Note

The synthesis and crystal structure of $[Cr(acacen)py_2][ZnCl_3py]$

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Abstract

The reduction of $CrCl_3$ by zinc dust in THF solution followed by slow addition to an ethanolic solution K(acacen) gave a brown powder, which when reacted with pyridine produced an intractable brown tar. Careful recrystallization of the tar from methanol gave a small quantity of crystalline $[Cr(acacen)py_2][ZnCl_3py]$. The structure consists of a set of two crystallographically independent complex cations and anions of the above formula. Crystal data: monoclinic space group $P2_1$, $a = 12.667(4)$, $b = 16.146(4)$, $c = 16.262(5)$ Å, $\beta = 108.57(1)°$, $V = 3153(2)$ Å^3, $Z = 4$. A total of 7657 reflections was collected with graphite monochromated Mo Kα radiation (to $2\theta = 54°$), of which 4536 were used in subsequent structure solution and refinement ($I \geq 3\sigma(I)$). The structure was solved by direct methods, and least-squares refinement converged at $R = 0.037$.

Key words: Crystal structures; Chromium complexes; Bidentate ligand complexes; Chelate complexes; Zinc complexes

Introduction**

Recently, we attempted to prepare $[Cr(acacen)(H_2O)_2]Cl$ via a modification of the literature method [1]. Ultimately, we had hoped to react this complex with pyridine in order to form pyCr(acacen)Cl. However, our modified procedure led instead to the serendipitous isolation of a small quantity of crystals of the title complex, the synthesis and solid state structure of which are reported here.

Experimental

Synthesis of $[Cr(acacen)py_2][ZnCl_3py]$

This method is similar, but not identical, to that given in ref. 1. The initial stages utilized standard Schlenk techniques under dry N_2. A mixture of KOH (1.81 g, 32.2 mmol) and acacenH_2 [2] (3.57 g, 15.9 mmol) in absolute ethanol (50 ml) was stirred until all the KOH had dissolved. The resulting light yellow solution was sparged with N_2 for 25 min, then transferred via syringe to a Schlenk flask attached to a Soxhlet apparatus. The thimble of the apparatus had previously been charged with anhydrous $CrCl_3$ (2.52 g, 15.9 mmol), zinc dust (0.230 g) and dry THF (40 ml) [3], under N_2. The reaction mixture was allowed to reflux for 3.25 h, at which time it was determined that all the $CrCl_3$ had been extracted. The red–brown mixture was cooled to room temperature and opened to air. THF (200 ml) was added and the precipitated KCl was filtered with the aid of Celite. The filtrate was evaporated to give 2.35 g of brown product. This material was dissolved in a minimum amount of pyridine. Repeated attempts to isolate the solid product via slow evaporation only produced intractable brown tars. Finally, the pyridine solvent was allowed to evaporate to dryness and the brown tar was dissolved in a minimum amount of methanol. Slow evaporation yielded a small amount of beautiful brown crystals which were collected. Evaporation of the supernatant gave only brown tars which were not investigated further.

X-ray diffraction study

Crystal data

A brown prismatic crystal of $[Cr(acacen)py_2]$-$[ZnCl_3py]$ of dimensions $0.40 \times 0.40 \times 0.60$ mm was mounted in a glass capillary. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.70930$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Cell constants were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $12 < \theta < 18°$ [4]: $a = 12.667(4)$, $b = 16.146(4)$, $c = 16.262(5)$ Å, $\beta = 108.57(1)°$, $V = 3153(2)$ Å^3, $Z = 4$. A total of 7657 reflections of which 4536 reflections were observed ($I \geq 3\sigma(I)$) was measured with the $\omega/2\theta$ scan technique ($2\theta_{max} = 54°$) at 24 °C. From the systematic absences of $0k0$, $k = 2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1$ with two independent units of $[Cr(acacen)py_2]^+$ and $[ZnCl_3py]^-$. Lorentz–

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**Abbreviations: acacen = N,N'-ethylenebis(acetylacetoneiminato), py = pyridine, salen = N,N'-ethylenebis(salicylideneiminato).

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polarization, empirical absorption and secondary extinction [5] corrections were applied to the data. Anomalous dispersion effects were included in F_c [6], and the value of $R_w^-/R_w^+ = 1.26$ confirmed the correct assignment of absolute configuration [7].

Solution and refinement of the structure

The structure was solved by direct methods [8]. A total of 40 atoms was located from an E-map, while the remaining atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were placed at calculated positions and added to the structure factor calculations ($B = 1.3 \times B_{eq}$ of the atom to which they are bonded) with their parameters not refined. The structure was refined via full-matrix least-squares with unit weights. Scattering factors and values for f' and f'' were taken from Cromer and Waber [9]. The final cycle of refinement converged at $R = 0.037$, $R_w = 0.038$. Final non-hydrogen positional parameters are given in Table 1. All calculations were performed on a μVax 2000 computer using the SDP/VAX package [10].

