3OD): δ 1.08 (s) [18 H, $CH_2C(CH_3)_3$]; 2.38 (s) (6 H, 3-CH_3); 2.71 (s) [4 H, $CH_2C(CH_3)_3$]; 7.14 (t), 7.35 (t) and 7.79 (d) (10 H, NC_6H_5).

[{BaQ_2(phen)}$_2$] 15. To a solution of BaQ_2 **14** (0.680 g, 1 mmol) in dichloromethane (30 ml), phen (0.182 g, 1 mmol) was added. The clear solution was stirred to reflux for 2 h, then solvent was removed on the rotary evaporator and the crude product treated with diethyl ether (20 ml). A colourless precipitate was obtained which was filtered off, washed with *n*-hexane (10 ml) and dried *in vacuo*. Yield 86%, mp 275–277 °C (decomp.) (Found: C, 61.25; H, 5.22; N, 9.70. Calc. for $C_{44}H_{46}BaN_6O_4$: C, 61.44; H, 5.39; N, 9.77%). IR (Nujol): 1624s (br), ν(C=O). ^{1}H NMR ($CDCl_3$): δ 0.76 (s) [18 H, $CH_2C(CH_3)_3$], 2.23 (s) [10 H, 3-CH_3, $CH_2C(CH_3)_3$]; 6.89 (t), 7.09 (t), 7.75 (d) (10 H, NC_6H_5); 7.39 (m), 8.16 (d) and 9.02 (d) (8 H, CH_{phen}). Molecular weight ($CHCl_3$, 40 °C, c = 0.01 m): 1685.

Reaction between [BaQ_2(Pypy)]·2H_2O 9 and $CdCl_2$. To a solution of [BaQ_2(Pypy)]·2H_2O **9** (0.950 g, 1 mmol) in methanol (30 ml) $CdCl_2$ (0.183 g, 1 mmol) was added. A light-brown precipitate immediately formed. The reaction mixture was stirred overnight to reflux, then filtered to separate the precipitate, which was washed with diethyl ether (10 ml), dried under vacuum and shown to be [$(CdCl_2)_2$(Pypy)] **16**. Yield 83%, mp >350 °C (decomp.) (Found: C, 28.30; H, 1.73; N, 9.35. Calc. for $C_7H_5CdCl_2N_2$: C, 27.98; H, 1.68; N, 9.32%). IR (Nujol): 1596s, 1572m, ν(C=C, C=N). ^{1}H NMR (DMSO-d_6): δ 7.35 (t), 7.90 (m) (4 H, CH_{Pypy}); 8.34 (d) (2 H, CH_{Pypy}) and 8.40 (s) (2 H, CH_{Pypy}). From the solution a colourless crystalline powder slowly formed, which has been shown to be [$Ba_2Q_4(H_2O)_4$] **1**.

Structure determination

Diffraction data for compounds **1**, **2**, **5** and **11** were collected at low temperatures on an IPDS (Stoe) diffractometer using graphite monochromatised Mo-Kα radiation. Crystallographic data are presented in Table 1. The crystallographic calculations were performed using SHELXS 86[25] (solution) and SHELXL-93[26] (refinement) program packages. No absorption corrections were applied. The structures were refined anisotropically for all non-hydrogen atoms. Hydrogen atoms of only one water molecule of structure **1** could be found in the Fourier-difference synthesis. Other hydrogen atoms for all three structures were placed in calculated positions and refined in the riding mode.

CCDC reference number 186/1402.

See http://www.rsc.org/suppdata/dt/1999/1555/ for crystallographic files in .cif format.

Results and discussion

The dinuclear derivative [{$BaQ_2(H_2O)_2$}$_2$] **1** can be prepared in high yield from the reaction of two moles of the proligand 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-one (HQ) with one mole of metallic Ba in MeOH, whereas the colourless mixed-ligand complexes **2**–**13** were obtained when the same reaction was carried out in ethanol in the presence of neutral mono-, bi- or poly-dentate *O*- or *N*-donor ligands L, eqn. (1)

$$\mathrm{Ba} + 2\mathrm{HQ} + n\mathrm{L} \xrightarrow[\mathrm{EtOH}]{\mathrm{H_2O}} \mathrm{BaQ_2L}_n(\mathrm{H_2O})_m \qquad (1)$$

2–13

(L = phen, bipy, Cupr, PPh_3O, Him, 1-MeIm or 2-MeImH, n = 2; L = tetraglyme, triglyme, diglyme, terpy or Pypy, n = 1; m = 1 or 2).

