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Inorganica Chimica Acta 318 (2001) 23–30

Inorganica Chimica Acta

Chelate-stabilized zinc complexes of alcohols and carbonyl compounds: pyridylphenylketone and pyridylphenylmethanol

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Received 8 January 2001; accepted 14 February 2001

Abstract

The reactions of various zinc salts with the chelating ketone pyridylphenylketone (PPK) and the chelating alcohol pyridylphenylmethanol (PPM) were studied. 2:1 reactions of PPK with ZnX_2 yielded octahedral complexes $(PPK)_2ZnX_2$ with $X = OSO_2CF_3$, Cl, Br, NCS. 1:1 reactions yielded the square pyramidal complexes $[(PPK)_2ZnHal]_2ZnHal_4$ with X = Br, I and the trigonal-bipyramidal complex $[(PPK)Zn(NCS)_2]_2$. With $Zn(SC_6F_5)_2$ the tetrahedral 1:1 complex $(PPK)Zn(SC_6F_5)_2$ resulted. Methanol as a coligand was incorporated in the octahedral complex $[(PPK)_2Zn(CH_3OH)_2](BF_4)_2$. Of the PPM complexes, only $(PPM)_2Zn(OSO_2CF_3)_2$ was analogous to the corresponding PPK complex. The zinc halides produced the octahedral complexes $[(PPM)_3Zn]ZnHal_4$ with X = Cl, Br. $Zn[N(SiMe_3)_2]_2$ and PPM yielded polymeric zinc pyridylphenylmethoxide.

Keywords: Crystal structures; Zinc complexes; Ketone complexes; Alcohol complexes

1. Introduction

Zinc-containing species play an important role in the catalytic activation of organic carbonyl compounds. This is so for both industrial organic chemistry [1] and biological processes [2]. Specifically, for the zinc containing alcoholdehydrogenase enzymes [2,3] it extends to the activation of both the carbonyl and alcoholic functions in their mutual redox interconversions. These facts provide ample justification for investigating the coordination chemistry of zinc with aldehydes, ketones, alcohols and terminal alkoxides as ligands.

However, except for alkoxides, these species are weak ligands and bind to zinc only when better ligands or donor solvents are absent. Typically, recrystallization from methanol can produce methanol adducts of zinc complexes [4], and we were the first to determine the crystal structures of hexa(alcohol)zinc complexes [5]. Similarly, prior to our own extensive studies [6–8] the aldehyde complexes of zinc were laboratory and structural curiosities [6]. The situation is somewhat more favourable with ketones [9]. Not counting the frequent zinc porphyrin solvates, four zinc–acetone [10,11] and one zinc–benzophenone complexes [12] have been structurally characterized. Again, we were the first to describe the structures of hexa(aldehyde)zinc complexes [6], and until today no hexa(ketone) complex of zinc has been fully characterized.

The evasiveness of the simple zinc–alcohol and zinc–aldehyde complexes has induced others [13–17] and ourselves [8,18,19] to resort to chelate assistance by employing pyridine-derived alcohols and aldehydes. Thereby, convincing structural [19] and functional [13,14] models of alcoholdehydrogenase could be obtained.

The present paper continues along these lines. In order to avoid the pitfalls of aldehyde chemistry in the presence of zinc ions, a chelating ketone was used. In order to allow comparisons of bonding and stability, the corresponding alcohol was also employed. The systems chosen were pyridylphenylketone (PPK) and pyridylphenylmethanol (PPM), which are the phenylated analogues of pyridine–carbaldehyde and pyridyl–methanol used by us previously [18,19]. We are not

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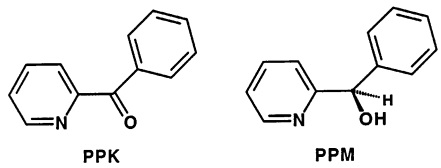
0020-1693/01/$ - see front matter
PII: S0020-1693(01)00395-4

aware of any zinc complex chemistry of these two ligands, but several copper complexes of PPK were described by Goher et al. [20].



2. Results and discussion

2.1. Complexes of PPK

The common anhydrous zinc salts were reacted with PPK in 1:2 and 1:1 stoichiometric ratios. The 1:2 reactions were straightforward for $Zn(CF_3SO_3)_2$, $ZnCl_2$, $ZnBr_2$ and $Zn(NCS)_2$ yielding the octahedral 1:2 complexes **1**–**4** $(PPK)_2ZnX_2$ [X = CF_3SO_3 (**1**), Cl (**2**), Br (**3**), NCS (**4**)].

When a 1:1 stoichiometric ratio was employed for $Zn(CF_3SO_3)_2$, complex **1** resulted again. However, with $ZnBr_2$ and ZnI_2, products with a 3:4:6 ratio of zinc, PPK and halide resulted, which were identified as $[(PPK)_2ZnHal]_2ZnHal_4$ (Hal = Br (**5**), I (**6**)). Yet another composition (1:1:2) was observed with $Zn(NCS)_2$, the resulting complex being identified as the thiocyanate-bridged dimer $[(PPK)Zn(NCS)_2]_2$ (**7**).

