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Pentagonal-Bipyramidal Complexes. Synthesis and Characterization of Cobalt(II) and Zinc(II) Complexes of Neutral and Dianionic 2,6-Diacetylpyridinebis(2'-pyridylhydrazone)[1]

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The synthesis and characterization of three complexes involving the ligand 2,6-diacetylpyridinebis(2'-pyridylhydrazone), H_2dapp, are described. The Co(II) and Zn(II) complexes have the stoichiometry $[M(H_2dapp)(H_2O)_2]^{2+},2Cl^-$ and are isomorphous. The unit cell dimensions are $a = 8.004$ (3) Å, $b = 27.373$ (11) Å, $c = 10.341$ (2) Å, and $\beta = 105.39$ (2)° for M = Co and $a = 7.887$ (2) Å, $b = 27.751$ (6) Å, $c = 10.377$ (3) Å, and $\beta = 105.23$ (2)° for M = Zn. The space group is $P2_1/n$ and $Z = 4$ for both complexes. The final unweighted R value was 0.046 for 2814 reflections for the Co complex and 0.040 for 2249 reflections for the Zn complex. The cation in both complexes has a pentagonal-bipyramidal geometry with H_2dapp forming the equatorial plane and two axial water molecules. The differences in distances and angles in the two complexes reflect both the ionic sizes as well as nonbonded contacts. The zinc complex formed by deprotonation of the ligand crystallizes with both a chloroform and a water of crystallization and has the stoichiometry $Zn(dapp)\cdot CHCl_3\cdot H_2O$. The unit cell dimensions are $a = 18.842$ (7) Å, $b = 11.072$ (5) Å, and $c = 22.893$ (5) Å, with $\beta = 94.93$ (3)°. There are 8 molecules per monoclinic cell with the space group being $C2/c$. The final unweighted R was 0.080 for the 1568 reflections used in the analysis. However, the zinc species is dimeric, i.e., $Zn_2(dapp)_2$, with the dimer having a twofold axis of symmetry. Each zinc atom in the dimer is surrounded by four nitrogens from two different ligands, and two nitrogens from the bridging pyridine groups complete the distorted octahedral arrangement. The deprotonated ligand, $dapp^{2-}$, is not planar but twisted about both C(central pyridine ring)–C(side chain) bonds.

Seven is an unusual coordination number for most elements and is particularly rare in the first-row transition elements. The only seven-coordinate complexes definitely characterized for the elements Sc–Zn before 1972 were a Ti(III),[2] a Mn(II),[3] and four Fe(III)[4] complexes although subsequently a V(III)[5] and another Mn(II)[6] species were reported. However, our preparation of a variety of pentagonal-bipyramidal (henceforth PBP) complexes using the planar pentadentate ligand 2,6-diacetylpyridinebis(semicarbazone), DAPSC,[7,8] suggested that PBP complexes might be prepared with other appropriate planar pentadentate ligands.

Another interesting planar pentadentate ligand, 2,6-diacetylpyridinebis(2'-pyridylhydrazone), henceforth H_2dapp, was reported, together with a cobalt complex $Co(H_2dapp)I^+$, presumed to be six-coordinate.[9] Our results with DAPSC suggested that H_2dapp might also yield PBP complexes. Moreover, the fact that the ligand could be deprotonated[10,11] to the dianion, $dapp^{2-}$, provided another incentive for investigating the H_2dapp ligand system. A preliminary report[12] has shown that the $[M(H_2dapp)(H_2O)_2]^{2+},2Cl^-$, M = Co or Zn, are PBP complexes but that the Zn(dapp) species is actually an octahedral dimer.

Experimental Section

The 2,6-diacetylpyridine was purchased from Pfaltz & Bauer, Inc., Flushing, N.Y., and used as received. All other materials were the usual reagent chemicals. The ligand, H_2dapp, was prepared as reported.[9]

Preparation of Diaqua[2,6-diacetylpyridinebis(2'-pyridylhydrazone)]cobalt(II) and -zinc(II) Complexes. To a warm solution of 0.886 g (2.5 mmol) of H_2dapp in 35 ml of 95% ethanol was added 0.595 g (2.5 mmol) of $CoCl_2\cdot 6H_2O$ in 23 ml of 95% ethanol, followed by 0.5 ml of concentrated HCl. The deep reddish brown solution was boiled, cooled, and filtered. Slow evaporation of the ethanol produced 0.58 g (45%) of orange-brown crystals, mp >360 °C, suitable for x-ray diffraction studies.

The corresponding zinc complex, II, was prepared in a similar manner using methanol–water (9:1) as the solvent. The yield was 0.63 g (49%) of yellow crystals, mp of 230 °C.

Magnetic Measurement of $[Co(H_2dapp)(H_2O)_2]^{2+},2Cl^-$. The magnetic moment for $[Co(H_2dapp)(H_2O)_2]^{2+},2Cl^-$ was determined by NMR techniques.[13] The average moment from five measurements of the shift was 5.25 ± 0.08 BM.

Preparation of the Deprotonated Zinc Complex, III. A warm solution of 0.886 g (2.5 mmol) of H_2dapp in 50 ml of acetone was added dropwise to a slurry of 0.3401 g (2.5 mmol) of $ZnCl_2$ in 25 ml of acetone. A reddish orange precipitate formed. A solution of KOH in water was added dropwise to produce a red solution and a black precipitate. The mixture was extracted with $CHCl_3$ and the extracts were dried over $MgSO_4$. Slow evaporation of the solvent produced beautiful red crystals, III, which slowly lost solvent and turned black.

Table I. Crystal Data for the Diaqua[2,6-diacetylpyridinebis(2'-pyridylhydrazone)] Complexes of Co, I, and Zn, II, and the Zinc Dimer, III

	I	II	III
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	8.004 (3)	7.887 (2)	18.842 (7)
b, Å	27.373 (11)	27.751 (6)	11.072 (5)
c, Å	10.341 (2)	10.377 (3)	22.893 (5)
β, deg	105.39 (2)	105.23 (2)	94.93 (3)
Vol., Å^3	2184.5 (12)	2191.5 (9)	4758 (3)
Mol wt	511.28	517.72	546.16
Z	4	4	8
d(calcd), g/cm^3	1.555	1.569	1.525
d(measd), g/cm^3	1.55	1.57	1.48
Crystal size, mm^3	0.16 × 0.19 × 0.33	0.13 × 0.20 × 0.25	0.11 × 0.11 × 0.16
Radiation	Mo	Mo	Cu
μ, cm^{-1}	10.9	14.3	14.3
2θ range, deg	0–50	0–45	0–100
No. of independent reflections	3878	2889	2364
No. of "reliable" reflections	2814	2249	1568

Data Collection and Reduction. Preliminary Weissenberg and precession photographs were taken of all three compounds. The complexes I and II appeared to be isomorphous from the preliminary photographs. Crystals of III were coated with Apiezon T grease to prevent loss of solvent and subsequent decomposition.

