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A Synthetic and X-ray Crystallographic Study of Zinc and Platinum Complexes of 4,5-Diazafluoren-9-one (Dafone) and Dicobalt Hexacarbonyl Derivatives of 9-Phenylethynyl-4,5-Diazafluoren-9-ol: Chelation versus Monocoordination

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Keywords: Metal-nitrogen linkages / Asymmetric bonds / Hydrogen bonds / Coordination modes / Zinc / Platinum / Cobalt

Reaction of 4,5-diazafluoren-9-one (dafone, **6**) and zinc dichloride yields [(dafone)$ZnCl_2(H_2O)$] (**11**) in which the $ZnCl_2$ moiety is coordinated to a single nitrogen atom and also to a molecule of water. Hydrogen bonding, not only to the uncomplexed nitrogen atom of dafone but also to the ketonic oxygen atom of a neighbouring molecule, leads to a zigzag chain structure. In contrast, reaction with anhydrous zinc iodide forms *cis*-(dafone)$_2ZnI_2$ (**12**) in which the metal–nitrogen distances – 2.170(5) and 2.456(5) Å – are significantly different. Dafone, in the presence of dimethyl sulfoxide, reacts with K_2PtCl_4 to produce square-planar (dafone)$PtCl_2$(dmso) (**13**), whereas with K_2PtBr_6 the octahedral complex (dafone)$PtBr_4$ (**14**) is formed in which the ligand chelates in a symmetrical fashion. Treatment of dafone with phenylethynyllithium furnishes 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**), which forms a square-planar nitrogen-bonded $PtCl_2$ complex, **15**. Reaction of **7** with $Co_2(CO)_8$ yields the (μ-alkyne)hexacarbonyldicobalt cluster **17**, which undergoes protonation at the nitrogen atom to form **20** rather than at the alcohol to form a cobalt-complexed propargyl cation. Alkynol **7** also reacts with HBr by addition across the triple bond to form Z-9-[(2-bromo-2-phenyl)ethenyl]-4,5-diazafluoren-9-ol (**10**). X-ray crystal structures are reported for **6**, **7**, **10**–**15**, **17** and **20**, and their differing hydrogen-bonding motifs are discussed.
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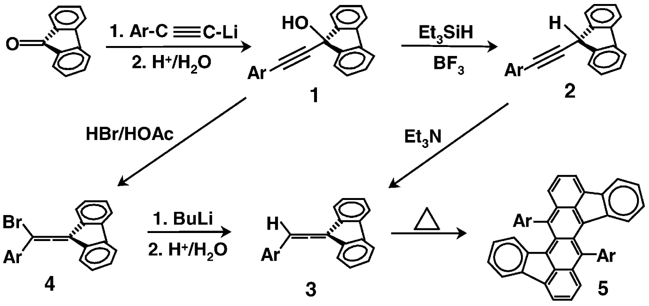
Introduction

We have recently reported a route to electroluminescent tetracenes through dimerisation of fluorenylideneallenes.[1–3] As depicted in Scheme 1, treatment of fluorenone with an alkynyllithium yields the corresponding 9-alkynylfluoren-9-ol, **1**. Conversion to the required 3,3-(biphenyl-2,2′-diyl)-1-arylallene **3** can be accomplished either by reaction with BF_3/Et_3SiH (to form an alkyne **2**, which readily rearranges under basic conditions)[4–6] or by formation of the bromoallene **4**,[7] followed by lithiation and hydrolysis.[8] Subsequent thermolysis of the allenes yields tetracenes **5**. This general procedure has since been extended to include allene dimers containing halogens, and also silyl,[8,9] phosphane[10] and ferrocenyl[11] substituents.



Scheme 1. Synthetic routes to diindenotetracenes **5**.

We here describe the preparation of 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**), an attempt to convert it into the corresponding allene **8** and the synthesis and characterisation of a series of metal complexes of **7** and **8**.

Results and Discussion

With the goal of preparing an allene **8** en route to a tetraazatetracene **9**, with potentially interesting photophysical properties, 4,5-diazafluoren-9-one (dafone, **6**) was treated with phenylethynyllithium to yield the alkynol **7**, as shown

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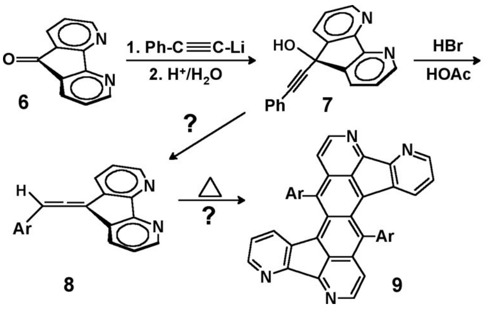
in Scheme 2. The structure of dafone (**6**) determined at 293 K has already been reported;[12] however, as X-ray quality crystals were at hand, a data set was collected at 100 K. The changes in bond lengths and angles are minor. Alkynol **7** is almost insoluble in many common solvents but can be recrystallised from 95:5 dichloromethane/methanol, and its molecular structure is shown in Figure 1. More interestingly, it can be obtained in two crystalline forms: as an anhydrous dimeric version with hydrogen bonds ($N\cdots HO$ 2.059 Å) linking a nitrogen atom of one molecule with a hydroxyl group of its neighbour, as shown in Figure 2, and also as a hydrated molecule that exists as a dimer with water molecules bridging both nitrogen atoms of one diazafluorenyl unit to the hydroxyl group of a neighbouring alkynol ($N\cdots H_2O$ 1.975 Å; $H_2O\cdots HO$ 1.754 Å), as depicted in Figure 3.



Scheme 2. Potential route to tetraazatetracenes **9**.

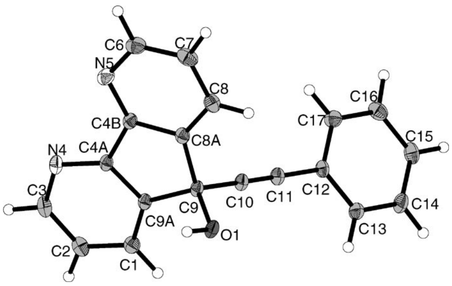


Figure 1. Molecular structure of 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**).