Starting with $Zn(SC_6F_5)_2$, one PPK ligand could be incorporated, resulting in the tetrahedral complex $(PPK)Zn(SC_6F_5)_2$ (**8**). In an attempt to prepare a complex bearing only PPK ligands, the very labile methanol complex $[Zn(MeOH)_6](BF_4)_2$ was treated with PPK. Irrespective of the stoichiometric ratio of the reagents, only two PPK ligands were attached to zinc in the product $[(PPK)_2Zn(MeOH)_2](BF_4)_2$ (**9**).

2.2. Complexes of PPM

As expected, PPM proved to be a weaker ligand than PPK. Furthermore, the racemic nature of PPM as resulting from the reduction of PPK seems to hamper crystallization, and hence an unambiguous characterization of the resulting compounds. Thus the structural assignments given for the PPM complexes rest mostly on their analytical compositions.

Only with $Zn(CF_3SO_3)_2$ was a product obtained that is analogous to that containing PPK: complex $(PPM)Zn(CF_3SO_3)_2$ (**10**) resulted in good yields. With $ZnCl_2$ and $ZnBr_2$ a dismutation of the zinc halide seems to occur again, this time leading to cationic constituents having three of the O,N-chelating PPM ligands per zinc ion. The resulting complexes $[(PPM)_3Zn]ZnHal_4$ [Hal = Cl (**11**), Br (**12**)] were the only isolated products, irrespective of the stoichiometric ratio of $ZnHal_2$ and PPM.

In order to introduce deprotonated PPM as an alkoxide ligand, PPM was reacted with $Zn[N(SiMe_3)_2]_2$, in which the silylamide ligands act as a base and a good leaving group. The complex $[Zn(pyridylphenylmethoxide)_2]_x$ (**13**) was obtained, which is likely to be an alkoxide-bridged oligomer.

2.3. Structural considerations

The ^1H NMR spectra of the complexes (see Section 3), showing mostly aromatic resonances, are of little diagnostic value. In contrast, the IR data of the PPK complexes (Table 1) are quite informative. They prove both O and N coordination of PPK in all cases by the typical lower-wavenumber shift of the ν(CO) absorptions and the typical higher-wavenumber shift of the ν(CN) pyridine ring absorptions. Although the ν(CN) bands move little, there are characteristic variations among the ν(CO) bands: in those complexes where a high coordination number and/or good coligands are present (**2**–**4**) there is the least shift of ν(CO). When the number of good donors is small or when the complexes are cationic (**1**, **5**, **6**, **9**) there is the highest shift of ν(CO). The complexes of PPM (**10**–**13**) lack such characteristic IR features, showing as typical bands only the broad OH absorptions between 3100 and 3300 cm^{-1}.

Of the 1:2 complexes **1**–**4**, **1** was chosen for a structure determination, the result of which is shown in Fig. 1. The ligand arrangement around zinc in the centrosymmetrical molecule is close to octahedral. The Zn–O(ketone) bond length is relatively short when compared with Zn–O(aldehyde) bond lengths in related complexes of pyridine–carbaldehyde [8]. This corresponds to the expectation that the ketonic ligands are better donors than the aldehydes towards zinc. In contrast, the Zn–O(sulfonate) bonds are comparatively long, as might have been expected considering the

Table 1
IR data (KBr, cm^{-1}) of the PPK complexes

	$\tilde{\nu}$(C=O)	$\tilde{\nu}$(CN) [a]
PPK	1668	1578
1	1624	1598
2	1648	1594
3	1649	1595
4	1659	1597
5	1622	1585
6	1619	1584
7	1635	1595
8	1638	1595
9	1625	1598

[a] Pyridine ring vibration.

