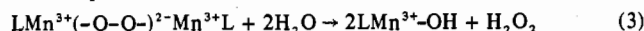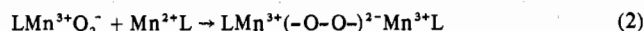which contains no O–H stretch or Mn–OH deformation in its infrared spectrum. The addition of H_2O to this material dissolved in an appropriate organic solvent gives a compound similar to Mn(5-NO₂SALDPT)(OH). Preliminary analytical and spectroscopic evidence suggests that a peroxo species is the initial product.[24] Consequently we propose the tentative mechanistic scheme given by eq 1–4 recognizing that eq 4 is

$$Mn^{2+}L + O_2 \rightarrow LMn^{3+}O_2^- \tag{1}$$

$$LMn^{3+}O_2^- + Mn^{2+}L \rightarrow LMn^{3+}(-O-O-)^{2-}Mn^{3+}L \tag{2}$$

$$LMn^{3+}(-O-O-)^{2-}Mn^{3+}L + 2H_2O \rightarrow 2LMn^{3+}-OH + H_2O_2 \tag{3}$$

$$LMn^{3+}-OH + [O] \rightarrow L'Mn^{3+}-OH \tag{4}$$

significant in the early stages only for Mn(XSALDPT) and that L′ corresponds to an oxidized product of XSALDPT.

In summary, evidence has been presented which shows the irreversibility of the reaction between O_2 and Mn(II) complexes containing a pentadentate O_2N_3 ligand field. In the majority of cases reaction with O_2 does not stop with conversion to Mn(III) but continues with oxidation of the ligand even under strictly anhydrous conditions. Oxidized products from nonanhydrous reactions are isolated for the nitro-substituted complexes which have the formulation Mn(5-NO₂SALDPT)(OH) and Mn(5-NO₂SALMeDPT)(OH).

Registry No. Mn(5-ClSALDPT), 61916-28-7; Mn(5-BrSALDPT), 61916-11-8; Mn(5-NO₂SALDPT), 61916-12-9; Mn(3-CH₃OSALDPT), 61916-13-0; Mn(5-BrSALMeDPT), 61951-29-9; Mn(5-NO₂SALMeDPT), 61916-14-1; Mn(SALPrDPT), 61916-15-2; Mn(SALPhDPT), 61916-16-3; Mn(5-NO₂SALDPT)(OH), 61967-10-0; Mn(5-NO₂SALMeDPT)(OH), 61916-17-4; Mn(3-CH₃OSALDPT)(OH), 61916-18-5; Mn(SALDPT), 15378-52-6; Mn(SALMeDPT), 61916-19-6.

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Infrared and Crystal Structure Study of σ vs. π Bonding in Tetrahedral Zinc(II) Complexes. Crystal and Molecular Structures of Dichlorobis(4-substituted pyridine)zinc(II) Complexes

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The crystal structures of three ZnCl₂(4-R-py)₂ (py = pyridine) complexes where R = vinyl (vin), acetyl (ac), and cyano (CN) have been determined by x-ray techniques. The far-infrared spectra for the R = methyl, vinyl, acetyl, and cyano and the unsubstituted pyridine derivatives have also been measured. The Zn–N bond length in the ZnCl₂(4-R-py)₂ complexes is directly proportional to the ligand pK_b, suggesting that π-bonding effects are minimal in the series. The Zn–Cl bond distance is virtually independent of the ligand pK_b, where R is anything but an H atom. ZnCl₂(4-H-py)₂ has longer Zn–Cl distances presumably because of a unique packing arrangement. The trends found in the structural studies are not obvious from the infrared data regarding chemical bonding. The complex ZnCl₂(4-vin-py)₂ crystallizes in the triclinic space group $P\bar{1}$. The cell dimensions are $a = 7.501$ (4), $b = 7.522$ (5), and $c = 14.482$ (6) Å with $\alpha = 90.41$ (4), $\beta = 90.53$ (4), and $\gamma = 105.29$ (5)°. There are two molecules of the complex per unit cell. The final R value was 0.048 for the 1566 reflections used in the analysis. There are eight molecules of ZnCl₂(4-ac-py)₂ in a monoclinic cell, space group $C2/c$, with the dimensions $a = 19.340$ (15), $b = 18.084$ (18), and $c = 9.678$ (6) Å and $\beta = 100.13$ (5)°. The final R value was 0.052 for the 1067 reflections used in the analysis. The ZnCl₂(4-CN-py)₂ complex forms monoclinic crystals with the space group $I2/a$. There are eight molecules in the unit cell of dimensions $a = 17.229$ (2), $b = 7.443$ (9), and $c = 22.500$ (3) Å with $\beta = 90.53$ (1)°. The final R value was 0.048 for the 1602 reflections used in the analysis. The data for all three complexes were measured using a computer-controlled diffractometer. The radiation was from graphite-monochromatized molybdenum, and a variable-speed θ–2θ scan technique was used in the intensity measurements.

Introduction

The relative roles of σ vs. π bonding in zinc(II) complexes have generated considerable controversy. A study of the far-infrared spectra of a series of ZnCl₂(4-R-py)₂ complexes was reported to indicate that both the Zn–Cl and Zn–N bonds increased in strength with any substitution.[2–4] When R was more electron donating than hydrogen, the Zn–N σ-bond was strengthened, increasing the electron density on the zinc atom.

Table I. Crystal Data

	$ZnCl_2(4\text{-vin-py})_2$	$ZnCl_2(4\text{-ac-py})_2$	$ZnCl_2(4\text{-CN-py})_2$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$I2/a$
a, Å	7.501 (4)	19.340 (15)	17.229 (2)
b, Å	7.522 (5)	18.084 (18)	7.443 (9)
c, Å	14.482 (6)	9.678 (6)	22.500 (3)
α, deg	90.41 (4)		
β, deg	90.53 (4)	100.13 (5)	90.53 (1)
γ, deg	105.29 (5)		
Vol., Å³	788.1 (8)	3332 (4)	2885.3 (7)
Mol wt	346.58	378.58	344.52
Z	2	8	8
ρ(calcd), g/cm³	1.460	1.509	1.586
ρ(measd), g/cm³	1.46	1.51	1.64
Crystal size, mm³	$0.21 \times 0.21 \times 0.57$	$0.41 \times 0.15 \times 0.12$	$0.60 \times 0.36 \times 0.21$
μ, cm⁻¹	19.2	18.4	21.1
2θ range, deg	0-45	0-35	0-45
Reflections measd	2070	1549	1896
Reflections used	1566	1067	1602

The increased electron density was removed via $d\pi$–$d\pi$ bonds to the chlorine atoms, increasing the Zn–Cl bond strength. If R was more electron withdrawing than hydrogen, the Zn–N σ bond was weakened but the $d\pi$–π* (of the ligand) bonds became important, and the Zn–N interaction was strengthened. The Zn–Cl bond was strengthened via the σ pathway to restore the electron density on the zinc atom. Thus, the Zn–N and Zn–Cl bonds were strengthened relative to pyridine regardless of the substituent.