The unit cell dimensions and intensity data were measured using a Syntex $P\bar{1}$ diffractometer. The pertinent crystal data, together with the radiation used for the intensity measurements and the 2θ limits, are given in Table I. A variable speed (1–24°/min for I and II and 2–24°/min for III) θ–2θ scan technique was used in measuring the intensity. A series of four standard reflections was measured after each 96 measurements and showed only a slight (2%) drop for I. However, in the case of II the deterioration was more pronounced (30%) and data collection was terminated at that point. In the case of III the standards dropped by more than 50% which was presumably due to decomposition of the crystal. The data collection was terminated at that point. The values for the four standard reflections were then used to correct the data for the change in the crystal with time. The

Table II. Final Positional and Thermal Parameters[a] ($\times 10^4$) for the Nonhydrogen Atoms of $[M(dappH)(H_2O)_2]Cl_2$ (M = Co, Zn) with Their Respective Estimated Standard Deviations in Parentheses[b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M = Co	1352 (1)	1331 (1)	408 (1)	94 (1)	7 (1)	42 (1)	3 (1)	27 (1)	1 (1)
M = Zn	1393 (1)	1344 (1)	348 (1)	119 (1)	10 (1)	58 (1)	2 (1)	38 (1)	2 (1)
Cl1	6959 (2)	669 (1)	2113 (1)	152 (2)	11 (1)	77 (1)	20 (1)	53 (3)	9 (1)
	7034 (2)	698 (1)	2056 (1)	178 (3)	12 (1)	90 (2)	18 (1)	60 (4)	11 (1)
Cl2	5360 (2)	1611 (1)	7957 (1)	145 (2)	14 (1)	75 (1)	6 (1)	79 (3)	18 (1)
	5418 (2)	1610 (1)	7917 (1)	169 (3)	16 (1)	82 (2)	0 (1)	77 (4)	19 (1)
O1	4052 (4)	1389 (1)	488 (3)	117 (6)	14 (1)	80 (4)	13 (3)	71 (7)	15 (2)
	4077 (5)	1386 (1)	410 (4)	152 (7)	16 (1)	89 (5)	10 (4)	91 (9)	25 (3)
O2	−1353 (4)	1324 (1)	362 (4)	116 (6)	19 (1)	86 (4)	−8 (3)	56 (8)	8 (3)
	−1289 (5)	1349 (2)	301 (4)	134 (7)	19 (1)	96 (5)	−13 (4)	41 (9)	16 (3)
N1	2091 (5)	1012 (1)	2442 (3)	100 (6)	9 (1)	46 (4)	−2 (3)	20 (7)	2 (2)
	2141 (5)	1027 (2)	2417 (4)	119 (8)	12 (1)	55 (4)	−1 (4)	24 (10)	6 (3)
N2	1925 (5)	529 (1)	329 (4)	114 (7)	10 (1)	51 (4)	2 (3)	7 (8)	−2 (2)
	1936 (6)	526 (2)	319 (4)	143 (9)	10 (1)	62 (5)	−2 (4)	27 (10)	−3 (3)
N3	1794 (6)	341 (2)	−917 (4)	189 (9)	10 (1)	57 (4)	11 (4)	20 (9)	−6 (3)
	1796 (7)	327 (2)	−902 (5)	228 (11)	13 (1)	73 (5)	9 (5)	41 (13)	−3 (3)
N4	318 (5)	1052 (1)	−1719 (4)	115 (7)	9 (1)	66 (4)	3 (3)	38 (8)	−5 (2)
	381 (6)	1037 (2)	−1780 (4)	154 (9)	10 (1)	77 (5)	2 (4)	37 (11)	−4 (3)
N5	1310 (5)	1906 (1)	1943 (4)	111 (6)	9 (1)	59 (4)	2 (3)	40 (8)	1 (2)
	1410 (6)	1921 (2)	1924 (4)	130 (8)	10 (1)	70 (5)	1 (4)	51 (10)	−1 (3)
N6	813 (5)	2359 (1)	1463 (4)	174 (8)	8 (1)	58 (4)	5 (3)	66 (9)	−2 (2)
	939 (6)	2369 (2)	1451 (4)	182 (10)	11 (1)	80 (5)	6 (4)	87 (12)	−1 (3)
N7	1256 (5)	2079 (1)	−529 (4)	122 (7)	8 (1)	62 (4)	7 (3)	60 (8)	−1 (2)
	1309 (6)	2095 (2)	−576 (4)	146 (9)	10 (1)	69 (5)	4 (4)	64 (10)	−2 (3)
C1	2683 (6)	554 (2)	2630 (4)	101 (7)	9 (1)	53 (4)	1 (4)	16 (9)	4 (3)
	2722 (7)	573 (2)	2610 (5)	114 (10)	12 (1)	74 (6)	−3 (5)	18 (12)	16 (4)
C2	3303 (7)	358 (2)	3915 (5)	159 (10)	11 (1)	68 (5)	7 (4)	38 (11)	8 (3)
	3337 (8)	383 (2)	3890 (6)	188 (13)	15 (1)	74 (6)	1 (6)	14 (15)	10 (4)
C3	3281 (7)	644 (2)	5008 (5)	170 (10)	16 (1)	59 (5)	19 (5)	36 (12)	18 (4)
	3345 (9)	671 (3)	4972 (6)	211 (14)	18 (1)	76 (7)	16 (6)	45 (16)	14 (4)
C4	2657 (7)	1116 (2)	4808 (5)	141 (9)	14 (1)	54 (5)	1 (4)	40 (11)	4 (3)
	2714 (8)	1134 (2)	4775 (6)	165 (11)	17 (1)	63 (6)	−2 (6)	50 (13)	1 (4)
C5	2068 (6)	1290 (2)	3513 (4)	91 (7)	11 (1)	52 (4)	−6 (4)	41 (9)	−2 (3)
	2137 (7)	1311 (2)	3468 (5)	118 (10)	12 (1)	55 (5)	−3 (5)	28 (11)	1 (3)
C6	2612 (6)	282 (2)	1376 (4)	110 (8)	8 (1)	59 (5)	−6 (3)	8 (9)	7 (3)
	2630 (7)	294 (2)	1379 (5)	137 (11)	12 (1)	73 (6)	−2 (5)	15 (13)	3 (4)
C7	3323 (7)	−223 (2)	1412 (5)	187 (11)	9 (1)	79 (5)	3 (4)	26 (12)	4 (3)
	3375 (9)	−204 (2)	1448 (6)	222 (14)	11 (1)	109 (7)	−1 (6)	60 (17)	6 (4)
C8	806 (6)	602 (2)	−1975 (5)	115 (8)	7 (1)	65 (5)	6 (3)	42 (10)	−4 (3)
	809 (7)	588 (2)	−1984 (5)	138 (10)	11 (1)	70 (6)	3 (5)	43 (13)	−9 (3)
C9	311 (7)	382 (2)	−3230 (5)	158 (9)	12 (1)	62 (5)	17 (5)	44 (11)	−10 (3)
	331 (8)	348 (2)	−3209 (6)	215 (14)	12 (1)	89 (7)	14 (6)	62 (16)	−6 (4)
C10	−768 (8)	631 (2)	−4263 (5)	198 (11)	14 (1)	60 (5)	18 (5)	40 (12)	−4 (3)
	−736 (9)	602 (2)	−4275 (6)	247 (15)	17 (1)	74 (7)	6 (7)	39 (16)	−3 (4)
C11	−1339 (7)	1090 (2)	−4010 (5)	151 (10)	15 (1)	68 (5)	18 (5)	16 (11)	4 (4)
	−1267 (8)	1062 (2)	−4074 (6)	183 (12)	15 (1)	81 (7)	17 (6)	14 (14)	7 (4)
C12	−786 (6)	1285 (2)	−2743 (5)	131 (8)	9 (1)	81 (5)	14 (4)	48 (11)	0 (3)
	−715 (8)	1262 (2)	−2831 (6)	171 (12)	11 (1)	91 (7)	1 (5)	56 (15)	−3 (4)
C13	1481 (6)	1796 (2)	3190 (4)	108 (8)	10 (1)	60 (5)	1 (4)	52 (10)	−4 (3)
	1559 (7)	1812 (2)	3156 (5)	122 (10)	13 (1)	71 (6)	−6 (5)	65 (12)	−8 (4)
C14	1153 (8)	2130 (2)	4234 (5)	241 (13)	13 (1)	68 (5)	19 (5)	105 (14)	−9 (3)
	1214 (9)	2135 (2)	4193 (6)	221 (14)	16 (1)	91 (7)	10 (6)	97 (16)	−9 (4)
C15	927 (6)	2452 (2)	174 (4)	108 (8)	9 (1)	50 (4)	5 (3)	32 (9)	−3 (3)
	1038 (6)	2465 (2)	163 (5)	111 (9)	10 (1)	63 (6)	7 (4)	31 (12)	1 (3)
C16	712 (7)	2932 (2)	−288 (5)	145 (9)	8 (1)	77 (5)	3 (4)	52 (11)	0 (3)
	867 (7)	2940 (2)	−294 (6)	152 (11)	10 (1)	87 (6)	−2 (5)	56 (13)	−1 (4)
C17	898 (7)	3028 (2)	−1544 (5)	190 (11)	10 (1)	76 (5)	3 (5)	68 (12)	9 (3)
	1012 (8)	3034 (2)	−1564 (6)	196 (13)	12 (1)	94 (7)	8 (6)	63 (15)	11 (4)
C18	1334 (7)	2647 (2)	−2282 (5)	193 (11)	12 (1)	66 (5)	−1 (5)	88 (12)	0 (3)
	1361 (9)	2658 (2)	−2328 (6)	230 (14)	14 (1)	71 (6)	3 (6)	112 (15)	5 (4)
C19	1513 (6)	2187 (2)	−1747 (5)	151 (9)	9 (1)	60 (5)	0 (4)	60 (11)	0 (3)
	1516 (8)	2202 (2)	−1793 (5)	177 (12)	11 (1)	74 (6)	−4 (5)	85 (14)	−5 (4)

