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FULL PAPER

Copper and calcium complexes with the anionic O_2-donor 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato (Q^-). Influence of hydrogen-bond interactions on lattice architecture in the crystal structures of $[CuQ_2(H_2O)]$ and $[CaQ_2(EtOH)_2]$

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

[a] *Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino, 1, 62032 Camerino (MC), Italy. E-mail: pettinar@camserv.unicam.it*

[b] *Department of Chemistry, Moscow State University, Vorobjevy Gory, 119899 Moscow, Russia. E-mail: drozdov@inorg.chem.msu.ru*

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By interaction of 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-one (HQ) with $Cu(O_2CCH_3)_2 \cdot H_2O$ in EtOH, the derivative $[CuQ_2(H_2O)]$ **1** has been synthesized. It possesses a square-pyramidal structure with the asymmetric β-diketonate ligands arranged in an "*anti*" configuration to each other and with a molecule of H_2O at the apex of polyhedron. Both protons of H_2O are involved in an intermolecular hydrogen-bonding network with pyridinic nitrogen atoms of Q donors belonging to two neighbouring complexes. Compound **1** reacts with substituted phenanthrolines (2,9-Me_2Phen with 4,7-Ph_2Phen) in Et_2O to give $[CuQ_2(2,9\text{-}Me_2Phen)]$ and $[CuQ_2(4,7\text{-}Ph_2Phen)]$ derivatives. During the reaction of **1** with an excess of 2,9-Me_2Phen in EtOH reduction of copper(II) to copper(I) was observed with formation of the ionic diamagnetic copper(I) derivative $[Cu(2,9\text{-}Me_2Phen)]Q$. Ethylenediamine (en) reacted with **1** affording the ionic complex $[Cu(en)_3]Q_2 \cdot 2H_2O$. By interaction of **1** with *N*-methylimidazole (N-MeIm) the compound $[CuQ_2(N\text{-}MeIm)_2]$ has been isolated. Finally the P-donors triphenylphosphine and tricyclohexylphosphine (PCy_3) reduced copper(II) affording the copper(I) derivatives $[CuQ(PPh_3)_2]$ and $[CuQ(PCy_3)_2]$. The reaction between HQ and $CaCl_2$ in basic (KOH) EtOH produced the derivative $[CaQ_2(EtOH)_2]$. It contains the calcium atom in an axially distorted octahedral environment with the two β-diketonate ligands in "*anti*" positions and the EtOH molecules *trans* to each other. The O–Ca–O axis is bent [172.86(6)°]. The protons of the solvent molecules are involved in a hydrogen-bonding network with the nitrogen atoms of Q donors of other molecular units, and the structure is constituted of infinite chains. The derivatives $[CaQ_2(ROH)_2]$ have been obtained in alcoholic ROH solvents when R = Me, Et or Pr^i, whereas the $[CaQ_2(H_2O)_2]$ complex formed when R = Bu^t, $HC{\equiv}CCH_2$ or $Pr^i(Bu^t)CH$. The interaction between $[CaQ_2(EtOH)_2]$ and 1,10-phenanthroline afforded the adduct $[Ca(Q)_2(Phen)_2]$.

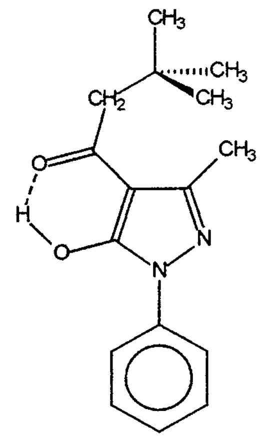
There is a great interest in discovering new co-ordination compounds as suitable molecular precursors to inorganic thin films, useful for the modern electronics and computer hardware industries.[1] A vast literature reports on the applications of copper(II)-β-diketonates to CVD processes[2] and several papers are focused on the structures of $[Cu^{II}(\beta\text{-dike})_2L]$ ($L = H_2O$, NH_3, pyridine, *etc.*) and on the influence of monodentate donors L on the volatility and stability of the precursors.[3–5] Alkaline-earth metal β-diketonate complexes also have recently provoked a growing interest as suitable precursors in the synthesis of high T_c superconducting films.[6–12] Knowledge of the crystal structure of such derivatives gives us not only sufficient information about the nuclearity of the complex molecule, but is important in understanding the behaviour of these compounds in the vapour phase, and the mechanisms of sublimation and decomposition. However, only a few calcium β-diketonato complexes have been crystallographically studied so far.[13–18] We have recently undertaken a systematic study of the chemical and structural properties and of the co-ordination behaviour of a family of asymmetric β-diketones named 4-acylpyrazol-5-ones (HQ) toward metal acceptors such as tin,[19–26] cadmium[27,28] and copper,[29] which are currently used in the synthesis of electronic devices. The acylpyrazolones are extensively employed as metal extractants[30–33] and as pigments for dyes.[34] They possess a pyrazole ring fused to the β-diketone moiety, which induces changes in the physico-chemical properties of their metal and organometallic derivatives, with respect to analogous acetylacetonato compounds. In the acylpyrazolone ligands the carbonyl fused to the heterocyclic ring generally forms the stronger metal–oxygen bond as compared with another one in the 4-acyl moiety. Complexes MQ_2L_2 generally contain two sets of M–O bond distances with the Q donors always arranged in a "*syn*" configuration around the metal, thus leading to a distorted octahedral geometry.[19–26,35,36] These ligands possess an additional donor centre, the pyridinic nitrogen atom of the pyrazole, which in some cases is involved in secondary bonding interactions and influences the whole structure of the metal derivatives. For example, in lead(II) bis(4-acylpyrazol-5-onate), the lead atom is found to be six-co-ordinated, being surrounded by four oxygen atoms of the two donors and also by the nitrogen atoms of two donors belonging to other molecular units.[37] In the analogous tin(II) derivative the tin atom is only co-ordinated by the four oxygen atoms.[38] Additionally, in triorganotin(IV) complexes the nitrogen atom participates in an intermolecular hydrogen-bond network (with water absorbed from atmospheric moisture), thus stabilising the trialkylmonoaquatin(IV) 4-acylpyrazol-5-onate complexes in an unexpected *TBPY* (trigonal bipyramidal) geometry.[39,40]

In a previous work[29] we have reported the synthesis and spectroscopic characterisation of copper-(I) and -(II) derivatives with 4-acylpyrazol-5-one donors containing not very hindered R^1 moieties. During recent years some papers regarding the

† Corresponding author for the crystal structures.

interaction of acylpyrazolonates with alkaline-earth metals appeared, but no structural determination of such derivatives has been reported.[41,42]

A well known strategy to induce changes in the properties of co-ordination complexes is based on the introduction of hindered substituents in peripheral positions of the corresponding polydentate donors. In this paper we present the synthesis, spectroscopic and structural characterisation of copper(II) and calcium derivatives of 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-one (HQ), a novel ligand containing a bulky neopentyl radical in the 4-acyl moiety. The reactivity of these compounds towards mono- and bi-dentate neutral N- and P-donors has also been investigated.