The $N\cdots N$ distances in **7** and in **7**·H_2O are 3.061 and 3.076 Å, respectively, whereas in dafone itself the $N\cdots N$ distance is 3.053 Å. The metric parameters of **7**, and of **7**·H_2O, closely resemble those found in dafone, except, of course, for those around the tetrahedral carbon atom C9, which bears the newly introduced alkynol functionality. The distances between the facing biaryl planes in the dimers **7** and **7**·H_2O are 3.359 Å and 3.279 Å, respectively.

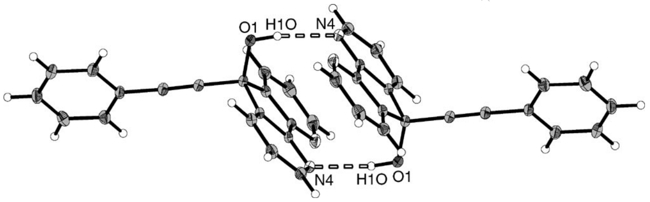


Figure 2. The $OH\cdots N$ hydrogen bonding in 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**).

As noted above, the conventional route to allenes from alkynols requires treatment with boron trifluoride and triethylsilane to furnish the corresponding alkyne, with subsequent base-promoted isomerisation to the allene;[4–6] in the present case, one might suspect that the Lewis acidic BF_3 would preferentially bind to a ring nitrogen atom and so preclude this approach. An alternative approach (Scheme 1) involves the reaction of the alkynol with cold dilute HBr to yield a bromoallene that can be lithiated and then quenched with water or dilute acid.[7,8] However, as shown in Scheme 2, when **7** was treated with HBr, the resulting product was shown to arise instead from addition across the triple bond to give *Z*-9-[(2-bromo-2-phenyl)ethenyl]-4,5-diazafluoren-9-ol (**10**), which was unequivocally characterised by X-ray crystallography (Figure 4). As with the alkynol precursor **7**, the system crystallises as a dimer, in which the hydroxyl moiety is hydrogen-bonded ($OH\cdots N$ 2.082 Å) to a nitrogen atom in the other molecule (Figure 5); the distance between the facing biaryl planes in the dimer of **10** is 3.295 Å.

It was therefore decided to consider the possibility of protecting **6** or **7** by complexation of the nitrogen atoms to a range of transition-metal centres, and here we discuss the syntheses and characterisation of several such complexes. The structures of a number of dafone derivatives of Mn,[13] Co,[14] Ni,[15] Cu,[16] Zn,[17] Cd,[18] Pd,[19] Ru,[20] Eu,[21] and Sn[22] have been previously reported. Comparisons of the $N\cdots N$ distances with those (≈2.62–2.65 Å) in the widely-studied bipyridyl or 1,10-phenanthrolene systems, which have a noticeably smaller bite, must be made. Evidently, the

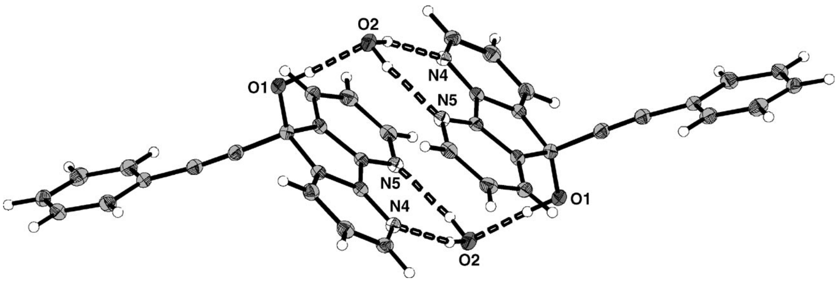


Figure 3. The hydrogen-bonding motif in 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**·H_2O).

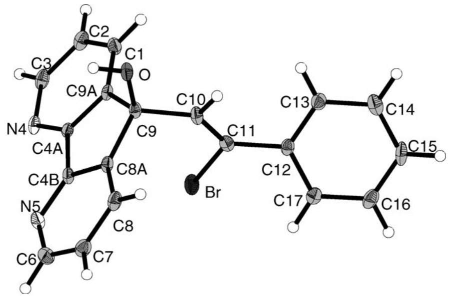


Figure 4. Molecular structure of *Z*-9-[(2-bromo-2-phenyl)ethenyl]-4,5-diazafluoren-9-ol (**10**).

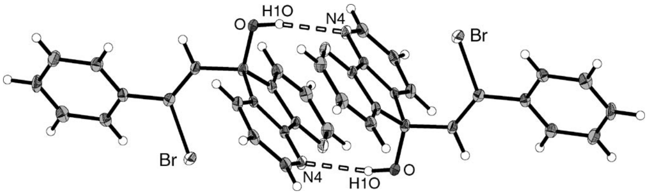


Figure 5. The intermolecular OH···N hydrogen bonding in **10**.

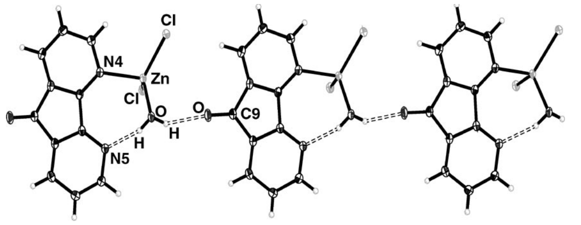


Figure 6. Bird's eye view of the hydrogen-bonding pattern in [(dafone)ZnCl$_2$(H$_2$O)] (**11**).

