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A Zwitterionic Complex: Crystal and Molecular Structure of Trichloro(*N*-(4′-pyridyl)-4-ethoxypyridinium)zinc(II)

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Received July 21, 1977

The reaction of $ZnCl_2$ with 4-chloropyridine in ethanol yields trichloro(*N*-(4′-pyridyl)-4-ethoxypyridinium)zinc(II). The crystal and molecular structures of the zwitterionic complex were determined by x-ray diffraction techniques. The complex crystallizes with the orthorhombic space group *Pbca* and unit cell dimensions of a = 11.975 (4), b = 16.403 (6), and c = 15.848 (7) Å. There are eight zwitterions per unit cell. A total of 1661 reflections with $I \geq 2\sigma(I)$ were used in the analysis, and the final residual R was 0.059. The geometry about the zinc ion is that of a distorted tetrahedron, with Zn–Cl distances of 2.237 (2), 2.246 (3), and 2.247 (3) Å and the Zn–N distance of 2.055 (8) Å. The two pyridine rings are not coplanar but twisted by 40.5° so that the pyridinium ion behaves essentially like pyridine. The Zn–Cl distances are midway between those found in L_2ZnCl_2 complexes and in the $ZnCl_4^{2-}$ ion. The increasing Zn–Cl distances are attributed to electronic rather than steric factors.

Introduction

The ligands in a coordination complex are usually neutral or anionic species. However, there are a few examples[2-11] where the ligand has a formal positive charge somewhat removed from the metal–ligand bond. An intriguing question is whether the donor properties of the ligand are influenced by the presence of the cationic site. The majority of the studies[2-10] (there is one exception[11]) suggest that a remote positive charge has little or no effect on the donor properties of the ligand. However, in only two cases[2,3] were the donor atom and cationic site separated by an aromatic system which could transmit charge effects. We now report the first structural study of a complexed pyridinium ion, trichloro(*N*-(4′-pyridyl)-4-ethoxypyridinium)zinc(II), henceforth (EtOPy-Py)$ZnCl_3$. Our results show that even if the donor atom and cationic site are connected via an aromatic system, the positive charge has little or no effect on the donor properties of the ligand.

Experimental Section

Preparation of (EtOPy-Py)$ZnCl_3$. A solution of 4-chloropyridine was prepared by reacting 1.500 g (10 mmol) of 4-chloropyridine hydrochloride in 40 mL of absolute ethanol with 0.400 g (10 mmol) of NaOH in 40 mL of absolute ethanol and removing the precipitated NaCl by filtration. To the ligand solution was added 0.681 g (5 mmol) of $ZnCl_2$ in a minimum of absolute ethanol, and the mixture was stirred and refluxed for several hours. The fine, light yellow solid which formed was removed by filtration. The solid was redissolved in absolute ethanol with heating to give a clear, light blue solution which was slowly cooled. Clear, colorless plates formed slowly and were collected by filtration, mp 205 °C. Anal. Calcd for (EtOPy-Py)$ZnCl_3$: C, 38.64; H, 3.51; Cl, 28.52; N, 7.51. Found: C, 38.41; H, 3.51; Cl, 28.63; N, 7.47.

Crystal Data for $C_{12}H_{13}Cl_3N_2OZn$: mol wt 372.98, orthorhombic, space group *Pbca*, a = 11.975 (4) Å, b = 16.403 (6) Å, c = 15.848 (7) Å, V = 3113 (2) Å^3, Z = 8, ρ(calcd) = 1.591 g cm^{-3}, ρ(obsd) 1.59 g cm^{-3}, crystal size = 0.59 × 0.26 × 0.26 mm^3, μ(Mo radiation) = 21.2 cm^{-1}.

Collection of X-Ray Diffraction Data. The cell constants and intensity data were measured with a Syntex $P\bar{1}$ diffractometer with graphite monochromatized Mo Kα radiation. The procedure was similar to that previously described.[12] The 1661 reflections (out of 2051 possible for $2\theta \leq 45°$) with $I \geq 2.0\sigma(I)$ were considered reliable and used in the analysis. No absorption corrections were made, and the transmission factors were estimated to be from 0.53 to 0.35.