In contrast x-ray studies of tetrahedral $ZnCl_2L_2$ complexes have suggested that the Zn–Cl bond length was a function of the donor properties of L.[5,6] A compilation of metal–donor distances in $ZnCl_2L_2$ complexes[6] indicated that when L was an aromatic nitrogen donor, the average Zn–Cl distance was significantly less than when L was a chloride ion. This shortening, analogous to a trans effect in square-planar complexes, was interpreted in terms of π bonding between the zinc ion and base via the $d\pi$–π* path. The π-bonding mechanism was also used to explain the accelerating effect of zinc chloride on the radical polymerization of 4-vinyl-pyridine.[7]

However, the $d\pi$–π* model of back-bonding in tetrahedral zinc complexes is not universally accepted. The nonexistence of zinc(II) carbonyls has been explained by lack of participation of the $3d^{10}$ state in π bonding.[8] Similar conclusions were reached in a study of the donor–acceptor properties of isocyanides[9] which are comparable to carbonyls in the π*-acceptor properties. Finally, a study of the infrared intensities of the C≡N group in some 3-cyanopyridine complexes was interpreted as indicating that σ bonding was much stronger than π bonding in the zinc(II) complex.[10]

The majority of the conclusions on the bonding in $ZnCl_2L_2$ complexes have been derived from infrared data with only a few reported structural studies on $ZnCl_2L_2$ complexes. Therefore, we undertook a systematic investigation of the infrared and structural properties of a series of $ZnCl_2L_2$ complexes, where L was a 4-substituted pyridine. The $ZnCl_2(py)_2$[11] and the $ZnCl_2(4\text{-CH}_3\text{-py})_2$[12] structures have been reported elsewhere. We now wish to report our structural studies of the 4-vinyl (4-vin-py), 4-acetyl (4-ac-py), and 4-cyano (4-CN-py) complexes. In addition we have determined the far-infrared frequencies of all five complexes for comparison with our structural results. Excluding the case of $ZnCl_2(py)_2$ which has a unique packing arrangement, the results suggest that π-bonding effects are minimal in $ZnCl_2L_2$ complexes.

Experimental Section

Synthesis. The $ZnCl_2(4\text{-R-py})_2$ complexes were prepared by adding 0.0100 mol of the pyridine ligand to a solution of 0.6814 g (0.005 00 mol) of $ZnCl_2$ in 50 mL of absolute ethanol. Liquid ligands were

Table II. Scheme of Refinement for the $ZnCl_2L_2$ Complexes[a]

	L		
	4-vin-py	4-ac-py	4-CN-py
R from all-atom Fourier synthesis	0.18	0.24	0.23
R after three least-squares cycles, isotropic thermal parameters	0.12	0.16	0.12
R after three least-squares cycles, anisotropic thermal parameters	0.055	0.062	0.067
R after three least-squares cycles with H atoms included	0.048	0.052	0.048
F_{low} for weighting	40.0	12.0	60.0
F_{high} for weighting	80.0	48.0	120.0

[a] The R values ($R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$) are given for various stages in the structure determination and refinement.

added directly while solid ligands were added as ethanolic solutions; 2–4 mL of triethyl orthoformate was added to the $ZnCl_2$ solution to remove any trace amounts of water. The solutions (or mixtures) formed on addition of the ligand were refluxed for several hours, filtered while hot (if necessary), and allowed to cool. The reactions were carried out under a nitrogen atmosphere. The colorless products were recrystallized from absolute ethanol.

Infrared spectra from 4000 to 500 cm⁻¹ were recorded on a Beckman model IR 10 grating spectrophotometer, with samples as Nujol mulls between sodium chloride disks. The infrared spectra in the region 500–190 cm⁻¹ were kindly measured by Professor A. J. Carty of the University of Waterloo, Waterloo, Ontario, Canada. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Anal. Calcd for $ZnCl_2(4\text{-CH}_3\text{-py})_2$: C, 44.68; H, 4.38; N, 8.68; Cl, 21.99. Found: C, 44.79; H, 4.26; N, 8.74; Cl, 21.80; mp 168 °C. Calcd for $ZnCl_2(4\text{-vin-py})_2$: C, 48.52; H, 4.07; N, 8.08; Cl, 20.46. Found: C, 48.61; H, 4.18; N, 8.05; Cl, 20.31; mp 126–128 °C. Calcd for $ZnCl_2(py)_2$: C, 40.78; H, 3.43; N, 9.51; Cl, 24.08. Found: C, 40.71; H, 3.52; N, 9.48; Cl, 23.90; mp 207–209 °C. Calcd for $ZnCl_2(4\text{-ac-py})_2$: C, 44.42; H, 3.73; N, 7.40; Cl, 18.73. Found: C, 44.37; H, 3.72; N, 7.38; Cl, 18.63; mp 180 °C. Calcd for $ZnCl_2(4\text{-CN-py})_2$: C, 41.84; H, 2.34; N, 16.26; Cl, 20.58. Found: C, 42.02; H, 2.30; N, 16.30; Cl, 20.60; mp 208 °C.

Collection of X-Ray Diffraction Data. The crystal system, space group, and preliminary cell constants for $ZnCl_2(4\text{-vin-py})_2$, $ZnCl_2(4\text{-ac-py})_2$, and $ZnCl_2(4\text{-CN-py})_2$ were determined from Weissenberg and/or precession photographs. The final unit cell dimensions and orientation matrix were determined from a least-squares fit of 2θ, ω, ϕ, and χ values for 15 reflections measured on a Syntex $P\bar{1}$ four-circle diffractometer. The crystals of $ZnCl_2(4\text{-vin-py})_2$ and $ZnCl_2(4\text{-CN-py})_2$ were air sensitive and were coated with Apiezon T grease to retard decomposition.

The intensity data were collected on the Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo Kα radiation (λ 0.710 69 Å) and a variable-speed θ–2θ scan technique. The scan rate was determined by a preliminary 3-s scan of the reflection and varied linearly from 24°/min to 1°/min. The background was measured for a time equal to half the total scan time at a point 1° to each side of the α_1 and α_2 peaks. Four standard reflections were measured at 100 reflection intervals and were used to correct for any variation of intensities

Table III. Final Parameters of Nonhydrogen Atoms in $ZnCl_2(\text{4-vin-py})_2{}^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	537 (13)	−586 (12)	24998 (6)	3302 (21)	2947 (19)	656 (4)	2286 (29)	683 (13)	556 (13)
Cl(1)	1197 (3)	2971 (2)	2482 (1)	529 (7)	278 (4)	99 (1)	250 (9)	95 (5)	73 (4)
Cl(2)	−2970 (3)	−1198 (3)	2517 (1)	314 (5)	493 (6)	100 (1)	261 (9)	83 (4)	86 (5)
N(1a)	1177 (7)	−1106 (8)	1401 (3)	293 (13)	304 (15)	63 (3)	217 (22)	25 (10)	44 (11)
C(2a)	1876 (9)	−57 (10)	678 (4)	340 (19)	320 (19)	70 (4)	157 (30)	41 (14)	56 (14)
C(3a)	2569 (10)	−751 (12)	−70 (5)	332 (20)	446 (24)	65 (5)	200 (35)	58 (15)	23 (16)
C(4a)	2607 (10)	−2558 (13)	−96 (5)	347 (23)	457 (28)	69 (5)	321 (42)	−11 (16)	−99 (20)
C(5a)	1882 (12)	−3632 (10)	649 (5)	472 (26)	336 (20)	82 (5)	275 (37)	56 (18)	−6 (17)
C(6a)	1193 (10)	−2878 (10)	1371 (5)	435 (23)	299 (19)	78 (5)	247 (33)	66 (16)	32 (15)
C(7a)	3413 (13)	−3148 (15)	−960 (8)	467 (29)	478 (31)	159 (9)	353 (50)	−116 (24)	−214 (28)
C(8a)	3656 (16)	−4643 (19)	−1009 (8)	588 (39)	705 (47)	133 (9)	323 (71)	−40 (27)	−154 (34)
N(1b)	1087 (8)	−1177 (7)	3595 (3)	314 (16)	289 (13)	65 (3)	153 (23)	43 (12)	20 (10)
C(2b)	41 (10)	−1884 (9)	4321 (5)	353 (21)	314 (18)	69 (4)	164 (31)	60 (15)	33 (14)
C(3b)	723 (12)	−2578 (10)	5063 (5)	428 (24)	317 (19)	66 (5)	234 (34)	30 (17)	30 (15)
C(4b)	2438 (13)	−2600 (9)	5101 (5)	448 (30)	279 (20)	66 (5)	217 (40)	−74 (20)	−23 (15)
C(5b)	3606 (11)	−1907 (11)	4340 (6)	362 (23)	461 (25)	82 (5)	282 (39)	−4 (18)	19 (18)
C(6b)	2861 (10)	−1209 (10)	3622 (5)	300 (20)	429 (22)	73 (5)	222 (34)	21 (15)	64 (16)
C(7b)	3140 (16)	−3426 (14)	5934 (8)	543 (35)	489 (29)	131 (9)	373 (53)	−194 (29)	−114 (24)
C(8b)	4648 (19)	−3688 (16)	6010 (8)	679 (48)	565 (36)	154 (9)	215 (69)	−225 (36)	−103 (27)