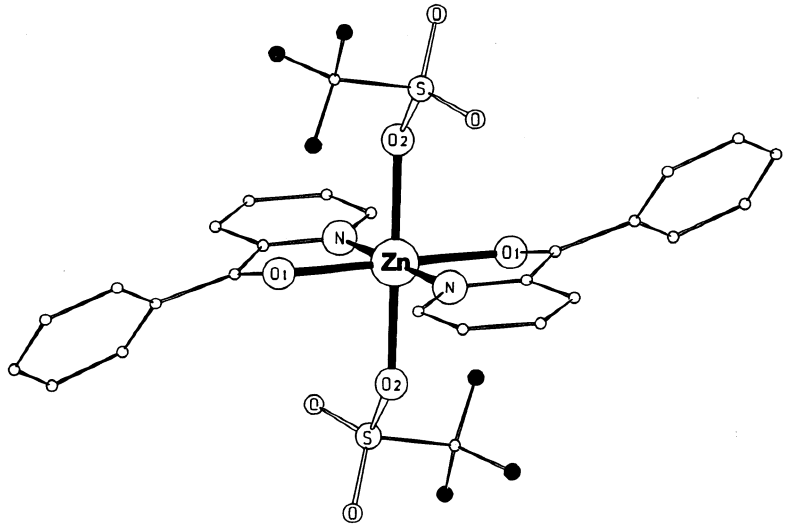


Fig. 1. Molecular structure of the centrosymmetrical complex $(PPK)_2Zn(CF_3SO_3)_2$ (**1**). Bond lengths (Å): Zn–N, 2.049(3); Zn–O1, 2.117(2); Zn–O2, 2.185(3); O1=C, 1.229(4); O2–S 1.453(3). Bond angles (°): N1–Zn–O1, 79.06(10); N1–Zn–O1′, 100.94(10); Zn–O1–C, 112.1(2); Zn–O2–S, 138.0(2).

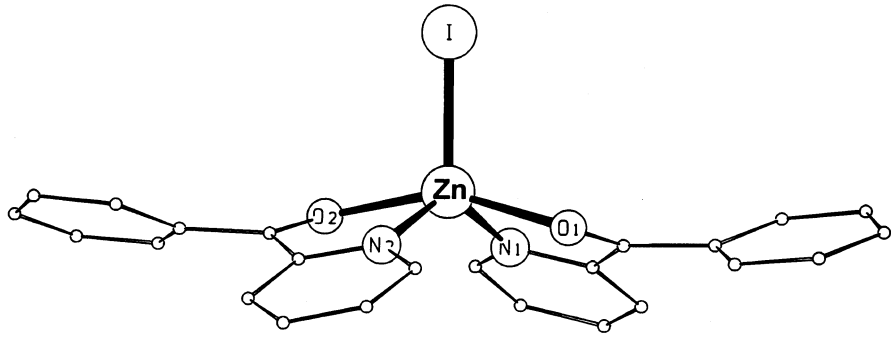


Fig. 2. Structure of the $[(PPK)_2ZnI]$ cations in **6**. Bond lengths (Å): Zn–N1, 2.067(5); Zn–N2, 2.055(5); Zn–O1, 2.156(4); Zn–O2, 2.161(4); Zn–I, 2.523(1); O1=C, 1.235(7); O2=C, 1.240(7). Bond angles (°): N1–Zn–O1, 76.8(2); N2–Zn–O2, 77.0(2); N1–Zn–O2, 92.3(2); N2–Zn–O1, 91.8(2); I–Zn–N1, 115.7(1); I–Zn–N2, 114.3(1); I–Zn–O1, 105.0(1); I–Zn–O2, 101.1(1).

mediocre ligating qualities of the triflate ion. As observed for the aldehyde complexes [6–8], the C=O bond length changes little upon coordination.

This suggests that complexes **2**–**4** assume structures like that of **1**. There is no evidence for or against this assumption other than the IR data, which group **2**–**4** together and differentiate them from **1**. However, pyridine–carbaldehyde forms octahedral L_2ZnHal_2 complexes for Hal = Cl, Br, I, which have the halide ligands in a cis-orientation [8]. Accordingly a cis-structure must also be considered for **2**–**4**.

Of the two 3:4:6 complexes, **6** was chosen for a structure determination. Fig. 2 shows the cationic constituents of **6**. Their square-pyramidal structure corresponds in nearly all molecular details to that of the corresponding pyridine–carbaldehyde zinc complex [8]. The only difference worth mentioning concerns the Zn–O bond lengths: they are about 0.1 Å shorter in **6** than in the aldehyde complex, again confirming the better donor qualities of the ketone PPK. The structure gives no clue as to why for certain zinc halide/NO ligand combinations the $[L_2ZnHal]_2ZnHal_4$ constitution is preferred.

The 1:1 composition of the thiocyanate complex **7** had led us to assume it to have a tetrahedral structure with both thiocyanate ligands attached via their sulfur atoms, as observed by us in several cases for $(chelate)Zn(SR)_2$ complexes [19]. The observed dinuclear structure (see Fig. 3) is unique for us: firstly because we have never observed it for pyridine-derived aldehydes or alcohols [8,19], and secondly because it is the first case of a trigonal-bipyramidal coordination of zinc in such species. The bond lengths and angles in the molecule are in the normal range, with the noteworthy observation that the axial and bridging NCS ligand has a shorter Zn–N bond than the equatorial and terminal NCS ligand. Obviously, the Zn–S coordination at one terminus of the bridging NCS ligand does not reduce the donor qualities at the other terminus and hence the strength of the axial Zn–N bond.

The structure of the tetrahedral 1:1 complex **8** can be deduced with some certainty from several similar structures of (NO ligand)$Zn(SC_6F_5)_2$ complexes determined by us before [19]. The $ZnONS_2$ coordination pattern corresponds to that in alcoholdehydrogenase [3], and the tetrahedral arrangement should be severely distorted with a small O–Zn–N and a large S–Zn–S angle.