Results and discussion

The copper derivative $[CuQ_2(H_2O)]$ **1** has been obtained from HQ and $Cu(O_2CCH_3)_2{\cdot}H_2O$ in ethanol at room temperature. It is a dark green high melting solid, soluble in dmso, acetone, acetonitrile and chlorinated solvents forming non-electrolyte solutions. The IR spectrum shows a very strong and broad absorption between 2400 and 3500 cm^{-1} attesting the presence of an extensive intermolecular hydrogen-bond interaction. The ν(C=O) shifts to lower frequencies (from 1642 to 1602 cm^{-1}) upon co-ordination and several medium to strong absorption bands appear at 466, 451, 369, 274 and 269 cm^{-1} assignable to Cu–O stretching modes.[43] The UV/VIS spectrum in chloroform shows two strong bands at 256 and 294 nm due to intraligand transitions and a broad and very weak band at 672 nm ($\varepsilon = 40$ dm^3 mol^{-1} cm^{-1}), likely due to an envelope of absorptions caused by d–d transitions.[44]

The compound **1** has a molecular structure with the copper atom in a square-pyramidal environment (Fig. 1). Selected bond angles and distances are reported in Table 1. The oxygen atoms of the two β-diketonate ligands lie in the plane of a square pyramid. The values of the Cu–O bond distances are in the range 1.91–1.96 Å that is typical for copper(II) diketonates, *e.g.* acetylacetonate (1.92 Å),[45] benzoylacetonate (1.91–1.93 Å),[46] and hexafluoroacetylacetonate (1.911 Å).[47] The water molecule occupies the apex in the pyramid, with Cu–O distance 2.25 Å. A description as a five-co-ordinated species can be made in terms of the distance ρ (Å) from copper to the average plane of the four ligands.[48] In **1** the copper atom is situated 0.14 Å above the square plane ($\rho = 0.14$ Å), and the bites of the Q ligands are 93.0 and 92.5°.

A quantitative measure suggested[49] for comparing real structural parameters to idealised limiting geometries on the Berry pathway (*i.e.* a square pyramid and a trigonal bipyramid) and quantifying the degree of stereochemical distortion is the geometric parameter $\tau = 100(\beta - \alpha)/60$, where $\beta > \alpha$ and α and β are the *trans* angles not involving a unique ligand; τ values range from zero to 100% on going from perfectly tetragonal-pyramidal to trigonal-bipyramidal geometries, respectively.

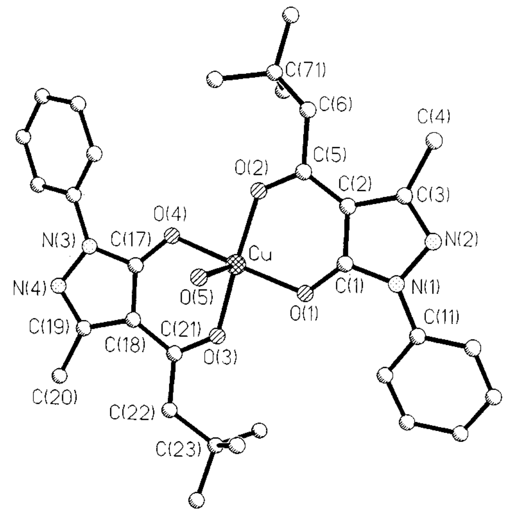


Fig. 1 Molecular structure of $[CuQ_2(H_2O)]$.

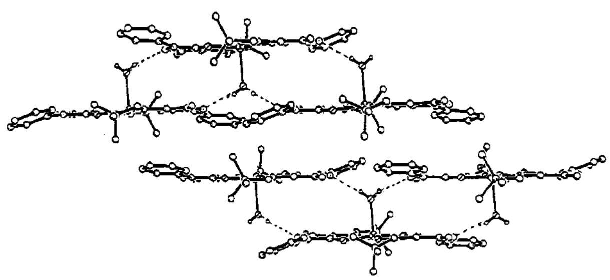


Fig. 2 Formation of hydrogen bonded chains in the crystal structure of $[CuQ_2(H_2O)]$.

By this criterion, structure **1** [$\alpha = 170.79(14)$ and $\beta = 172.1(2)°$] is 2.17% distorted from the ideal square-pyramidal geometry, less than $[Cu(hfac)_2(H_2O)]$ (Hhfac = 1,1,1,5,5,5-hexafluoroacetylacetone).[5]

The oxygen atoms of the acyl moieties of the two donors are *trans* in the plane, so that the Q donors are arranged in "*anti*" positions to each other, as previously found in the structure of bis(1-phenylbutane-1,3-dionato)copper(II).[46]

Both hydrogen atoms of H_2O are involved in hydrogen bonds with pyridinic nitrogen atoms of Q donors ligands of two different complex molecules (O···N distances are 2.902 or 2.886 Å, and O–H···N angles are 171.0 or 165.0°, respectively). The system of hydrogen bonds connects the molecules into infinite chains as shown in Fig. 2, whereas only van der Waals contacts have been established between the chains.

Intramolecular hydrogen-bonding interactions are also present: the distance between the *ortho*-H of phenyl in Q and the oxygen in the 5-carbonyl is less than the sum of van der Waals radii of H and O atoms (H···O 2.21 or 2.34 Å and C–H···O 125.3 or 117.8° respectively). Similar to it is the interaction between the oxygen O(2) and a hydrogen atom of the neopentyl group in the 4-acyl moiety of Q (H···O 2.30 or 2.37 Å and C–H···O 124.2 or 119.3° respectively). The former contact has also been found in other complexes with acylpyrazolonato donors, but the latter is new, being a particular feature of this ligand with the sterically hindered neopentyl group in the 4-acyl moiety. According to a recent study[50] on the hydrogen bonds involving H atoms linked to carbon atoms, we do not consider the contacts between carbonyl oxygens and phenyl or *tert*-butyl fragments in the structure as hydrogen bonds. The rotation of phenyl fragments around N–C bonds (15–17°) are indicative of repulsive interactions with carbonyl oxygens. For instance, H···O distances in our structure are 2.21–2.37 Å but not 1.98 Å as in 1-methoxy-15,16-dihydrocyclopenta[*a*]phenanthren-17-one treated as an example of intramolecular hydrogen bonding.[50]

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Cu–O(1)	1.911(3)	N(3)–C(17)	1.365(6)
Cu–O(2)	1.938(3)	N(3)–N(4)	1.401(5)
Cu–O(3)	1.956(3)	N(3)–C(27)	1.411(5)
Cu–O(4)	1.923(3)	N(4)–C(19)	1.302(6)
Cu–O(5)	2.248(4)	C(1)–C(2)	1.414(6)
O(1)–C(1)	1.279(5)	C(2)–C(5)	1.394(7)
O(2)–C(5)	1.266(6)	C(2)–C(3)	1.431(6)
O(3)–C(21)	1.262(5)	C(3)–C(4)	1.505(6)
O(4)–C(17)	1.281(5)	C(5)–C(6)	1.519(8)
N(1)–C(1)	1.359(5)	C(17)–C(18)	1.414(6)
N(1)–N(2)	1.398(4)	C(18)–C(21)	1.414(6)
N(1)–N(11)	1.409(5)	C(18)–C(19)	1.431(6)
N(2)–C(3)	1.293(6)	C(19)–C(20)	1.507(6)
O(1)–Cu–O(4)	170.79(14)	C(3)–N(2)–N(1)	106.8(3)
O(1)–Cu–O(2)	92.95(13)	C(17)–N(3)–N(4)	110.8(3)
O(4)–Cu–O(2)	87.27(13)	C(17)–N(3)–C(27)	129.7(3)
O(1)–Cu–O(3)	86.01(12)	N(4)–N(3)–C(27)	119.3(3)
O(4)–Cu–O(3)	92.50(13)	C(19)–N(4)–N(3)	106.2(3)
O(2)–Cu–O(3)	172.1(2)	O(1)–C(1)–N(1)	122.8(4)
O(1)–Cu–O(5)	94.99(14)	O(1)–C(1)–C(2)	130.5(4)
O(4)–Cu–O(5)	94.2(2)	N(1)–C(1)–C(2)	106.7(3)
O(2)–Cu–O(5)	94.4(2)	C(5)–C(2)–C(1)	122.5(4)
O(3)–Cu–O(5)	93.5(2)	C(5)–C(2)–C(3)	133.0(4)
C(1)–O(1)–Cu	122.0(3)	C(1)–C(2)–C(3)	104.3(4)
C(5)–O(2)–Cu	129.9(3)	N(2)–C(3)–C(2)	111.7(4)
C(21)–O(3)–Cu	129.8(3)	N(2)–C(3)–C(4)	118.7(4)
C(17)–O(4)–Cu	121.1(3)	C(2)–C(3)–C(4)	129.7(3)
C(1)–N(1)–N(2)	110.5(3)	O(2)–C(5)–C(2)	121.7(4)
C(1)–N(1)–C(11)	130.2(3)	O(2)–C(5)–C(6)	118.0(5)
N(2)–N(1)–C(11)	118.9(3)		