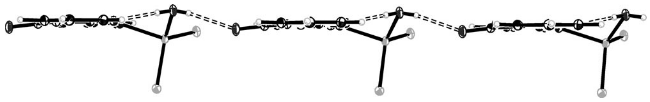


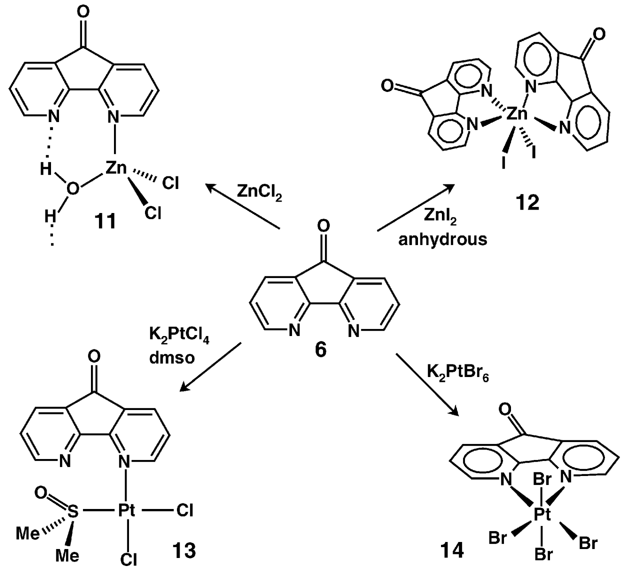
Figure 7. Side view of the hydrogen bonding in **11**, which illustrates the zigzag pattern.

presence of the five-membered ring in dafone pulls the nitrogen atoms further apart, increases the rigidity of the system, and makes chelate formation somewhat more challenging for small metals.[16d]

Metal Complexes of 4,5-Diazafluoren-9-one (dafone)

The reaction of a thf solution of ZnCl$_2$ with dafone in dichloromethane yielded X-ray quality crystals, which were analysed to be [(dafone)ZnCl$_2$(H$_2$O)] (**11**). As shown in Figure 6, the zinc is tetrahedrally coordinated to a single nitrogen atom [Zn–N 2.0932(12) Å] and to two chlorine atoms, as well as to a water molecule [Zn–O 1.9886(11) Å]; the N···N distance in **11** (3.148 Å) is slightly longer than that in the free ligand. The coordinated water molecule is hydrogen bonded not only to the uncomplexed nitrogen atom in dafone (N···H 1.890 Å), but also to the carbonyl oxygen atom of a neighbouring molecule (C=O···H 2.085 Å). This results in a series of one-dimensional hydrogen-bonded zigzag chains, which stack in an antiparallel fashion; moreover, as illustrated in Figure 7, the chain is not planar but rather adopts a structure such that all the zinc atoms lie on one side of the plane defined by the dafone molecules and the bridging water molecules are situated above this plane. This is in contrast to the situation in [(dafone)$_2$Zn(H$_2$O)$_2$]$^{2+}$ (as either the nitrate or perchlorate salt), which adopts a *trans* octahedral geometry and forms a one-dimensional hydrogen-bonded chain structure.[17]

As depicted in Scheme 3, treatment of dafone with ZnI$_2$ under rigorously anhydrous conditions yielded crystals of *cis*-(dafone)$_2$ZnI$_2$ (**12**, Figure 8). The metal adopts a distorted octahedral environment in which the nitrogen atoms within each dafone molecule are asymmetrically bonded to the metal. The Zn–N bond *trans* to the iodine atom is long [2.456(5) Å], whereas the Zn–N linkage *trans* to the other dafone molecule is considerably shorter [2.170(5) Å]. The N···N distance within the dafone ligands in **12** (2.912 Å) is slightly contracted as a result of chelation to Zn^{2+}; the internal N–Zn–N angle is 77.8° and the I–Zn–I angle is 102.1°. Likewise, in the analogous complexes *cis*-(dafone)$_2$MnCl$_2$[13] and *cis*-(dafone)$_2$Co(NCS)$_2$,[14b] the metal–N bonds involving the nitrogen atoms *trans* to the halide or pseudohalide group are longer: Mn–N 2.445(2) and 2.323(2) Å, N–Mn–N 75.8° and Cl–Mn–Cl 103.3°; Co–N 2.266(3) and 2.224(3) Å, N–Co–N 79.8° and SCN–Co–NCS 96.8°. As noted above, the structure of [*trans*-(dafone)$_2$Zn(H$_2$O)$_2$]$^{2+}$ has been reported,[17] and, once again, the Zn–N bonds are not equivalent [2.276(4) and 2.151(4) Å, N–Zn–N 80.8° (perchlorate salt); 2.290(3) and 2.201(3) Å, N–Zn–N 81.3° (nitrate salt)], which demonstrates the difficulty in forming symmetrical chelate complexes of dafone with first row transition metals. The analogous copper complexes [*trans*-(dafone)$_2$CuX$_2$] exhibit even more dramatic differences for the metal–nitrogen bond lengths [2.785(6)



Scheme 3. Reactions of dafone (**6**) with metal salts.

and 1.966(5) Å in the dibromido complex],[16d] but such phenomena may be amplified by Jahn–Teller effects that, of course, do not operate in d^{10} Zn^{II} systems.

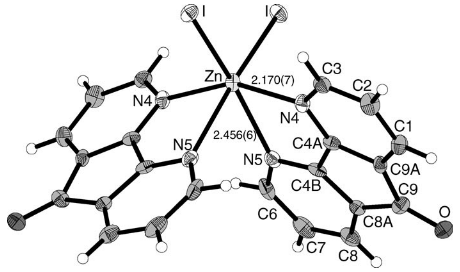


Figure 8. Molecular structure of *cis*-(dafone)$_2$ZnI$_2$ (**12**).

In the case of platinum, a metal with a larger ionic radius than zinc, chelation may be expected to be favoured. Treatment of a dichloromethane solution of dafone with an aqueous solution of K_2PtCl_4 containing some dmso, to help solubilise both reactants, furnished crystals of [(dafone)-PtCl$_2$(dmso)] (**13**). The X-ray crystal structure (Figure 9) reveals that the dichloridoplatinum moiety is coordinated to only one of the dafone nitrogen atoms – the square plane is completed by a sulfur-bonded dimethyl sulfoxide molecule. The N···N distance of 3.086 Å is scarcely changed from that in the free ligand, and the Pt–N bond length of 2.024(4) Å in **13** is significantly shorter than the Zn–N distance of 2.0932(12) Å in [(dafone)ZnCl$_2$(H$_2$O)] (**11**). A possible explanation lies in the extended structure seen in **11**, in which the hydrogen-bonding motif places the zinc out of the plane defined by the dafone ligands, which results in a somewhat stretched Zn–N distance.