[a] The form of the thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The coordinates of the atoms for each structure are listed according to the order of the metal atoms.

intensity was equal to [scan rate][total scan counts − background counts/background to scan ratio], with σ(intensity) equal to [total scan counts + (background count/background to scan ratio)^2]$^{1/2}$. Reflections with an intensity greater than or equal to twice σ(intensity) were considered reliable and were used in the analysis. The remaining reflections were flagged with a minus sign and were not used in the determination or refinement. The data were reduced to a set of structure amplitudes in the usual manner. The small values of μ (11–14) and the small crystal sizes made absorption corrections unnecessary.

Structure Determination and Refinement. The structures of I and III were determined by the heavy-atom method and refined by least-squares techniques. In both cases the metal atom was located in a Patterson function and the light atoms in successive Fourier syntheses. After all of the atoms had been located, R, the usual residual, was 0.18 for I and 0.21 for III. Three least-squares cycles using individual isotropic thermal parameters reduced R to 0.080 for I and 0.13 for III. In the case of I all atoms were allowed to vibrate anisotropically and R was reduced to 0.060 after three cycles using the block approximation. A difference Fourier synthesis was used

Table III. Final Parameters for the Hydrogen Atoms in $[(Co(H_2dapp)(H_2O)_2]^{2+},2Cl^-$ [a]

Atom [bonded to]	Distance	x	y	z	B
H1[C2]	1.02	368	0	400	4.4
H2[C3]	1.10	373	50	604	4.9
H3[C4]	1.00	279	132	563	4.2
H4[C7]	0.99	280	−42	200	4.4
H5[C7]	0.88	283	−39	68	4.4
H6[C7]	1.02	461	−16	153	4.4
H7[C14]	1.08	11	230	347	4.9
H8[C14]	0.81	157	240	439	4.9
H9[C14]	0.93	32	199	459	4.9
H10[N3]	1.05	215	0	−126	4.4
H11[C9]	1.09	88	2	−334	4.3
H12[C10]	1.04	−136	48	−520	4.8
H13[C11]	0.97	−219	130	−462	4.7
H14[C12]	0.96	−118	160	−250	4.1
H15[N6]	0.99	64	264	203	4.0
H16[C16]	0.98	64	319	36	4.1
H17[C17]	1.04	90	337	−198	4.4
H18[C18]	1.00	137	269	−324	4.5
H19[C19]	1.09	192	188	−227	3.8
H20[O1]	0.84	436	149	−19	4.2
H21[O1]	0.97	481	113	94	4.2
H22[O2]	0.81	−217	136	−29	4.8
H23[O2]	0.86	−179	115	89	4.8

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters (× 10^3), and the isotropic thermal parameter (in $Å^2$).

to locate the positions of all of the hydrogen atoms. The hydrogen atoms were assigned an isotropic thermal parameter one unit larger than that of the atom to which the hydrogen was bonded and were included in subsequent calculations but their parameters were not varied. Three additional least-squares cycles reduced R to 0.046. At this point only eight parameters had shifts of more than $^1/_3$ esd so that the refinement was terminated. After the isotropic refinement of III, the zinc and three chlorine atoms were assigned anisotropic thermal parameters and three least-squares cycles reduced R to 0.093. Three block-diagonal least-squares cycles with all atoms anisotropic reduced R to 0.085. Only 16 of the 20 hydrogen atoms could be located in the difference Fourier synthesis. The hydrogens were handled in the same way as in I and three least-squares cycles reduced R to 0.080. The shifts were all less than $^1/_3$ esd so that the refinement was terminated.