Complex **9** was subjected to a structure determination to find out whether the methanol constituents are actually bound to zinc and whether comparative information as to the ketone versus alcohol binding strengths can be obtained. Fig. 4 shows that the trans-octahedral $Zn(PPK)_2X_2$ arrangement of **9** is quite similar to that in **1**. The major difference between **1** and **9** consists in the fact that the alcohol in **9** has shorter Zn–O bonds than the sulfonate in **1**. The most important bonding information is that that there is no significant difference between the Zn–O(alcohol) and Zn–O(carbonyl) bond lengths. We have observed this situation before for zinc complexes containing alcohol and aldehyde ligands in the same molecule [6].

As suitable single crystals of the PPM complexes could not be obtained their structures had to be deduced by analogy. For **10** it can be concluded from the reaction course and solubility behaviour that its ligand arrangement corresponds to that of **1**. Convincing evidence for the structural assignment of **11** and **12** is lacking. The analytical composition is in accord with the given formulas, which imply octahedral tris(chelate) coordination of PPM. Previous experience with 2-pyridylmethanol [18] would have predicted a formulation as $[(PPM)_2ZnHal]_2ZnHal_4$, like in **6** and **7**. Though we have not observed tris(chelate) complexes of zinc with N,O-chelating alcohols before [18,19], we did so with N,O-chelating aldehydes [8]. Finally, complex **13** is unlikely to be a tetrahedrally coordinated monomer owing to its low solubility. We propose it to be an oligomer or polymer containing interconnected arrays

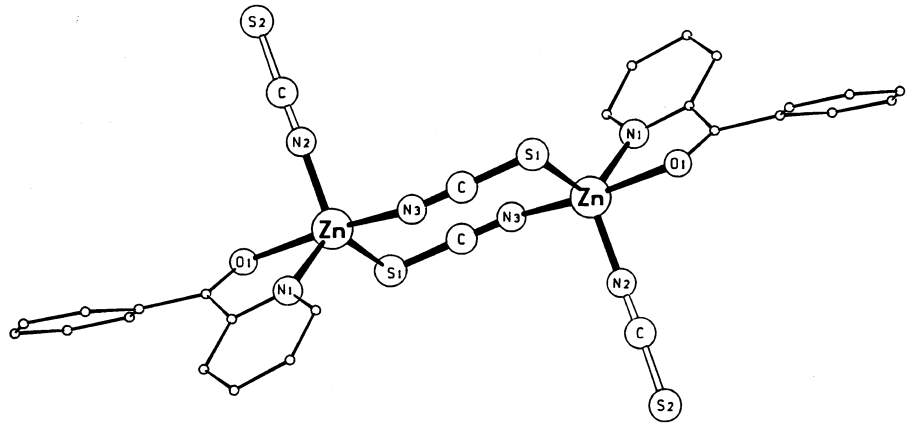


Fig. 3. Molecular structure of the centrosymmetrical dinuclear complex $[(PPK)Zn(NCS)_2]_2$ (**7**). Bond lengths (Å): Zn–N1, 2.053(3); Zn–N2, 1.923(3); Zn–N3, 2.072(3); Zn–O1, 2.236(2); Zn–S, 2.405(1); O1=C, 1.230(4). Bond angles (°): N1–Zn–O1, 75.7(1); N1–Zn–N2, 120.8(1); N2–Zn–S, 115.6(1); N1–Zn–S, 118.9(1); O1–Zn–N3, 171.8(1); Zn–N2–C, 174.9(3); Zn–N3–C, 152.9(2); Zn–S–C, 99.3(1).

