Pentagonal Bipyramidal Complexes of Cobalt(II) and Zinc(II). The X-Ray Crystal Structure of the Novel Deprotonated Zinc Dimer

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Summary Pentagonal bipyramidal complexes of cobalt (II) and zinc(II) with 2,6-diacetylpyridine bis-2-pyridylhydrazone have been prepared and the zinc complex has been shown to dimerize to an octahedral complex after deprotonation of the ligand, utilizing a pyridine bridge; the structures of the complexes have been determined by *X*-ray crystallography.

The recent preparation of pentagonal bipyramidal (PBP) complexes of Fe^{II}, Co^{II}, and Zn^{II} using planar pentadentate ligands[1] suggested that other PBP complexes could be synthesized. One possibility was to use 2,6-diacetylpyridine bis-2-pyridylhydrazone (H_2dapp) which could be deprotonated to give the dianion $dapp^{2-}$. We have synthesized complexes of the type $[M(H_2dapp)(H_2O)_2]Cl_2$ where (I; M = Co^{II}) and (II; M = Zn^{II}) and have shown that they are PBP complexes rather than the previously postulated octahedral species.[2]

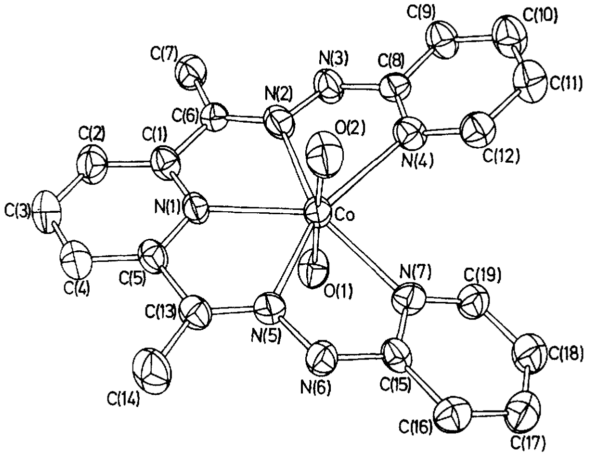

Figure 1. An ORTEP drawing of the diaqua-(2,6-diacetylpyridine bis-2-pyridylhydrazone)cobalt(II) cation illustrating the pentagonal bipyramidal geometry of the complex. The Zn derivative is isomorphous. Pertinent distances for the Co and Zn complexes are M–N(1), 2·207 and 2·251; M–N(2), 2·248 and 2·314; M–N(4), 2·268 and 2·305; M–N(5), 2·242 and 2·286; M–N(7), 2·258 and 2·288; M–O(1), 2·146 and 2·104; M–O(2), 2·153 and 2·103 Å; all distances are ± 0·004 Å.

However, after deprotonation a unique dimeric zinc complex $[Zn_2(dapp)_2],2HCCl_3,2H_2O$ (III) was isolated in which each zinc atom was surrounded by six nitrogen atoms in a distorted octahedral configuration. The octahedral arrangement around the zinc atom results from a bridging pyridine group, the first example of pyridine functioning in that manner.

The reaction of $[CoCl_2]6H_2O$ and H_2dapp in EtOH gives orange dichroic crystals of (I), and $ZnCl_2$ with H_2dapp in acidic MeOH yields yellow crystals of (II). Chloroform extraction of an alkali-treated mixture of $ZnCl_2$ and H_2dapp gives red crystals of (III). Elemental analyses were in agreement with the appropriate formulation, and *X*-ray crystal structure studies of these complexes were undertaken.

