Novel bis(acylpyrazolonato)cadmium(II) derivatives and their reactivity toward aromatic and aliphatic N₂-donor ligands

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By reaction of 1-phenyl-3-methyl-4-R-C(=O)-pyrazol-5-one (HQ$_T$: R = CH$_2$C(CH$_3$)$_3$; HQ$_C$: R = C$_6$H$_{11}$) with Cd(O$_2$CCH$_3$)$_2$·2H$_2$O in EtOH the derivatives [Cd(Q$_T$)$_2$(EtOH)$_2$] **1** and [Cd(Q$_C$)$_2$(EtOH)$_2$] **2** have been synthesised. Complex **1** has a molecular structure with a slightly distorted octahedral coordination of the cadmium atom with EtOH and Q$_T$ ligands *trans* to each other. When the reaction between HQ$_T$ or HQ$_C$ and Cd(O$_2$CCH$_3$)$_2$·2H$_2$O was carried out in the presence of bidentate N-donor ligands L (L = 1,10-phenanthroline, 2,2′-bipyridyl, *N*,*N′*,*N′*-trimethyl-ethylenediamine or tetramethylethylenediamine), [Cd(Q$_T$)$_2$(L)] and [Cd(Q$_C$)$_2$(L)] were always obtained. In the six-coordinate derivatives [Cd(Q$_C$)$_2$(1,10-phenanthroline)] and [Cd(Q$_T$)$_2$(tetramethylethylenediamine)] the cadmium atom is in a strongly distorted octahedral environment due to steric requirements of the bidentate N$_2$-donor ligands. All complexes synthesized have been characterized spectroscopically by IR, ^{1}H and ^{113}Cd NMR. The behavior in solution is also discussed.

We have recently undertaken a systematic investigation into the coordination chemistry of an interesting class of heterocyclic β-diketones, namely 4-acyl-5-pyrazolones (Fig. 1). This family of ligands, widely used as extractants for trace metals[1] and for dyes,[2] has only recently been the object of a growing interest, due to their low cost and versatility. The influence on the physicochemical properties of the metal and organometal acylpyrazolonates, exerted by the pyridinic nitrogen atom in the pyrazole ring, suitable for additional interaction with metal/hydrogen centres, has been shown in the case of R$_3$Sn(IV)-,[3] Cu(II)-, Ca(II)-[4] Ba(II)-[5] and Pb(II)-acylpyrazolonates.[6] In the literature only a few papers exist on the synthesis of cadmium acylpyrazolonates[7] but these works were mainly based on analytical and physicochemical topics and no spectroscopic or structural data were reported.

On the other hand there are several works dealing with the X-ray crystal data of cadmium-β-diketonate derivatives. In particular bis(acetylacetonato)cadmium was found to be polymeric, with each Cd atom octahedrally coordinated with one oxygen from each acetylacetonate ligand bridging between two metal centres.[8] In this compound the polymeric chains are formed due to the chelate-bridging functions of some acetylacetonate ligands, the Cd–O distances in the chelate ring being shorter than those for bridging bonds. Other examples are tris(β-diketonato)cadmium salts of K^{+}[9] and of NH$_4$$^{+}$,[10] where the anions contain six-coordinated cadmium atoms, with distorted trigonal prismatic stereochemistry.

We recently reported the synthesis of some Group 12 metal acylpyrazolonates[11] and their adducts with bis(pyrazolyl)methane and imidazoles.[12] We always found that these derivatives were hydrated or solvated, *e.g.* [Cd(Q)$_2$(ROH)$_n$], with one or two ROH (where R=H, Me or Et) molecules so, looking forward, we wanted to explore the interaction of new, more sterically hindered acylpyrazolones (Fig. 1) towards cadmium acceptors and to verify if it is possible to obtain anhydrous Cd-(acylpyrazolonate)$_2$ complexes, as in the case of the acetylacetonate ligand, or if the presence of the pyridine nitrogen in the acylpyrazolonate ligand favours the coordination of ROH solvent molecules, thus influencing their stoichiometry, structure and crystal packing, as observed in the case of Cu(II), Ca(II) and Ba(II) acylpyrazolonates.[4,5] Moreover we also wanted to obtain clear structural information about mixed-ligand derivatives such as [Cd(β-diketonato)$_2$(L)] [where L = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy)], since there are only a few papers on their synthesis and spectroscopic characterization,[13] and few X-ray data have been reported. We also present here the synthesis of the first [Cd(β-diketonato)$_2$(L)] [where L = trimethylethylenediamine (trime) or tetramethylethylenediamine (tmeda)] derivatives. In fact, till now, only cadmium(II) halide complexes containing these aliphatic N$_2$-donors have been reported.[14]