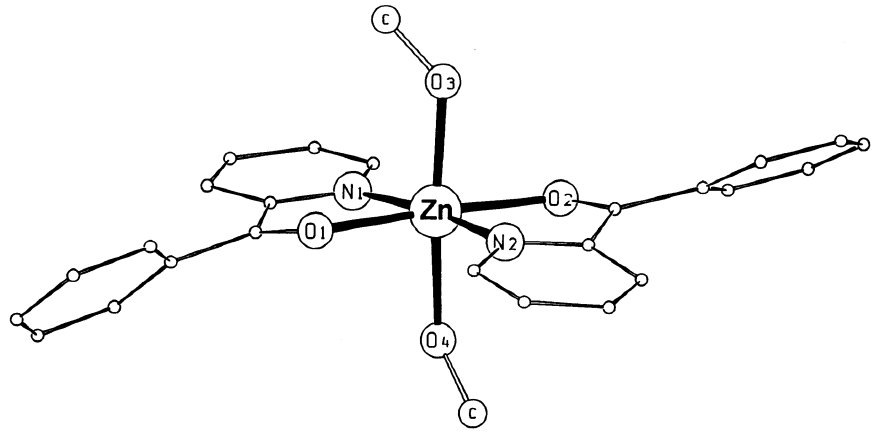


Fig. 4. Structure of the $[(PPK)_2Zn(MeOH)_2]$ cations in **9**. Bond lengths (Å): Zn–N1, 2.062(2); Zn–N2, 2.058(2); Zn–O1, 2.157(2); Zn–O2, 2.142(2); Zn–O3, 2.096(2); Zn–O4, 2.156(2); O1=C, 1.229(3); O2=C, 1.228(3). Bond angles (°): N1–Zn–O1, 76.8(1); N2–Zn–O2, 77.3(1); N1–Zn–O2, 109.8(1); N2–Zn–O1, 96.0(1); N1–Zn–N2, 171.9(1); O1–Zn–O2, 173.2(1); O3–Zn–O4, 171.8(1).

of ZnL_2 units held together by bridging alkoxide units, thereby giving the zinc ions an octahedral ZnN_2O_4 coordination as in **1** or **9**. Such an array of doubly O-bridged ZnN_2O_2 units, which occurs frequently in transition metal salen complexes, has, for instance, been found for tetrameric zinc oxinate [21]. Strong donors should be able to break the array up, and, in accordance with this, **13** dissolves in the strong donor solvent DMSO, in which it should exist as a $ZnL_2(DMSO)_2$ monomer.

2.4. Discussion

The PPK and PPM complexes described here provide a natural complement to the pyridine-derived aldehyde and alcohol complexes described by us before [8,18,19]. Frequently, compositions and structures are analogous, but the trans geometries of **1** and **9**, the ligand arrangement in dinuclear **7**, the 1:3 composition in the cations of **11** and **12**, and the composition and structure of **13** are novel. Again, it has been demonstrated that this type of N,O-chelate ligand goes along with a wide variety of coligands, which range from the softest donors, like iodide or sulfur species, to the hardest donors and weakest ligands, like triflate or even perchlorate [6].

In comparison with the monodentate aldehydes, ketones or alcohols, there is a significant enhancement of complex stabilities when using the chelating pyridine-derived species. The complexes of the latter can be prepared in donor solvents, their water sensitivity is low, complex formation does not require a large excess of the ligand, and their handling, e.g. for reactions or structure determinations, is greatly facilitated. This advantage is not outweighed by seriously altered Zn–(O-ligand) bonding situations, as has been demonstrated by the structural comparisons.

One important motivation for this work was to gather information for a comparison of the binding between zinc and the carbonyl or alcoholic functions. As the structural data in this and the preceding papers [5–8,18,19] have shown, there is little difference in terms of bond lengths or hydrolytic sensitivities. As a consequence, the replacement of alcohol by carbonyl ligands (this paper), as well as the replacement of carbonyl by alcohol ligands [6], is possible. This bears relevance in the context of the function of alcoholdehydrogenases, which are able to both oxidize alcohols and reduce carbonyl compounds [3].

Irrespective of the similarity in bonding capabilities, the chelating alcohols and carbonyl compounds display characteristic differences in terms of compositions and structures of their zinc complexes. This is most obvious in this paper for the zinc halide complexes (**2**–**7** versus **11** and **12**). Previously we had observed such differences for the alcohols and aldehydes derived from pyridine [18] and *N*,*N*-dimethylaniline [19]. Yet for the closest structural analogy to the alcoholdehydrogenases, the $ZnONS_2$ coordination in the $L{\cdot}Zn(SC_6F_5)_2$ complexes, there seems to be a uniform picture: all $Zn(SC_6F_5)_2$ complexes of O,N-chelating alcohols, aldehydes and ketones obtained by us so far (this paper and Ref. [19]) are mononuclear tetrahedral (O,N-ligand)$Zn(SR)_2$ species.

The final point of discussion concerns the coordination numbers of zinc in these complexes. It is commonplace that the coordination numbers of zinc in enzymes change frequently during enzymatic action. This is reflected in our work by the occurrence of coordination numbers 4, 5 and 6 for the same types of O,N ligand, exemplified here by the PPK complexes **8**, **7** and **1**. Furthermore, this paper and our previous work [6] have shown that alcohols and carbonyl compounds can be present as ligands in the same complex. Thus, although the chelating species employed in this work are not typical as substrates for alcoholdehydrogenase, they have provided ample information about the basic coordination chemistry in the enzyme.

3. Experimental

3.1. General procedures

For the general working and measuring procedures, see Ref. [22]. Ligand PPK and the zinc salts were obtained commercially. All reagents were stored and handled under anhydrous conditions.