a All values are ×10⁴, except those for Zn, which are ×10⁵. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table IV. Final Parameters of Nonhydrogen Atoms in $ZnCl_2(\text{4-ac-py})_2{}^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	34839 (7)	39660 (6)	15481 (13)	288 (6)	301 (5)	1348 (18)	−34 (9)	195 (15)	57 (15)
Cl(1)	2990 (2)	3064 (2)	2581 (4)	45 (1)	40 (1)	224 (5)	−20 (2)	53 (4)	38 (4)
Cl(2)	3876 (2)	5000 (2)	2616 (3)	43 (1)	36 (1)	152 (4)	−7 (2)	9 (4)	−23 (3)
N(1a)	4303 (5)	3482 (4)	778 (9)	31 (3)	28 (3)	136 (11)	4 (5)	29 (11)	−1 (10)
C(2a)	4755 (8)	3895 (6)	247 (11)	39 (5)	29 (4)	150 (15)	−9 (9)	50 (15)	32 (13)
C(3a)	5302 (7)	3622 (7)	−318 (12)	29 (5)	48 (5)	149 (15)	−10 (8)	57 (15)	14 (13)
C(4a)	5414 (8)	2862 (6)	−310 (12)	50 (6)	27 (4)	170 (16)	1 (10)	0 (16)	−8 (13)
C(5a)	4958 (10)	2432 (7)	287 (18)	76 (7)	19 (4)	378 (31)	13 (11)	129 (27)	−18 (18)
C(6a)	4397 (7)	2751 (7)	779 (15)	56 (6)	28 (5)	272 (24)	2 (10)	84 (21)	4 (17)
C(7a)	5999 (9)	2516 (8)	−926 (16)	58 (7)	41 (5)	286 (25)	30 (12)	104 (23)	−29 (18)
C(8a)	6526 (9)	2978 (8)	−1430 (20)	71 (7)	48 (6)	398 (36)	22 (12)	197 (27)	53 (24)
O(9a)	6045 (7)	1859 (6)	−900 (16)	93 (6)	45 (5)	603 (33)	24 (10)	231 (24)	−82 (19)
N(1b)	2729 (5)	4279 (5)	−98 (9)	33 (4)	27 (3)	152 (13)	4 (6)	25 (11)	−4 (11)
C(2b)	2381 (7)	3776 (6)	−981 (14)	42 (5)	24 (4)	191 (18)	−3 (8)	35 (17)	−15 (14)
C(3b)	1824 (7)	3953 (6)	−2007 (12)	42 (5)	37 (4)	143 (16)	−7 (9)	−24 (17)	−10 (14)
C(4b)	1611 (7)	4691 (7)	−2154 (12)	32 (5)	39 (5)	135 (14)	−2 (9)	−43 (17)	−1 (15)
C(5b)	1960 (7)	5210 (6)	−1295 (12)	35 (5)	38 (4)	151 (15)	2 (8)	−23 (15)	11 (14)
C(6b)	2524 (7)	4980 (6)	−280 (13)	43 (5)	40 (5)	145 (18)	−8 (9)	23 (18)	−24 (14)
C(7b)	992 (9)	4867 (9)	−3205 (17)	46 (7)	41 (7)	271 (26)	−14 (12)	−21 (24)	−20 (22)
C(8b)	861 (9)	5653 (8)	−3672 (15)	86 (8)	57 (6)	215 (23)	43 (12)	0 (22)	55 (19)
O(9b)	954 (8)	4381 (8)	−3712 (16)	90 (7)	70 (6)	530 (33)	0 (12)	−282 (25)	6 (24)

a All values are ×10⁴, except those for Zn, which are ×10⁵. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

with time. The variation increased approximately linearly from 1.000 to 1.189 for $ZnCl_2(\text{4-vin-py})_2$, to 1.570 for $ZnCl_2(\text{4-ac-py})_2$, and to 1.411 for $ZnCl_2(\text{4-CN-py})_2$. Those reflections with an intensity $I > 2.00\sigma(I)$ were considered reliable and were used in the structure analysis. The intensity data were reduced to a set of structure amplitudes by the usual application of Lorentz–polarization corrections. In all three cases the initial choice of the centric space group was based on calculated intensity statistics and was confirmed by the successful structure analysis. The relevant crystal data for each of the compounds are given in Table I.

For $ZnCl_2(\text{4-ac-py})_2$, a preliminary set of intensity data was collected using the method described above but with Cu Kα radiation (λ 1.5418 Å) and a 2θ range of 0–60°. However, the values of α and γ calculated from the least-squares fit of 15 reflections deviated by 0.15 and 0.12°, respectively, from the ideal value of 90°. Therefore, this data set was of questionable reliability and was used for the calculation of the Patterson function, the Fourier syntheses, and the isotropic least-squares refinement but not for the anisotropic least-squares refinement. Of the 1200 reflections measured in this preliminary data set, the 1042 reflections with $I > 2.00\sigma(I)$ were considered reliable and were used in the structure analysis. A second set of intensity data was measured using Mo Kα radiation and was used for the anisotropic least-squares refinement. The values listed in Table I for $ZnCl_2(\text{4-ac-py})_2$ are for the second set of data.

Solution and Refinement of Structures. All three structures were solved by the heavy-atom method. The zinc atom position was determined by use of a Patterson function; the other atoms in the coordination sphere were located by use of a Fourier synthesis. Subsequent Fourier syntheses were used to locate the rest of the nonhydrogen atoms. The structures were then refined using full-matrix least-squares calculations with isotropic and then anisotropic thermal parameters. At this point a difference Fourier synthesis was calculated to determine the positions of the hydrogen atoms, which were included in the final three cycles of least-squares calculatons but were not refined. The refinement was terminated when the indicated shifts in positional parameters were less than one-fourth of their estimated standard deviation. The scheme of refinement and the R index at various stages, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, are given in Table II.

The quantity minimized in the least-squares calculations was $\sum w[||F_o| - |F_c||]^2$ where $w^{1/2} = F_o/F_{low}$ if $F_o < F_{low}$, $w^{1/2} = 1$ if $F_{low} \leq F_o \leq F_{high}$, and $w^{1/2} = F_{high}/F_o$ if $F_{high} < F_o$. The values of F_{low} and F_{high} for each of the three compounds are given in Table II. The scattering factors for the zinc, chlorine, carbon, nitrogen, and oxygen atoms were taken from Hanson, Herman, Lea, and Skillmann;[13] those for the hydrogen atom were taken from Stewart, Davidson, and Simpson.[14] All scattering factors are uncorrected for the real and imaginary parts of the anomalous dispersion. The final atomic parameters for the nonhydogen atoms are given in Tables III–V; the hydrogen atom parameters are given in Tables VI–VIII. Tables of observed and calculated structure factor amplitudes are available.[15]

Results and Discussion

The approximately tetrahedral nature of the three complexes can be seen in Figures 1–3 which also give the atomic