Finally, to avoid interference from a potentially coordinating solvent such as dimethyl sulfoxide, an aqueous solution of K_2PtBr_6 was treated with dafone in methanol; crystals of (dafone)PtBr$_4$ (**14**) were obtained. As shown also in Figure 9, the platinum atom is in a very slightly perturbed octahedral environment, and the *cis*-Br–Pt–Br and *cis*-Br–Pt–N angles only range from 88° to 92°; the N–Pt–N angle is 82.7(2)°. The bulky bromido ligands limit the approach of the dafone nitrogen atoms to 2.099(5) and 2.103(4) Å, but the N···N distance of 2.778 Å is by far the shortest of all the molecules reported herein; the Pt–N bonds are not significantly different.

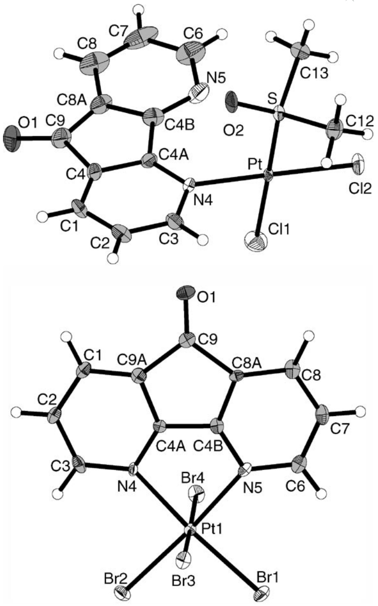
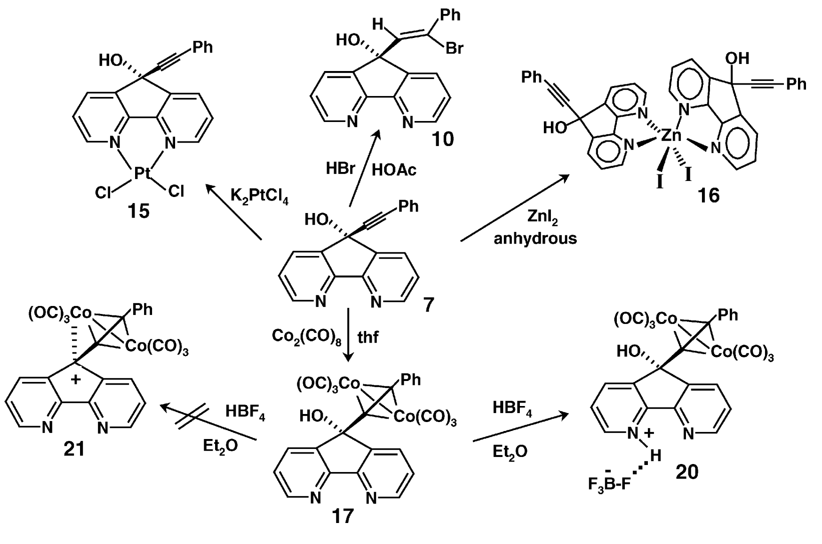


Figure 9. Molecular structures of [(dafone)PtCl$_2$(dmso)] (**13**) and (dafone)PtBr$_4$ (**14**).

Metal Complexes of 9-Phenylethynyl-4,5-diazafluoren-9-ol

In addition, we prepared some metal complexes of the alkynol **7**, not only by coordination to the nitrogen atoms, but also by addition to the alkyne unit, as shown in Scheme 4. It was found that the reaction with K_2PtCl_4 gave a square-planar complex, **15**; although the connectivity is



Scheme 4. Reactions of 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**).

evident (Figure 10), the crystal quality[23] did not permit a detailed discussion of the bond lengths. Moreover, reaction of **7** with anhydrous ZnI_2 led to the formation of bis(9-phenylethynyl-4,5-diazafluoren-9-ol)ZnI_2 (**16**), which presumably is analogous to (dafone)$_2$$ZnI_2$ (**12**); however, it was not possible to obtain X-ray quality crystals of **16**.

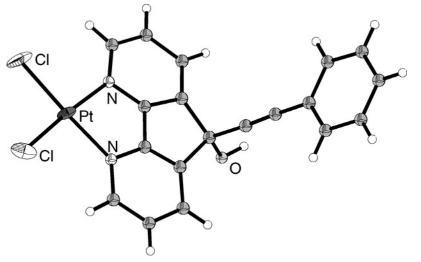
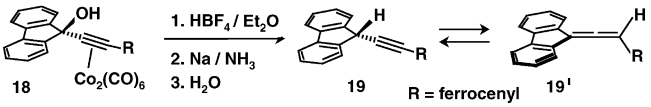


Figure 10. Structure of dichlorido(9-phenylethynyl-4,5-diazafluoren-9-ol)platinum(II) (**15**).

Alkynol **7** also reacted readily with dicobalt octacarbonyl to yield the anticipated (μ-alkyne)hexacarbonyldicobalt cluster **17**. As with the free ligand, **7**·H_2O, the system crystallises as a dimer in which water molecules bridge both nitrogen atoms of one diazafluorenyl unit to the hydroxyl group of the neighbouring alkynol [N4···H_2O 2.048 Å; N5···H_2O 2.153 Å; H_2O···HO 1.880 Å], as depicted in Figure 11.

It is well established that propargyl cations are greatly stabilised when complexed to a $Co_2(CO)_6$ moiety.[24] Moreover, it has been reported that protonation of the closely analogous (9-ferrocenylethynyl-fluoren-9-ol)$Co_2(CO)_6$ cluster (**18**), and subsequent reduction of the resulting cation, yields the corresponding alkyne **19**, which was proposed to be in equilibrium with its isomeric allene **19′**, as shown in Scheme 5.[25]



Scheme 5. Proposed conversion of a ferrocenylalkynol to an allene.