The similarity in cell constants and intensity data suggested that I and II were isomorphous. A difference Fourier synthesis using the refined parameters from I revealed no significant changes, and since R was 0.18, isotropic refinement was started. After three least-squares cycles, R was 0.074, and three cycles with anisotropic thermal parameters reduced R to 0.056. A difference Fourier synthesis indicated the hydrogen positions were very close to the positions in I so these coordinates were utilized with adjusted thermal parameters. Three additional least-squares cycles reduced R to 0.040 and the refinement was terminated. The final parameters for the nonhydrogen atoms in I and II are given in Table II with the hydrogen parameters from Co complex presented in Table III. The corresponding parameters for the dimer III are given in Tables IV and V. Tables of observed and calculated structure amplitudes are available.[14]

The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$ where $w^{1/2} = F_o/F(\text{low})$ if $F_o < F(\text{low})$, $w^{1/2} = 1$ if $F(\text{low}) \leq F_o \leq F(\text{high})$, and $w^{1/2} = F(\text{high})/F_o$ if $F(\text{high}) < F_o$. The values of F(low) were 8.0, 8.0, and 12.0 and those of F(high) were 32.0, 32.0 and 47.0 for the complexes I, II, and III, respectively. The atomic scattering factors for the nonhydrogen atoms were taken from Hanson, Herman, Lea, and Skillman[15] and the hydrogen curve was from Stewart, Davidson, and Simpson.[16] All calculations were carried out on an IBM 370/165 using programs written or modified by G.J.P.

Results and Discussion

$[M(H_2dapp)(H_2O)_2]Cl_2$ Complexes. The atomic numbering and thermal ellipsoids in the $[Co(H_2dapp)(H_2O)_2]^{2+}$ cation are shown in Figure 1. The pentagonal-bipyramidal nature of the cation is easily seen. The geometry of the cation is a direct result of the planar pentadentate nature of the H_2dapp ligand. The main distortions (vide infra) involve nonbonded

Table IV. Final Positional and Thermal Parameters[a] (× 10^4) for the Nonhydrogen Atoms of $Zn(dapp)\cdot CHCl_3\cdot H_2O$ with Their Respective Estimated Standard Deviations in Parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	226 (1)	391 (1)	1774 (1)	32 (1)	72 (1)	25 (1)	4 (2)	−6 (1)	3 (2)
Cl1	1931 (4)	4424 (6)	5104 (3)	86 (3)	188 (8)	61 (2)	−36 (8)	62 (4)	−2 (7)
Cl2	1420 (4)	2106 (5)	5450 (3)	110 (4)	114 (5)	49 (2)	49 (7)	17 (4)	17 (5)
Cl3	554 (4)	3535 (7)	4632 (2)	94 (3)	278 (10)	28 (1)	20 (9)	−4 (3)	20 (6)
N1	889 (5)	576 (9)	2809 (4)	32 (4)	60 (10)	21 (2)	−8 (10)	17 (5)	−10 (8)
N2	547 (5)	−1283 (9)	2048 (4)	35 (4)	66 (10)	16 (2)	37 (11)	−8 (5)	10 (8)
N3	245 (6)	−2237 (8)	1727 (5)	38 (4)	56 (9)	21 (2)	9 (11)	−2 (5)	−13 (9)
N4	−274 (5)	−668 (9)	1138 (4)	26 (4)	70 (10)	19 (2)	−3 (10)	−10 (5)	5 (8)
N5	−24 (5)	2206 (9)	1738 (4)	28 (4)	64 (10)	15 (2)	4 (10)	4 (5)	−1 (8)
N6	499 (5)	2959 (9)	1582 (4)	25 (4)	85 (11)	19 (3)	−22 (11)	17 (5)	5 (9)
N7	1121 (5)	1137 (9)	1493 (4)	21 (4)	77 (11)	21 (3)	16 (10)	−4 (5)	7 (9)
C1	1330 (7)	−373 (12)	2765 (5)	32 (5)	84 (13)	13 (3)	16 (14)	7 (6)	−10 (10)
C2	2061 (8)	−289 (14)	2957 (6)	36 (6)	111 (16)	26 (4)	17 (16)	0 (7)	17 (13)
C3	2332 (8)	790 (14)	3159 (7)	29 (5)	112 (17)	32 (4)	0 (16)	−2 (7)	19 (13)
C4	1897 (7)	1789 (14)	3196 (6)	20 (5)	139 (18)	28 (4)	−3 (15)	6 (7)	−5 (14)
C5	1156 (6)	1641 (11)	3027 (5)	20 (4)	76 (13)	21 (3)	2 (12)	17 (6)	0 (10)
C6	1039 (8)	−1473 (11)	2469 (6)	42 (6)	66 (13)	20 (3)	40 (14)	8 (7)	18 (11)
C7	1314 (8)	−2715 (12)	2651 (6)	54 (7)	60 (14)	26 (4)	14 (15)	−22 (8)	−1 (12)
C8	−193 (7)	−1853 (12)	1251 (5)	29 (5)	88 (13)	15 (3)	3 (14)	7 (6)	2 (10)
C9	−534 (8)	−2757 (12)	891 (6)	44 (6)	87 (15)	20 (3)	−8 (15)	−10 (7)	−31 (11)
C10	−977 (8)	−2391 (13)	403 (6)	39 (6)	116 (17)	20 (3)	−5 (16)	−10 (7)	−16 (12)
C11	−1048 (8)	−1165 (15)	284 (7)	41 (6)	126 (19)	27 (4)	7 (17)	−12 (8)	7 (14)
C12	−691 (8)	−318 (14)	652 (6)	50 (6)	116 (17)	21 (3)	14 (18)	−12 (7)	−23 (14)
C13	641 (7)	2568 (12)	3134 (5)	31 (5)	86 (14)	14 (3)	−11 (13)	9 (6)	−8 (10)
C14	838 (8)	3920 (13)	3096 (6)	37 (6)	87 (15)	27 (4)	−18 (15)	12 (7)	14 (12)
C15	1080 (6)	2378 (12)	1423 (5)	20 (4)	101 (14)	16 (3)	−19 (13)	−1 (6)	−12 (10)
C16	1636 (6)	3014 (13)	1204 (6)	20 (5)	108 (15)	24 (3)	−18 (14)	4 (6)	−12 (12)
C17	2231 (7)	2432 (12)	1050 (6)	19 (5)	104 (15)	26 (3)	−23 (14)	15 (6)	−12 (12)
C18	2284 (6)	1162 (14)	1138 (6)	13 (4)	132 (17)	29 (4)	0 (14)	−3 (6)	−32 (13)
C19	1727 (7)	599 (12)	1347 (6)	23 (5)	106 (16)	22 (3)	−16 (14)	−10 (6)	−8 (12)
C20	1183 (10)	3569 (15)	5237 (7)	71 (9)	117 (18)	26 (4)	−12 (20)	15 (10)	−7 (14)
O1	4159 (5)	490 (8)	3547 (4)	44 (4)	89 (10)	32 (3)	−6 (11)	14 (5)	1 (9)