Table V. Final Parameters of Nonhydrogen Atoms in $ZnCl_2(4\text{-}CN\text{-}py)_2{}^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	24 605 (5)	5924 (11)	12 769 (3)	417 (4)	1247 (17)	118 (2)	−77 (16)	−86 (3)	−21 (10)
Cl(1)	1 685 (1)	−1431 (3)	1 675 (1)	52 (1)	192 (4)	20 (0)	−50 (4)	−3 (1)	13 (2)
Cl(2)	2 085 (1)	3141 (3)	851 (1)	59 (1)	136 (4)	18 (0)	31 (3)	−11 (1)	4 (2)
N(1a)	3 113 (3)	−721 (9)	649 (2)	35 (2)	162 (16)	12 (1)	6 (12)	−11 (3)	6 (8)
C(2a)	3 535 (5)	188 (9)	269 (3)	44 (4)	141 (15)	15 (2)	−13 (12)	−8 (4)	5 (8)
C(3a)	4 019 (4)	−617 (11)	−142 (3)	38 (3)	193 (16)	16 (1)	18 (14)	−7 (3)	1 (10)
C(4a)	4 044 (4)	−2476 (11)	−152 (3)	32 (3)	212 (20)	15 (1)	39 (12)	−8 (4)	−19 (9)
C(5a)	3 588 (4)	−3441 (10)	228 (3)	48 (3)	146 (15)	20 (2)	12 (13)	−5 (4)	−19 (9)
C(6a)	3 131 (5)	−2536 (8)	622 (3)	47 (4)	111 (14)	18 (2)	−13 (11)	−13 (4)	0 (8)
C(7a)	4 562 (5)	−3359 (13)	−559 (4)	44 (3)	264 (22)	23 (2)	44 (16)	−7 (4)	−7 (12)
N(8a)	5 001 (4)	−4027 (12)	−870 (3)	63 (3)	348 (24)	31 (2)	105 (16)	12 (4)	−19 (11)
N(1b)	3 249 (4)	1388 (8)	1 924 (2)	44 (3)	137 (13)	14 (1)	−57 (11)	−7 (3)	1 (7)
C(2b)	3 360 (5)	375 (11)	2 417 (3)	49 (4)	186 (18)	17 (2)	−40 (16)	−12 (4)	11 (10)
C(3b)	3 885 (5)	905 (12)	2 860 (3)	43 (4)	222 (24)	16 (2)	−7 (16)	−14 (4)	−1 (10)
C(4b)	4 287 (5)	2455 (10)	2 788 (4)	37 (4)	193 (17)	17 (2)	−25 (13)	−10 (5)	−20 (10)
C(5b)	4 180 (6)	3491 (13)	2 282 (4)	58 (5)	263 (21)	25 (2)	−109 (19)	−20 (6)	24 (13)
C(6b)	3 640 (6)	2886 (11)	1 864 (3)	59 (4)	237 (20)	19 (2)	−95 (16)	−19 (5)	21 (10)
C(7b)	4 818 (6)	3072 (12)	3 252 (4)	49 (4)	232 (20)	24 (2)	−31 (16)	−19 (6)	3 (12)
N(8b)	5 244 (5)	3568 (13)	3 596 (4)	74 (4)	368 (25)	38 (2)	−78 (17)	−57 (6)	−6 (13)

^{a} All values are $\times 10^4$, except those for Zn, which are $\times 10^5$. The estimated standard deviatiöns are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table VI. Final Parameters of the Hydrogen Atoms in $ZnCl_2(4\text{-}vin\text{-}py)_2{}^a$

Atom	x	y	z	B, Å^2	Distance, Å
H(2a)	174	141	74	7.1	1.14
H(3a)	306	24	−64	8.1	1.12
H(5a)	229	−501	81	8.5	1.18
H(6a)	79	−320	202	7.8	1.12
H7(7a)	431	−183	−155	10.6	1.35
H8(8a)	460	−496	−173	12.7	1.32
H9(8a)	308	−605	−36	12.7	1.40
H(2b)	−162	−200	421	7.1	1.24
H(3b)	−34	−302	568	7.9	1.19
H(5b)	504	−201	430	8.7	1.10
H(6b)	377	−77	300	7.8	1.13
H7(7b)	217	−394	672	10.7	1.36
H8(8b)	508	−446	677	12.4	1.33
H9(8b)	619	−317	588	12.4	1.13

^{a} The positional parameters are $\times 10^3$. The number in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column.

Table VII. Final Parameters of the Hydrogen Atoms in $ZnCl_2(4\text{-}ac\text{-}py)_2{}^a$

Atom	x	y	z	B, Å^2	Distance, Å
H(2a)	469	445	23	5.8	1.00
H(3a)	569	381	−87	6.1	1.05
H(5a)	496	192	24	8.0	0.93
H(6a)	411	225	109	8.7	1.13
H7(8a)	627	332	−216	9.7	1.00
H8(8a)	671	355	−129	9.7	1.09
H9(8a)	652	262	−224	9.7	1.01
H(2b)	260	318	−96	7.8	1.16
H(3b)	157	351	−257	6.5	1.03
H(5b)	183	581	−151	7.4	1.13
H(6b)	271	536	53	5.7	1.05
H7(8b)	62	583	−456	10.0	0.96
H8(8b)	55	542	−295	10.0	1.08
H9(8b)	72	610	−341	10.0	0.90

^{a} The positional parameters are $\times 10^3$. The number in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column.

Table VIII. Final Parameters of the Hydrogen Atoms in $ZnCl_2(4\text{-}CN\text{-}py)_2{}^a$

Atom	x	y	z	B, Å^2	Distance, Å
H(2a)	365	162	26	4.5	1.08
H(3a)	435	51	−42	4.8	1.20
H(5a)	353	−491	26	4.7	1.10
H(6a)	285	−345	87	4.5	1.00
H(2b)	303	−102	243	5.5	1.18
H(3b)	400	33	334	5.2	1.17
H(5b)	468	460	215	6.8	1.24
H(6b)	389	323	128	5.7	1.40

^{a} The positional parameters are $\times 10^3$. The number in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column.
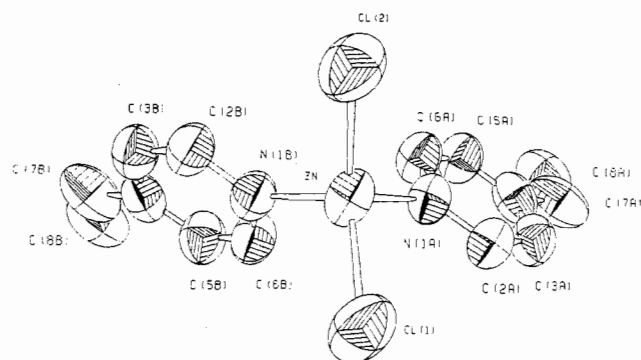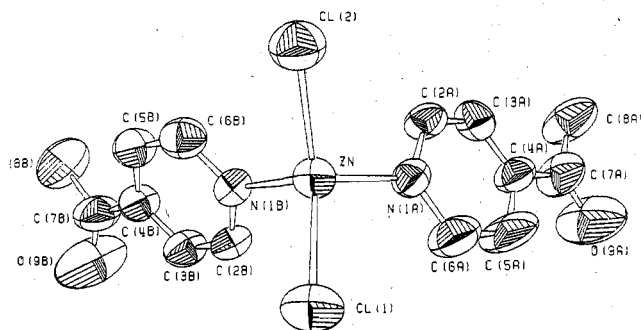