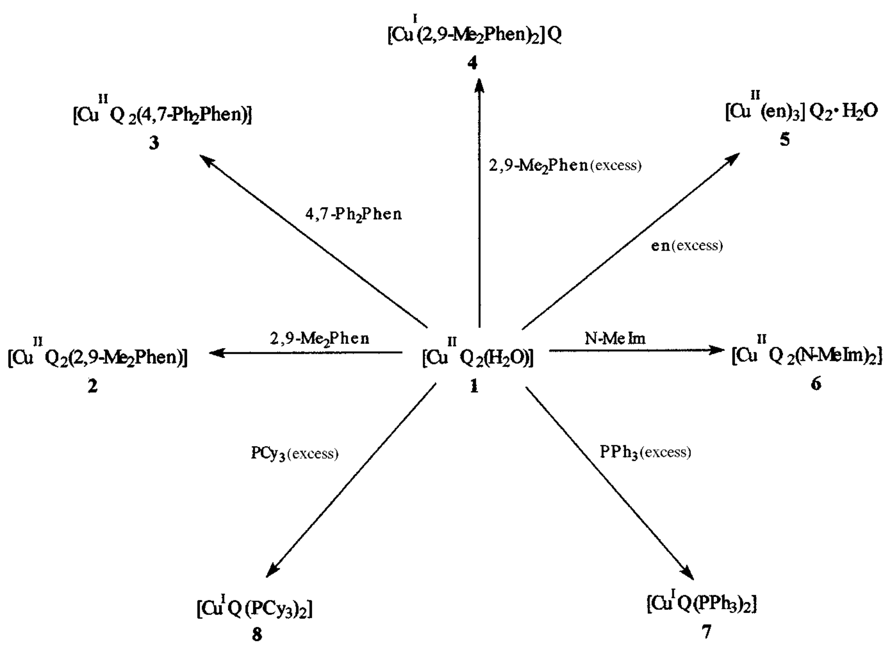
As for many other copper(II) β-diketonates, the compound **1** can be sublimed *in vacuo* with loss of the water molecule. Testing **1** as a precursor in a CVD reactor under nitrogen we succeeded in depositing a thin film of copper.

We have also tested the reactivity of compound **1** towards neutral mono- and bi-dentate donors (Scheme 1), such as *N*-methylimidazole (N-MeIm), triphenylphosphine (PPh_3), 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2Phen), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2Phen), and ethylenediamine (en). By the reaction between equimolar quantities of **1** and N_2-bidentate donors 2,9-Me_2Phen and 4,7-Ph_2Phen in diethyl ether the 1 : 1 adducts **2** and **3** have been isolated. They likely possess a distorted octahedral geometry, as previously found in similar [Cu(β-dike)$_2$(N_2-donor)] derivatives.[51–53]

By using an excess of 2,9-Me_2Phen in a mixture of Et_2O and EtOH the diamagnetic copper(I) compound [Cu(2,9-Me_2-Phen)$_2$Q] **4** has been obtained. The presence of a protic solvent such as ethanol seems to be necessary for the reduction of copper, which likely proceeds through a mechanism involving a β-diketonate ligand and a solvent molecule.[47,54] In the ^{1}H NMR spectrum the integration of the signals confirms the formulation proposed from elemental analyses. There is a unique set of resonances for the Q ligand and for the 2,9-Me_2Phen donors and, based on the conductivity value in dichloromethane (40.1 Ω^{-1} cm^2 mol^{-1}), it is possible to propose an ionic structure [Cu(2,9-Me_2Phen)$_2$]Q, with the copper atom tetrahedrally surrounded by two bidentate 2,9-Me_2Phen molecules, whereas the acylpyrazolonate Q ligand is out of the co-ordination sphere. Moreover, the ν(Cu–O) band is absent in the far-infrared region, indicating ionic character of the acylpyrazolonate also in the solid state. The UV/VIS spectrum of this derivative shows a medium to strong charge transfer absorption (ε = 3300 dm^3 mol^{-1} cm^{-1}) at 458 nm, which is the cause of the intense red colour of the complex.[55]

By the interaction of compound **1** with an excess of ethylenediamine in ethanol a blue-lilac derivative of empirical formula $CuQ_2(en)_3(H_2O)_2$ **5** has been isolated. The IR spectrum of **5** shows two strong absorption bands at 3261 and 3150 cm^{-1} due to co-ordinated NH_2 groups of ethylenediamine. All the six nitrogen atoms are likely bonded to copper as in the IR spectrum there is no absorption over 3500 cm^{-1} characteristic for a free NH_2 group.[56] Moreover, the ν(C=O) vibration falls to 1607 cm^{-1}. A broad band at 3430 cm^{-1} can be assigned to ν(O–H···O) of water, as indicated by elemental analysis. In conclusion we can suppose an ionic structure [Cu(en)$_3$]Q_2·2H_2O similar to that found for the complex [Cu(en)$_3$]SO_4.[57]

Conductivity measurements were carried out in different solvents to study the stability of compound **5** in solution. In dichloromethane and acetone decomposition occurs, the non-electrolyte solutions immediately changing from blue to green. Quite the reverse occurs in ethanol: a solution 10^{-3} mol dm^{-3} gives a conductivity value of 22.7 Ω^{-1} cm^2 mol^{-1}, indicative of a 1 : 1 electrolyte. This result can be explained in terms of formation of an intermediate species such as [Q(en)Cu$^+$]Q$^-$, an explanation previously proposed with similar derivatives.[56] The UV/VIS spectrum, which has been recorded in ethanol, seems to confirm this hypothesis, showing a medium to weak absorption (ε = 110 dm^3 mol^{-1} cm^{-1}) at 558 nm, very near to



Scheme 1

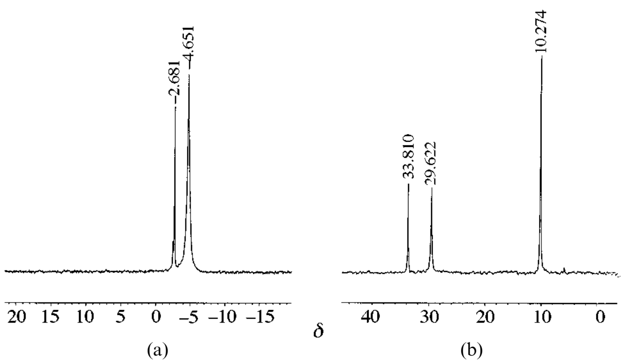


Fig. 3 The ^{31}P NMR spectra of (a) compound **7** at -10 °C, (b) **8** at -50 °C.

that (546 nm) for the complex $[Cu(en)_2]SO_4$.[56] In the species existing in ethanol solution the copper atom could be six-co-ordinated, with two bidentate donors (Q and en) in the equatorial plane and two axially co-ordinated solvent molecules (EtOH).