[a] The form of the thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Final Parameters for the Hydrogen Atoms in $[Zn(dapp)]_2 \cdot CHCl_3 \cdot H_2O$[a]

Atom [bonded to]	Distance	*x*	*y*	*z*	*B*
H1[C2]	1.01	225	−114	292	6.0
H2[C3]	1.18	295	88	315	6.4
H4[C7]	0.95	157	−257	302	6.0
H5[C7]	0.89	82	−329	265	6.0
H6[C7]	0.87	134	−338	245	6.0
H7[C14]	1.15	102	410	264	5.7
H8[C14]	1.03	119	396	346	5.7
H9[C14]	1.00	44	414	334	5.7
H12[C11]	1.10	−122	−71	−13	6.9
H13[C12]	1.03	−91	45	82	6.8
H14[C16]	1.10	155	400	121	5.2
H15[C17]	1.05	264	292	87	5.5
H16[C18]	1.06	284	106	120	5.8
H17[C19]	1.04	176	−30	149	5.3
H18[C20]	1.16	105	391	569	7.6
H21[O1]	0.85	395	40	326	6.5

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters ($\times 10^3$), and the isotropic thermal parameter (in $Å^2$).

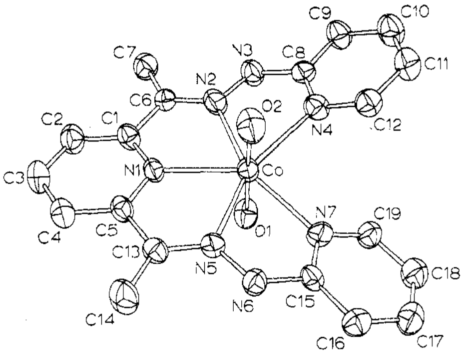

Figure 1. $[Co(H_2dapp)(H_2O)_2]^{2+}$ cation showing the atomic numbering and the thermal elipsoids. The Zn complex is isomorphous and virtually identical.

contacts between hydrogen atoms of the pyridine rings. The important point, however, is that PBP complexes of first-row transition elements can be prepared using an appropriate ligand.

The distances and angles in the three complexes are summarized in Tables VI and VII. The main differences in the bond distances in I and II are related to the difference in the size of the two metal ions. Excluding the bond M–N1 to the central pyridine rings, the remaining M–N bonds average 2.254 Å for the Co and 2.298 Å for the Zn complex. The Zn^{2+} ion is only slightly larger, as might be expected since the Co^{2+} complex is high spin. The magnetic moment of the Co complex was 5.25 ± 0.08 BM which is at the upper end of the range (4.7–5.2 BM) given for six-coordinate Co^{2+} in a pseudooctahedral field.[17] The value of 4.47 BM was reported for $Co(H_2dapp)I_2$[9] while values of 4.9–5.0 BM have been reported[11] for other cobalt complexes of pyridylhydrazones. However, there is no question that the Co complex is high spin as would be expected. The difference of about 0.044 Å in the M–N bonds is larger than expected from the data tabulated on ionic sizes of various ions.[18] However, since a similar difference has been observed[19] in the PBP complexes of Co^{2+} and Zn^{2+}, the extrapolation of the six-coordinate values is probably not valid. The axial water molecules, somewhat surprisingly, behave in an opposite manner, namely, are shorter (average Zn–O is 2.104 Å) in the Zn complex than in the Co case (average Co–O is 2.150 Å). The axial water to metal distances appear to be determined largely by nonbonded contacts involving the equatorial nitrogen atoms. As the in-plane metal–ligand distances increase, the corresponding nonbonded contacts increase if O···N was less than 3.0 Å and decrease or remain constant if the distance was greater than 3.0 Å. A somewhat similar pattern was noted in other PBP complexes involving a planar pentadentate ligand.[7,19]

Table VI. Intramolecular Distances (Å) in the Three Complexes

Coordination Sphere of the $[M(H_2dapp)(H_2O)_2]^{2+}$ Ions

	M = Co	M = Zn		M = Co	M = Zn
M–O1	2.146 (4)	2.104 (4)	O1–N2	2.884 (5)	2.911 (6)
M–O2	2.153 (4)	2.103 (4)	O1–N4	3.372 (5)	3.334 (6)
M–N1	2.207 (4)	2.251 (4)	O1–N5	3.292 (5)	3.292 (6)
M–N2	2.248 (4)	2.314 (4)	O1–N7	2.904 (5)	2.918 (6)
M–N5	2.242 (4)	2.286 (4)	O2–N2	3.416 (5)	3.415 (5)
M–N4	2.268 (4)	2.305 (4)	O2–N4	2.916 (5)	2.939 (6)
M–N7	2.258 (4)	2.288 (4)	O2–N5	2.812 (5)	2.830 (6)
O1–N1	3.048 (5)	3.054 (6)	O2–N7	3.240 (5)	3.209 (6)
O2–N1	3.132 (5)	3.133 (6)	N4–N7	3.080 (5)	3.200 (6)

Coordination Sphere of $Zn_2(dapp)_2$

Zn–N1	2.590 (10)	Zn–N1′	2.390 (10)	Zn–Zn′	3.503 (2)
Zn–N2	2.032 (10)	Zn–N4	2.036 (10)	Zn–N5′	2.064 (10)
Zn–N7′	2.031 (10)				