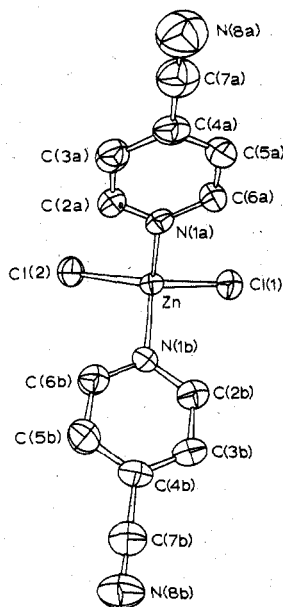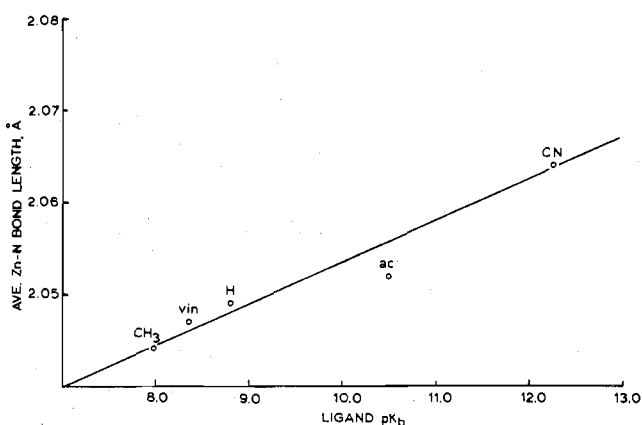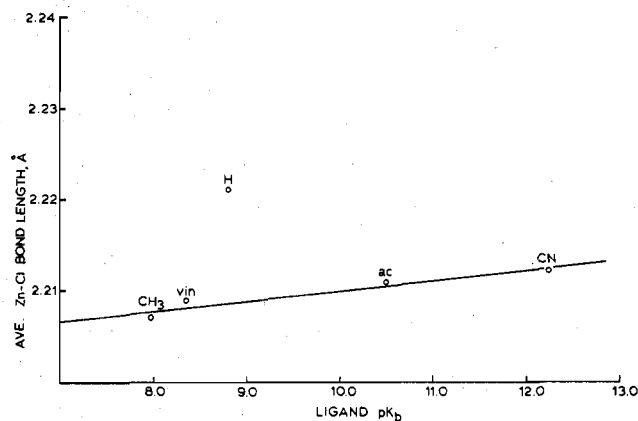**Figure 1.** ORTEP drawing of dichlorobis(4-vinylpyridine)zinc(II) showing the thermal ellipsoids and atomic numbering.

complexes in which the substituent in the 4 position has been systematically varied. The basicity of the pyridine in aqueous solution $(pK_b)^{16}$ varies with the substituent in the order CH_3 (7.97) > vin (8.38) > H (8.80) > ac (10.49) > CN (12.12). Therefore, we have a series in which the steric properties of the ligand are approximately constant while the donor properties vary.

A plot of the average Zn–Cl and Zn–N distances in the five complexes vs. the ligand pK_b is shown in Figure 4. In the case of the Zn–N distances a linear relationship Zn–N(av) = [2.004 (1) + 0.0050 (5)(pK_b)] Å can be obtained by a least-squares procedure.[17] The point for the ac complex was assigned a weight of $^1/_2$ because the esd's for the Zn–N bond were approximately twice those of the other complexes. The relationship illustrated in Figure 4 of the Zn–N bonds has

numbering. The bond lengths and angles in the coordination sphere are given in Table IX. The dimensions of the pyridine ligands together with the least-squares planes data are available.[15] These three complexes together with $ZnCl_2(py)_2{}^{11}$ and $ZnCl_2(4\text{-}CH_3\text{-}py)_2{}^{12}$ form a series of $ZnCl_2(4\text{-}R\text{-}py)_2$

Table IX. Bond Lengths (A) and Angles (deg) in the Coordination Sphere for the $ZnCl_2(4\text{-R-py})_2$ Complexes

	R		
	Vinyl	Acetyl	Cyano
		Lengths	
Zn-Cl(1)	2.214 (2)	2.216 (3)	2.207 (2)
Zn-Cl(2)	2.204 (2)	2.206 (3)	2.218 (2)
Zn-N(1a)	2.054 (5)	2.061 (9)	2.059 (5)
Zn-N(1b)	2.040 (5)	2.042 (9)	2.069 (6)
		Angles	
Cl(1)-Zn-Cl(2)	118.7 (1)	123.6 (1)	125.7 (1)
Cl(1)-Zn-N(1a)	106.9 (2)	105.7 (3)	106.9 (2)
Cl(1)-Zn-N(1b)	110.8 (2)	104.5 (3)	107.8 (2)
Cl(2)-Zn-N(1a)	110.7 (2)	107.9 (3)	105.5 (2)
Cl(2)-Zn-N(1b)	106.6 (2)	105.7 (3)	104.3 (2)
N(1a)-Zn-N(1b)	101.9 (2)	109.0 (4)	105.0 (2)

Figure 2. ORTEP drawing of dichlorobis(4-acetylpyridine)zinc(II) showing the thermal ellipsoids and atomic numbering.

Figure 3. ORTEP drawing of dichlorobis(4-cyanopyridine)zinc(II) showing the thermal ellipsoids and atomic numbering.

Figure 4. Average Zn–Cl and Zn–N bond distances in $ZnCl_2(4\text{-R-py})_2$ complexes vs. the ligand pK_b values. Abbreviations: CH_3, methyl; vin, vinyl; ac, acetyl; CN, cyano; H, unsubstituted complex.

important implications regarding the nature of the bonding in these tetrahedral $ZnCl_2$ complexes. The ligand pK_b's can be viewed as a measure of the strength of the interaction of the pyridine with a hydrogen ion. A smaller pK_b indicates a stronger pyridine–hydrogen interaction. Since there is no possibility for π bonding to a hydrogen ion (via a π* orbital of the pyridine), the pK_b can be viewed as an indication of the σ-donor strength of the pyridine. Consequently, the variation of the Zn–N distance with pK_b can be interpreted as being strictly a σ-bond effect. If, as has been suggested,[4] π bonding

were significant, then we might have anticipated that the Zn–N distance would not be linearly dependent on the pK_b value of the ligand. Therefore, we conclude that π bonding in these $ZnCl_2L_2$ complexes must be minimal.

The variation in Zn–Cl bond distances with pK_b as shown in Figure 4 is somewhat more complicated. If we exclude the point for pyridine (H), the relationship Zn–Cl(av) = [2.199 (2) + 0.0011 (4) (pK_b)] Å can be derived. The pyridine complex packs differently from the others, vide infra, which can explain the deviation of that point. The variation in Zn–Cl distance with the pK_b is so small that the average bond lengths are virtually independent of pK_b. In fact, the average bond lengths for the CH_3 case (2.207 Å) are not significantly different from those found in the CN complex (2.212 Å) using the usual test.[18] The zinc(II) ion presumably does not transmit changes in the σ-donor abilities of the pyridine ligands to the chloride ion. Consequently, a phenomenon analogous to the trans effect in square-planar complexes[19] does not appear to exist for the $ZnCl_2(4\text{-R-py})_2$ series.

Far-Infrared Studies. The infrared frequencies in the region 500–190 cm^{-1} observed for the five complexes are given in Table X. The Zn–Cl and Zn–N stretching frequencies were assigned by comparison with those reported for other $ZnCl_2(R\text{-py})_2$ complexes[4,20-26] as follows (cm^{-1}): ν_{Zn-N} 255, 240, and 199 for CH_3, 243 and 196 for vin, 222 and 203 for H, 245 and 202 for ac, 216 and 199 for CN; ν_{Zn-Cl} 335 and 304 for CH_3, 329 and 304 for vin, 330 and 297 for H, 337 and 302 for ac, 340 and 302 for CN.