Our aim is also to show how combined IR, ^{1}H and ^{113}Cd NMR spectroscopy, conductivity measurements and vaporimetric molecular weight determinations together with X-ray data allow us to study and discuss the solid state and solution chemistry of cadmium derivatives.
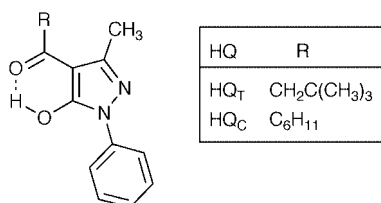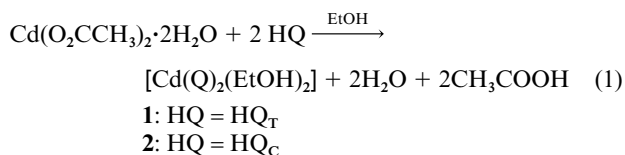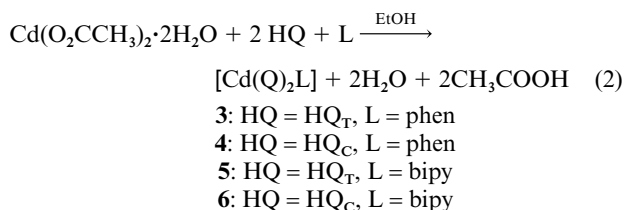
Results and discussion

Syntheses

Derivatives **1** and **2** have been synthesised by interaction of Cd(O$_2$CCH$_3$)$_2$·2H$_2$O with the proligands HQ$_T$ and HQ$_C$, respectively, in ethanol, in accordance with eqn. (1).

HQ	R
HQ$_T$	CH$_2$C(CH$_3$)$_3$
HQ$_C$	C$_6$H$_{11}$

Fig. 1 4-Acyl-pyrazolone proligands used in this work.

$$Cd(O_2CCH_3)_2 \cdot 2H_2O + 2\ HQ \xrightarrow{\ EtOH\ }$$

$$[Cd(Q)_2(EtOH)_2] + 2H_2O + 2CH_3COOH \quad (1)$$
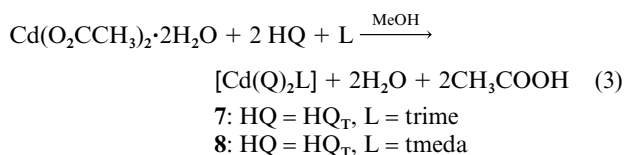
1: HQ = HQ$_T$
2: HQ = HQ$_C$

Derivatives **1** and **2** show quite broad melting ranges (2–5 °C); they are soluble in DMSO, chloroform, dichloromethane and acetone in which they are non-electrolytes. The vaporimetric molecular weight determinations (CHCl$_3$) indicate that complexes **1** and **2** exist as dinuclear or oligonuclear species in solution. Association of the independent molecules of **1** and **2** through H bonds observed in the solid state (see below) should occur also in solution. It is very interesting to note that under these reaction conditions cadmium pyrazolonate derivatives achieve six-coordination[15] through bonding of two O-donor solvent molecules, whereas zinc(II)-β-diketonates generally absorb only one molecule of water or of O-donor solvent yielding stable five-coordinate derivatives.[16]

Derivatives **3**–**6** can be obtained from the reaction of **1** and **2** (with the N$_2$-donors phen and bipy respectively) in CHCl$_3$ solution upon displacement of the EtOH molecules from the coordination sphere of cadmium. Alternatively **3**–**6** can also be prepared from the reaction of Cd(O$_2$CCH$_3$)$_2 \cdot$2H$_2$O with the pro-ligands HQ$_T$ and HQ$_C$, in ethanol, in the presence of an equimolar quantity of the N$_2$-donor ligand phen or bipy (eqn. (2)).

$$Cd(O_2CCH_3)_2 \cdot 2H_2O + 2\ HQ + L \xrightarrow{\ EtOH\ }$$

$$[Cd(Q)_2L] + 2H_2O + 2CH_3COOH \quad (2)$$

3: HQ = HQ$_T$, L = phen
4: HQ = HQ$_C$, L = phen
**5**: HQ = HQ$_T$, L = bipy
6: HQ = HQ$_C$, L = bipy

Derivatives **3**–**6** also have broad melting points. They are soluble in DMSO, acetone and chlorinated solvents, in which they are not electrolytes. Vaporimetric molecular weight determinations (CHCl$_3$) indicate that they exist in solution as poorly dissociated mononuclear species.

Derivatives **7** and **8** can be obtained following the procedure described above for complexes **3**–**6** by using MeOH as solvent (eqn. (3)).

$$Cd(O_2CCH_3)_2 \cdot 2H_2O + 2\ HQ + L \xrightarrow{\ MeOH\ }$$

$$[Cd(Q)_2L] + 2H_2O + 2CH_3COOH \quad (3)$$

7: HQ = HQ$_T$, L = trime
8: HQ = HQ$_T$, L = tmeda

Complexes **7** and **8** are sharp melting solids, very soluble in DMSO, acetone, CH$_2$Cl$_2$ and CHCl$_3$, and partially soluble in alcohols. They are not electrolytes in CH$_2$Cl$_2$ and acetone; in chlorinated solutions they partially dissociate into the neutral species (eqn. (4)), as evidenced by vaporimetric molecular

$$[Cd(Q)_2L] \rightleftharpoons [Cd(Q)_2] + L \quad (4)$$
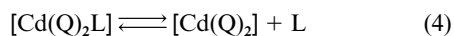
weight determination, the ratio r (r = FW/MW) being in the range 0.70–0.90. The dissociation generally increases with dilution.