Ligand in the Three Complexes

Atoms	I	II	III	Atoms	I	II	III
C1–C6	1.484 (6)	1.478 (8)	1.475 (18)	N7–C15	1.320 (6)	1.332 (7)	1.385 (17)
C5–C13	1.473 (7)	1.472 (8)	1.447 (18)	N7–C19	1.361 (6)	1.348 (7)	1.355 (16)
C6–N2	1.271 (6)	1.267 (7)	1.296 (17)	C1–C2	1.396 (7)	1.393 (8)	1.411 (19)
C13–N5	1.296 (6)	1.289 (7)	1.287 (16)	C2–C3	1.378 (8)	1.376 (9)	1.363 (21)
N2–N3	1.365 (6)	1.359 (6)	1.382 (14)	C3–C4	1.382 (8)	1.375 (10)	1.384 (21)
N5–N6	1.356 (6)	1.352 (6)	1.362 (14)	C4–C5	1.381 (6)	1.401 (8)	1.427 (18)
N3–C8	1.368 (6)	1.391 (7)	1.377 (16)	C8–C9	1.390 (7)	1.395 (8)	1.416 (19)
N6–C15	1.384 (6)	1.385 (7)	1.346 (16)	C9–C10	1.366 (8)	1.393 (9)	1.395 (20)
C6–C7	1.492 (7)	1.496 (8)	1.515 (19)	C10–C11	1.385 (8)	1.375 (10)	1.389 (22)
C13–C14	1.490 (7)	1.482 (8)	1.546 (19)	C11–C12	1.375 (7)	1.366 (8)	1.395 (22)
N1–C1	1.335 (6)	1.338 (7)	1.350 (16)	C15–C16	1.394 (7)	1.395 (8)	1.391 (18)
N1–C5	1.349 (6)	1.346 (7)	1.360 (16)	C16–C17	1.372 (7)	1.377 (8)	1.366 (18)
N4–C8	1.340 (6)	1.321 (7)	1.343 (16)	C17–C18	1.390 (8)	1.381 (9)	1.423 (20)
N4–C12	1.345 (6)	1.353 (7)	1.362 (18)	C18–C19	1.368 (7)	1.376 (8)	1.343 (18)

Table VII. Selected Bond Angles (deg) in the Three Complexes

Coordination Sphere of the $[M(H_2dapp)(H_2O)_2]^{2+}$ Ions

	M = Co	M = Zn		M = Co	M = Zn
O1–M–N1	88.9 (1)	89.0 (2)	O2–M–N1	91.8 (1)	92.0 (2)
O1–M–N2	82.0 (1)	82.3 (2)	O2–M–N2	101.8 (1)	101.2 (2)
O1–M–N4	99.6 (1)	98.1 (2)	O2–M–N4	82.5 (1)	83.5 (2)
O1–M–N5	97.2 (1)	97.1 (2)	O2–M–N5	79.5 (1)	80.2 (2)
O1–M–N7	82.4 (1)	83.2 (2)	O2–M–N7	94.5 (1)	93.8 (2)
N1–M–N2	69.1 (1)	68.0 (2)	M–N1–C1	120.4 (3)	120.3 (4)
N1–M–N5	69.8 (1)	69.0 (2)	M–N1–C5	120.0 (3)	119.2 (3)
N2–M–N4	70.2 (1)	69.1 (2)	M–N2–C6	122.3 (3)	121.7 (4)
N5–M–N7	70.2 (1)	69.9 (2)	M–N2–N3	115.9 (3)	116.1 (3)
N4–M–N7	85.8 (1)	88.3 (2)	M–N5–C13	121.6 (3)	121.7 (4)
M–N4–C8	116.7 (3)	117.7 (4)	M–N5–N6	116.2 (3)	115.8 (3)
M–N7–C15	117.0 (3)	116.9 (3)	O1–M–O2	176.1 (1)	176.5 (2)

Coordination Sphere of $Zn_2(dapp)_2$ III

N1–Zn–N2	71.4 (4)	N2–Zn–N4	78.7 (4)	N4–Zn–N7′	110.7 (4)
N1–Zn–N4	148.9 (4)	N2–Zn–N5′	163.9 (4)	N4–Zn–N1′	88.1 (4)
N1–Zn–N5′	92.8 (3)	N2–Zn–N7′	103.6 (4)	N5′–Zn–N7′	77.6 (4)
N1–Zn–N7′	84.8 (4)	N2–Zn–N1′	101.7 (4)	N5′–Zn–N1′	74.2 (4)
N1–Zn–N1′	89.9 (3)	N4–Zn–N5′	116.3 (4)	N7′–Zn–N1′	150.9 (4)
Zn–N4–C8	112.7 (8)	Zn–N2–C6	123.6 (9)	Zn–N5′–C13′	120.1 (8)
Zn–N7′–C15′	113.6 (8)	Zn–N2–N3	115.8 (7)	Zn–N5′–N6′	116.0 (7)
Zn–N1–C1	97.0 (7)	Zn–N1′–C1′	122.2 (8)	Zn–N1–Zn′	89.3 (3)
Zn–N1–C5	122.6 (8)	Zn–N1′–C5′	103.7 (7)		

Ligand in the Three Complexes

	I	II	III		I	II	III
C1–C6–C7	121.2 (4)	120.8 (5)	121.2 (12)	C5–C13–C14	121.3 (4)	121.2 (5)	120.7 (11)
C1–C6–N2	112.6 (4)	113.4 (5)	114.9 (11)	C5–C13–N5	112.8 (4)	112.6 (5)	116.7 (11)
C7–C6–N2	126.2 (4)	125.7 (5)	123.8 (12)	C15–C13–N5	125.9 (4)	126.2 (5)	122.6 (11)
C6–N2–N3	120.7 (4)	121.0 (5)	120.5 (10)	C13–N5–N6	121.3 (4)	121.5 (5)	123.9 (10)
N2–N3–C8	116.2 (4)	115.6 (5)	112.1 (10)	N5–N–C15	115.6 (4)	116.5 (5)	113.6 (10)
N3–C8–N4	117.4 (4)	118.3 (5)	120.3 (11)	N6–C15–N7	117.5 (4)	117.8 (5)	118.8 (11)
N3–C8–C9	118.8 (4)	116.5 (5)	117.0 (11)	N6–C15–C16	118.0 (4)	119.0 (5)	120.7 (11)
C6–C1–C2	124.1 (4)	123.6 (5)	120.8 (12)	C13–C5–C4	123.4 (4)	123.1 (5)	121.9 (11)
C1–C2–C3	119.0 (5)	119.0 (6)	119.4 (13)	C4–C5–N1	121.8 (4)	120.7 (5)	121.5 (11)
C2–C3–C4	119.4 (5)	119.8 (6)	120.9 (14)	C5–N1–C1	119.4 (4)	120.2 (5)	119.4 (10)
C3–C4–C5	118.9 (5)	119.0 (6)	117.6 (13)	N1–C1–C2	121.5 (4)	121.2 (5)	121.1 (12)
N4–C8–C9	123.8 (4)	125.2 (5)	122.6 (11)	N7–C15–C16	124.5 (4)	123.2 (5)	120.5 (11)
C8–C9–C10	118.5 (5)	116.4 (6)	118.1 (12)	C15–C16–C17	118.0 (5)	118.6 (5)	121.0 (11)
C9–C10–C11	118.6 (5)	119.5 (6)	118.8 (13)	C16–C17–C18	118.8 (5)	119.1 (6)	118.6 (12)
C10–C11–C12	119.5 (5)	119.0 (6)	120.4 (14)	C17–C18–C19	118.9 (5)	118.2 (6)	117.6 (13)
C11–C12–N4	123.0 (5)	123.5 (6)	121.1 (11)	C18–C19–N7	123.3 (5)	124.1 (5)	125.7 (12)
C12–N4–C8	116.5 (4)	116.1 (5)	119.0 (11)	C19–N7–C15	116.3 (4)	116.6 (5)	116.6 (10)