However, when (9-phenylethynyl-4,5-diazafluoren-9-ol)-hexacarbonyldicobalt (**17**) was treated with HBF_4, product **20** was obtained. It was isolated and characterised by X-ray

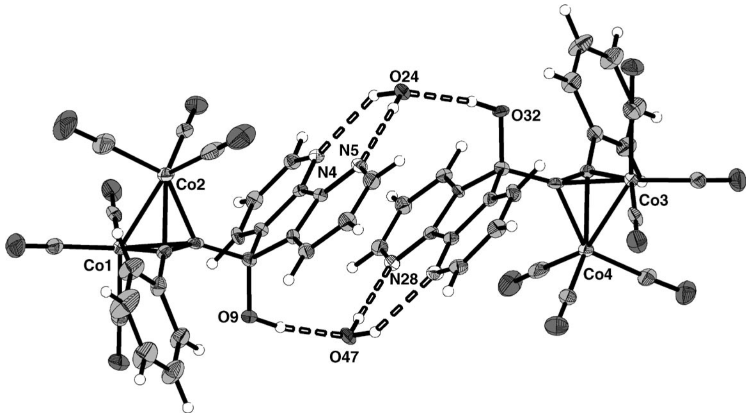


Figure 11. Structure of the cobalt cluster **17** illustrating the hydrogen bonding in the dimer, which is mediated by bridging water molecules.

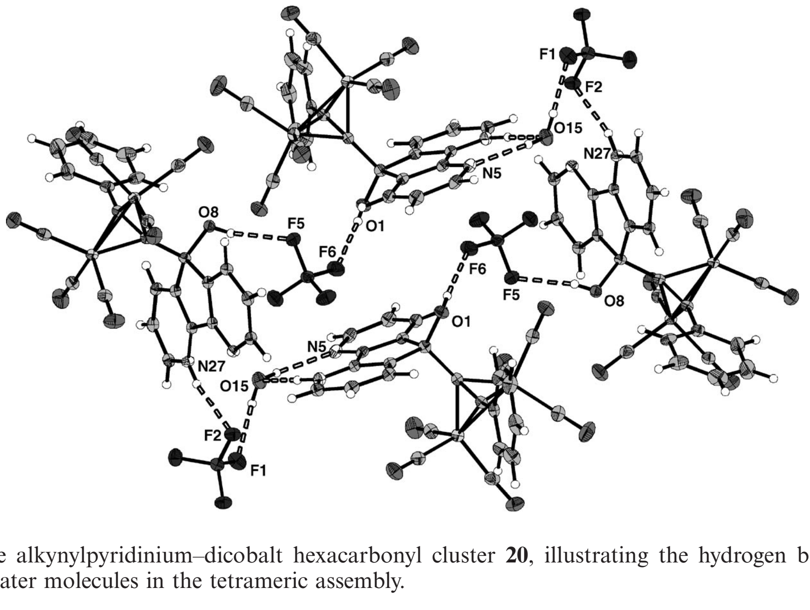


Figure 12. Structure of the alkynylpyridinium–dicobalt hexacarbonyl cluster **20**, illustrating the hydrogen bonding through the tetrafluoroborate groups and water molecules in the tetrameric assembly.

crystallography, which reveals that protonation occurs at a ring nitrogen atom rather than at the propargyl alcohol. Apparently, as shown in Scheme 4, formation of the cobalt-stabilised cationic cluster **21** is less favoured than generation of the pyridinium salt. Moreover, in the solid state, complex **20** exhibits a strikingly picturesque hydrogen-bonding motif in which a cationic N–H unit in one molecule is linked through a tetrafluoroborate and a water molecule to both the neutral nitrogen and the protonated nitrogen atoms of a proximate molecule. This “dimeric” fragment of two pyridinium cationic clusters sharing a single tetrafluoroborate anion is, in turn, hydrogen-bonded to its two hydroxyl units, through another pair of tetrafluoroborate anions, thus generating the tetrameric assembly shown in Figure 12.

Conclusions

As noted by a number of previous workers,[13–22] the rather long N···N distance in 4,5-diazafluoren-9-one (dafone) (**6**) frequently renders symmetrical chelate formation to be non-competitive, with monocoordination and incorporation of an additional ligand. The asymmetry of the M–N bond lengths is clearly apparent in both *cis*- and *trans*-(dafone)$_2$MX$_2$ complexes, and is particularly evident in d^9 Cu^{II} systems in which geometric distortions are amplified by Jahn–Teller effects.[16] However, with larger metal ions in high oxidation states, such as Pt^{IV}, dafone can function as a symmetrically bonded chelating ligand. The closely related molecule 9-phenylethynyl-4,5-diazafluoren-9-ol (**7**) likewise forms complexes with zinc and platinum and also reacts with $Co_2(CO)_8$ to yield the dicobalt hexacarbonyl cluster **17**, which undergoes preferential protonation at the nitrogen atom rather than the formation a cobalt-stabilised diazafluorenyl cation. Derivatives of **7** in which both the alkyne substituent and the ring nitrogen atoms are complexed by metals will be the topic of a future report.

Experimental Section

General: All experiments were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Varian VNMRS 300 MHz, 400 MHz or Inova 500 MHz spectrometers; the sparing solubility of some complexes resulted in very weak spectra. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer and were calibrated with polystyrene. Melting points were determined on an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin. 4,5-Diazafluoren-9-one (dafone) was prepared from 1,10-phenanthroline, potassium hydroxide and potassium permanganate by a literature method.[26]