The stoichiometry and the nuclearity strongly depend on the type of ligand employed: for example a 2:1 adduct was generally obtained by using *N*-donor mono- or bi-dentate ligands, 1:1 adducts by using tri- or tetra-dentate *N*-donor and tri-, tetra- or penta-dentate polyether *O*-donor ligands. Furthermore dinuclear compounds were preferred when monodentate Lewis bases were employed, whereas mononuclear complexes are likely when ligand:metal ratio is 1:1 and the donor is tetra- or penta-dentate, and also when the ligand:metal ratio is 2:1 and the ligand is bidentate.

When the derivative **1** is stored for 2 d *in vacuo* at *ca.* 100 °C the anhydrous derivative [$(BaQ_2)_n$] **14** can be obtained. When exposed to air this compound rapidly absorbs water to give back the hydrate derivative **1**.

From the reaction of compound **14** with an equimolar quantity of 1,10-phenanthroline in a dichloromethane–diethyl ether suspension the 1:1 adduct [{BaQ_2(phen)}$_2$] **15** has been obtained, for which, on the basis of molecular weight determination (the ratio r between the experimental molecular weight and the empirical formula weight being 1685:860 = 1.96:1) and previous reports on analogous derivatives,[27] a dinuclear structure has been proposed.

The derivative [BaQ_2(Pypy)]·2H_2O **9** reacts with an equimolar quantity of anhydrous $CdCl_2$ in methanol yielding both derivative **1** and [$(CdCl_2)$(Pypy)] **16** in accordance with eqn. (2).

$$2[\mathrm{BaQ_2(Pypy)}]\cdot 2\mathrm{H_2O} + 4\mathrm{CdCl_2} \xrightarrow{\mathrm{MeOH}} [\{\mathrm{BaQ_2(H_2O)_2}\}_2] + 2[(\mathrm{CdCl_2})_2(\mathrm{Pypy})] \qquad (2)$$

All the derivatives are high melting solids, soluble in chlorinated and aromatic solvents, alcohols, DMSO and acetone, in which they are not electrolytes. Vaporimetric molecular weight determinations (chloroform solution) carried out for selected derivatives (**1**, **2**, **5**, **8**, **9**, **10** and **11**) indicated that **1** exists as dinuclear molecule in solution, the r value being *ca.* 1.88. The derivatives **2** and **5** (for which a mononuclear structure has been found in the solid state, see below) and **8** and **9** exhibit values of r in the range 0.64–0.80 in accordance with the partial dissociation (3). Derivative **10** is extensively dissociated (r = 0.48). On

$$2\mathrm{BaQ_2L}_n(\mathrm{H_2O})_2 \xleftrightarrow{\mathrm{CDCl_3}} [\mathrm{BaQ_2(H_2O)_2}]_2 + 2n\mathrm{L} \qquad (3)$$

the other hand **11**, which exists in the solid state as a dinuclear species (see below), exhibits an r value of 0.99, suggesting the existence of a mononuclear species in chloroform solution.

It is very interesting that a ligand such as 2,3-bis(pyridyl)-pyrazine (Pypy), a tetradentate donor widely employed in building block chemistry and able to co-ordinate to at least two metal centres,[28] in compound **9** is likely bonded only to one barium atom not only in the solid state but also in solution.

In the case of compound [{BaQ_2(diglyme)}$_2$]·2H_2O **4** we suggest a dinuclear structure, analogously to those found for derivatives [$Ba_2(thd)_4$(diglyme)][29] and [$Ba_2(thd)_4$(diglyme)]·H_2O.[30] Our hypothesis is supported by the fact that the r value of **4** in $CHCl_3$ (1.96) is very close to that expected for a dinuclear derivative.

The presence of water (often strongly hydrogen bonded) in derivatives **1**, **4**, **8**, **9** and **10** is also confirmed by their infrared spectra, broad absorptions at *ca.* 3200–2500 cm^{-1} and medium to strong bands at *ca.* 1650 cm^{-1} being observed in all cases. The ν(C=O) of the ligand (Q^-) generally undergoes a shift to

higher frequencies upon complexation, with the exception of derivative **1** which shows a ν(C=O) at lower frequency with respect to the starting proligand HQ.