Solution and Refinement of the Structure. A Patterson function was calculated and the zinc–zinc vectors were easily identified. The x coordinate of the zinc was nearly $^1/_4$ which gives two possible values for the y coordinate. Since we initially anticipated a $ZnCl_2L_2$ species, both y coordinates were carefully considered. The existence of the $ZnCl_3$ unit was eventually accepted and least-squares refinement was initiated. After three cycles using isotropic thermal parameters and then three cycles using anisotropic thermal parameters, a difference Fourier synthesis was calculated. The hydrogen atoms were located and included in subsequent calculations but their parameters were not varied. After three more least-squares cycles, the R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) was 0.059, and the shifts were small (less than one-fifth of an esd) so that refinement was terminated.

The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$, where $w = (F_o/24.0)^2$ if $F_o < 24.0$, $w = 1$ if $24.0 \leq F_o \leq 96.0$, and $w = (96.0/F_o)^2$ if $F_o > 96.0$. The scattering factors were from the usual sources.[13] The final atomic parameters are given in Tables I and II, with the distances and angles in Table III. Tables of observed and calculated structure factors and the least-squares planes data are available.[14]

Results and Discussion

An ORTEP drawing showing the thermal ellipsoids and atomic numbering is given in Figure 1. The (EtOPy-Py)$ZnCl_3$ complex which results from the reaction of $ZnCl_2$ with 4-chloropyridine in absolute ethanol is formally a zwitterion with a positive charge on N(1b) and a negative charge on the $ZnCl_3$ group. The rearrangement of 4-halopyridines to *N*-pyridylpyridinium ions which was first observed by Wibaut and Brockman[15] is now a well-known reaction.[16] Halopyridines also undergo alcoholysis[17] and in fact halopyridinium ions are much more reactive toward methanolysis than the neutral halopyridine.[18]

The three Cl atoms and the N(1a) atom form a distorted tetrahedral arrangement around the zinc atom. The Zn–N bond length of 2.055 (8) Å is not significantly different from the Zn–N distance of 2.049 (5) Å in $ZnCl_2(py)_2$.[19] Since we have shown that in $ZnCl_2L_2$ complexes, where L is a 4-substituted pyridine, the Zn–N distance is a function of the pK_b of the ligand,[20] we conclude that the EtOPy-Py ligand has about the same pK_b as that of pyridine. Consequently, the cationic site on the second pyridine ring has virtually no effect on the donor properties of the ligand. Although the conclusion is somewhat surprising, the results are consistent with the other studies on nonaromatic systems. The lack of an appreciable effect may be related to the relative orientation of the two pyridine rings. The two rings are twisted by 40.5° from coplanarity because of the steric interactions between the 3,5 hydrogens on the "a" ring and the 2,6 hydrogens on the "b" ring. The contacts of H(3a)···H(2b) of 2.41 Å and H(5a)···H(6b) of 2.39 Å are essentially van der Waals contacts. Any attempt to make the rings coplanar would make these contacts intolerably small.

The three Zn–Cl distances average 2.243 Å which is definitely longer than in the $ZnCl_2L_2$ complexes where Zn–Cl ranges from 2.204 to 2.216 Å, with an average of 2.211 Å.[20] In trichloro(adeninium)zinc(II)[3] the three Zn–Cl distances range from 2.210 to 2.254 Å, with an average of 2.232 Å which is close to our value. In the $ZnCl_4^{2-}$ ion the Zn–Cl distances average 2.267 Å[21] and 2.270 Å,[22] somewhat longer than our value. The Zn–Cl distance appears to increase with increasing