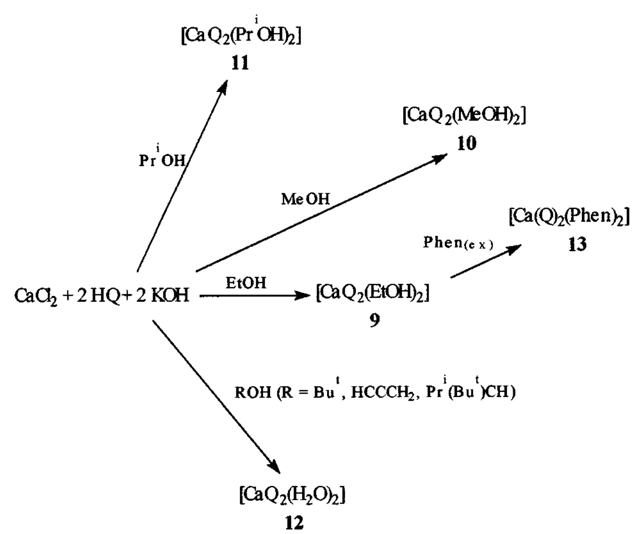
From the reaction between derivative **1** and *N*-methylimidazole in diethyl ether, $[CuQ_2(N\text{-}MeIm)_2]$ **6** has been obtained. On the basis of conductivity and far-IR data, a six-co-ordinate neutral structure is likely.

By the interaction of compound **1** with reducing agents such as triphenylphosphine (PPh_3) and tricyclohexylphosphine (PCy_3) the copper(I) derivatives $[CuQ(PPh_3)_2]$ **7** and $[CuQ(PCy_3)_2]$ **8** have been synthesized. In the ^{1}H NMR spectra the integration of the signals is in accordance with the formulation proposed. Derivative **7** likely contains a four-co-ordinated copper atom in a strongly distorted tetrahedron, as we have found in the crystal structure previously reported for an analogous copper(I) complex,[29] and a ^{31}P NMR study in the range from +20 to -70 °C showed that the absorbance at δ -3.73 at room temperature is split into two signals at -10 °C (Fig. 3). In the proton NMR spectrum two sets of resonances for each equivalent proton of Q have been detected, in accordance with the existence of an equilibrium between a four- and a three-co-ordinate species, containing a monodentate acylpyrazolonate donor.[29] In the IR spectrum of copper(I) derivative **7** the ν(C=O) is at higher frequencies (1622 cm^{-1}) with respect to those found for copper(II) derivatives **1**–**3** and **6**.[29] In the far-IR region the characteristic envelope of absorptions, caused by y modes of vibrations of triphenylphosphine,[58,59] has been detected at about 500 cm^{-1}, whereas the bands assignable to ν(Cu–O) have been found at slightly lower frequencies (444 cm^{-1} and below) with respect to those found for **1**–**3** and **6** (472 cm^{-1} and below), a fact explainable with the different oxidation state of copper which influences the strength of the Cu–O bonding.

In the proton NMR spectrum of derivative **8** we found the same multiplicity as observed for **7**. The room temperature ^{31}P NMR spectrum showed a sharp resonance at δ +34 and two broad absorbances at δ +29 and +11, which became sharp at -50 °C (Fig. 3). The latter is due to free PCy_3, whereas those at δ +29 and +34 are likely caused by the species $[CuQ(PCy_3)_2]$ and $[CuQ(PCy_3)]$ respectively.[60] In conclusion the following equilibrium in solution can be hypothesised: $[CuQ(PCy_3)_2] \rightleftharpoons [CuQ(PCy_3)] + PCy_3$.

The calcium derivative $[CaQ_2(EtOH)_2]$ **9** was synthesized from the interaction between HQ and $CaCl_2$ in basic ethanol at room temperature. The presence of ethanol has been confirmed by the ^{1}H NMR spectrum. Calcium co-ordinates molecules of solvent to increase its co-ordination number from 4 to 6. We sought to test how steric hindrances in the solvent (ROH) can influence the stoichiometry and the stability of corresponding metal derivatives (Scheme 2).

By using MeOH or Pr^{i}OH, which do not contain sterically hindered R groups, we have obtained the corresponding



Scheme 2

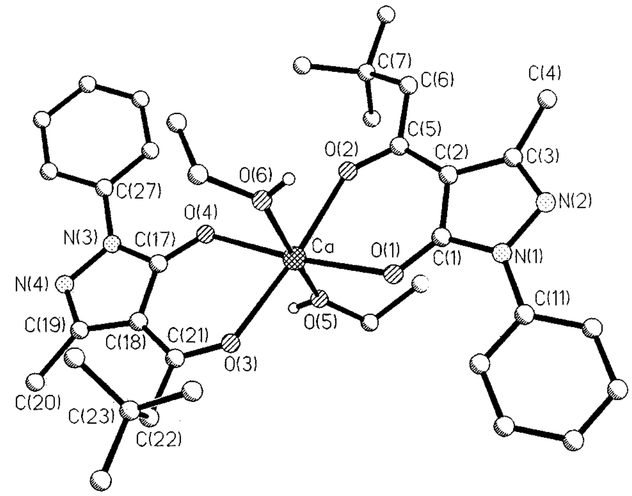


Fig. 4 Molecular structure of $[CaQ_2(EtOH)_2]$.

calcium derivatives $[CaQ_2(MeOH)_2]$ **10** and $[CaQ_2(Pr^iOH)_2]$ **11**, whereas in the reaction with Bu^{t}OH, HC≡CCH$_2$OH or Pr^i(Bu^t)CHOH in all the cases the hydrated product $[CaQ_2(H_2O)_2]$ **12** has been isolated.

The crystal structure of $[CaQ_2(EtOH)_2]$ **9** consists of discrete mononuclear units, in which calcium is situated in a distorted octahedral environment, surrounded by two acylpyrazolonate ligands and two ethanol molecules in *trans* positions (Fig. 4). Selected bond distances and angles are reported in Table 2. The acylpyrazolonate anions act as bidentate O-donor ligands similar to aliphatic β-diketonates. Thus, Ca–O(Q) distances in **9** (2.29–2.31 Å) are similar to those in $[Ca(acac)_2(H_2O)_2]$ (2.32–2.34 Å, calcium atom being also six-co-ordinated)[18] and are shorter than Ca–O (acac) distances in $[Ca(MeCO_2)(acac)(H_2O)_2]$ (2.39 Å, calcium atom is eight-co-ordinated).[14] The acylpyrazolonate ligands in **9** are situated in *trans* positions, not *cis* as in $[Ca(acac)_2(H_2O)_2]$[18] and $[Mg(acac)_2(H_2O)_2]$.[61] The calcium atom is located in the plane of the two six-membered β-diketonate rings. The distances Ca–O (EtOH) in **9** (2.35, 2.37 Å) are close to those in $[Ca_4(dbzm)_8(EtOH)_2]$ (2.41 Å) (Hdbzm = dibenzoylmethane).[13]

The O(5)–Ca–O(6) axis is bent [172.86(6)°]. The bites of the Q donors are 75.97(6) and 76.33(6)°, much less than the value of 90° expected for an ideal octahedron and also less than the bites found in the structure of copper derivative **1**. However, they are similar to those found in other calcium β-diketonates.[13–18] The tetragonal distortion can be ascribed to the lower donor power of the oxygen atoms of ethanol molecules with respect to