Spectroscopy

IR spectroscopy gave several indications about the solid state structures of **1**–**8**. In derivatives **1**, **2** and **7** the broad absorption in the region 3100–3300 cm^{-1} indicates the presence of extensive H-bonding, between the N atom of the heterocyclic ring and the OH group of EtOH (**1** and **2**) or the NH of trime (**7**). The ν(C=O) band due to ligands Q$_T$ and Q$_C$ shifts to lower
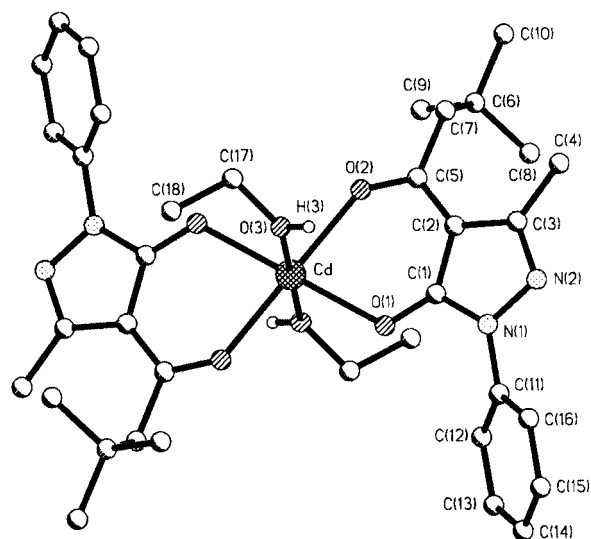
Fig. 2 Centrosymmetric molecular structure of [Cd(Q$_T$)$_2$(EtOH)$_2$] (**1**) with atom labelling.

frequency upon coordination. In addition several medium to strong absorption bands appear in the range 350–450 cm^{-1}, likely due to Cd–O stretching modes.[17] In complexes **3**–**6** absorption bands at *ca.* 230 cm^{-1}, absent in the spectra of the neutral and anionic ligands, are due to Cd–N stretching vibrations.

In the ^{1}H NMR spectra of all the complexes (**1**–**8**) we have found that the signals due to the 3-Me group are always shifted to high field upon coordination, whereas the opposite trend has been observed for the aromatic protons N–Ph, in accordance with previous work for this kind of donor.[3,5] In derivatives **3**–**8** all signals due to N$_2$-aromatic and aliphatic donors appear as very broad resonances, suggesting the existence of dissociation equilibria, like that shown in eqn. (4), or ligand fluxionality.

[113]Cd NMR spectroscopy has been recently employed in the study of Cd(β-diketonate) derivatives: the [113]Cd chemical shift for [tris(pyrazolyl)borate]cadmium(2,4-pentanedione) which possesses a CdN$_3$O$_2$ central core were found in the range 150–180 ppm,[18] whereas cadmium[bis(4-acylpyrazolonate)-(imidazole)$_n$][12b] (n = 1 or 2) (CdO$_4$N$_2$ or CdO$_4$N central core) derivatives exhibit resonances in the range 59–82 ppm. Complexes **1**–**8**, which have a CdO$_6$ or CdO$_4$N$_2$ central core, show a sharp resonance in the range 25–28 ppm. These results indicate that ligand binding through oxygen increases shielding of the cadmium nucleus, whereas ligand binding through nitrogen produces a marked deshielding.

X-Ray crystallography

The compounds **1**, **4** and **8** have molecular structures with a distorted octahedral coordination around the Cd atom. In the case of bidentate ligands L (phen and tmeda) the octahedral coordination of Cd is more distorted due to small bite angles N–Cd–N, less than 90°. Selected bond lengths and angles are reported in Table 1.

In the structure of [Cd(Q$_T$)$_2$(EtOH)$_2$] **1**, the Cd atom has a centrosymmetric slightly distorted octahedral coordination by six O atoms from two Q$_T$ ligands and two EtOH molecules (Fig. 2). Due to the arrangement of similar ligands *trans* to each other, the difference in Cd–O distances (Cd–O(1): 2.225(2); Cd–O(2): 2.259(2) Å for O(Q$_T$)) are less ($\Delta = 0.03$) than in other complexes of Cd. The larger difference between Cd–O(1); (O2) and Cd–O(3) (EtOH) could be due to the difference in the donating ability (supported by chelating effect for Q$_T$ and its negative charge). Due to the presence of an acidic H atom in EtOH, there are intermolecular H bonds O(3)–H(3)$\cdots$N(2) ($\angle$176°) and O(3)$\cdots$N(2) (2.744 Å) connecting the [Cd-

Table 1 Selected bond distances (Å) and angles (°) for derivatives **1**, **4** and **8**