Table I. Final Parameters of the Nonhydrogen Atoms in (EtOPy-Py)$ZnCl_3$[a]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	25114 (9)	10029 (7)	6905 (6)	320 (5)	572 (7)	442 (6)	−37 (6)	−9 (5)	−58 (6)
Cl(1)	4366 (2)	973 (2)	855 (2)	33 (1)	77 (2)	58 (2)	−1 (1)	−3 (1)	−6 (2)
Cl(2)	1438 (2)	1070 (2)	1851 (2)	42 (1)	98 (2)	45 (1)	6 (2)	3 (1)	−12 (2)
Cl(3)	1953 (2)	1928 (2)	−266 (2)	39 (1)	82 (2)	88 (2)	−7 (1)	5 (1)	35 (2)
N(1a)	2144 (6)	−108 (5)	159 (4)	30 (4)	85 (6)	35 (4)	4 (4)	0 (4)	9 (4)
C(2a)	1193 (7)	−507 (6)	346 (6)	39 (5)	60 (7)	38 (5)	−6 (5)	5 (4)	3 (5)
C(3a)	797 (7)	−1168 (5)	−116 (6)	33 (5)	45 (6)	51 (6)	−1 (4)	3 (5)	−3 (4)
C(4a)	1426 (7)	−1433 (5)	−794 (5)	31 (5)	54 (5)	39 (5)	−1 (5)	0 (4)	2 (5)
C(5a)	2434 (8)	−1071 (6)	−961 (5)	42 (5)	54 (5)	47 (5)	−3 (6)	11 (5)	−6 (5)
C(6a)	2753 (7)	−419 (5)	−481 (6)	35 (6)	43 (5)	53 (5)	−1 (4)	4 (4)	−9 (4)
N(1b)	1014 (5)	−2096 (4)	−1310 (4)	33 (4)	42 (5)	39 (4)	0 (4)	−2 (3)	1 (4)
C(2b)	486 (7)	−2738 (6)	−973 (6)	35 (5)	54 (6)	39 (5)	−9 (4)	−4 (4)	9 (5)
C(3b)	45 (7)	−3359 (6)	−1456 (6)	37 (5)	57 (7)	49 (6)	−2 (5)	−2 (4)	5 (5)
C(4b)	184 (7)	−3293 (6)	−2343 (6)	38 (6)	53 (7)	51 (7)	0 (5)	−6 (5)	−8 (5)
C(5b)	738 (8)	−2626 (5)	−2677 (6)	63 (7)	49 (6)	45 (7)	−8 (6)	1 (5)	−6 (5)
C(6b)	1144 (8)	−2028 (6)	−2166 (6)	54 (6)	49 (7)	43 (5)	−6 (5)	5 (5)	6 (5)
O	−173 (6)	−3862 (4)	−2891 (4)	60 (4)	61 (5)	62 (4)	−7 (4)	3 (4)	−17 (4)
C(1)	−946 (10)	−4480 (8)	−2618 (8)	71 (7)	70 (7)	71 (8)	−14 (7)	−6 (6)	−9 (7)
C(2)	−2081 (10)	−4130 (8)	−2490 (8)	59 (6)	124 (11)	84 (9)	−21 (7)	−2 (6)	7 (9)

[a] The positional parameters are $\times 10^4$ except for the Zn atom, which are $\times 10^5$. The *U* values are $\times 10^4$ for the Zn atom and $\times 10^3$ for the remaining atoms. The temperature factor is of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. The estimated standard deviations are given in parentheses.

Table II. Final Parameters of Hydrogen Atoms in (EtOPy-Py)$ZnCl_3$[a]

Atom	*x*	*y*	*z*	*B*, Å^2	Dist, Å
H(2a)	83	−27	91	4.7	1.06
H(3a)	7	−147	5	4.2	1.03
H(5a)	294	−129	−144	4.8	1.03
H(6a)	353	−9	−58	4.5	1.08
H(2b)	38	−288	−32	4.2	1.07
H(3b)	−31	−389	−114	4.9	1.09
H(5b)	79	−269	−339	5.3	1.13
H(6b)	147	−152	−243	4.6	1.01
H1(1)	−94	−497	−312	6.3	1.13
H2(1)	−66	−479	−207	6.3	1.06
H3(2)	−214	−376	−193	7.3	1.07
H4(2)	−231	−394	−296	7.3	0.86
H5(2)	−261	−470	−236	7.3	1.15

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

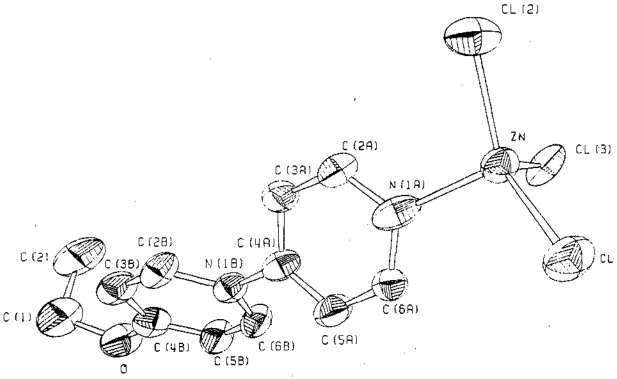

Figure 1. An ORTEP drawing of trichloro(*N*-(4′-pyridyl)-4-ethoxypyridinium)zinc(II) showing the atomic numbering and thermal ellipsoids.