Table 2 Selected bond lengths (Å) and angles (°) for compound **9**

Ca–O(1)	2.291(2)	N(2)–C(3)	1.315(3)
Ca–O(2)	2.290(2)	N(3)–C(17)	1.380(3)
Ca–O(3)	2.310(2)	N(3)–N(4)	1.394(3)
Ca–O(4)	2.293(2)	N(3)–C(27)	1.419(3)
Ca–O(5)	2.345(2)	N(4)–C(19)	1.320(3)
Ca–O(6)	2.368(2)	C(1)–C(2)	1.432(3)
O(1)–C(1)	1.262(2)	C(2)–C(3)	1.425(4)
O(2)–C(5)	1.244(3)	C(2)–C(5)	1.429(3)
O(4)–C(17)	1.254(3)	C(3)–C(4)	1.500(4)
O(3)–C(21)	1.245(3)	C(5)–C(6)	1.518(3)
O(5)–C(33)	1.428(3)	C(6)–C(7)	1.543(4)
O(6)–C(35)	1.436(3)	C(7)–C(10)	1.518(4)
N(1)–C(1)	1.378(3)	C(7)–C(9)	1.522(4)
N(1)–N(2)	1.396(3)	C(7)–C(8)	1.536(4)
N(1)–C(11)	1.420(3)		
O(2)–Ca–O(1)	75.97(6)	C(5)–O(2)–Ca	140.2(2)
O(2)–Ca–O(4)	98.19(6)	C(17)–O(4)–Ca	129.78(14)
O(1)–Ca–O(4)	174.15(6)	C(21)–O(3)–Ca	138.34(14)
O(2)–Ca–O(3)	174.35(6)	C(33)–O(5)–Ca	135.7(2)
O(1)–Ca–O(3)	109.52(6)	C(35)–O(6)–Ca	131.2(2)
O(4)–Ca–O(3)	76.33(6)	C(1)–N(1)–N(2)	111.2(2)
O(2)–Ca–O(5)	90.42(7)	C(1)–N(1)–C(11)	129.0(2)
O(1)–Ca–O(5)	94.95(7)	N(2)–N(1)–C(11)	119.7(2)
O(4)–Ca–O(5)	85.00(7)	C(3)–N(2)–N(1)	106.2(2)
O(3)–Ca–O(5)	90.54(7)	C(17)–N(3)–N(4)	111.2(2)
O(2)–Ca–O(6)	85.07(7)	C(17)–N(3)–C(27)	128.8(2)
O(1)–Ca–O(6)	89.33(7)	N(4)–N(3)–C(27)	119.2(2)
O(4)–Ca–O(6)	90.16(7)	C(19)–N(4)–N(3)	106.4(2)
O(3)–Ca–O(6)	93.51(7)	O(1)–C(1)–N(1)	122.8(2)
O(5)–Ca–O(6)	172.86(6)	O(1)–C(1)–C(2)	131.3(2)
C(1)–O(1)–Ca	129.47(14)	N(1)–C(1)–C(2)	105.9(2)

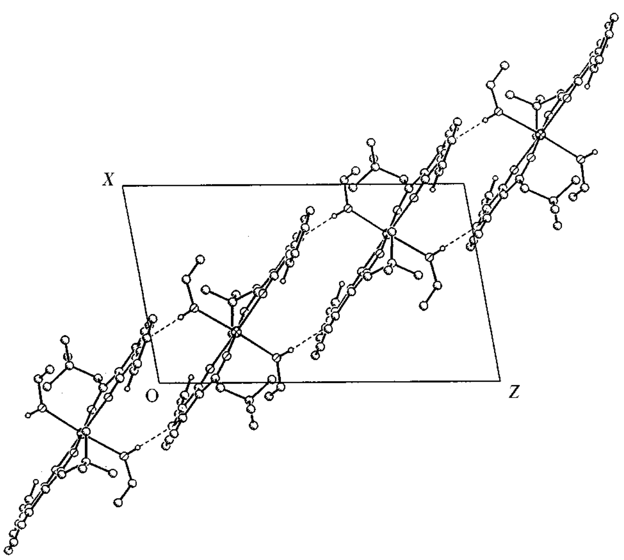


Fig. 5 Formation of hydrogen bonded chains in the crystal structure of $[CaQ_2(EtOH)_2]$.

those of the Q donors, co-ordinated in the O_2-bidentate monoanionic form. Also in this structure the two Q donors are arranged in "*anti*" configurations.

The protons of ethanol molecules are involved in a system of intermolecular hydrogen bonds with the pyridinic nitrogens (O–H · · · N 2.26 or 2.27 Å and 121.1 or 121.4°) of Q donors of other molecular units, to form infinite chains (Fig. 5).

Derivative **9** reacts with phenanthroline in hot chloroform giving the mixed-ligand complex $[CaQ_2(Phen)_2]$ **13** with a melting point lower than that of derivatives **9**–**12** and being soluble in chlorinated solvents, acetone and dmso. The IR spectrum shows a shift of ν(C=O) to higher frequencies (from 1591 to 1635 cm^{-1}) in agreement with a lengthening of the Ca–O bonds. In the far-IR region two strong absorptions at 242 and 225 cm^{-1} have been detected that are absent in the IR spectrum of **9**, and therefore can be tentatively assigned to Ca–N stretching modes.[62] The proton NMR spectrum shows a general downfield shift of the Q ligand resonances with respect to those of **9**, as a consequence of the lowering of electronic flow from acylpyrazolonates toward calcium. In the UV/VIS spectrum the band at 236 cm^{-1} has $\varepsilon = 39880$ dm^3 mol^{-1} cm^{-1} due to a Q intraligand transition, whereas that at 266 cm^{-1} possesses $\varepsilon = 88950$ dm^3 mol^{-1} cm^{-1}, thus confirming the presence not only of two Q ligands but also of two Phen donors. All this evidence is in accordance with the increase of the co-ordination number of calcium from 6 (in the starting derivative **9**) to 8 (in the adduct **13**), as previously found in the crystal structure of the analogous $[Ca(thd)_2(phen)_2]$ (Hthd = 2,2,6,6-tetramethylhepta-3,5-dione) complex.[17]

Conclusion

4-Acylpyrazol-5-onato derivatives of copper(II) and calcium(II) have been structurally characterised for the first time: the co-ordination environments of the metal atoms are similar to those found in analogous metal acetylacetonato complexes, but the supramolecular lattice structures are strongly influenced by the presence of the peripheral nitrogen atoms in the 4-acylpyrazol-5-onato donors, which are involved in a network of intermolecular hydrogen-bonding interactions with protic molecules directly bonded to the metal atoms. It is well known that the copper(II) β-diketonates crystallise without water in all the cases when the ligand is unfluorinated. The presence of a water molecule in the inner co-ordination sphere of **1** could be explained by a system of hydrogen bonds due to the presence of nitrogen atoms of azoles. The copper derivative reacts with several mono- and bi-dentate neutral donors to give some new neutral or ionic adducts. Moreover, copper(II) can be reduced to copper(I) not only by ethanol solutions of triphenylphosphine or tricyclohexylphosphine, but also by ethanol solutions of 2,9-Me_2Phen.

The calcium complex **9** is obtained in basic ethanol and is mononuclear, as shown by its crystal structure. It is interesting that, apart from the mixed polydentate ligand derivatives $[Ca(hfac)_2(triglyme)]$ (triglyme = 2,5,8,11-tetraoxadodecane),[16] $[Ca(hfac)_2(tetraglyme)]$ (tetraglyme = 2,5,8,11,14-pentaoxapentadecane)[16] and $[Ca(thd)_2(phen)_2]$,[17] the only mononuclear calcium β-diketonato compound previously crystallographically characterised is $[Ca(acac)_2(H_2O)_2]$.[18] Analogous $[CaQ_2(ROH)_2]$ derivatives have been obtained when R is not sterically hindered, otherwise the compound $[CaQ_2(H_2O)_2]$ was afforded. The interaction of **9** with Phen produced the likely eight-co-ordinate calcium adduct **13**.