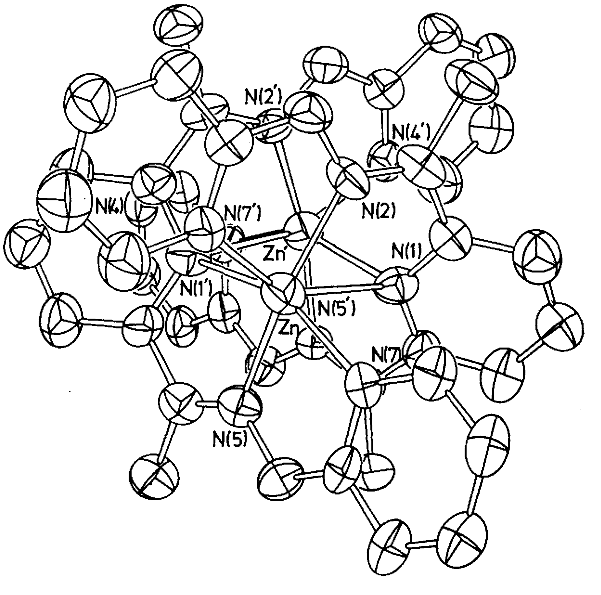

Figure 2. A view of the dimeric zinc complex obtained from the pentagonal bipyramidal complex upon deprotonation of the ligand. A 2-fold axis passes through the molecule. The numbering is identical to that shown in Figure 1.

Crystal data: (I) $a = 8·004(3)$, $b = 27·373(11)$, $c = 10·341(2)$ Å, $\beta = 105·39(2)°$, $D_m = 1·55$ g cm^{-3}, $Z = 4$, space group $P2_1/n$. (II) $a = 7·887(2)$, $b = 27·751(6)$, $c = 10·377(3)$ Å, $\beta = 105·23(2)°$, $D_m = 1·57$ g cm^{-3}, $Z = 4$, space group $P2_1/n$. (III) $a = 18·842(7)$, $b = 11·072(5)$, $c = 22·893(5)$ Å, $\beta = 94·93(3)°$, $D_m = 1·48$ g cm^{-3}, $Z = 4$ dimers, space group $C2/c$. The intensity data for all compounds were measured using a Syntex $P\bar{1}$ diffractometer with a variable speed scan technique, with graphite-monochromatized Mo-K_α radiation for (I) and (II) and Ni-filtered Cu-K_α radiation for (III). The structures of (I) and (III) were solved by the heavy atom method and refined using least-squares techniques to an R value of 0·046 for 2814 reflections for (I) and 0·085 for 1568 reflections for (III). Since (II) was isomorphous with (I), the final parameters for (I) were used as the starting parameters for a least-squares refinement. The final R was 0·040 for the 2249 reflections used in the analysis of (II).

An ORTEP drawing of the cobalt complex (I) (Figure 1) clearly shows the PBP nature of the cation. The zinc complex (II) is isomorphous and virtually identical to (I). The reported conductivity measurements for $[Co(H_2dapp)]I_2$ indicated a two-to-one electrolyte[2] which is in agreement with the formulation found in our study. The principal distortions from an ideal PBP geometry appear to be related to steric interactions between the hydrogen atoms on C(12) and C(19). The two pyridine rings are twisted and tipped until the H · · · H distance between the two hydrogen atoms is increased to 2·56 Å in (I). The deviations from planarity in (II) are slightly less than in (I) because of the larger Zn–N in-plane distance. The non-bonded interactions between the ligand and the two axial water molecules are reduced so that Zn–OH_2 is shorter than the Co–OH_2. A similar dependence of non-bonded contacts on the axial bond lengths was observed in the PBP complexes of Fe^{II}, Co^{II}, and Zn^{II}.[1]

An unusual rearrangement occurs upon deprotonation of the $[Zn(H_2dapp)(H_2O)_2]^{2+}$ ion. The $dapp^{2-}$ ion does not function as a planar pentadentate ligand, and the dimeric species illustrated in Figure 2 is formed. Although an explanation for the difference in the two cases is not obvious, steric factors may be important. If the in-plane metal distances in the dianion were to decrease because of the increased negative charge, the steric interactions between the two pyridyl rings could become too great. The so-called helical co-ordination found in bis-(2-mercaptobenzylideneamine)-2,6-diacetylpyridinezinc(II)[3] then represents an intermediate configuration between the PBP configuration in (II) and the dimer found in (III). Another unexpected feature of the zinc dimer (III) is the presence of the bridging pyridine ring which to our knowledge is the first example reported. A final question is whether similar dimerizations might account for the abnormal magnetic moments found in complexes with the related ligand 1,3-bis-(2-pyridyl)-1,2-diazaprop-2-ene.[4]

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