3.2. Preparations

Ligand PPM [23] was prepared by a new route: 20.65 g (0.113 mol) of PPK in 120 ml of methanol at 0°C were treated in small portions with 5.00 g (0.132 mol) of solid $NaBH_4$. After stirring for 2.5 h at room temperature, 250 ml of water were added slowly and the mixture stirred for another 0.5 h. Then it was extracted with five 75 ml portions of CH_2Cl_2 and the organic extracts dried over $MgSO_4$. After removal of the solvent in vacuo the solid residue was recrystallized from *n*-heptane/benzene (1:1), yielding 16.58 g (79%) of colourless PPM, m.p. 132°C. IR (KBr): 3112 vs, br (OH). ^{1}H NMR ($CDCl_3$): $\delta = 5.75$ (s, 1H, CH), 7.30 (m, 8H, aromatic), 7.60 (s, br, 1H, OH), 8.55 (m, 1H, aromatic).

3.2.1. Complex *1*

1.00 g (2.75 mmol) of anhydrous $Zn(CF_3SO_3)_2$ and 1.00 g (5.50 mmol) of PPK were dissolved in 25 ml of absolute methanol and stirred for 15 min. After removal of the solvent in vacuo the residue was crystal-

lized from acetonitrile, yielding 1.45 g (72%) of **1** as colourless crystals, m.p. 252°C.

Anal. Found: C, 42.78; H, 2.49; N, 3.84; Zn, 8.97%. Calc. for $C_{26}H_{18}F_6N_2O_8S_2Zn$ (729.95): C, 42.78; H, 2.44; N, 3.94; Zn, 9.58.

^{1}H NMR (CD_3CN): 7.60 (m, 2H), 7.78 (m, 1H), 7.89 (m, 2H), 8.08 (m, 1H), 8.37 (m, 2H), 9.03 (m, 1H).

3.2.2. Complex **2**

Like **1**, from 1.10 g (6.00 mmol) PPK and 0.41 g (3.00 mmol) of anhydrous $ZnCl_2$ in 15 ml of acetonitrile. Yield 0.80 g (53%) of **2**, colourless crystals, m.p. 128°C.

Anal. Found: C, 57.33; H, 3.61; N, 5.57; Zn, 13.02%. Calc for $C_{24}H_{18}Cl_2N_2O_2Zn$ (502.71): C, 56.79; H, 3.57; N, 5.82; Zn, 12.88.

^{1}H NMR ($CDCl_3$): 7.40 (m, 2H), 7.53 (m, 1H), 7.71 (m, 2H), 7.81 (m,1H), 8.03 (m, 2H), 9.19 (m, 1H).

3.2.3. Complex **3**

1.10 g (6.00 mmol) of PPK and 0.68 g (3.00 mmol) of anhydrous $ZnBr_2$ in 15 ml of warm absolute ethanol were stirred for 15 min. Upon cooling, complex **3** (1.41 g, 80%) was precipitated as colourless crystals, m.p. 134°C.

Anal. Found: C, 48.72; H, 3.07; N, 4.73; Zn, 11.05%. Calc. for $C_{24}H_{18}Br_2N_2O_2Zn$ (591.62): C, 48.76; H, 3.28; N, 4.67; Zn, 11.06.

^{1}H NMR ($CDCl_3$): 7.44 (m, 2H), 7.55 (m, 1H), 7.77 (m, 3H), 8.02 (m, 2H), 9.20 (m, 1H).

3.2.4. Complex **4**

0.60 g (3.30 mmol) of $Zn(NCS)_2$ and 1.21 g (6.60 mmol) of PPK in 15 ml of acetonitrile were stirred for 30 min. Careful layering with diethyl ether and storage at 4°C yielded 1.45 g (80%) of **4** as colourless crystals, m.p. 154°C, which were dried in vacuo.

Anal. Found: C, 56.99; H, 3.31; N, 10.23; Zn, 11.94%. Calc. for $C_{26}H_{18}N_4O_2S_2Zn$ (547.98): C, 56.10; H, 3.28; N, 10.43; Zn, 12.08.

^{1}H NMR ($CDCl_3$): 7.40 (m, 2H), 7.53 (m, 1H), 7.76 (m, 3H), 8.02 (m, 2H), 9.04 (m, 1H).

3.2.5. Complex **5**

1.10 g (6.00 mmol) of PPK and 1.35 g (6.00 mmol) of anhydrous $ZnBr_2$ in 15 ml of acetonitrile were stirred for 30 min. Keeping the solution at 4°C for 48 h resulted in the precipitation of 1.60 g (55%) of **5** as colourless crystals, m.p. 164°C.

Anal. Found: C, 41.43; H, 2.71; N, 4.83; Zn, 13.54%. Calc. for $C_{48}H_{36}Br_6N_4O_4Zn_3{\cdot}CH_3CN$ (1408.43 + 41.05): C, 41.33; H, 2.71; N, 4.84; Zn, 13.26.

^{1}H NMR (CD_3CN): 1.93 (s, 3H, CH_3CN), 7.62 (m, 8H), 7.76 (m, 4H), 7.98 (m, 12H), 8.27 (m, 8H), 9.20 (m, 4H).