[Cd(Q$_T$)$_2$(EtOH)$_2$] (1)		[Cd(Q$_C$)$_2$(phen)] (4) Molecule 1		Molecule 2		Molecule 3		Molecule 4		[Cd(Q$_T$)$_2$(tmeda)] (8)	
Cd–O(1)	2.225(2)	Cd(1)–O(1)	2.224(11)	Cd(2)–O(5)	2.223(12)	Cd(3)–O(9)	2.192(14)	Cd(4)–O(13)	2.228(13)	Cd–O(1)	2.229(2)
Cd–O(2)	2.259(2)	Cd(1)–O(2)	2.269(11)	Cd(2)–O(6)	2.260(10)	Cd(3)–O(10)	2.290(12)	Cd(4)–O(14)	2.279(12)	Cd–O(2)	2.312(3)
Cd–O(3)	2.328(3)	Cd(1)–O(3)	2.204(12)	Cd(2)–O(7)	2.264(11)	Cd(3)–O(11)	2.209(9)	Cd(4)–O(15)	2.198(11)	Cd–N(3)	2.373(3)
		Cd(1)–O(4)	2.272(10)	Cd(2)–O(8)	2.243(10)	Cd(3)–O(12)	2.294(10)	Cd(4)–O(16)	2.277(12)		
		Cd(1)–N(5)	2.356(13)	Cd(2)–N(11)	2.341(13)	Cd(3)–N(17)	2.385(11)	Cd(4)–N(23)	2.363(11)		
		Cd(1)–N(6)	2.359(13)	Cd(2)–N(12)	2.369(13)	Cd(3)–N(18)	2.407(14)	Cd(4)–N(24)	2.340(11)		
O(1)–Cd–O(1)#	180.0	O(1)–Cd(1)–O(2)	80.9(4)	O(5)–Cd(2)–O(6)	81.3(4)	O(9)–Cd(3)–O(10)	81.0(5)	O(13)–Cd(4)–O(14)	81.7(4)	O(1)–Cd–O(1)#	109.42(14)
O(1)–Cd–O(2)#	97.73(7)	O(3)–Cd(1)–O(4)	80.4(4)	O(7)–Cd(2)–O(8)	81.4(4)	O(11)–Cd(3)–O(12)	82.8(4)	O(15)–Cd(4)–O(16)	81.1(4)	O(1)–Cd–O(2)	80.21(9)
O(1)–Cd–O(2)	82.27(7)	N(5)–Cd(1)–N(6)	70.4(4)	N(11)–Cd(2)–N(12)	70.8(4)	N(17)–Cd(3)–N(18)	68.8(4)	N(23)–Cd(4)–N(24)	70.9(4)	O(1)–Cd–O(2)#	89.95(10)
O(2)#–Cd–O(2)	180.0									O(2)–Cd–O(2)#	163.0(2)
O(2)–Cd–O(3)#	94.68(9)									N(3)–Cd–N(3)#	77.2(2)
O(1)–Cd–O(3)	93.63(8)										
O(2)–Cd–O(3)	85.32(9)										
O(3)#–Cd–O(3)	180.0										

(Q$_T$)$_2$(EtOH)$_2$] molecules in pairs to infinite linear chains running in the x direction (Fig. 3). The packing mode found for this structure is very similar to that determined for the analogous [Ca(Q$_T$)$_2$(EtOH)$_2$].[4]

In [Cd(Q$_C$)$_2$(phen)] **4** (Fig. 4), the bonding of the Q$_C$ ligand is distorted, with a small difference between the shorter (av. 2.222 Å) and the longer (av. 2.272 Å) Cd–O bonds (Δ_{av} = 0.05 Å). The structure of [Cd(Q$_C$)$_2$(phen)] has four crystallographically different complexes in the asymmetric unit. The packing of molecules in this structure has some special features resulting in high unit cell dimensions (Fig. 5). The central Cd atoms can be considered as lying in the layers parallel to (xy0) at heights $z \approx 0$ or ≈ 1 (Cd1 and Cd2) and $z \approx 0.5$ (Cd3 and Cd4). In the layer at $z \approx 0$, all the complexes nearly perfectly obey a translation period of 0.5 in the x direction.

On the other hand, the complexes in the layer at $z \approx 0.5$ obey a translation period of 0.5 in the y direction. Thus, these pseudo translations by $\frac{1}{2}a$ and $\frac{1}{2}b$ act only within the layer and the crystallographic translations are doubled in both the x and y directions. Apparently, such a packing mode accounts for the strong tendency for twinning found for crystals of [Cd(Q$_C$)$_2$-(phen)].

In [Cd(Q$_T$)$_2$(tmeda)] **8**, the molecule is symmetric around a two-fold axis going through the Cd atom and the centre of the C–C bond in the tmeda donor ligand (Fig. 6). Also in this molecule the bonding of the Q$_T$ ligand is distorted with the shorter Cd–O(1) 2.23 Å and the longer Cd–O(2) 2.31 Å distance (Δ = 0.08 Å) perhaps due to the *trans* position of O(1) with respect to N(3) of the tmeda ligand.

Average bond distances and angles of Cd environment in previous cadmium-β-diketonate crystal structures[8–10,13] and those reported in this work are very similar, the range of Cd–O being 2.20–2.33 Å and the bite angles falling in the range 79.5–82.3°.

Conclusion

This study gives detailed information into structural and spectroscopic properties of a number of derivatives containing cadmium(II) acylpyrazolonates and monodentate O-donor or bidentate N$_2$-donor ancillary ligands. We have also found that the nature of the ancillary ligands does not affect the nuclearity and coordination number of our compounds, whereas steric hindrance and the presence of acidic H atoms on the ligands can modify the supramolecular architecture both in the solid and solution state through extended intermolecular hydrogen bonds with acceptor N atoms in acylpyrazolonates.