In the far-IR region for all derivatives **1**–**15** it is very difficult to assign with certainty ν(Ba–O) and ν(Ba–N) modes due to the fact that they are often overlapped with some typical skeletal modes of the O_2-donor acylpyrazolonate and of the ancillary *N*- or *O*-donor ligands employed. However we have found in the spectra of derivatives **5**–**9**, **11**–**13** and **15** some absorptions at *ca*. 300 cm^{-1}, absent in the spectra of the free ancillary *N*-donor ligand and of BaQ_2 species, which have been tentatively assigned to Ba–N stretching vibrations.[31] In addition all the derivatives show a similar complex pattern of absorption in the 350–400 cm^{-1} region which is likely due to Ba–O stretching vibrations.[32] It is also interesting that derivatives **1** and **14** have completely different spectra in accordance with their different structure and nuclearity.

The ^{1}H NMR spectra of the proligand HQ and of the barium complexes **1**–**15** were recorded in $CDCl_3$ and for some derivatives also in methanol. The spectra are strongly dependent on the nature of the neutral ancillary ligand, on the stoichiometry and also on the solvent employed. For example in the spectra ($CDCl_3$ solution) of complexes containing *N*-donor ligands the signals due to the acylpyrazolonate moiety are always displaced toward higher field with respect to the same signals of the uncomplexed starting reagent HQ. The observed higher field shift is additional evidence in favour of the existence of the complexes in this solvent. We also observed that Δ (= difference in chemical shift of a given proton signal of the complex with respect to that of the "free" ligand) is generally greater for the 2:1 adducts containing bidentate chelating ligands than for the 4:2 adducts containing monodentate imidazoles, whereas in the spectra of derivatives **2**–**4** the displacement of the proton signals on going from the free proligand HQ to the anionic (Q^-) in the complex is often negligible. In some cases (for example the *para* protons of the phenyl group) the signals are even displaced towards lower field upon coordination. It is also interesting that the ^{1}H NMR spectra of **1** and **14** are very similar suggesting the existence of the same species in solution.

On the other hand in deuteriated methanol the spectra of derivatives **1**–**15** are very similar to each other in accordance with an extensive solvation and almost complete ancillary neutral ligand dissociation in this co-ordinating solvent.

In the spectrum of $[BaQ_2(phen)_2]$ **5** the two phen ligands appear symmetrical in solution due to a fluxional/exchange process in contrast to the lack of symmetry in the crystal structure determination (see below), likely due to a weak Ba–N bonding interaction. We have also observed that, while at room temperature only one set of signals has been found for each equivalent group of protons in the spectra of **1** and **5**, at 223 K each broad resonance type splits into at least two or three absorptions with different intensity, indicating that these species, containing four and two acylpyrazolonato ligands respectively, are fluxional at room temperature but not at 223 K.

In the case of derivative $[BaQ_2(PPh_3O)_2]\cdot H_2O$ **10** also a ^{31}P NMR variable study has been carried out: it has been found that this compound is completely dissociated in solution in accordance with eqn. (3) not only at 293 but also at 223 K, the δ(^{31}P) being similar to that found at the same temperatures for the free donor PPh_3O (δ 32.1).

Crystal structures

Selected bond distances and angles for compounds **1**, **2**, **5** and **11** are reported in Table 2.

The crystal structure of $[\{BaQ_2(H_2O)_2\}_2]\cdot 2CHCl_3$ **1** (Fig. 1) consists of centrosymmetric dimers $Ba_2Q_4(H_2O)_4$, each containing two eight-co-ordinate barium atoms with Ba···Ba′ distance of 3.974 Å. The structure also contains solvated chloroform molecules.