Plots of the average Zn–Cl and Zn–N stretching frequencies vs. ligand pK_b are shown in Figure 5. There is no systematic change of either Zn–Cl or Zn–N with pK_b of the ligand. The

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Table X. Infrared Spectra in the Region 500–190 cm^{-1} for Some ZnCl$_2$(4-R-py)$_2$ and ZnBr$_2$(4-R-py)$_2$ Complexes[a]

Compd	Absorption peaks, cm^{-1}
ZnCl$_2$(4-CH$_3$-py)$_2$	494 sp, 489 sp, 388 w, 358 w, 335 s, 304 s, 255 m, 240 m, 199 s
ZnCl$_2$(4-vin-py)$_2$	466 br, 452 br, 329 s, 304 s, 243 w, 196 s
ZnCl$_2$(py)$_2$	424 sp, 418 sp, 330 s, 297 s, 222 m, 203 w
ZnCl$_2$(4-ac-py)$_2$	429 m, 388 br, 337 s, 302 s, 245 m, 202 m
ZnCl$_2$(4-CN-py)$_2$	391 sp, 384 sp, 340 s, 302 s, 216 m, 199 s
ZnBr$_2$(py)$_2$	425 sp, 417 sp, 256 s, 222 s, 185 m
ZnBr$_2$(4-CN-py)$_2$	390 sp, 387 sp, 272 s, 214 m, 205 w, 190 m

[a] Relative intensities: s, strong; m, moderate; w, weak; br, broad; sp, sharp.
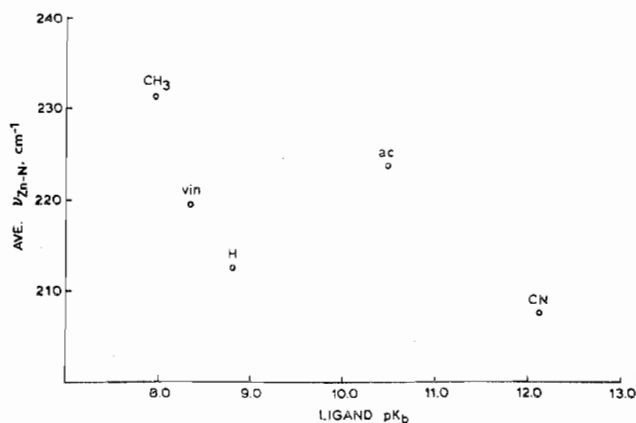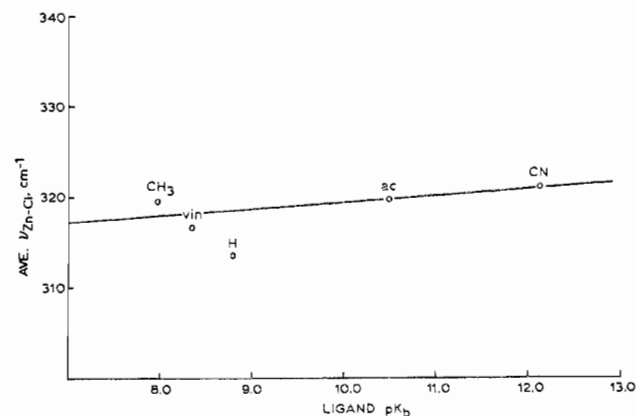
Figure 5. Average Zn–Cl and Zn–N stretching frequencies in some ZnCl$_2$(4-R-py)$_2$ complexes vs. ligand pK_b values. The abbreviations are the same as in Figure 4.

Figure 6. Packing diagram for the dichlorobis(4-vinylpyridine)zinc(II) complex.

A$_1$ mode for the Zn–Cl stretch at about 300 cm^{-1} and the B$_1$ mode at about 330–340 cm^{-1} are virtually independent of the ligand pK_b in agreement with our structural studies. The Zn–N frequencies show a bit more scatter and are not as constant as a function of pK_b. The symmetric stretch, A$_1$, shows some tendency to decrease with pK_b although the value for the 4-ac derivative is higher than might be expected. The asymmetric stretch at about 196–204 cm^{-1} appears to be virtually independent of pK_b. A calculation was made to correct for the difference in mass of the various derivatives[27] but it did not reveal any variations with pK_b. A normal-coordinate analysis of the ZnCl$_2$(py)$_2$ complex[4,23] has shown that there is little or no coupling between the Zn–Cl and Zn–N stretching modes which might affect the correlation of the frequencies with ligand pK_b.

The earlier study of the ZnCl$_2$(py)$_2$ complex[4] assigned values of 219.2 and 152.6 cm^{-1} to the Zn–N stretch.[4] The lower value

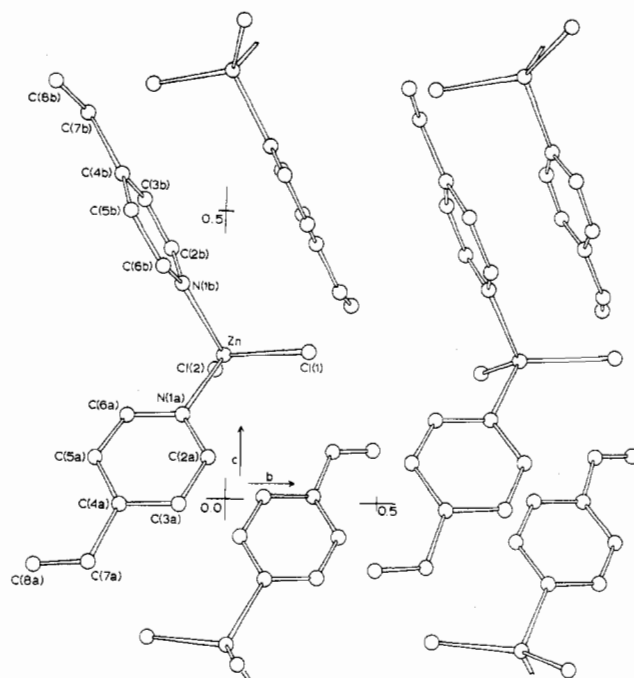was particularly important in their arguments regarding substituent effects. Our measurements of 222 and 203 cm^{-1} for Zn–N in ZnCl$_2$(py)$_2$ are in agreement with the values reported by others: 222.4 and 203.9,[23] 222,[24] 221,[20] and 220 cm^{-1}.[25] Consequently, it appears that the earlier conclusions[4] may have been based on an incorrect assignment of the Zn–N frequencies.

Packing Effects. The plot of the average Zn–Cl distances vs. ligand pK_b given in Figure 4 shows that the four substituted pyridines fall on a straight line. However, a much longer Zn–Cl distance was found in the unsubstituted case (point H) which appears to be related to the unique packing arrangement found in the ZnCl$_2$(py)$_2$ complex. The packing diagrams for the vin, ac, and CN complexes are given in Figures 6–8 while similar diagrams are available for the py[11] and CH$_3$[12] complexes. In the py case one set of rings (the "a rings") are stacked across a center of symmetry to give a dimerlike unit. The inter-ring distances of 3.7–3.8 Å are about the shortest found in the ZnCl$_2$L$_2$ series. The dimerlike units have longer contacts between the "b rings" of about 4.2 Å with the rings tipped by about 25 °C relative to each other. When there is a bulky substituent in the 4 position, the dimerlike pair is prevented from forming because of steric factors and the rings are much further apart, 4.8–5.2 Å. For example in the vin complex, Figure 7, although the a and b rings appear to stack across centers of symmetry, the rings are displaced along the *a* axis so that the ring centers are very far apart.