Synthesis of 9-Phenylethynyl-4,5-diazafluoren-9-ol (7): *n*-Butyllithium (27.5 mL of a 1.6 M solution, 44 mmol) was added dropwise to phenylacetylene (4.8 mL, 44 mmol) in dry thf (120 mL) at 0 °C, and the solution was then held in a warm water bath (approximately 45 °C) for about 20 min. 4,5-Diazafluoren-9-one (4.01 g, 22.0 mmol) was added slowly at room temperature, and the solution was stirred for 72 h. The solution was quenched with water (10 mL), and the precipitate was filtered and washed with thf. Chromatography on alumina (eluent dichloromethane/methanol, 95:5) and removal of solvent yielded **7** as a colourless powder (5.37 g, 18.9 mmol, 86%). M.p. 219 °C. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from CH_2Cl_2/MeOH, 95:5. ^{1}H NMR (500 MHz, CD_3OD): δ = 8.69 (dd, J = 5.0, J = 1.5 Hz, 2 H, H^{3,6}), 8.22 (dd, J = 7.5, J = 1.5 Hz, 2 H, H^{1,8}), 7.51 (dd, J = 7.5, J = 5.0 Hz, 2 H, H^{2,7}), 7.41 (dd, J = 7.5, J = 1.5 Hz, 2 H, H^{13,17}), 7.34 (m, 1 H, H^{15}), 7.31 (m, 2 H, H^{14,16}), 5.49 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 157.5 (C^{4a,4b}), 152.0 (C^{3,6}), 144.8 (C^{8a,9a}), 134.0 (C^{1,8}), 132.8 (C^{13,17}), 130.0 (C^{15}), 129.5 (C^{14,16}), 126.0 (C^{2,7}), 123.2 (C^{12}), 88.6 (C^{10}), 84.2 (C^{11}), 72.1 (C^9) ppm. MS (ES): *m/z* = 285 [M + H]. IR (KBr): $\tilde{\nu}$ = 3456 (OH), 2222 (C≡C) cm^{-1}. $C_{19}H_{12}N_2O$ (284.32): calcd. C 80.27, H 4.25, N 9.85; found C 79.90, H 4.35, N 9.69.

Synthesis of *Z*-9-[(2-Bromo-2-phenyl)ethenyl]-4,5-diazafluoren-9-ol (10): Alkynol **7** (43.2 mg, 0.152 mmol) in acetic acid (1.5 mL) was treated with a fourfold excess of HBr in acetic acid, and the solution stirred at room temperature for 2 h. After removal of acetic acid, dissolution of the residue in dichloromethane, and washing with aqueous sodium carbonate, the solution was dried with sodium sulfate. Removal of the solvent furnished **10** (26.8 mg, 0.073 mmol; 48%). X-ray quality crystals were obtained from dichloromethane/diethyl ether. ^{1}H NMR (300 MHz, CD_3OD): δ = 8.34 (d, J = 5.0 Hz, 2 H, H^{3,6}), 7.82 (d, J = 7.3 Hz, 2 H, H^{1,8}), 7.47 (m, 2 H, H^{2,7}), 7.30–7.01 (m, 5 H, phenyl H) ppm. $C_{19}H_{13}BrN_2O\cdot C_4H_{10}O$ (439.35): calcd. C 62.88, H 5.28, Br 18.19, N 6.38; found C 63.04, H 4.95, Br 18.05, N 6.32.

Synthesis of Dichloridoaqua(4,5-diazafluoren-9-one)zinc(II) (11): Dafone (100 mg, 0.55 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and layered with benzene (4 mL). $ZnCl_2$ (75 mg, 0.55 mmol) was dissolved in thf (4 mL) and carefully layered onto the benzene. The mixture was left for 4 d to allow formation of yellow crystals at the interface. Filtration yielded $ZnCl_2$(dafone)(H_2O) (**11**) (101 mg, 0.30 mmol; 54%). $C_{11}H_6Cl_2N_2OZn\cdot H_2O$ (336.49): calcd. C 39.26, H 2.40, N 8.33; found C 39.51, H 2.35, N 8.63.

Synthesis of *cis*-Diiodido-bis(4,5-diazafluoren-9-one)zinc(II) (12): Dafone (200 mg, 1.10 mmol) dissolved in dry CH_2Cl_2 (4 mL) was layered onto a solution of anhydrous ZnI_2 (530 mg, 1.66 mmol) dissolved in dry thf (4 mL), and the sample was sealed for 20 h, after which time crystal formation had occurred at the interface. Filtration yielded (dafone)$_2$ZnI$_2$ (**12**) (320 mg, 0.47 mmol; 85%). ^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD): δ = 8.75 (br., 4 H, H^{3,6}), 7.98 (d, J = 7.3 Hz, 4 H, H^{1,8}), 7.36 (br., 4 H, H^{2,7}) ppm. $C_{22}H_{12}I_2N_4O_2Zn\cdot CH_2Cl_2$ (768.49): calcd. C 35.95, H 1.84, N 7.29; found C 35.63, H 1.84, N 6.85. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from CH_2Cl_2.

Synthesis of Dichlorido(4,5-diazafluoren-9-one)(dimethylsulfoxide)-platinum(II) (13): Dafone (200 mg, 1.10 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and layered onto benzene (4 mL). K_2PtCl_4 (457 mg, 1.10 mmol) was dissolved in water (3 mL) and dmso (5 mL) and carefully layered onto the benzene. The mixture was left for 4 d to allow formation of yellow crystals at the interface. Filtration yielded (dafone)PtCl$_2$(dmso) (**13**) (390 mg, 0.74 mmol; 67%). $C_{13}H_{12}Cl_2N_2O_2PtS$ (526.3): calcd. C 29.67, H 2.30, N 5.32; found C 29.50, H 2.35, N 5.53. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from CH_2Cl_2.

Synthesis of Tetrabromido(4,5-diazafluoren-9-one)platinum(IV) (14): Dafone (200 mg, 1.10 mmol) was dissolved in methanol (4 mL) and carefully layered onto a solution of K_2PtBr_6 (828 mg, 1.10 mmol) in water (4 mL). The reaction occurred immediately with formation of a bright orange precipitate. Filtration yielded (dafone)$PtBr_4$ (**14**) (620 mg, 0.89 mmol; 81 %). $C_{11}H_6Br_4N_2OPt$ (696.9): calcd. C 18.96, H 0.87, Br 45.86, N 4.02; found C 19.30, H 1.01, Br 46.02, N 4.23. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from CH_2Cl_2.