Table III. Bond Lengths and Angles in (EtOPy-Py)$ZnCl_3$ with Their Estimated Standard Deviations in Parentheses

(a) Bond Lengths (Å)

Zn–Cl(1)	2.237 (2)	C(4a)–N(1b)	1.447 (11)
Zn–Cl(2)	2.246 (3)	N(1b)–C(2b)	1.339 (11)
Zn–Cl(3)	2.247 (3)	C(2b)–C(3b)	1.379 (13)
Zn–N(1a)	2.055 (8)	C(3b)–C(4b)	1.420 (14)
N(1a)–C(2a)	1.347 (12)	C(4b)–C(5b)	1.384 (14)
C(2a)–C(3a)	1.390 (13)	C(5b)–C(6b)	1.362 (14)
C(3a)–C(4a)	1.383 (12)	C(6b)–N(1b)	1.371 (11)
C(4a)–C(5a)	1.371 (13)	C(4b)–O	1.345 (12)
C(5a)–C(6a)	1.368 (13)	O–C(1)	1.440 (13)
C(6a)–N(1a)	1.350 (11)	C(1)–C(2)	1.489 (17)

(b) Bond Angles (deg)

Cl(1)–Zn–Cl(2)	118.3 (1)	C(3a)–C(4a)–N(1b)	119.3 (8)
Cl(1)–Zn–Cl(3)	112.9 (1)	C(5a)–C(4a)–N(1b)	121.1 (8)
Cl(1)–Zn–N(1a)	103.9 (2)	C(4a)–N(1b)–C(2b)	121.8 (7)
Cl(2)–Zn–Cl(3)	110.4 (1)	C(4a)–N(1b)–C(6b)	117.3 (7)
Cl(2)–Zn–N(1a)	104.8 (2)	C(6b)–N(1b)–C(2b)	120.8 (7)
Cl(3)–Zn–N(1a)	105.0 (2)	N(1b)–C(2b)–C(3b)	122.7 (8)
Zn–N(1a)–C(2a)	121.5 (6)	C(2b)–C(3b)–C(4b)	116.6 (9)
Zn–N(1a)–C(6a)	121.8 (6)	C(3b)–C(4b)–C(5b)	119.6 (9)
C(6a)–N(1a)–C(2a)	116.0 (8)	C(4b)–C(5b)–C(6b)	120.8 (9)
N(1a)–C(2a)–C(3a)	123.5 (8)	C(5b)–C(6b)–N(1b)	119.3 (9)
C(2a)–C(3a)–C(4a)	117.9 (8)	C(3b)–C(4b)–O	123.3 (9)
C(3a)–C(4a)–C(5a)	119.6 (8)	C(5b)–C(4b)–O	117.0 (9)
C(4a)–C(5a)–C(6a)	118.5 (8)	C(4b)–O–C(1)	119.9 (8)
C(5a)–C(6a)–N(1a)	124.3 (8)	O–C(1)–C(2)	110.9 (9)

numbers of Cl atoms bonded to the zinc atom which could be due to steric or electronic factors. A somewhat similar observation was made for the Cu–P bond in various copper(I)-phosphine complexes[23] although no conclusions regarding the relative influence of steric vs. electronic effects were made. The zinc–chlorine case is somewhat simpler because of the monoatomic nature of the chloride ion. A comparison of the nonbonded Cl···Cl contacts shows a decrease from about 3.88 Å in the L_2ZnCl_2 case to 3.74 Å in the $ZnCl_3^-$ complexes and finally 3.70 Å for the $ZnCl_4^{2-}$ ion. In all cases the contacts are greater than the van der Waals contact for two Cl atoms of 3.60 Å.[24] Therefore, if we assume that the van der Waals radius for Cl is approximately correct, the increase in the Zn–Cl distances must be due to electronic factors. Support for the electronic argument arises also from the work on $Zn_2Cl_6^{2-}$ where the terminal Zn–Cl bonds average 2.175 Å, with the Cl···Cl contact of 3.627 Å.[25]