The intramolecular H···Cl contacts in the pyridine case also appear to be slightly different from the substituted complexes. The H···Cl contacts (Table XI) usually consist of one short contact of about 2.8 Å and a long contact of greater than 3.1 Å for each ring. For comparison, the van der Waals radii for H and Cl[28] give a nonbonded contact of about 3.0 Å. The difference in the two contacts of a given ring simply represents a rotation about the Zn–N bond. These rotations about the Zn–N bond of the individual molecules can also be seen in Figures 1–3. Presumably, the significantly different packing arrangement in the ZnCl$_2$(py)$_2$ complex causes small rotations in the pyridine rings and a slight weakening of the Zn–Cl bond distances. The fact that the Zn–N distances are a function of pK_b also suggests that π-bonding arguments are not im-
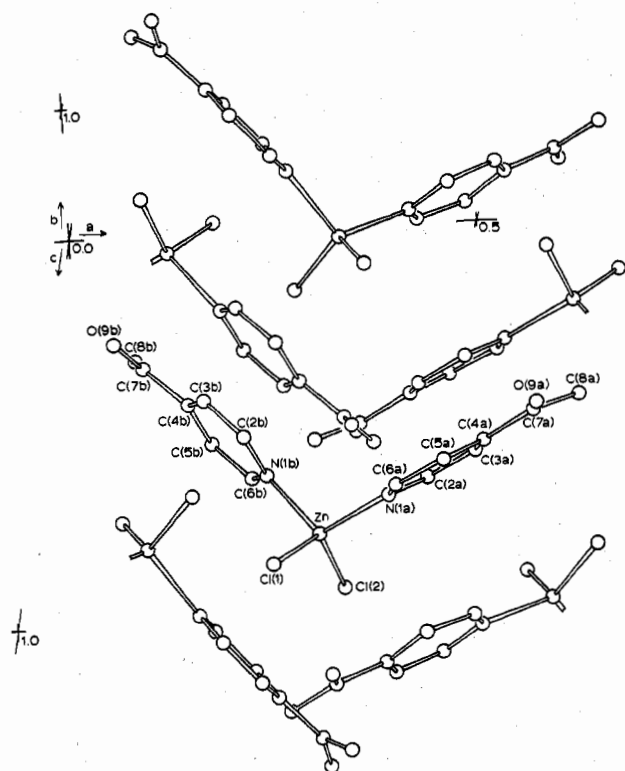
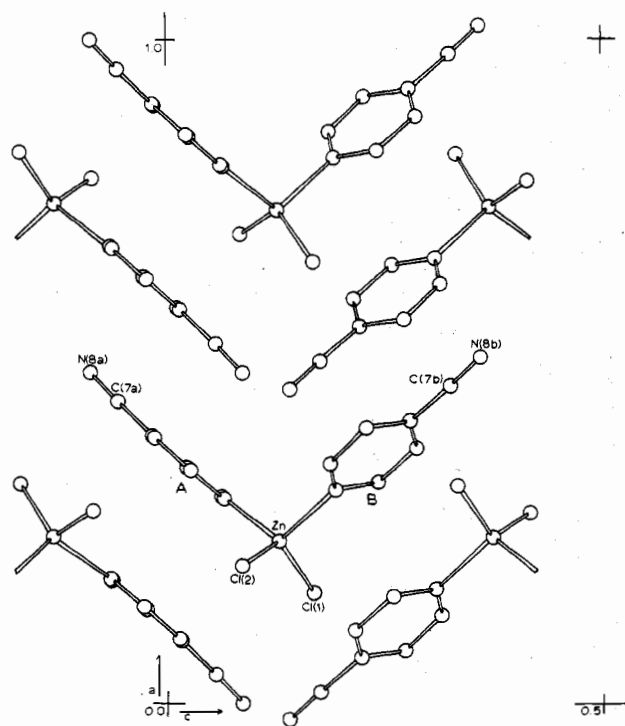**Figure 7.** Packing diagram for the dichlorobis(4-acetylpyridine)zinc(II) complex.

Figure 8. Packing diagram for the dichlorobis(4-cyanopyridine)zinc(II) complex. Only the two cyano groups have been labeled but the A denotes the a ring and B the b ring.

Table XI. Comparison of the Cl· · ·Cl and Cl· · ·H Intramolecular Contacts (in Å) for the $ZnCl_2(4$-R-py$)_2$ Complexes

	R				
	CH$_3$[a]	vin	H	ac	CN
Cl(1)· · ·Cl(2)	3.86	3.80	3.87	3.90	3.94
H(a)· · ·Cl(1)	3.12	2.85	3.26	3.17	2.87
H(a)· · ·Cl(2)	2.86	3.85	3.01	3.18	3.23
H(b)· · ·Cl(1)	2.98	3.89	3.05	3.39	3.10
H(b)· · ·Cl(2)	3.11	2.77	3.05	2.83	3.24

[a] Calculated from the data in ref 12.

of increasing pK_b values of the ligand. The Zn–Cl distances fall within a comparatively narrow range of 2.228–2.198 Å if the $ZnCl_2(NH_3)_2$[31] and $ZnCl_2(imid)_2$[32] (imid = imidazole) cases are excluded. The $ZnCl_2(NH_3)_2$ structure is rather old and should probably be redone. In this complex the existence of N–H···Cl hydrogen bonds could easily account for the long Zn–Cl bonds. There are N–H···Cl hydrogen bonds in the $ZnCl_2(imid)_2$ structure and the Zn–Cl bonds are a bit longer than might be expected. In the remaining cases the Zn–Cl distances are only slightly dependent on the ligand pK_b.

The dependence of the Zn–N distance on the ligand pK_b is more pronounced but again we see small changes due to steric effects. The dmphen vs. phen is a particularly interesting example where the Zn–N distance is increased slightly due to steric factors. The Zn–N distance of about 2.00 Å appears to be a lower limit, but as noted above, the $ZnCl_2(NH_3)_2$ data are not up to modern standards. In conclusion, we see that in tetrahedral $ZnCl_2L_2$ complexes with L as a nitrogen donor the Zn–N distances roughly parallel the ligand pK_b values with small perturbations due to steric effects.

The reported Zn–N and Zn–Cl stretching frequencies for various $ZnCl_2L_2$ complexes with L as a nitrogen donor are given as a function of the ligand pK_b in Table XIII. A perusal of the various values does not reveal any obvious trends in the two stretching frequencies as a function of ligand pK_b. The lack of a correlation is not too surprising since even in our limited series, as seen in Figure 5, there was no obvious relationship between the stretching frequency and pK_b. Presumably, the packing effects are sufficient to mask any small changes in the frequencies. Consequently, spectroscopic data alone may not be sufficient to interpret trends in bonding of molecular complexes.

Structures of the Three Pyridine Ligands. Although the various pyridine rings are planar (see supplementary material[15]), the dimensions, as expected, do not correspond to those of a regular hexagon. The C–N bonds average 1.335 (4) Å[41] compared to the value in gaseous pyridine of 1.340 (1) Å[42] or of 1.330 Å in the glucitol–pyridine complex.[43] The C–C distances average 1.375 (3) Å[41] compared to the value of 1.394 (1) Å in gaseous pyridine and 1.367 Å in the glucitol complex. The shorter C–C bonds may be related to libration effects. The average C–N–C, N–C–C, and C–C–C angles of 117.8 (3), 122.7 (3), and 118.9 (3)° are very similar to the values of 116.8, 123.9, and 118.5° observed in gaseous pyridine. Consequently, there appears to be very little change in the pyridine ring dimensions which is reasonable if the Zn–N bonding is nearly pure σ with very little π interaction. This observation is in agreement with our earlier discussion.

The structure of uncomplexed 4-cyanopyridine has been reported[44] and the pyridine distances and angles are virtually identical with the average values found in our studies. Furthermore, the C–C distance of 1.439 (8) Å and the C–N distance of 1.137 (8) Å in the uncomplexed ligand are virtually identical with the corresponding values of 1.449 (11) and 1.135 (12) Å observed in the $ZnCl_2$ complex. If π effects were important, then the C–N–ring interactions might be altered and the CN dimensions would be different in the complexed

portant and that the longer Zn–Cl distances in the py derivative are a result of crystal-packing effects.

Comparison of $ZnCl_2(4$-R-py$)_2$ Structures with Those of Other $ZnCl_2L_2$ Complexes. The Zn–N and Zn–Cl distances in a number of $ZnCl_2L_2$ complexes where L is a nitrogen donor are given in Table XII. The entries are arranged in order

Table XII. Comparison of Zn-N and Zn-Cl Bond Distances in Some Tetrahedral ZnCl₂L₂ Complexes, Where L is a Nitrogen Donor

Compd[a]	pK_b	Ref	Zn-N, A	Zn-Cl, A	Ref
ZnCl₂(NH₃)₂	4.74	29	2.01	2.30	31
ZnCl₂(imid)₂	7.01	16	1.995 (11), 2.020 (11)	2.258 (3), 2.239 (3)	32
ZnCl₂(4-CH₃-py)₂	7.97	16	2.046 (5), 2.042 (5)	2.211 (2), 2.204 (2)	12
ZnCl₂(dmphen)[a]	8.15	16	2.059 (11), 2.074 (9)	2.204 (3), 2.219 (3)	6
ZnCl₂(4-vin-py)₂	8.38	30	2.040 (5), 2.054 (5)	2.204 (2), 2.214 (2)	This work
ZnCl₂(py)₂	8.80	16	2.052 (6), 2.046 (5)	2.228 (2), 2.215 (2)	11
ZnCl₂(phen)[a]	9.04	16	2.050 (7), 2.072 (7)	2.207 (3), 2.198 (3)	33
ZnCl₂(4-ac-py)₂	10.49	16	2.042 (9), 2.061 (9)	2.216 (3), 2.206 (3)	This work
ZnCl₂(4-CN-py)₂	12.12	16	2.069 (6), 2.059 (5)	2.218 (2), 2.207 (2)	This work

[a] imid is imidazole; dmphen is 2,9-dimethyl-1,10-phenanthroline; phen is 1,10-phenanthroline.