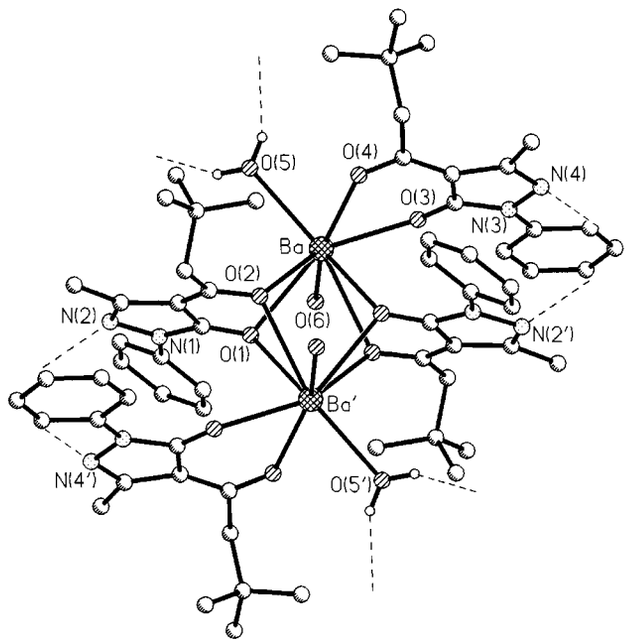


Fig. 1 Molecular structure of $[\{BaQ_2(H_2O)_2\}_2]$.

In the environment of the metal there is a terminal (t) bidentate acylpyrazolonate ligand, two bridging (b) tetradentate ones and two water molecules. To our knowledge this is the first structure containing an acylpyrazolonate acting as bridging tetradentate. As expected, the Ba–$O_{(t)}$ distances, 2.575(3) and 2.625(3) Å, are longer than Ba–$O_{(b)}$, 2.819–2.948 Å. The distances Ba–O_{water} are 2.726(3) and 2.998(4) Å. Two of the four water molecules are involved in an intermolecular hydrogen-bond network connecting each dimer with other four units (Fig. 1), O(5) and O(5′) acting as hydrogen donors and N(2), N(2′), N(4) and N(4′) as hydrogen acceptors, so that eight interactions are observed for each molecule. All these hydrogen bonds practically lie in a plane, so that the dimers are arranged in the 4^4 net connected by four pairs of hydrogen bonds. The $CHCl_3$ molecules are near the water molecules O(6) and O(6′) and are likely responsible for the fact the latter are not involved in hydrogen-bonding interactions.

The structure of compound **1** is remarkably similar to the dimeric $[\{Ba(thd)_2(NH_3)_2\}_2]$[33] in which the Ba···Ba distance, 3.83 Å, is shorter presumably due to the lack of intermolecular interactions. Compound **1** is built up from dimeric units linked by bridging water molecules. In fact, it can be considered as the final product of hydration, as was shown for thd–Ba derivative.[33] The differences between these two structures are due to the presence of nitrogen in the pyrazole ring acting as a Lewis base centre in ligand Q.

The crystal structure of $[\{BaQ_2(Him)_2\}_2]\cdot C_6H_6$ **11** (Fig. 2) consists of dimeric units connected by two bridging diketonate ligands similar to the structure of compound **1**. Apparently, due to the different donor abilities of imidazole and water, Ba–O terminal distances are longer than in **1** [2.617(2); 2.684(2) Å], whereas Ba–O bridging bonds are a little bit shorter [2.785(2)–2.865(2) Å]. As in **1**, two Ba–N distances to imidazole molecule differ from each other: 2.790(3) and 2.896(3) Å. Both protonated nitrogen atoms of imidazole are involved in the system of hydrogen bonds: N(6)–H(6)···N(4) and N(8)–H(8)···N(4) are 3.02 and 2.94 Å respectively. Each dimeric unit is connected by four pairs of hydrogen bonds to four neighbour dimeric units.

The structure of $[BaQ_2(tetraglyme)]$ **2** (Fig. 3) is composed of discrete molecules, as there are no intermolecular contacts shorter than the van der Waals ones. The barium atom is