Experimental

General comments

Solvents were used as supplied or distilled using standard methods. All the chemicals were purchased from Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried in vacuum to constant weight (20 °C, $ca.$ 0.1 Torr). Elemental analyses (C,H,N) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Molecular weight determinations were performed in chloroform (m = mol kg^{-1} of solvent) at 313 K with a Knauer membrane osmometer. IR spectra were recorded from 4000 to 100 cm^{-1} using a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H and ^{113}Cd spectra were recorded on a VXR-300 Varian spectrometer operating at 293 K (300 MHz for ^{1}H, 66.55 MHz for ^{113}Cd). Proton chemical shifts are reported in ppm $vs.$ Me$_4$Si while cadmium chemical shifts are reported in ppm $vs.$ Cd(ClO$_4$)$_2$. The electrical conductances (reported as Ω^{-1} cm^2 mol^{-1}) of the dichloromethane and acetone solutions (M = mol l^{-1}) were measured with a Crison CDTM 522 conductimeter at room temperature.
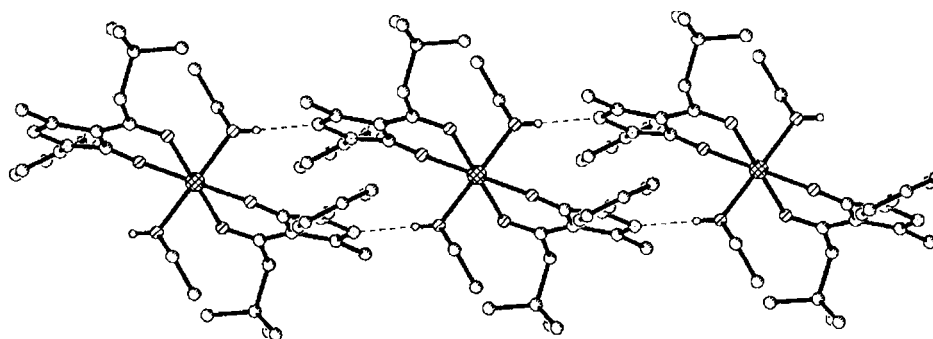
Fig. 3 Linear chain of [Cd(Q_T)$_2$(EtOH)$_2$] (**1**) molecules connected by pairs of hydrogen bonds O–H···N. Only hydroxyl H atoms are shown.

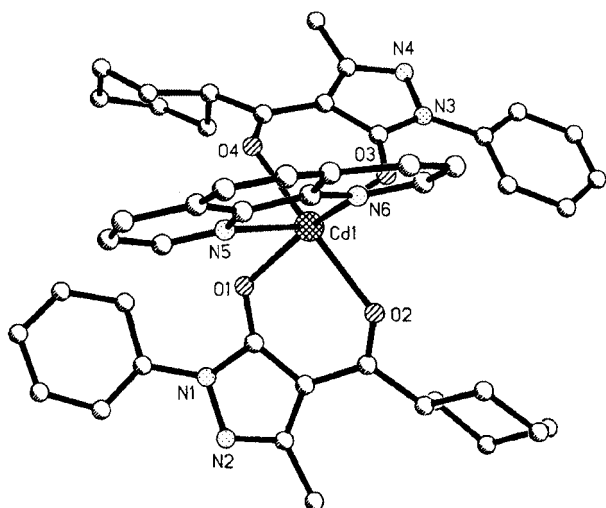**Fig. 4** Molecular structure of [Cd(Q_C)$_2$(phen)] (**4**) exemplified by the complex with Cd(1). H atoms are omitted for clarity.

Syntheses

The proligands HQ_C and HQ_T were synthesised according to the procedure previously described.[4,19]

[Cd(Q_T)$_2$(EtOH)$_2$] 1. Compound **1** has been obtained by interaction of Cd(O$_2$CCH$_3$)$_2$·2H$_2$O (0.266 g, 1.0 mmol) with the proligand HQ_T (0.545 g, 2.0 mmol) in 30 ml of EtOH. From the solution a pale-yellow solid slowly precipitated. After 4 h the suspension was filtered off, the precipitate was washed with Et$_2$O and dried to constant weight under reduced pressure and recrystallised from CHCl$_3$–n-hexane, 88% yield. Mp 150–155 °C. Calc. for C$_{36}$H$_{50}$CdN$_4$O$_6$: C, 57.87; H, 6.74; N, 7.50. Found: C, 57.55; H, 6.61; N, 7.67%. IR (Nujol, cm^{-1}): 3140br (OH···N), 1655m (OH···N), 1607vs (C=O), 452s (br), 348s (br) (Cd–O). ^{1}H NMR (CDCl$_3$): δ, 0.98 (s) (18H, CH$_2$C(CH_3)$_3$), 1.25 (t) (6H, CH_3 $_{EtOH}$), 2.45 (s) (6H, 3-CH_3), 2.48 (s) (4H, CH_2C(CH$_3$)$_3$), 3.65 (q) (4H, CH_2 $_{EtOH}$), 7.0–7.7 (m) (10H, N-Ph). ^{113}Cd NMR (CDCl$_3$): δ, 27.2. MW (CHCl$_3$): 2813 ($c = 3.1 \times 10^{-2}$ m); 2196 ($c = 1.4 \times 10^{-2}$ m).