Experimental

General comments

All the chemicals were purchased from Alfa (Karlsruhe) or Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried *in vacuo* to constant weight (20 °C, *ca.* 0.1 Torr). Elemental analyses (C, H, N) were performed with a Fisons Instruments 1108 CHNS-O Elemental Analyser. The IR spectra were recorded from 10000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument, ^{1}H and ^{31}P NMR spectra on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H and 121.4 MHz for ^{31}P). Proton chemical shifts are reported in ppm *vs.* $SiMe_4$ while phosphorus chemical shifts are in ppm *vs.* 85% H_3PO_4. The UV/VIS spectra were recorded in chloroform and ethanol solutions from 200 to 820 nm with a HP8452A diode array spectrophotometer. Melting points were taken on an IA 8100 Electrothermal Instrument. The electrical conductance of dichloromethane, acetone and ethanol solutions was measured with a Crison CDTM 522 conductometer at room temperature. The magnetic susceptibilities were measured at room temperature (20 °C) by the Gouy method, with a Sherwood Scientific Magnetic Balance MSB-Auto, using $HgCo(NCS)_4$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The magnetic moments (in μ_B) were calculated from the equation $\mu_{eff} = 2.84 (\chi_m^{corr.}T)^{\frac{1}{2}}$.

Syntheses

4-*tert*-Butylacetyl-3-methyl-1-phenylpyrazol-5-one HQ. 3-Methyl-1-phenylpyrazol-5-one (15.0 g, 0.088 mol) was placed in a flask equipped with a stirrer, separating funnel and a reflux condenser. Dry 1,4-dioxane (80 ml) was added by warming and to the clear solution calcium hydroxide (12.0 g, 0.162 mol) and then *tert*-butylacetyl chloride (11.9 g, 0.086 mol) was added, the latter dropwise for 10 min. The mixture was heated to reflux for 4 h and then poured into 2 mol dm^{-3} HCl (300 ml) to decompose the calcium complex. A light brown precipitate immediately formed, which was separated by filtration from the solution and dried under reduced pressure at 50 °C. Recrystallisation was performed by treating the solid with hot methanol: slow cooling of the solution afforded a yellow crystalline powder. Yield 84%, mp 85–87 °C (Found: C, 70.5; H, 7.5; N, 10.3. Calc. for $C_8H_{10}NO$: C, 70.6; H, 7.4; N, 10.3%). IR (Nujol): 1642vs, ν(C=O); 579s, 509vs, 448w, 419w, 396w, 370m, 356m, 333m, 305w, 270m, 243w and 224w (far-IR). ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 3 H, C^3–CH_3); 2.63s (2 H), 1.12s (9 H, $C_4H_9CH_2C$=O); 7.25 (t), 7.46 (t), 7.90 (d), (5 H, aromatics); and 11.5 (br, 1 H, OH···O). UV/VIS ($CDCl_3$): 246 (sh) (11740) and 268 nm (15380 dm^3 mol^{-1} cm^{-1}).

Aquabis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)copper(II), [CuQ$_2$(H$_2$O)] 1. An ethanolic solution (30 ml) of HQ (2 mmol) was added to copper acetate monohydrate (1 mmol) dissolved in 20 ml of warm ethanol. A green precipitate immediately formed. After ½ h the precipitate was separated by filtration, washed with ethanol (10 ml) and dried under reduced pressure at 50 °C. Recrystallisation was performed in hot dichloromethane: on cooling green crystals suitable for X-ray structural analyses formed. Yield 88%, mp 260–262 °C (Found: C, 61.85; H, 6.62; N, 9.12. Calc. for $C_{32}H_{40}CuN_4O_5$: C, 61.57; H, 6.46; N, 8.98%). $\mu_{eff} = 1.79$ μ_B. IR (Nujol): 2300–3200 (br), ν(O–H···N); 1645w, $\delta(OH_2)$; 1602vs, ν(C=O); 466m, 451m, ν_{sym}(Cu–O); 369m, $\nu(Cu–OH_2)$; 274vs, 269 (sh), ν_{asym}(Cu–O). UV/VIS ($CHCl_3$): 256 (42310), 294 (26890) and 672 nm (40 dm^3 mol^{-1} cm^{-1}). The substance was heated *in vacuo* (0.01 Torr) at 75 °C for 30 min (to eliminate water) and then sublimed at 170–190 °C as CuQ_2. The copper film deposition was carried out in a hot wall horizontal CVD reactor under a nitrogen flow at 90 mmHg and 200–230 °C.

Bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)(2,9-dimethylphenanthroline)copper(II), [CuQ$_2$(2,9-Me$_2$Phen)] 2. After 2,9-Me$_2$Phen (1 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in Et$_2$O (40 ml) the mixture immediately changed from green to dark brown. The dark precipitate was stirred for 4 h and then filtered off, washed with Et$_2$O and dried to constant weight under reduced pressure. Yield 86%, mp 168 °C (decomp.) Found: C, 67.62; H, 6.25; N, 10.34. Calc. for $C_{46}H_{50}CuN_6O_4$: C, 67.84; H, 6.19; N, 10.32%). $\mu_{eff} = 1.91$ μ_B. IR (Nujol): 16029, ν(C=O); 451s, 416s, ν(Cu–O); 286m, 264m, ν(Cu–N). UV/VIS ($CHCl_3$): 238 (40080), 266 (53760), 420 (sh) (380) and 680 nm (30 dm^3 mol^{-1} cm^{-1}).

Bis-(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)-(4,7-diphenylphenanthroline)copper(II), [CuQ$_2$(4,7-Ph$_2$Phen)] 3. The compound 4,7-Ph$_2$Phen (1 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in Et$_2$O (40 ml). The mixture immediately changed from green to brown. After 4 h of stirring the brown precipitate was filtered off, washed with Et$_2$O and dried to constant weight under reduced pressure. Yield 88%, mp 176 °C (decomp.) Found: C, 71.55; H, 5.91; N, 9.01. Calc. for $C_{56}H_{54}CuN_6O_4$: C, 71.66; H, 5.80; N, 8.95%). $\mu_{eff} = 1.92$ μ_B. IR (Nujol): 1609, ν(C=O); 453m, 409m, ν(Cu–O); 294s, 238s, ν(Cu–N). UV/VIS ($CHCl_3$): 242 (sh) (51130), 274 (65880) and 704 nm (60 dm^3 mol^{-1} cm^{-1}).

Bis(2,9-dimethylphenanthroline)copper(I) 4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onate [Cu(2,9-Me$_2$Phen)$_2$]Q 4. The compound 2,9-Me$_2$Phen (3 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in Et$_2$O–EtOH (1 : 1, 40 ml). The mixture immediately changed from green to brown-red. After 4 h of stirring the red precipitate was filtered off, washed with Et$_2$O and dried to constant weight under reduced pressure. Yield 76%, mp 215–220 °C (Found: C, 70.14; H, 5.85; N, 11.13. Calc. for $C_{44}H_{50}CuN_6O_2$: C, 70.33; H, 5.77; N, 11.18%). Λ_M (in CH_2Cl_2) = 40.1 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): 2.43 (s, 3 H, 3-CH_3); 3.01 (s, 2 H), 1.06 (s, 9 H, $CH_2C_4H_9$); 6.85 (t), 7.21 (t), 8.16 (d) (5 H, NC_6H_5); 2.37 (s, 12 H, 2,9-CH_3); 7.69 (d, 4 H), 7.94 (s, 4 H), 8.39 (d, 4 H) (2,9-Me$_2$Phen). IR (Nujol): 1609, ν(C=O); 299s, 242m, ν(Cu–N). UV/VIS ($CHCl_3$): 238 (47860), 272 (65280) and 458 nm (3330 dm^3 mol^{-1} cm^{-1}).