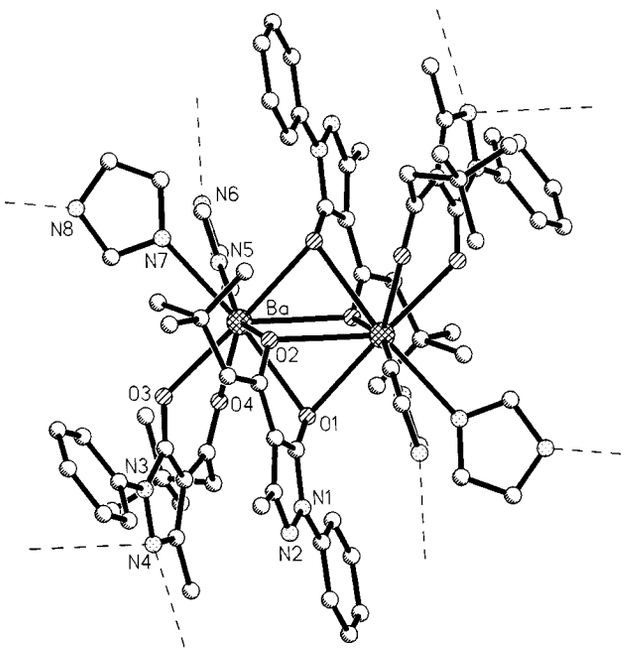


Fig. 2 Molecular structure of $[\{BaQ_2(Him)_2\}_2]$.

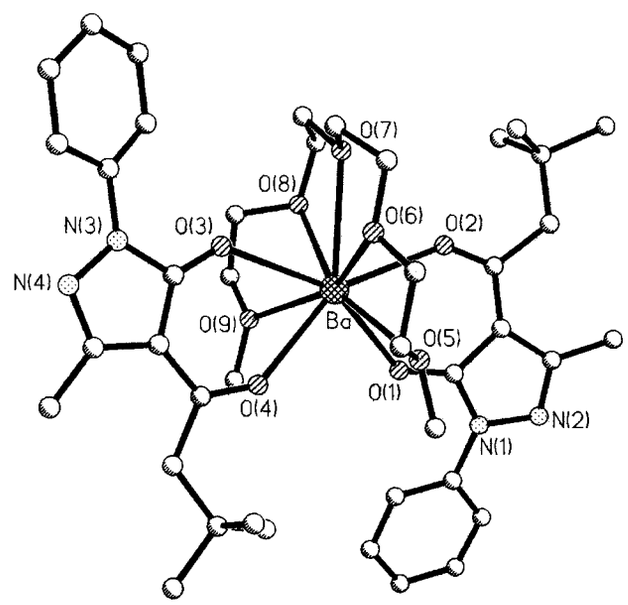


Fig. 3 Molecular structure of $[BaQ_2(tetraglyme)]$.

nine-co-ordinate, four oxygen atoms being of the two Q ligands and five of the tetraglyme. Other crystal structures of Ba(β-diketonate)$_2$(tetraglyme) compounds are well known (see for example ref. 34). When asymmetric chelating O_2 ligands are used {as in $[Ba(pta)_2(tetraglyme)]$[35]} (Hpta = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione) they are arranged in *syn* position to each other, whereas in **2** the Q ligands are in *anti* positions. However the longer distances Ba–O(2) [2.751(3) Å] and Ba–O(3) [2.718(3) Å] are those situated closer to tetraglyme, due to repulsion and steric hindrance exerted by the latter. The $Ba–O_{(tetraglyme)}$ distances are a little bit longer than those reported for analogous compounds,[34] the central Ba–O(7) bond [2.912(3) Å] being the longest one.

The structure of $[BaQ_2(phen)_2]\cdot C_6H_6$ **5** (Fig. 4) consists of discrete molecules with barium lying on a twofold axis. The barium co-ordination number is eight, 4O + 4N. The structure of **5** is very similar to that of $[Ba(thd)_2(phen)_2]$[36] with shorter Ba–N distances (mean values are 2.92 and 2.95 Å, respectively) but a little bit longer Ba–O distances (mean values are 2.70 and 2.67 Å). Moreover, the phen ligands are not in parallel planes, forming a dihedral angle of 34.7°. In contrast, the Q-chelating