[Cd(Q_C)$_2$(EtOH)$_2$] 2. Compound **2** has been obtained by the same method as that described for **1**. Recrystallised from CHCl$_3$–n-hexane, 92% yield. Mp 194–196 °C. Calc. for C$_{38}$H$_{50}$CdN$_4$O$_6$: C, 59.18; H, 6.53; N, 7.26. Found: C, 58.95; H, 6.53; N, 7.26%. IR (Nujol, cm^{-1}): 3150br (OH···N), 1670m (OH···N), 1614vs (C=O), 430m, 405m (Cd–O). ^{1}H NMR (CDCl$_3$): δ, 1.1–1.9 (m) (28H, C$_6$H$_{11}$ + CH_3 $_{EtOH}$), 2.40 (s) (6H, 3-CH_3), 3.50 (q) (4H, CH_2 $_{EtOH}$), 7.0–7.7 (m) (10H, N-Ph). ^{113}Cd NMR (CDCl$_3$): δ, 26.3. MW (CHCl$_3$): 1628 ($c = 1.4 \times 10^{-2}$ m); 2964 ($c = 0.9 \times 10^{-2}$ m).

[Cd(Q_T)$_2$(phen)] 3. Compound **3** has been obtained by interaction of Cd(O$_2$CCH$_3$)$_2$·2H$_2$O (0.266 g, 1.0 mmol) with the proligand HQ_T (0.545 g, 2.0 mmol) and 1,10-phenanthroline (phen, 0.180 g, 1.0 mmol) in 30 ml of EtOH. From the solution a light-

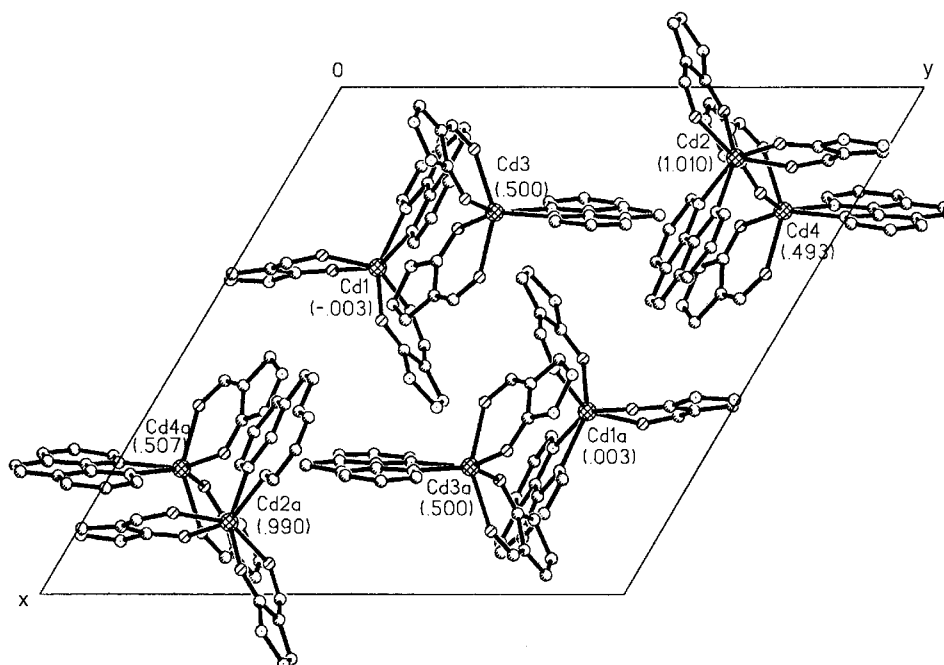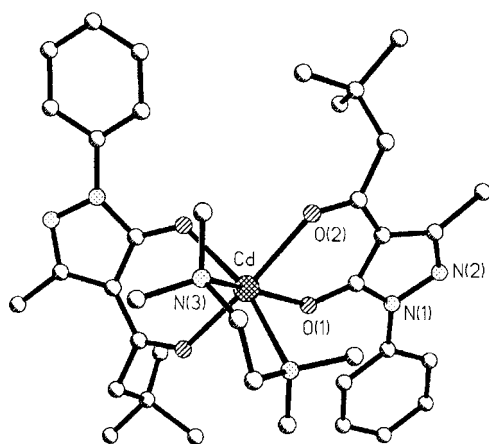**Fig. 5** Packing of [Cd(Q_C)$_2$(phen)] (**4**) molecules in the unit cell. The numbers in brackets indicate z coordinates of Cd atoms. All methyl, phenyl and cyclohexyl substituents as well as H atoms are omitted for clarity.