3.2.6. Complex **6**

Like **5**, from 0.73 g (4.00 mmol) of PPK and 1.28 g (4.00 mmol) of anhydrous ZnI_2: yield 0.80 g (35%) of **6**, colourless crystals, m.p. 148°C.

Anal. Found: C, 34.68; H, 2.27; N, 4.04; Zn, 11.33%. Calc. for $C_{48}H_{36}I_6N_4O_4Zn_3{\cdot}CH_3CN$ (1690.43 + 41.05): C, 34.51; H, 2.23; N, 4.01; Zn, 11.73.

^{1}H NMR ($CDCl_3$): 1.96 (s, 3H, CH_3CN), 7.55 (m, 2H), 7.69 (m, 4H), 7.86 (m, 8H), 7.92 (m, 12H), 8.17 (m, 8H), 8.98 (m, 4H).

3.2.7. Complex **7**

Like **4**, from 0.63 g (3.50 mmol) of $Zn(NCS)_2$ and 0.64 g (3.50 mmol) of PPK. The product was precipitated with diethyl ether and recrystallized from acetonitrile/chloroform (1:1), yielding 0.89 g (35%) of **7** as colourless crystals, m.p. 234°C.

Anal. Found: C, 46.10; H, 2.49; N, 11.52; Zn, 17.93%. Calc. for $C_{28}H_{18}N_6O_2S_4Zn_2$ (729.53): C, 45.21; H, 2.43; N, 11.33; Zn, 18.64.

^{1}H NMR (CD_3CN): 7.63 (m, 2H), 7.78 (m, 1H), 7.95 (m, 3H), 8.25 (m, 2H), 8.95 (m, 1H).

3.2.8. Complex **8**

0.148 g (0.809 mmol) of PPK and 0.375 g (0.809 mmol) of $Zn(SC_6F_5)_2$ were dissolved in 5 ml of chloroform and the solution layered with hexane. Within 6 days, 0.258 g (49%) of **8** had separated as yellow crystals, m.p. 144°C.

Anal. Found: C, 44.55; H, 1.39; N, 2.17; Zn, 10.12%. Calc. for $C_{24}H_9F_{10}NOS_2Zn$ (646.84): C, 44.32; H, 1.37; N, 2.06; Zn, 10.01.

^{1}H NMR ($CDCl_3$): 7.71 (m, 2H), 7.99 (m, 4H), 8.34 (m, 2H), 9.09 (m, 1H).

3.2.9. Complex **9**

0.71 g (3.90 mmol) of PPK and 0.56 g (1.30 mmol) of $[Zn(CH_3OH)_6](BF_4)_2$ were dissolved in 6 ml of nitromethane and the solution layered with *n*-heptane/diethyl ether (1:1). After 3 days, 0.68 g (78%) of **9** had separated as colourless crystals, m.p. 282°C.

Anal. Found: C, 46.64; H, 3.91; N, 4.18; Zn, 9.77%. Calc. for $C_{26}H_{26}B_2F_8O_4Zn$ (669.50): C, 46.48; H, 3.85; N, 4.00; Zn, 9.88.

^{1}H NMR (CD_3CN): 3.32 (s, 6H, CH_3), 7.66 (m, 4H), 7.83 (m, 2H), 7.90 (m, 4H), 8.10 (m, 4H), 8.35 (m, 6H), 9.00 (m, 2H).

3.2.10. Complex **10**

1.00 g (5.50 mmol) of PPM and 1.00 g (2.75 mmol) of $Zn(CF_3SO_3)_2$ were dissolved in 30 ml of hot acetonitrile. After cooling to room temperature, the solvent was removed in vacuo and the residue recrystallized from acetonitrile/chloroform (3:1), yielding 1.39 g (71%) of **10** as colourless crystals, m.p. 151°C.

Anal. Found: C, 42.54; H, 3.00; N, 3.82; Zn, 8.91%. Calc. for $C_{26}H_{22}F_6N_2O_8S_2Zn$ (733.98): C, 42.45; H, 3.02; N, 3.80; Zn, 9.57.

^{1}H NMR (CD_3CN): 6.16 (s, 1H, CH(OH)), 7.30 (m, 7H), 7.60 (m, 1H), 8.00 (m, 1H), 8.60 (m, 1H).

3.2.11. Complex **11**

0.74 g (4.00 mmol) of PPM and 0.55 g (4.00 mmol) of anhydrous $ZnCl_2$ were dissolved in 6 ml of warm anhydrous acetonitrile. Upon cooling to room temperature, 0.66 g (40%) of **11** were precipitated as a colourless powder, m.p. 148°C.

Anal. Found: C, 52.50; H, 4.17; N, 6.44; Zn, 15.04%. Calc. for $C_{36}H_{33}Cl_4N_3O_3Zn_2{\cdot}CH_3CN$ (828.27 + 41.05): C, 52.43; H, 4.05; N, 6.07; Zn, 15.15.