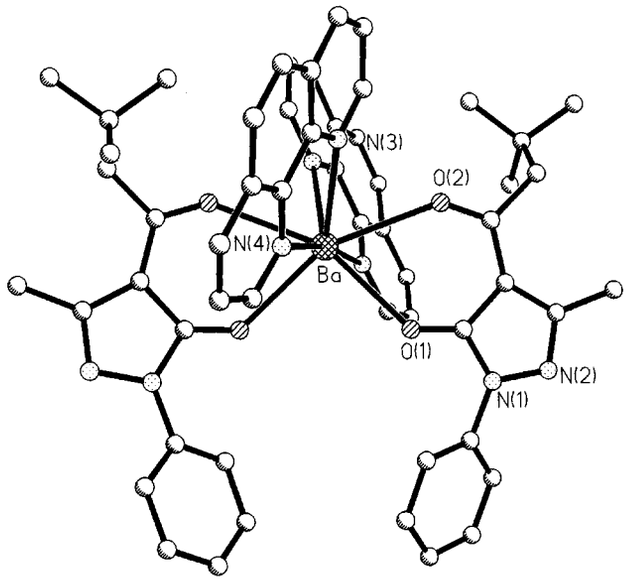


Fig. 4 Molecular structure of $[BaQ_2(phen)_2]$.

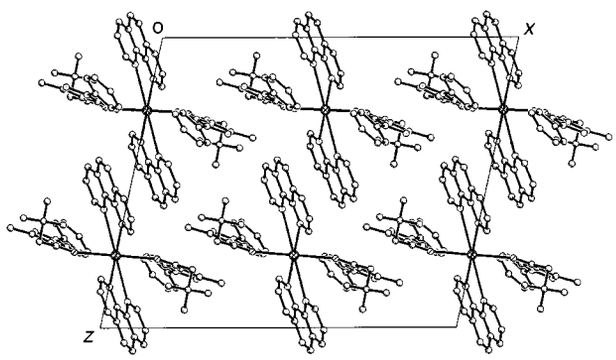


Fig. 5 Packing diagram for $[BaQ_2(phen)_2]$.

rings are almost parallel (only 6°). Differently from $[BaQ_2(tetraglyme)]$, the Q ligands are now *syn* to each other. One could speculate on the preference of Q donors to place themselves *syn* or *anti*: many factors can be invoked to explain the different behaviour, such as packing forces or polarity of the donors around barium. However, more crystallographic data are required to find trends and to formulate hypotheses.

The packing of the molecules (Fig. 5) is influenced by stacking interactions between phen ligands of neighbouring molecules at the interplane distances of 3.47 Å. The phen ligands are parallel and a little bit shifted to form chains along the *z* axis with a Ba · · · Ba distance of 9.32 Å. The more distant Ba · · · Ba separations between chains (>13 Å) are due to van der Waals contacts of Ph and Bu^t groups of Q ligands from different molecules.

Conclusion

Our study provides detailed insight into structural aspects of a number of systems containing barium(II) β-diketonates and mono- or poly-dentate *N*- and *O*-donor ligands. This work demonstrates that a combination of acylpyrazolonates, a new class of β-diketonates, and ancillary ligands such as *O*-donor polyethers or mono-, bi-, tri- and tetra-dentate *N*-donor ligands give rise to mononuclear or dinuclear complexes, depending on the nature of the ligand and some other factors. Generally, one can observe this tendency by examining a number of barium diketonate complexes with known crystal structures.[34] Among the factors that cause the formation of either mono- or dinuclear complexes we mention the stoichiometry of the reagents and the steric hindrance of the ligands involved in co-ordination as well as the realisation of supramolecular struc-

Table 1 Crystal data and summary of data collection and refinement for compounds **1**, **2**, **5** and **11**

	1	**2**	**5**	**11**
Formula	$C_{66}H_{86}Ba_2Cl_6N_8O_{12}$	$C_{42}H_{60}BaN_4O_9$	$C_{56}H_{54}BaN_8O_4$	$C_{76}H_{92}Ba_2N_{16}O_8$
M	1670.80	902.28	1040.43	1710.44
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
a/Å	14.067(3)	7.955(2)	22.025(6)	13.467(2)
b/Å	18.070(4)	13.973(3)	13.830(4)	16.232(2)
c/Å	15.153(3)	20.565(5)	18.302(5)	18.730(3)
α/°		78.21(3)		
β/°	108.34(3)	87.52(2)	102.42(3)	98.09(2)
γ/°		77.08(2)		
V/Å^3	3656.1(13)	2181.0(9)	5444(3)	4053.6(10)
Z	4	2	4	4
D_c/g cm^{-3}	1.518	1.374	1.365	1.401
μ/mm^{-1}	1.353	0.967	0.785	1.030
T/K	130(2)	180(2)	180(2)	180(2)
Reflections collected	26096	17085	20198	23994
Reflections unique	7146	7972	5212	6317
Data/parameters	6153/444	6043/515	3998/343	5560/495
$R1$, $wR2$	0.0519, 0.1131	0.0366, 0.0658	0.0340, 0.0664	0.0295, 0.0771