An explanation of the increase in the Zn–Cl bond distance could invoke electroneutrality arguments[26] or the s-character arguments of Bent.[27] The latter arguments are particularly attractive and relatively simple. In the L_2ZnCl_2 complexes the Zn–Cl bonds have greater s character as indicated by the large Cl–Zn–Cl angles which are greater than 109°28′. As additional Cl atoms are added, the amount of s character per Zn–Cl bond decreases as the limiting tetrahedral sp^3 case is reached in $ZnCl_4^{2-}$. Since the length of the Zn–Cl bond reflects the amount of s character, the distance increases in going from L_2ZnCl_2 to $ZnCl_4^{2-}$. It is tempting to extrapolate these observations to the copper(I)–phosphine system and attribute the increasing Cu–P bond lengths with increasing numbers of phosphines to an electronic effect.

The length of the C(4a)–N(1b) bond between the two pyridine rings is 1.447 (11) Å which is not significantly different from the values of 1.459 (5)[28] and 1.471 (12) Å[29] reported for other *N*-phenylpyridinium ions. The remaining distances and angles in the ligand are all within the generally accepted values. The intermolecular distances less than 3.5 Å were calculated and no abnormally short contacts between the zwitterions were found.

Acknowledgment. We thank the Center for Instructional and Research Activities, University of Florida, for a grant of computer time.

Registry No. (EtOPy-Py)$ZnCl_3$, 65982-74-3; 4-chloropyridine hydrochloride, 7379-35-3; $ZnCl_2$, 7646-85-7.

Supplementary Material Available: A listing of observed and calculated structure factors and a table of least-squares planes data (10 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Bidentate Difluorophosphines. 2. Complexes of 1,2-Bis(difluorophosphino)cyclohexane with Chromium(0), Molybdenum(0), and Tungsten(0)[1,2]

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Received October 28, 1977

The reactions of 1,2-bis(difluorophosphino)cyclohexane with hexacarbonyls of Cr(0), Mo(0), and W(0) and with the norbornadiene tetracarbonyl compounds of Cr(0), Mo(0), and W(0) have been investigated. The hexacarbonyls react, either under photolytic or thermolytic conditions, to produce carbon monoxide and oily mixtures of products of the general formulation $(M(CO)_4P_2F_4C_6H_{10})_x$, where x varies apparently from 1 to 3. The higher values of x correspond to species involving bridging ligands. The dienetetracarbonyls react to produce chelates of the general formulation $M(CO)_4P_2F_4C_6H_{10}$. $Mo(CO)_4P_2F_4C_6H_{10}$ will react with more $P_2F_4C_6H_{10}$ to give $(Mo(CO)_2(P_2F_4C_6H_{10})_2)_x$. Analysis of the infrared spectra of these chelates indicates that the ligand fits into a sequence of π-acceptor strength as $PF_3 > PCl_3 \sim P_2F_4C_6H_{10} > RN(PF_2)_2 \gg Ph_2PCH_2CH_2PPh_2$. NMR, IR, and mass spectral data for the chelates are presented and discussed.

Introduction

Transition-metal complexes containing bidentate phosphine ligands or monodentate fluorophosphine ligands have been studied for many years.[3,4] A large number of phosphine-substituted derivatives of the group 6B metal carbonyls have been described[5] and attempts have been made to classify series of ligands according to π-acceptor ability.[6] For example, Nixon et al.[4] have developed such a series for fluorophosphine ligands. Until recently, bidentate fluorophosphine ligands containing carbon–hydrogen backbones have not been available.[7] The ligand, 1,2-bis(difluorophosphino)cyclohexane, is the first example of a bidentate ligand that contains fluorine atoms located on the phosphorus atoms which in turn are positioned across a hydrocarbon backbone. We have chosen this particular ligand for initial coordination studies due to the relative ease of its preparation and molecular rigidity.

The reaction of $Ni(CO)_4$ with 1,2-bis(difluorophosphine)cyclohexane, $P_2F_4C_6H_{10}$, which resulted in the preparation of the complex bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) was reported by this laboratory.[2] Due to the stability of the complex and the relatively mild conditions required for the complete displacement of CO from $Ni(CO)_4$, in contrast to the conditions required for the displacement of PF_3, this ligand was assumed to exhibit strong π-acceptor and chelating character.

In a continuation of our study of the coordinating properties of bidentate fluorophosphines, we now describe analogous reactions of $P_2F_4C_6H_{10}$ with the group 6B metal carbonyls