The distortions from a plane pentagon are also related to nonbonded contacts. Although the three pyridine rings are planar (see Table VIII), they are not coplanar with each other but twisted by relatively larger amounts (16–40°). The twists appear to be related to steric interaction between the hydrogen on C12, H14, with the corresponding one on C19, H19. The distance H14···H19 in the Co complex is 2.56 Å which is very close to the expected van der Waals contact of 2.4 Å. Obviously, any attempt to make the two rings coplanar would result in an intolerably close contact between the two H atoms. The pattern of distortions is very similar to the "helical" coordination found in bis(2-thiobenzaldimino)-2,6-diacetylpyridinezinc(II)[20] if one considers the deviations from planarity relative to the central pyridine ring N1, C1–C5. However, the metal atom is significantly out of the plane of the pyridine ring so that "helical" might not be the best description. In any case, the best plane through the five donor nitrogen atoms shows appreciable deviations from planarity in an alternating manner from N1. Since PBP complexes of Co^{2+} and Zn^{2+} with DAPSC[19] have smaller deviations from planarity than in I and II, the ligand geometry must be the overriding factor.

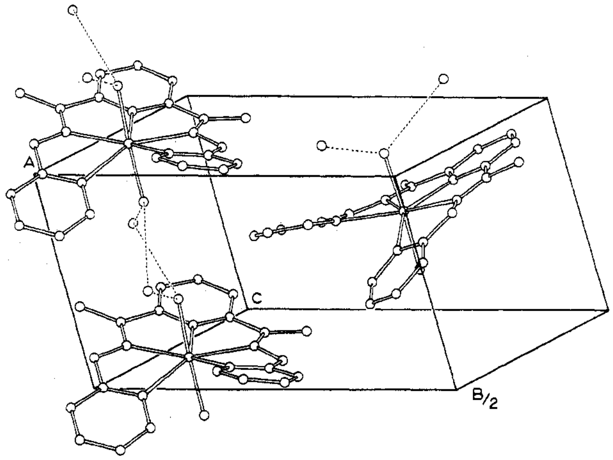

Figure 2. Partial packing diagram for the $[M(H_2dapp)(H_2O)_2]^{2+}$, Cl^- ions. The hydrogen bonds from the apical water molecules to the chloride ions are shown by dotted lines.

The packing of the $[M(H_2dapp)(H_2O)_2]^{2+}$ ions in the unit cell is illustrated in Figure 2. The two apical water molecules are hydrogen bonded to the two chloride ions to form an infinite chain parallel to the *a* axis. The distances and angles of the hydrogen bonds are summarized in Table IX. The O···Cl distances range from 3.102 (4) to 3.202 (4) Å and are similar to the values found in other metal chloride hydrates.[21]

$Zn_2(dapp)_2$ Complex. Although the deprotonation of pyridylhydrazones is well documented, to our knowledge no structural data on the deprotonated complexes have been reported. The fact that the zinc complex changes from a PBP complex to an octahedral dimer on deprotonation was

Table VIII. Least-Squares Planes[a] and Parameters

	Planes								
	1	2	3	4	5	6	7	8	9
M	185	32	−145	189	18	−122	−1867	−164	−116
O1	2258			2220					
O2	−1854			−1802					
N1	4*	−779	566	2*	−773	562	−1*	−596	2465
N2	−89	−414	−107	−113	−400	−35	−917	14	407
N3	−80	−114	−483	−114	−104	−363	−1175	29	−589
N4	−375	19*	−1352	−352	27*	−1235	−2679	−11*	−1900
N5	331	−99	327	348	−159	302	−2377	−574	−80
N6	471	284	98	494	183	66	−3194	442	48
N7	995	1246	−26*	993	1159	−22*	−3132	1614	−8*
C1	−4*			−5*			−19*		
C2	2*			−1*			20*		
C3	0*			10*			−3*		
C4	−1*			−13*			−17*		
C5	−1*			7*			19*		
C6	−25			−37			−184		
C7	48			70			455		
C8	−356	−13*		−377	−18*		−2112	1*	
C9		−2*			−2*			9*	
C10		11*			12*			−10*	
C11		−5*			−3*			1*	
C12		−10*			−16*			10*	
C13	84			83			214		
C14	−94			−128			−374		
C15	927		17*	946		12*	−3641		5*
C16			5*			6*			7*
C17			−17*			−14*			−15*
C18			8*			4*			12*
C19			14*			14*			−1*
	Parameters for the Planes ($\times 10^{+4}$)								
l	9432	8820	8987	9486	9013	9173	−2251	8348	3401
m	3295	4051	1645	3149	3601	1331	−2752	−334	1341
n	370	−2406	4066	310	−2404	3752	9269	−5496	9308
p	1946	2201	1782	1948	2146	1670	5478	−2010	3965

[a] The deviations from the plane (Å × 10^3) are given for the specified atom. Equation of the plane: deviation (Å) = $lX + mY + nZ - p$ when X, Y, and Z are the orthogonal coordinates (in Å) relative to a, b, and $c \sin \beta$, and p is the distance of the plane from the origin. The atoms used to define the planes are noted by an asterisk following the deviations. Planes 1-3 are for I with M = Co, 4-6 are for II with M = Zn, and 7-9 are for III with M = Zn. Angles of interest between the planes are 1-2 = 16.9°, 1-3 = 23.5°, 2-3 = 40.4°, 4-5 = 16.0°, 4-6 = 22.5°, 5-6 = 38.3°, 7-8 = 44.5°, 7-9 = 42.3°, and 8-9 = 76.6°.