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **5** and **11**

	1	**2**	**5**	**11**
Ba–O(1)	2.822(3)	2.665(3)	2.644(2)	2.815(2)
Ba–O(2)	2.819(4)	2.751(3)	2.753(2)	2.794(2)
Ba–O(3)	2.575(3)	2.718(3)		2.617(2)
Ba–O(4)	2.625(3)	2.682(3)		2.684(2)
Ba–O(5)	2.726(3)	2.848(3)		
Ba–O(6)	2.998(4)	2.841(3)		
Ba–O(7)		2.912(3)		
Ba–O(8)		2.892(3)		
Ba–O(9)		2.795(3)		
Ba′–O(1)	2.881(3)			2.865(2)
Ba′–O(2)	2.948(3)			2.785(2)
Ba–N(3)			2.898(3)	
Ba–N(4)			2.946(3)	
Ba–N(5)				2.896(3)
Ba–N(7)				2.790(3)
Ba · · · Ba′	3.9738(8)			3.8681(6)
O(1)–Ba–O(2)	59.00(9)	64.42(9)	64.81(7)	60.61(6)
O(1)–Ba–N(3)			115.73(9)	
O(1)–Ba–N(4)			99.08(8)	
O(2)–Ba–N(3)			70.55(8)	
O(2)–Ba–N(4)			109.16(9)	
N(3)–Ba–N(4)			55.90(8)	
O(3)–Ba–O(4)	66.79(11)	65.60(8)		66.39(7)
O(1)–Ba–O(4)	150.49(10)	91.28(9)		73.74(6)
O(1)–Ba–O(3)	139.07(10)			78.33(6)
O(2)–Ba–O(4)	91.83(10)			127.18(6)
O(2)–Ba–O(3)	141.93(9)	141.00(9)		79.08(6)
O(5)–Ba–O(6)	97.32(11)	58.46(9)		
O(6)–Ba–O(7)		57.71(9)		
O(7)–Ba–O(8)		58.96(10)		
O(8)–Ba–O(9)		57.74(9)		
O(4)–Ba–O(9)		72.29(10)		
O(4)–Ba–O(7)		133.79(9)		
O(5)–Ba–O(9)		136.74(9)		
N(5)–Ba–N(7)				76.48(10)
O(3)–Ba–N(5)				116.49(8)
O(3)–Ba–N(7)				87.21(9)
O(4)–Ba–N(5)				73.22(8)
O(4)–Ba–N(7)				123.52(9)
Ba–O(1)–Ba′	88.34(8)			85.84(6)
Ba–O(2)–Ba′	87.07(9)			87.79(6)
O(2)–Ba–O(5)	94.53(11)			
O(2)–Ba–O(6)	116.69(10)			

tures in the crystal. The role of steric hindrance can be seen when comparing the complexes with mono-, di- and tri-dentate neutral ligands on one hand and tetra- or penta-dentate ligands (triglyme, tetraglyme and others) on the other.[34] Concerning the compounds discussed in this paper, the important factor stabilising the structure is the ability of the ligands to form intermolecular hydrogen bonds, especially, favoured by the presence of the hydrogen donor and acceptor atoms in one molecule. In the case of the ligands that contain a conjugated aromatic system (for example, phenanthroline), π–π stacking interaction can be an important reason for the stability of a supramolecular network in the crystal structure.[36]

The use of *N*- and *O*-donors such as phen and tetraglyme results in mononuclear species, whereas in the case of the additional ligands containing protonated donor atoms (imidazole, alcohol or water) the dimeric structure is preferable due to the formation of the hydrogen bonding system.