Table 2 Crystal data and summary of data collection and refinement for compounds **1**, **4** and **8**

Compound	$[Cd(Q_T)_2(EtOH)_2]$ (**1**)	$[Cd(Q_C)_2(phen)]$ (**4**)	$[Cd(Q_T)_2(tmeda)]$ (**8**)
Empirical formula	$C_{36}H_{50}CdN_4O_6$	$C_{46}H_{44}CdN_6O_4$	$C_{38}H_{54}CdN_6O_4$
FW	747.20	857.27	771.27
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
Crystal system	Triclinic	Triclinic	Monoclinic
$a/\text{Å}$	8.992(2)	19.691(4)	23.324(6)
$b/\text{Å}$	10.358(3)	19.747(4)	7.577(2)
$c/\text{Å}$	10.678(3)	24.343(7)	21.702(6)
$\alpha/°$	85.69(3)	96.82(3)	
$\beta/°$	71.72(3)	94.56(3)	97.00(3)
$\gamma/°$	74.19(3)	119.71(2)	
$V/\text{Å}^3$	908.6(4)	8057(3)	3807(2)
Z	1	8	4
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	6.49	5.94	6.20
T/K	170	160	180
Reflections collected	8088	35406	13432
Reflections unique	3625	22215	3680
R_1	0.0347	0.0907	0.1098
wR_2	0.0992	0.1993	0.1098

Fig. 6 Molecular structure of $[Cd(Q_T)_2(tmeda)]$ (**8**) with a two-fold axis going through the Cd atom and the middle of the C–C bond in the tmeda ligand.

brown precipitate was slowly formed. After 6 h stirring the suspension was filtered off, the precipitate was washed with Et_2O and dried to constant weight under reduced pressure. Recrystallised from $CHCl_3$–n-hexane, 85% yield. Mp 228–230 °C. Calc. for $C_{44}H_{46}CdN_6O_4$: C, 63.27; H, 5.55; N, 10.06. Found: C, 63.08; H, 5.73; N, 9.98%. IR (Nujol, cm^{-1}): 1598vs (C=O), 435s (br) 420s, 387s (Cd–O), 244m (Cd–N). ^{1}H NMR (CDCl$_3$): δ, 0.93 (s, br) (18H, CH$_2$C(CH$_3$)$_3$), 2.41 (s) (6H, 3-CH$_3$), 2.50 (s, br) (4H, CH$_2$C(CH$_3$)$_3$), 7.0–7.8 (m) (10H, N-*Ph*), 7.92 (s), 8.08 (t, br), 8.41 (d), 9.32 (d, br) (8H, CH$_{phen}$). ^{113}Cd NMR (CDCl$_3$): δ, 25.2. This compound can also be obtained by interaction of **1** with phen in CHCl$_3$ (70% yield).

[Cd(Q$_C$)$_2$(phen)] 4. Compound **4** has been obtained by an identical method to **3**. Recrystallised from $CHCl_3$–n-hexane, 82% yield. Mp 234–237 °C. Calc. for $C_{46}H_{46}CdN_6O_4$: C, 64.30; H, 5.40; N, 9.78. Found: C, 64.18; H, 5.54; N, 9.70%. IR (Nujol, cm^{-1}): 1632vs (C=O), 420s, 401m, 347s (Cd–O), 247m (Cd–N). ^{1}H NMR (CDCl$_3$): δ, 1.1–1.9 (m), 2.8 (t) (22H, C$_6$H$_{11}$), 2.40 (s) (6H, 3-CH$_3$), 7.08 (t, br), 7.30 (t, br), 7.86 (d, br) (10H, N-*Ph*), 7.92 (s), 7.98 (t, br), 8.45 (d), 9.31 (d, br) (8H, CH$_{phen}$). ^{113}Cd NMR (CDCl$_3$): δ, 24.7. MW (CHCl$_3$): 845 ($c = 1.4 \times 10^{-2}$ m); 837 ($c = 1.3 \times 10^{-2}$ m). This compound can also be obtained by interaction of **2** with phen in CHCl$_3$ (60% yield).

[Cd(Q$_T$)$_2$(bipy)] 5. Compound **5** has been obtained by an identical method to **3**. Recrystallised from $CHCl_3$–n-hexane, 78% yield. Mp 217–219 °C. Calc. for $C_{42}H_{46}CdN_6O_4$: C, 62.18; H, 5.72; N, 10.36. Found: C, 62.10; H, 5.83; N, 10.38%. IR

(Nujol, cm^{-1}): 1600vs (C=O), 413vs, 386m, 345m (Cd–O), 239m (Cd–N). ^{1}H NMR (CDCl$_3$): δ, 0.96 (s, br) (18H, CH$_2$C(CH$_3$)$_3$), 2.40 (s) (4H, CH$_2$C(CH$_3$)$_3$), 2.50 (s) (6H, 3-CH$_3$), 7.06 (t), 7.28 (t), 8.02 (t) (10H, N-*Ph*), 7.92 (s), 7.52 (t), 7.95 (t), 8.18 (d), 9.08 (d) (8H, CH$_{bipy}$). ^{113}Cd NMR (CDCl$_3$): δ, 26.5. MW (CHCl$_3$): 719 ($c = 1.4 \times 10^{-2}$ m); 702 ($c = 0.9 \times 10^{-2}$ m). This compound can also be obtained by interaction of **1** with bipy in CHCl$_3$ (73% yield).