Table IX. Hydrogen Bonds in $[Co(H_2dapp)(H_2O)]^{2+},2Cl^-$

Bond D-H···A[a]	Position of A	D-H, Å	H···A, Å	D···A, Å	D-H···A, deg
O1-H21-Cl1	i	0.97	2.21	3.170 (4)	167
O1-H20-Cl2	ii	0.84	2.29	3.127 (4)	168
O2-H23-Cl1	iii	0.86	2.24	3.102 (4)	174
O2-H22-Cl2	iv	0.81	2.40	3.202 (4)	169

[a] Donor-hydrogen···acceptor. D-H is at x, y, z. The acceptor A is at i (x, y, z), ii ($x - 1, y, z$), iii ($x, y, z - 1$), or iv ($x - 1, y, z - 1$).

unexpected. A view of only the nitrogen atoms around each zinc atom is given in Figure 3. The central pyridine nitrogen atom in the anion $dapp^{2-}$ bridges the two zinc atoms (see Figure 4) at relatively long Zn–N distances (Zn–N1 is 2.590 (10) and Zn–N1' is 2.390 (10) Å) which is very unusual for a pyridine group. In fact to our knowledge, this is the first reported bridging pyridine ligand although very recently a pyrrole ring was found to bridge two $Re(Co)_3$ or $Tc(Co)_3$ groups.[22] The remaining Zn–N distances average 2.04 Å and are not unusual. There appears to be no significant differences between the bond lengths in the neutral or deprotonated form of the ligand. Unfortunately, the gradual decomposition of the crystals of III has reduced the accuracy of the determination so that small changes may be masked by large esd's. Nevertheless, the most striking changes have taken place in the conformation of the anion $dapp^{2-}$ compared to that of H_2dapp. The large distortions from planarity of $dapp^{2-}$ can be appreciated by considering the various dihedral angles given in Table X. The pattern in I and II is that of a nearly planar H_2dapp, with only small twists required to satisfy both the metal atom and internal strain. The dihedral angles about N3–C8 and N6–C15 indicate the small twists of the terminal pyridine ring. In contrast in $dapp^{2-}$ the side chains C6–C8 and C13–C15 show slightly smaller deviations from planarity but a much larger rotation about the C1–C6 and C5–C13 bonds. The net result is that the side chains are definitely twisted out of the plane of the central pyridine ring. However, since the steric interactions between the terminal pyridine rings have been decreased, the rings are more nearly coplanar with the side chain.

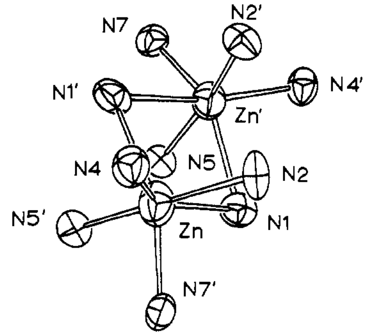

Figure 3. View of the coordination sphere of the dimeric deprotonated zinc complex, $Zn_2(dapp)_2$. A twofold axis relates the unprimed to primed atoms. Note the $dapp^{2-}$ ion is coordinated to both zinc atoms with the central pyridine ring nitrogen, N1, bridging the two zinc atoms.

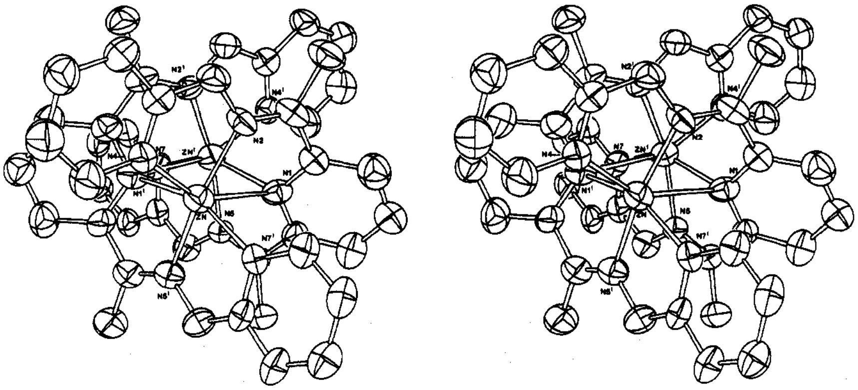

Figure 4. Stereoscopic view of the $Zn_2(dapp)_2$ dimer. The numbering scheme for the ligand is identical with that given in Figure 1 for the protonated ligand. Only the five nitrogen atoms of each ligand are labeled.

Table X. Selected Dihedral Angles (deg) in the Three Complexes[a]

Atoms a-b-c-d	I	II	III
N1-C1-C6-N2	−2.7	−2.9	32.6
C2-C1-C6-C7	−4.0	−6.2	36.3
C7-C6-N2-N3	−0.7	0.5	−0.9
C6-N2-N3-C8	170.4	171.9	−171.6
N2-N3-C8-N4	11.4	12.5	1.2
N2-N3-C8-C9	−166.1	−166.7	−179.8
N1-C5-C13-N5	−8.8	−10.4	29.2
C4-C5-C13-C14	−12.3	−12.4	34.9
C14-C13-N5-N6	0.9	1.6	−4.8
C13-N5-N6-C15	170.7	172.0	−175.1
N5-N6-C15-N7	9.6	10.5	−6.9
N5-N6-C15-C16	−169.6	−169.0	174.5

[a] The angles are defined for the atoms a-b-c-d as the positive clockwise rotation from a to d when viewed down the bond from b to c.

A somewhat similar twist was observed in one side chain of the deprotonated form of 2,6-diacetylpyridinebis(picolinoylhydrazone), H_2dip, coordinated to a Cu(II) ion.[23] In the Cu(dip) complex the twist is about the N-N bond rather than around the C(central pyridine ring)-C(side chain) bonds, C1-C6 and C5-C13, as in III.

The reasons for the dimerization upon deprotonation of I and II are not obvious. Although the protons are removed from N3 and N6, developing a formal negative charge, neither of these two atoms is coordinated to the zinc atom in II or III. In contrast in the Cu(dip) complex the Cu(II) ion is bonded to the two nitrogens with the formal negative charge. Additional structural studies on other complexes of both deprotonated and protonated pyridylhydrazones are needed before the dimerization reaction can be fully understood.

The H_2dapp and $dapp^{2-}$ Ligands. The C-C and C-N bond distances in the three pyridine rings average 1.381 (10) and 1.342 (14) Å in I, 1.384 (11) and 1.340 (12) Å in II, and 1.392 (25) and 1.359 (14) Å in III and are not significantly different. Similarly, the various C-C, C-N, and N-N distances in the side chains (see Table VI) appear to be similar, although as noted the esd's for III are somewhat larger and may mask small changes. However, for a related system no differences in bond lengths were found between the ligand Hsip,[24] *N*-picolinylidene-*N'*-salicylolhydrazine, and the nickel complex $Ni(sip)_2$,[25] involving the deprotonated form of the ligand. Furthermore, the distances in the side chains of H_2dapp, $dapp^{2-}$, Hsip, and sip^- are all virtually identical with the dimensions in benzaldehyde semicarbazone,[26] suggesting similar electronic structures in all cases. Therefore, little or no change takes place in the electronic structure of the various ligands either upon deprotonation or complex formation.

Conclusions. One result of the present study is the demonstration that PBP complexes of the first-row transition elements can be prepared using appropriate pentadentate ligands. A second important point is the realization that the deprotonation of various ligands need not follow identical and apparently simple paths.

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Registry No. I, 55428-24-5; II, 55469-05-1; III, 55428-30-3.

Supplementary Material Available: Listings of structure factor amplitudes (36 pages). Ordering information is given on any current masthead page.

References and Notes

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