Synthesis of Dichlorido(9-phenylethynyl-4,5-diazafluoren-9-ol)-platinum(II) (15): 9-Phenylethynyl-4,5-diazafluoren-9-ol (57 mg, 0.200 mmol) in methanol (2 mL) was added dropwise to a hot (70 °C) solution of K_2PtCl_4 (83 mg, 0.200 mmol) in 0.1 M HCl (6 mL), and the mixture was heated at reflux for 2 h. The resulting precipitate was filtered and washed thoroughly with water, methanol and diethyl ether to yield **15** as a yellow powder (100 mg, 0.182 mmol; 91 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 5.7 Hz, 2 H, $H^{3,6}$), 8.34 (d, J = 7.7 Hz, 2 H, $H^{1,8}$), 7.65 (m, 2 H, $H^{2,7}$), 7.42 (d, J = 8 Hz, 2 H, *o*-phenyl), 7.35 (m, 3 H, *m*-, *p*-phenyl) ppm. IR (KBr): $\tilde{\nu}$ = 3316 (OH), 2232 (C≡C) cm^{-1}. $C_{19}H_{12}Cl_2N_2OPt$ (550.3): calcd. C 41.47, H 2.20, Cl 12.88, N 5.09; found C 41.23, H 2.00, Cl 12.61, N 5.40. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from CH_2Cl_2.

Synthesis of Diiodido-bis(9-phenylethynyl-4,5-diazafluoren-9-ol)-zinc(II) (16): 9-Phenylethynyl-4,5-diazafluoren-9-ol (151 mg, 0.533 mmol) and ZnI_2 (88 mg, 0.275 mmol) were stirred in thf (20 mL) for 20 h at room temperature. Removal of the solvent and recrystallisation from dichloromethane yielded **16** (145 mg, 0.163 mmol; 61 %) as a beige powder. ^{1}H NMR (300 MHz, [D$_6$]-acetone): δ = 8.55 (d, J = 5.1 Hz, 4 H, $H^{3,6}$), 8.05 (d, J = 7.6 Hz, 4 H, $H^{1,8}$), 7.41–7.26 (m, 14 H, $H^{2,7}$, phenyl H), 5.87 (s, 1 H, OH) ppm. $C_{38}H_{24}I_2N_4O_2Zn\cdot 0.5CH_2Cl_2$ (930.3): calcd. C 49.71, H 2.71, N 6.02; found C 49.77, H 2.68, N 5.61.

Synthesis of (9-Phenylethynyl-4,5-diazafluoren-9-ol)hexacarbonyl-dicobalt (17): 9-Phenylethynyl-4,5-diazafluoren-9-ol (**7**) (77 mg, 0.272 mmol) and dicobalt octacarbonyl (94 mg, 0.274 mmol) were stirred in dry thf (20 mL) for 24 h at room temperature. The sample was reduced to a volume of 1 mL; addition of diethyl ether and cooling yielded **17** (153 mg, 0.269 mmol; 99 %) as dark red crystals. M.p. 62 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.52 (d, J = 4.3 Hz, 2 H, $H^{3,6}$), 7.89 (d, J = 7.6 Hz, 2 H, $H^{1,8}$), 7.81 (m, 7 H, $H^{2,7}$), 7.40–7.16 (m, 5 H, phenyl H), 5.96 (s, 1 H, OH) ppm. $C_{25}H_{12}Co_2N_2O_7\cdot(C_2H_5)_2O$ (644.4): calcd. C 54.06, H 3.44, N 4.35; found C 53.91, H 3.73, N 4.36. Upon addition of $HBF_4\cdot OEt_2$ to an ethereal solution of the alkyne–dicobalt complex **17** at 0 °C, a red precipitate was eventually formed, which was recrystallised from acetone to yield X-ray quality crystals of **20**.

Table 1. Crystallographic data for **6**, **7**, **7·H$_2$O**, **10** and **11**.

	6	**7**	**7·H$_2$O**	**10**	**11**
Formula	$C_{11}H_6N_2O$	$C_{19}H_{12}N_2O$	$C_{19}H_{14}N_2O_2$	$C_{19}H_{13}BrN_2O$	$C_{11}H_8Cl_2N_2O_2Zn$
Formula mass	182.18	284.31	302.32	365.22	336.46
Temperature [K]	100(2)	293(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a [Å]	9.8958(9)	8.1451(14)	7.9361(10)	8.2371(12)	5.8614(6)
b [Å]	12.3746(12)	9.5973(16)	10.2148(13)	9.3676(14)	9.4507(9)
c [Å]	6.6687(6)	9.8067(16)	10.4803(13)	10.2678(15)	11.4436(11)
α [°]	90	86.894(3)	85.197(2)	85.532(3)	94.299(1)
β [°]	99.509(2)	66.943(2)	67.872(2)	81.873(2)	94.028(1)
γ [°]	90	89.281(3)	69.493(2)	84.309(3)	107.718(1)
V [Å^3]	805.41(13)	704.3(2)	736.00(16)	778.8(2)	599.25(10)
Z	4	2	2	2	2
$\rho_{calcd.}$ [g cm^{-3}]	1.502	1.341	1.364	1.557	1.865
μ [mm^{-1}]	0.100	0.085	0.090	2.645	2.487
F(000)	376	296	316	368	336
Crystal size [mm]	0.70 × 0.70 × 0.50	0.40 × 0.40 × 0.40	0.30 × 0.20 × 0.20	0.80 × 0.50 × 0.02	0.50 × 0.10 × 0.05
θ range [°]	2.09 to 28.28	2.13 to 28.30	2.10 to 27.00	2.01 to 28.00	1.79 to 28.51
Index ranges	$-13 \le h \le 13$	$-10 \le h \le 10$	$-10 \le h \le 10$	$-10 \le h \le 10$	$-7 \le h \le 7$
	$-16 \le k \le 16$	$-12 \le k \le 12$	$-13 \le k \le 12$	$-12 \le k \le 12$	$-12 \le k \le 12$
	$-8 \le l \le 8$	$-12 \le l \le 12$	$-13 \le l \le 13$	$-13 \le l \le 13$	$-14 \le l \le 15$
Reflections collected	6553	11896	6933	7532	10085
Independent reflections	1883	3284	3204	3721	2796
R_{int}	0.0236	0.0211	0.0219	0.0373	0.0157
Completeness to θ_{max} [%]	94.2	93.9	99.6	98.9	92.1
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.9516 and 0.6695	0.9670 and 0.8973	0.9822 and 0.7742	0.9490 and 0.4566	0.8857 and 0.6093
Data/restraints/parameters	1883/0/151	3284/0/247	3204/0/264	3721/0/209	2796/0/195
Goodness-of-fit on F^2	1.043	1.019	1.037	1.094	1.064
Final R values [$I > 2\sigma(I)$]					
R_1	0.0438	0.0424	0.0412	0.0463	0.0196
wR_2	0.1146	0.1064	0.1014	0.1383	0.0520
R values (all data)					
R_1	0.0460	0.0533	0.0464	0.0518	0.0202
wR_2	0.1171	0.1132	0.1051	0.1437	0.0523
Largest diff. peak/hole [e Å^{-3}]	0.359 and –0.502	0.279 and –0.145	0.353 and –0.237	0.944 and –0.741	0.493 and –0.213

Table 2. Crystallographic data for **12**, **13**, **14**, **17** and **20**.