[Cd(Q$_C$)$_2$(bipy)] 6. Compound **6** has been obtained by the same method as that described for **3**. Recrystallised from $CHCl_3$–n-hexane, 80% yield. Mp 215–218 °C. Calc. for $C_{44}H_{46}CdN_6O_4$: C, 63.27; H, 5.55; N, 10.06. Found: C, 63.38; H, 5.64; N, 10.20%. IR (Nujol, cm^{-1}): 1628vs (C=O), 409vs, 401sh, 342vs (Cd–O), 247m (Cd–N). ^{1}H NMR (CDCl$_3$): δ, 1.1–1.9 (m), 2.82 (t) (22H, C$_6$H$_{11}$), 2.40 (s) (6H, 3-CH$_3$), 7.10 (t), 7.30 (t), 7.98 (d, br) (10H, N-*Ph*), 7.53 (t, br), 7.92 (t, br), 8.12 (d, br), 9.01 (d, br) (8H, CH$_{bipy}$). ^{113}Cd NMR (CDCl$_3$): δ, 26.1. This compound can also be obtained by interaction of **2** with bipy in CHCl$_3$ (55% yield).

[Cd(Q$_T$)$_2$(trime)] 7. Compound **7** has been obtained by interaction of $Cd(O_2CCH_3)_2 \cdot 2H_2O$ (0.266 g, 1.0 mmol) with the proligand HQ$_T$ (0.545 g, 2.0 mmol) and N,N',N''-trimethylethylenediamine (trime, 0.102 g, 1.0 mmol) in 30 ml of MeOH. The transparent solution was stirred overnight, then its volume was reduced to one half under vacuum. Upon cooling at 0 °C a dark-green precipitate slowly formed. The suspension was filtered off, the precipitate washed with Et_2O and dried to constant weight under reduced pressure. Recrystallised from $CHCl_3$–n-hexane, 75% yield. Mp 179–181 °C decomp. Calc. for $C_{37}H_{52}CdN_6O_4$: C, 58.69; H, 6.92; N, 11.10. Found: C, 58.39; H, 6.85; N, 11.13%. IR (Nujol, cm^{-1}): 3220br (NH $\cdots$ N), 1650 (NH $\cdots$ N), 1633vs (C=O), 453s, 433vs, 388m (Cd–O). ^{1}H NMR (CDCl$_3$): δ, 0.99 (s) (18H, CH$_2$C(CH$_3$)$_3$), 2.41 (s) (6H, 3-CH$_3$), 2.48 (s) (4H, CH$_2$C(CH$_3$)$_3$), 2.50 (s), 2.52 (s) (9H, NCH$_3$ $_{trime}$), 2.59 (t), 2.63 (t) (4H, N–CH$_2$ $_{trime}$), 2.90 (br) (1H, NH) 7.08 (t), 7.29 (t), 7.92 (t) (10H, N-*Ph*). ^{113}Cd NMR (CDCl$_3$): δ, 28.4. MW (CHCl$_3$): 614 ($c = 1.4 \times 10^{-2}$ m); 590 ($c = 0.9 \times 10^{-2}$ m).

[Cd(Q$_T$)$_2$(tmeda)] 8. Compound **8** has been obtained by the same method as that described for **7**. Recrystallised from $CHCl_3$–n-hexane, 72% yield. Mp 201–203 °C decomp. Calc. for $C_{38}H_{54}CdN_6O_4$: C, 59.18; H, 7.06; N, 10.90. Found: C, 59.13; H, 7.14; N, 11.06%. IR (Nujol, cm^{-1}): 1612vs (C=O), 450m, 439s, 411m, 377m (Cd–O). ^{1}H NMR (CDCl$_3$): δ, 0.98 (s) (18H, CH$_2$C(CH$_3$)$_3$), 2.40 (s) (6H, 3-CH$_3$), 2.47 (s) (4H, CH$_2$C(CH$_3$)$_3$), 2.49 (s) (12H, NCH$_3$ $_{tmeda}$), 2.64 (t) (4H, N–CH$_2$ $_{tmeda}$), 7.05 (t), 7.28 (t), 7.93 (t) (10H, N-*Ph*). ^{113}Cd

NMR (CDCl$_3$): δ, 26.6. MW (CHCl$_3$): 642 ($c = 1.3 \times 10^{-2}$ m); 633 ($c = 0.9 \times 10^{-2}$ m).

Crystal structure determination

Diffraction data for compounds **1**, **4** and **8** were collected at low temperatures on a IPDS (Stoe) diffractometer using graphite monochromated Mo-Kα radiation. Crystallographic data are presented in Table 2. The structures **1**, **4** and **8** were solved by direct methods using SHELXS-86 [20] and refined anisotropically for all non-hydrogen atoms using SHELXL-93 [21]. No absorption corrections were applied. In **1** the hydroxyl H atom of EtOH was refined isotropically. The other H atoms in **1**, **4** and **8** were placed in calculated positions and refined in a riding mode. Most of the crystals of [Cd(Q$_C$)$_2$(phen)] **4** were twinned. Data collection was carried out for a small weak reflecting crystal. In addition the presence of pseudo translations for the pairs of four crystallographically independent [Cd(Q$_C$)$_2$(phen)] molecules resulted in higher correlation coefficients. Therefore, the refinement was performed using constraints (SAME [21]) concerning the geometry of phen ligands in four molecules of [Cd(Q$_C$)$_2$(phen)] complex. In [Cd(Q$_T$)$_2$(tmeda)] **8**, 'Bu groups were found to be disordered around the C–'Bu bond with occupancy factors 0.56(2) and 0.44(2).

CCDC reference number 186/1814.

See http://www.rsc.org/suppdata/dt/a9/a908913f/ for crystallographic files in .cif format.

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