^{1}H NMR (CD_3CN): 1.93 (s, 3H, CH_3CN), 6.14 (s, 3H, CH(OH)), 7.36 (m, 18H), 7.47 (m, 3H), 7.93 (m, 3H), 8.61 (m, 3H).

3.2.12. Complex **12**

Like **11**, from 0.79 g (4.25 mmol) of PPM and 0.49 g (2.12 mmol) of anhydrous $ZnBr_2$. Yield 0.75 g (69%) of **12** as a colourless powder, m.p. 148°C.

Anal. Found: C, 43.59; H, 3.47; N, 5.35; Zn, 12.49%. Calc. for $C_{36}H_{33}Br_4N_3O_3Zn_2{\cdot}CH_3CN$ (1006.07 + 41.05): C, 43.29; H, 3.49; N, 5.87; Zn, 12.33.

^{1}H NMR (CD_3CN): 1.95 (s, 3H, CH_3CN), 5.98 (s, 3H, CH(OH)), 7.25 (m, 21H), 7.77 (m, 3H), 8.45 (m, 3H).

3.2.13. Complex **13**

0.44 g (1.30 mmol) of $Zn[N(SiMe_3)_2]_2$ were added to a solution of 0.50 g (2.70 mmol) of PPM in 40 ml of anhydrous CH_2Cl_2. After stirring for 1 h the solution was layered with hexane. After 3 days, 0.35 g (60%) of **13** had separated as a colourless powder, m.p. 99°C.

Anal. Found: C, 66.45; H, 4.65; N, 6.46; Zn, 15.07%. Calc. for $C_{24}H_{20}N_2O_2Zn$ (433.82): C, 66.19; H, 4.61; N, 6.25; Zn, 14.75.

^{1}H NMR (DMSO-d_6): 5.84 (s, 1H, CH(OH)), 6.46–8.35 (m, 9H).

3.3. Structure determinations

The crystals were obtained directly from the reaction solutions and used without drying in vacuo. They were immersed in fluorinated polyether oil and immediately placed in the nitrogen stream of the diffractometer's cooling system. Diffraction data were recorded with the ω–2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (Kα, $\lambda = 0.7107$ Å) and a graphite monochromator. No absorption corrections

Table 2
Crystallographic details

	1	**6**	**7**	**9**
Formula	$C_{26}H_{18}F_6N_2O_8S_2Zn$	$C_{48}H_{36}I_6N_4O_4Zn_3{\cdot}CH_3CN$	$C_{28}H_{18}N_6O_2S_4Zn_2$	$C_{26}H_{26}B_2F_8N_2O_4Zn$
Molecular mass	729.95	1690.43 + 41.05	729.53	669.50
Crystal size (mm^3)	0.8 × 0.7 × 0.6	0.7 × 0.3 × 0.3	0.5 × 0.3 × 0.2	0.8 × 0.8 × 0.6
Space group	*Pbca*	*C*2/*c*	$P\bar{1}$	$P2_1/n$
Z	4	4	1	4
a (Å)	10.028(1)	27.219(5)	7.167(3)	15.248(3)
b (Å)	14.931(2)	15.776(3)	8.266(6)	12.165(2)
c (Å)	19.342(2)	14.270(3)	13.607(3)	15.704(3)
α (°)	90	90	97.34(4)	90
β (°)	90	111.67(3)	101.85(3)	104.29(3)
γ (°)	90	90	107.25(5)	90
V (Å^3)	2896.0(4)	5694.6(16)	737.9(6)	2822.8(9)
d_{calc} (g cm^{-3})	1.67	2.00	1.64	1.58
Temperature (K)	293	293	183	183
μ(Mo Kα) (mm^{-1})	1.08	4.55	1.95	0.96
hkl range				
h	0 to 12	−33 to 31	−8 to 8	−18 to 7
k	0 to 18	0 to 19	−10 to 0	−14 to 14
l	−23 to 0	0 to 17	−16 to 16	−18 to 19
Reflections measured	2837	5821	3103	11 179
Independent reflections	2835	5581	2892	5526
Observed reflections ($I > 2\sigma(I)$)	2021	3945	2513	5029
Parameters	205	309	190	388
Reflections refined	2835	5581	2892	5526
R_1 (observed reflections)	0.038	0.037	0.033	0.038
wR_2 (all reflections)	0.118	0.108	0.094	0.101
Residual electron density (e Å^{-3})	+0.3, −0.3	+1.4, −1.3	+0.8, −0.7	+0.5, −0.5

were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite [24]. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma |F_o - F_c| / \Sigma F_o$ and $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL [25]. Table 2 lists the crystallographic data.

4. Supplementary material

The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC-149836 (for **1**), 149837 (for **7**), 149838 (for **6**) and 149839 (for **9**). Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: teched@chemcrys.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. We are indebted to Mrs P. Klose for help with the preparative work.

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