Table XIII. Comparison of Zn-N and Zn-Cl Stretching Frequencies in Some Tetrahedral ZnCl₂L₂ Complexes, Where L is a Nitrogen Donor

Compd[a]	pK_b	Ref	ν_{Zn-N}, cm⁻¹	ν_{Zn-Cl}, cm⁻¹	Ref
ZnCl₂(NH₃)₂	4.74	29	422	286	34
ZNCl₂(2-CH₃-imid)₂	6.14	16	240	302, 287	35
ZnCl₂(N-CH₃-imid)₂	6.75	16	235	306, 285	36
ZnCl₂(imid)₂	7.01	16	253, 237	301, 289	34
ZnCl₂(4-CH₃-py)₂	7.97	16	255, 240, 199	335, 304	This work
ZnCl₂(2-CH₃-py)₂	8.04	16	224, 209	318, 297	21
ZnCl₂(3-CH₃-py)₂	8.30	16	204	329, 284	20
ZnCl₂(4-vin-py)₂	8.38	30	243, 196	329, 304	This work
ZnCl₂(4-CH₂OH-py)₂	8.59	2	233, 173	311, 294	4
ZnCl₂(Ph-hyd)₂	8.80	16	394, 376	297	37
ZnCl₂(py)₂	8.80	16	222, 203	330, 297	This work
ZnCl₂(3,4-xyld)₂	8.83	30	413	307, 294	38
ZnCl₂(p-told)₂	8.92	16	417, 395[b]	298	38
ZnCl₂(m-told)₂	9.29	16	417, 385[b]	303	38
ZnCl₂(anil)₂	9.42	16	402, 362	294	39
ZnCl₂(2,5-xyld)₂	9.47	30	386[b]	315, 295	38
ZnCl₂(o-told)₂	9.60	16	411, 390[b]	303, 285	38
ZnCl₂(2,6-xyld)₂	10.05	16	390, 357[b]	315	38
ZnCl₂(p-Cl-anil)₂	10.05	16	411, 396	304	40
ZnCl₂(4-Br-py)₂	10.25	16	223	324, 298	21
ZnCl₂(4-ac-py)₂	10.49	16	245, 202	337, 302	This work
ZnCl₂(m-Cl-anil)₂	10.55	16	420, 391	308, 298	40
ZnCl₂(4-CONH₂py)₂	10.57	2	227, 210	328, 294	4
ZnCl₂(4-COOCH₃-py)₂	10.76	2	230, 204	329, 298	4
ZnCl₂(4-CN-py)₂	12.12	16	216, 199	340, 302	This work
ZnCl₂(2-Cl-py)₂	13.51	30	210	321, 308	21

[a] Ph-hyd is phenylhydrazine; xyld is 3,4-xylidine; told is toluidine; anil is aniline.   [b] Listed as "other modes".

and uncomplexed states. Consequently, the indications, once again, support the postulate of mainly a σ interaction between the Zn atom and pyridine base.

The dimensions of the acetyl and vinyl groups are not particularly remarkable. The C≡C distance in the vinyl group of 1.195 Å is short, but the thermal parameters are large and libration and/or disorder could account for these apparently short distances.

Summary

The structural data on ZnCl₂(4-R-py)₂ complexes have been correlated with the pK_b of the pyridine ligand. The average Zn–N distance varies linearly with the ligand pK_b. Since the ligand pK_b is strictly a σ-bond effect, the importance of π bonding in the above series must be minimal. When R is a bulky group, the Zn–Cl distances appear to be independent of the ligand pK_b, again suggesting a minimum π-type interaction. Finally, the dimensions of the various ligands are consistent with the σ-bond model. The ZnCl₂(py)₂ complex is anomalous because the small H atom in the 4 position permits a significantly different packing arrangement. Our conclusions are the opposite of other reports which emphasize the importance of π bonding in the above series.

The far-infrared data for ZnCl₂L₂ complexes, where L is a nitrogen donor, do not appear to be dependent upon the ligand pK_b in any simple way. Presumably, mass differences, crystal packing, and coupling of modes can produce small effects which obscure the changes due to the ligand pK_b. In addition, the problem of the correct bond assignment is always present. Therefore, one should use the results of infrared studies cautiously in discussing the nature of the bond in ZnCl₂L₂ complexes and, by extension, in other systems as well.

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Binuclear Complexes. Synthesis and Characterization of the Binuclear Ligand 1,4-Dihydrazinophthalazine Bis(2'-pyridinecarboxaldimine) and the Nickel Complex μ-Chloro-tetraaqua[1,4-dihydrazinophthalazine bis(2'-pyridinecarboxaldimine)]dinickel(II) Chloride Dihydrate

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The synthesis and characterization by x-ray diffraction techniques of a binuclear ligand and its corresponding dinickel complex are described. The ligand dhphpy, 1,4-dihydrazinophthalazine bis(2'-pyridinecarboxaldimine), is formed by the reaction of pyridinecarboxaldehyde with the 1,4-dihydrazinophthalazine, dhph, in the presence of the Ni(II) ion. The protonated ligand $H_2dhphpy(NO_3)_2 \cdot 2H_2O$ (I) forms monoclinic crystals with unit cell dimensions of $a = 20.480\ (3)$, $b = 11.166\ (2)$, and $c = 10.704\ (2)$ Å with $\beta = 102.99\ (2)°$. The space group is $C2/c$ and, with 4 molecules per cell, the ligand I lies on a twofold axis. The structure was solved by direct methods and refined to an R value of 0.050. The dinickel complex II also forms monoclinic crystals (green) with the space group $C/2c$. With 8 dinuclear units per cell, no symmetry is required; however, there is in essence a twofold axis in the complex. The unit cell dimensions are $a = 15.016\ (6)$, $b = 15.527\ (6)$, and $c = 28.704\ (17)$ Å with $\beta = 115.78\ (3)°$. The final R was 0.048. The main differences between the ligand I and the dinickel complex II are the angles in the "hydrazone arms" which change slightly after complex formation. The magnetic moment in solution of the dinickel complex is 2.74 μ_B, slightly lower than the spin-only value. Since the cations are well separated in the crystal and presumably in solution, the lowering of the moment must represent a nickel–nickel interaction. Both the ligand I and the dinickel complex II (excluding the axial water molecules) are remarkably planar and show extensive delocalization. Therefore, the preparation of binuclear ligands from dhph and various aldehydes appears to be virtually limitless.

Introduction

Multidentate ligands which incorporate two metal atoms are useful in studying the magnetic interactions between metal ions. The binuclear complexes themselves are of interest as models of metalloenzymes and in applications to catalysis. Ligands which yield binuclear complexes are not common[2] and have generally involved either substituted diformylphenols,[3-5] heptatriones,[6,7] or 1,4-dihydrazinophthalazine[8,9] although a few other examples are known.[10,11] However, in the majority of cases the bridging groups are determined by the geometry of the ligand and cannot be altered. Therefore, we decided to prepare a binuclear ligand where only the bridging atom was undefined and could presumably be varied.

The reaction of 1,4-dihydrazinophthalazine with appropriate aldehydes should yield hydrazones with six donor atoms arranged in a manner which would favor the formation of bi-