	12	**13**	**14**	**17**	**20**
Formula	$C_{22}H_{12}N_4O_2ZnI_2\cdot CH_2Cl_2$	$(C_{13}H_{12}N_2O_2SCl_2Pt)_2\cdot CH_2Cl_2\cdot H_2O$	$(C_{11}H_6N_2OBr_4Pt)_2\cdot CH_2Cl_2$	$(C_{25}H_{12}N_2O_7Co_2H_2O)_8\cdot (C_5H_{12})_3\cdot C_4H_8O_2$[a]	$\{[C_{25}H_{13}N_2O_7Co_2][BF_4]\}_2\cdot H_2O$
Formula mass	768.45	1135.50	1478.74	5010.48	1334.10
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	*C*2 (#5)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	*C*2/*c* (#15)	$P\bar{1}$ (#2)
a [Å]	8.412(2)	8.3870(12)	14.4297(14)	24.928(3)	8.8436(6)
b [Å]	13.620(3)	9.8490(14)	18.2910(17)	24.901(3)	16.2401(11)
c [Å]	10.905(3)	11.3912(16)	12.4507(12)	34.744(4)	18.5611(13)
α [°]	90	66.705(2)	90	90	84.299(1)
β [°]	99.380(4)	86.617(2)	92.513(2)	98.148(2)	84.169(1)
γ [°]	90	78.209(2)	90	90	80.154(1)
V [Å^3]	1232.6(5)	845.8(2)	3283.0(5)	21349(4)	2603.8(3)
Z	2	1	4	4	2
$\rho_{\text{calcd.}}$ [g cm^{-3}]	2.071	2.265	2.992	1.559	1.702
μ [mm^{-1}]	3.747	8.903	18.443	1.297	1.354
F(000)	732	546	2664	10168	1332
Crystal size [mm]	0.20 × 0.20 × 0.01	0.60 × 0.50 × 0.40	0.15 × 0.10 × 0.02	0.60 × 0.40 × 0.02	0.45 × 0.30 × 0.20
θ range [°]	1.89 to 26.00	1.95 to 28.46	1.80 to 26.00	1.16 to 26.00	1.11 to 27.00
Index ranges	$-9 \le h \le 10$	$-11 \le h \le 11$	$-17 \le h \le 17$	$-30 \le h \le 30$	$-11 \le h \le 11$
	$-16 \le k \le 16$	$-13 \le k \le 13$	$-22 \le k \le 22$	$-30 \le k \le 21$	$-20 \le k \le 20$
	$-13 \le l \le 13$	$-14 \le l \le 14$	$-15 \le l \le 15$	$-42 \le l \le 42$	$-23 \le l \le 23$
Reflections collected	4769	14331	50321	57148	47610
Independent reflections	2407	3949	6451	20794	11365
R_{int}	0.0356	0.0453	0.0557	0.0437	0.0321
Completeness to θ_{max} [%]	99.8	92.3	100.0	99.0	100.0
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.9635 and 0.6521	0.1249 and 0.0214	0.7093 and 0.3889	0.9822 and 0.7742	0.7735 and 0.6961
Data/restraints/parameters	2407/1/155	3949/0/192	6451/0/370	20794/18/1451[a]	11365/0/860
Goodness-of-fit on F^2	1.015	1.088	1.098	1.031	1.052
Final *R* values [$I>2\sigma(I)$]					
R_1	0.0334	0.0253	0.0276	0.0624	0.0316
wR_2	0.0702	0.0589	0.0528	0.1567	0.0792
R values (all data)					
R_1	0.0376	0.0269	0.0352	0.0853	0.0396
wR_2	0.0720	0.0594	0.0549	0.1677	0.0843
Largest diff. peak/hole [e Å^{-3}]	1.679 and –0.738	2.496 and –1.974	1.228 and –0.761	1.182 and –0.690	0.783 and –0.263

[a] A SAME restraint was used to make both halves of the disordered pentane molecule [C90 to C94] equivalent. Also DELU restraints were applied to these atoms.

X-ray Measurements for 6, 7, 7·H$_2$O, 10–14, 17, 20: Crystal data were collected using a Bruker SMART APEX CCD area detector diffractometer and are listed in Tables 1 and 2. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudoempirical absorption correction based on redundant reflections was performed by the program SADABS.[27] The structures were solved by direct methods by using SHELXS-97,[28] and refined by full-matrix least-squares on F^2 for all data by using SHELXL-97.[29] Hydrogen-atom treatment varied from compound to compound, depending on the crystal quality. In **6**, **7**, **7·H$_2$O** and **20**, all hydrogen atoms were located in the difference Fourier map and allowed to refine freely with isotropic thermal displacement factors. The same applies to the water protons in **17**. All other hydrogen atoms were added at calculated positions and refined by using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom to which the H atom is attached. Anisotropic temperature factors were used for all non-hydrogen atoms. In **13** and **17**, the PLATON "squeeze" procedure[30] was used to treat regions of diffuse solvent(s) that could not be modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed, and modified F_o^2 written to a new HKL file. The number of electrons thus located was assigned to appropriate solvent molecules (one molecule of dichloromethane and one molecule of water in **13**, and one molecule of ethyl acetate in **17**). These solvents are included in the formula, formula weight, calculated density, μ and *F*(000). CCDC-716985 (**6**), -716990 (**7**), -716992 (**7·H$_2$O**), -716994 (**10**), -716987 (**11**), -716988 (**12**), -716986 (**13**), -716989 (**14**), -716991 (**17**) and -716993 (**20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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