Tris(ethylenediamine)copper(II) bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onate) dihydrate, [Cu(en)$_3$]Q$_2$·H$_2$O 5. Ethylenediamine (3 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in EtOH (40 ml). The green mixture immediately changed to a dark blue solution. After 1 h the solvent was removed on a rotary evaporator and Et$_2$O (30 ml) added. A blue-lilac precipitate was filtered off, washed with Et$_2$O and dried to constant weight under reduced pressure. Yield 68%, mp 159–160 °C (Found: C, 55.44; H, 8.21; N, 17.22. Calc. for $C_{38}H_{66}CuN_{10}O_4$: C, 55.49; H, 8.09; N, 17.03%). $\mu_{eff} = 1.81$ μ_B. Λ_M (in EtOH) = 22.7 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3430 (br), ν(O–H···O); 3261s, 3150s, ν(N–H); 1607s, ν(C=O); 291s, 241m, ν(Cu–N). UV/VIS ($CHCl_3$): 204 (47500), 262 (47870) and 558 nm (110 dm^3 mol^{-1} cm^{-1}).

Bis (4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis-(*N*-methylimidazole)copper(II), [CuQ$_2$(N-MeIm)$_2$] 6. *N*-Methylimidazole (2 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in Et$_2$O (40 ml). The dark green mixture slowly changed to a light green-yellow. After 4 h the green-yellow precipitate was filtered off, washed with Et$_2$O and dried to constant weight under reduced pressure. Yield 62%, mp 169–172 °C (Found: C, 62.18; H, 6.68; N, 14.64. Calc. for $C_{40}H_{50}CuN_8O_4$: C, 62.36; H, 6.54; N, 14.54%). $\mu_{eff} = 1.91$ μ_B. IR (Nujol): 1602s, ν(C=O); 472m, 458s, ν_{asym}(Cu–O); 279s, 267m, ν_{sym}(Cu–O); 253vs, 247vs, ν(Cu–N). UV/VIS ($CHCl_3$): 236 (30910), 258 (44250), 296 (27450) and 578 (25 dm^3 mol^{-1} cm^{-1}).

(4-*tert*-Butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis-(triphenylphosphine)copper(I), [CuQ(PPh$_3$)$_2$] 7. Triphenylphosphine (3 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in EtOH (40 ml). During one night of refluxing the green precipitate dissolved giving a yellow solution, that was reduced in volume to ¼ on a rotary evaporator and cooled at −20 °C. A colourless microcrystalline powder precipitated. Yield 75%, mp 165–168 °C (Found: C, 72.54; H, 5.84; N, 3.29. Calc. for $C_{52}H_{49}CuN_2O_2P_2$: C, 72.67; H, 5.75; N, 3.26%). IR (Nujol): 1622vs, ν(C=O); 516s, 504vs, 495vs (PPh$_3$, y mode); 444s, 419m, ν_{asym}(Cu–O); 268m, ν_{sym}(Cu–O). ^{1}H NMR ($CDCl_3$): δ 2.41 (s), 2.39 (s) (3 H, 3-CH_3); 2.62 (s), 2.48 (s) (2 H), 1.12 (s), 0.91 (s) (9 H, $CH_2C_4H_9$); 7.03 (t), 7.19–7.40 (m), 7.52 (m), 7.68 (m), 7.86 (d), 7.93 (d) (35 H, aromatics). ^{31}P NMR ($CDCl_3$): δ −3.73 (s) (+20 °C), −2.68 (s), 4.65 (s) (−10 °C).

(4-*tert*-Butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis-(tricyclohexylphosphine)copper(I), [CuQ(PCy$_3$)$_2$] 8. Tricyclohexylphosphine (3 mmol) was added to a suspension of [CuQ$_2$(H$_2$O)] (1 mmol) in EtOH (40 ml). The mixture was left

Table 3 Crystal data and structure refinement parameters for $[CuQ_2(H_2O)]$ **1** and $[CaQ_2(EtOH)_2]$ **9***

	$[CuQ_2(H_2O)]$	$[CaQ_2(EtOH)_2]$
Molecular formula	$C_{32}H_{40}CuN_4O_5$	$C_{36}H_{50}CaN_4O_6$
M	624.22	674.88
Crystal size/mm	0.4 × 0.3 × 0.2	0.4 × 0.2 × 0.1
T/K	295(2)	160(2)
a/Å	9.169(2)	9.652(2)
b/Å	13.410(3)	11.476(2)
c/Å	14.350(3)	16.828(3)
α/°	65.93(3)	97.51(3)
β/°	73.23(3)	100.22(3)
γ/°	78.72(3)	90.10(3)
V/Å^3	1536.3(6)	1818.1(6)
D_c/Mg m^{-3}	1.349	1.233
μ/mm^{-1}	0.757	0.221
F(000)	658	724
Data collection range/°	$1.60 < \theta < 22.0$	$1.79 < \theta < 22.53$
Index ranges	$-9 \leqslant h \leqslant 9, -12 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 15$	$-10 \leqslant h \leqslant 10, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 17$
Reflections collected	3745	10632
Independent reflections (R_{int})	3744 (0.0000)	4499 (0.0568)
Data, parameters, restraints	3744, 412, 5	4270, 441, 0
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0502, 0.1315	0.0387, 0.0890
(all data)	0.0609, 0.1392	0.0566, 0.1242
Goodness of fit on F^2	1.072	0.926
Peak, hole in final difference map/e Å^{-3}	0.563, −0.377	0.258, −0.245

* Details in common: λ 0.71073 Å; triclinic, space group $P\bar{1}$; $Z = 2$.

for one night under refluxing and sufficient stirring. The green precipitate disappeared giving a yellow solution. Then the volume was reduced to ¼ on a rotary evaporator and the solution was cooled at −20 °C. A colourless microcrystalline powder of the complex precipitated. Yield 71%, mp 142–144 °C (Found: C, 69.34; H, 9.64; N, 3.22. Calc. for $C_{52}H_{85}CuN_2O_2P_2$: C, 69.73; H, 9.56; N, 3.13%). IR (Nujol): 1623vs, ν(C=O); 511vs, 488s (PCy_3); 450m, 402m, ν(Cu–O). ^{1}H NMR ($CDCl_3$): δ 2.47 (br) (3 H, 3-CH_3), 2.65 (m br, 2 H), 1.09 (s), 1.28 (s) (9 H, $CH_2C_4H_9$); 7.15 (m br), 7.40 (m br), 7.90–8.15 (m br) (5 H, aromatics); 1.32–1.94 (m br, PCy_3). ^{31}P NMR ($CDCl_3$): δ 33.8 (s), 29.1 (br), 11.2 (br) (+20 °C), 33.8 (s), 29.6 (s), 10.3 (s), (−50 °C).

Bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis(ethanol)calcium(II), $[CaQ_2(EtOH)_2]$ 9. An ethanolic solution (30 ml) of HQ (2 mmol) and KOH (2 mmol) was added to an aqueous solution (10 ml) of calcium dichloride (1 mmol). In a few minutes a white precipitate formed. After 1 h the precipitate was filtered off, washed with water (10 ml) and dried under reduced pressure at 50 °C. Recrystallisation from hot ethanol gave on cooling light colourless crystals. Yield 84%, mp 329–331 °C (Found: C, 63.82; H, 7.55; N, 8.46. Calc. for $C_{36}H_{50}CaN_4O_6$: C, 64.07; H, 7.47; N, 8.30%). IR (Nujol): 2400–3500 (br), ν(O–H···N); 1644s, δ(OH); 1591vs, ν(C=O); 440 vs, 409m, ν_{sym}(Ca–O); 377m, ν[Ca–O(H)Et]; 253vs (br), 233m, ν_{asym}(Ca–O). ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 6 H, C^3–CH_3), 2.43 (s, 4 H), 0.90 (s, 18 H) ($C_4H_9CH_2C$=O); 7.05 (t), 7.24 (t), 6.67 (d) (10 H, aromatics); 2.15 (br, 2 H), 3.64 (q, 4 H), 1.71 (t, 6 H) (EtOH).

Bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis(methanol)calcium(II), $[CaQ_2(MeOH)_2]$ 10. Upon addition of a methanolic solution (30 ml) of HQ (2 mmol) and KOH (2 mmol) to calcium dichloride (1 mmol) dissolved in water (20 ml) a white precipitate immediately formed. After 1 h of stirring it was filtered off, washed with water (10 ml) and dried under reduced pressure at 50 °C. Recrystallisation was performed in hot methanol: on cooling slow formation of light colourless crystals was observed. Yield 91%, mp 158–161 °C (Found: C, 62.85; H, 7.05; N, 8.52. Calc. for $C_{34}H_{46}CaN_4O_6$: C, 63.13; H, 7.17; N, 8.66%). IR (Nujol): 2800–3300 (br), ν(O–H···N); 3617m, ν(O–H); 1624vs br, ν(C=O); 434m, 413m, ν_{sym}(Ca–O); 381m, ν[Ca–O(H)Me]; 253vs (br), ν_{asym}(Ca–O). ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 6 H, C^3–CH_3); 2.45 (s, 4 H), 0.89 (s, 18 H) ($C_4H_9CH_2C$=O); 7.05 (t), 7.24 (t), 7.71 (d) (10 H, aromatics); 1.90 (br, 2 H), 1.22 (s, 6 H) (MeOH).

Bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis(isopropyl alcohol)calcium(II), $[CaQ_2(Pr^iOH)_2]$ 11. A Pr^iOH solution (30 ml) of HQ (2 mmol) and KOH (2 mmol) was added to an aqueous solution (20 ml) of calcium dichloride (1 mmol). In a few minutes a white precipitate formed. After 1 h the mixture was filtered, the precipitate washed with water (10 ml) and dried under reduced pressure at 50 °C. Recrystallisation was performed in hot Pr^iOH: on cooling the solution slow formation of light colourless crystals was observed. Yield 88%, mp 315–317 °C (Found: C, 64.72; H, 7.75; N, 8.24. Calc. for $C_{38}H_{54}CaN_4O_6$: C, 64.93; H, 7.74; N, 7.97%). IR (Nujol): 3100 (br), ν(Pr^iOH···N); 1624s, ν(C=O); 432 (sh), 428vs, ν(Ca–O). ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6 H, C^3–CH_3); 2.45 (s, 4 H), 0.95 (s, 18 H) ($C_4H_9CH_2C$=O); 7.04 (t), 7.25 (t), 7.84 (d) (10 H, aromatics); 4.02 (h, 2 H), 1.21 (s), 1.18 (s, 12 H) (Pr^iOH).

Diaquabis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)calcium(II), $[CaQ_2(H_2O)_2]$ 12. A solution containing HQ (2 mmol) and KOH (2 mmol) in propargylic alcohol (HC≡CCH$_2$OH) (30 ml) was added to an aqueous solution (20 ml) of calcium dichloride (1 mmol). In a few minutes a white precipitate formed. After 1 h the mixture was filtered, the precipitate washed with propargylic alcohol (10 ml), dried under reduced pressure at 50 °C and shown to be compound **12**. Yield 85%, mp 262–265 °C (Found: C, 62.35; H, 6.93; N, 9.53. Calc. for $C_{32}H_{43}CaN_4O_6$: C, 62.11; H, 6.84; N, 9.05%). IR (Nujol): 3185 (br), ν(H_2O); 1680m, δ(H_2O); 1620s, ν(C=O); 437vs, 414vs, 395s, 381 (sh), ν(Ca–O). ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6 H, C^3–CH_3); 2.46 (s, 4 H), 0.95 (s, 18 H) ($C_4H_9CH_2C$=O); 7.05 (t), 7.25 (t), 7.79 (d) (10 H, aromatics); 1.65 (s br, 4 H, H_2O).

Alternatively, a solution of HQ (2 mmol) and KOH (2 mmol) in *tert*-butyl alcohol (30 ml) was added to an aqueous solution (20 ml) of calcium dichloride (1 mmol). Within half an hour a white precipitate slowly formed. The mixture was stirred overnight, then the precipitate was separated by filtration, washed with *tert*-butyl alcohol (10 ml) and dried under reduced pressure at 50 °C. By using *tert*-amyl alcohol in a similar procedure, a white crystalline precipitate (compound **12**) was afforded only after several days on cooling (4 °C) the reaction solution.

Bis(4-*tert*-butylacetyl-3-methyl-1-phenylpyrazol-5-onato)bis-(1,10-phenanthroline)calcium(II), [$CaQ_2(Phen)_2$] 13. To [CaQ_2-$(EtOH)_2$] (1 mmol) dissolved in 30 ml of chloroform a solution (10 ml) of 1,10-phenanthroline (2 mmol) in the same solvent was added. The clear solution was refluxed with stirring overnight. Then the solvent was removed on a rotary evaporator and diethyl ether (30 ml) added: the white precipitate formed was filtered off, washed with diethyl ether (10 ml) and dried under reduced pressure at 50 °C. Recrystallisation was performed in hot *n*-hexane: on cooling a microcrystalline powder was obtained. Yield 90%, mp 261–262 °C (Found: C, 70.97; H, 5.84; N, 11.77. Calc. for $C_{44}H_{46}CaN_8O_4$: C, 71.31; H, 5.77; N, 11.88. IR (Nujol): 3054m, $\nu(C_{arom}–H)$; 1635s, ν(C=O); 436m, 416vs, ν(Ca–O); 242s, 225vs, ν(Ca–N). ^1H NMR ($CDCl_3$): δ 2.32 (s, 6 H, $C^3–CH_3$); 2.35 (s, 4 H), 0.80 (s, 18 H) ($C_4H_9CH_2C$=O); 7.08 (t), 7.25 (t), 7.98 (d) (10 H, aromatics); 7.56 (dd), 7.79 (s), 8.28 (d), 9.21 (d) (16 H, Phen). UV/VIS ($CHCl_3$): 236 (39880) and 266 nm (88950 dm^3 mol^{-1} cm^{-1}).

Crystal structure determination and refinement

The data collection for compound **1** was carried out on an IPDS diffractometer (Stoe) (Mo-Kα radiation, graphite monochromator), that for **9** on a STADI-4 (Stoe) diffractometer (θ–2θ scan mode). The unit cell parameters were determined from the positions of 951 reflections for **1** and 24 centred reflections for **9**. The structure solution by direct methods (SHELXS 86)[63] was difficult in the proper space group $P\bar{1}$ due to the planarity of the molecules. However, the solution could be readily found in the non-centrosymmetric space group *P*1. After the positions of most of the atoms had been determined, the transformation to the correct space group was performed. All non-hydrogen atoms in both structures were refined anisotropically (SHELXL 93).[64] The hydrogen atoms of the water molecule (structure **1**) and OH groups of ethanol molecules (structure **9**) have been found in the Fourier-difference map and refined isotropically. All other hydrogen atoms were placed in calculated positions and refined in a rigid mode.

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See http://www.rsc.org/suppdata/dt/1998/3325/ for crystallographic files in .cif format.

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