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References

1 T. Ozawa, *Thermochim. Acta*, 1991, **174**, 185.
2 H. Zama and Sh. Oda, *Jpn. J. Appl. Phys.*, 1990, **29**, L1072.
3 A. D. Berry, D. K. Gaskill, R. T. Holm, E. J. Cukauskas, R. Kaplan and R. L. Henry, *Appl. Phys. Lett.*, 1988, **52**, 1743.
4 A. Glezies, A. Drozdov and S. Troyanov, *Koord. Khim.*, 1994, **20**, 922.
5 A. Drozdov and S. Troyanov, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1619.
6 D. C. Bradley, M. Hasan, M. B. Hursthouse, M. Motevalli, O. F. Z. Khan, R. C. Pritchard and J. O. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 575.
7 R. E. Sievers, S. B. Turnipseed, L. Huang and A. F. Lagalante, *Coord. Chem. Rev.*, 1993, **128**, 285.
8 E. C. Okafor and B. A. Uzoukwu, *Synth. React. Inorg. Met.-Org. Chem.*, 1991, **21**, 1375.
9 E. C. Okafor. P. U. Adiukwu and B. A. Uzoukwu, *Synth. React. Inorg. Met.-Org. Chem.*, 1993, **23**, 97.
10 C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, E. Mundorff, M. Rossi and F. Caruso, *J. Organomet. Chem.*, 1998, **557**, 187 and refs. therein.
11 C. Pettinari, F. Accorroni, A. Cingolani, F. Marchetti, A. Cassetta and L. Barba, *J. Organomet. Chem.*, 1998, **566**, 187.
12 F. Marchetti, C. Pettinari, A. Cingolani, D. Leonasi, M. Camalli and A. Pifferi, *Polyhedron*, 1996, **15**, 3835.
13 F. Marchetti, C. Pettinari, A. Cingolani, D. Leonesi, A. Drozdov and S. Troyanov, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3325.
14 Y. A. Zolotov and N. M. Kuzmin, in *Metal Extraction with Acylpyrazolones*, Izdat Nauka, Moscow, 1977.

15 E. C. Okafor, *Z. Naturforsch.*, *Teil B*, 1981, **36**, 213.
16 S. Umetani and H. Freiser, *Inorg. Chem.*, 1987, **26**, 3179.
17 E. C. Okafor and B. A. Uzoukwu, *Radiochim. Acta*, 1990, **51**, 167.
18 K. Venkataraman, in *The Chemistry of Dyes*, Academic Press, New York, 1952, vol. 1.
19 M. F. McMahon, K. C. Molloy, B. A. Omotowa and M. A. Mesubi, *J. Organomet. Chem.*, 1996, **511**, 227.
20 M. F. McMahon, K. C. Molloy, B. A. Omotowa and M. A. Mesubi, *J. Organomet. Chem.*, 1996, **525**, 239.
21 D. S. Schulz, B. J. Hinds, C. L. Stern and T. J. Marks, *Inorg. Chem.*, 1993, **32**, 249.
22 T. J. Marks, *Pure Appl. Chem.*, 1995, **67**, 313.
23 B. A. Uzoukwu, P. U. Adiukwu, S. S. Al-Juaid, P. B. Hitchcock and J. D. Smith, *Inorg. Chim. Acta*, 1996, **250**, 173.
24 S. R. Drake, S. A. S. Miller and D. J. Williams, *Inorg. Chem.*, 1993, **32**, 3227.
25 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.
26 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
27 A. Drozdov and S. Troyanov, *Polyhedron*, 1993, **12**, 2973.
28 S. Roffia, M. Marcaccio, C. Paradisi, F. Paolucci, V. Balzani, G. Denti, S. Serroni and S. Campagna, *Inorg. Chem.*, 1993, **32**, 3003.
29 A. Drozdov and S. Troyanov, *Koord. Khim.*, 1994, **20**, 171.
30 S. R. Drake, M. B. Hursthouse, K. M. A. Malik and S. A. S. Miller, *Inorg. Chem.*, 1993, **32**, 4653.
31 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley Interscience, New York, 1986, ch. III, pp. 208–213.
32 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley Interscience, New York, 1986, ch. III, pp. 259–268.
33 W. S. Rees, M. W. Carris and W. Hesse, *Inorg. Chem.*, 1991, **30**, 4479.
34 A. Drozdov and S. Troyanov, *Main Group Met. Chem.*, 1996, **19**, 547.
35 N. Kuzmina, A. Drozdov, T. Zotova, G. Kupryanova, A. Pisarevsky and Yu Struchkov, *Koord. Khim.*, 1994, **20**, 743.
36 N. Kuzmina, V. Ivanov, S. Troyanov and L. Martynenko, *J. CVD*, 1994, **3**, 32.

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