Results and discussion

Synthesis of [Cr(acacen)py$_2$][ZnCl$_3$py]

Although there are two literature reports concerning the synthesis of pyCr(acacen)Cl [11, 12], we wished to investigate whether this complex could be obtained via recrystallization of [Cr(acacen)(H_2O)$_2$]Cl from pyridine, by analogy to known chemistry involving Cr salen complexes [13]. Although our modified preparation of [Cr(acacen)(H_2O)$_2$]Cl by zinc dust reduction of $CrCl_3$ in THF followed by slow addition to an ethanolic solution of K(acacen) initially appeared to occur without incident, it soon became apparent that in fact all had not gone as planned. The recrystallization from pyridine of the brown powder initially obtained in our [Cr(acacen)(H_2O)$_2$]Cl synthesis led to the formation of an intractable tar, from which we were eventually able to obtain a small quantity of brown crystals of [Cr(acacen)py$_2$][ZnCl$_3$py].

It is likely that our less rigorous purification of the initially obtained [Cr(acacen)(H_2O)$_2$]$^+$ product led to our isolation of a mixture of composition [Cr(acacen)(H_2O)$_2$]$_n$X^{n-}, where X^{n-} was possibly Cl$^-$, $ZnCl_4^{2-}$ etc. Finally, solution of this brown powder in pyridine resulted in substitution by solvent at both Cr and Zn sites and eventual isolation of the title compound by a fortuitous fractional recrystallization. It is interesting to note that the reduction of V(salen)Cl_2 with zinc dust in THF, followed by the addition of pyridine, similarly gave [V(salen)py$_2$][ZnCl$_3$py] [14].

Structural chemistry

An ORTEP drawing of one independent unit of complex ions, [Cr(acacen)py$_2$]$^+$ and [ZnCl$_3$py]$^-$, is shown in Fig. 1. The Cr(III) center in [Cr(acacen)py$_2$]$^+$ exhibits a distorted octahedral geometry. The tetradentate acacen ligand occupies the four equatorial positions whereas the two py ligands are *trans*-bonded. The dihedral angles between the two pyridine ligands in the two crystallographically independent cations A and B are 76.1(3) and 84.7(3)°, respectively. The acacen ligand exhibits almost the same kind of distortion in both complex ions. The two chemically equivalent halves of the acacen ligand are bent away from the py ligand that crosses the five-membered ring, making dihedral angles of 19.7(3)° (A) and 27.8(2)° (B). The torsional angles around the CH_2–CH_2 bond are −38(1)° (A) and 24(1)° (B).

The mean values for the four Cr–O and Cr–N coordination distances of the chelate system in the two cations are 1.939(4) and 1.995(5) Å, respectively, and are in good agreement with the corresponding bond lengths observed in [Cr(salen)(H_2O)$_2$]Cl [13]. As might be expected, these bond distances in the Cr(III) Schiff base complexes are intermediate in length compared to those in a lower valent Cr(II) compound, Cr(acacen) [15], and those found in higher valent Cr(V) substituted-salen complexes [16]. The bond distances within the acacen ligand agree very well with the mean values reported for several V, Cu and Co acacen derivatives [17].

The axial Cr(III)–N(py) distances in the cations range from 2.079(6) to 2.124(6) Å with a mean value of 2.101(10) Å, which is only slightly shorter than the Cr(II)–N(py) mean value of 2.131(10) Å observed in Cr(TTP)py$_2$ (TPP = *meso*-tetraphenylporphinato) [18]. The relatively wide distribution of Cr–N(py) bond lengths in the present case corresponds to different orientations of the py ligands with respect to the equatorial moiety (Fig. 2). These orientations, mainly dictated by crystal packing forces, appear to determine the Cr–N(py) distances owing to the interactions between the py ligand and the equatorial N and O atoms. In fact, the longer Cr–N(py) distances are found for lower values of dihedral angle between the pyridine plane and coordination plane defined by the two N atoms of pyridine and the two *trans*-bonded N and O atoms of the acacen ligand (Fig. 2).

In the [ZnCl$_3$py]$^-$ anions, the three Cl atoms and the N atom of the py ligand form a distorted tetrahedral arrangement about the zinc atom. The bond distances and angles in the coordination spheres of the two crystallographically independent [ZnCl$_3$py]$^-$ anions are reported in Table 2 together with their mean values and appear to be significantly different. In fact, the Zn–N distance in anion A is shorter than that in anion

TABLE 1. Positional parameters for non-hydrogen atoms for [Cr(acacen)py_2][$ZnCl_3py$] (e.s.d.s in parentheses)[a]

Atom	Unit A				Unit B			
	x	*y*	*z*	*B* (Å^2)	*x*	*y*	*z*	*B* (Å^2)
Cr	0.23101(8)	0.500	0.65068(6)	3.22(2)	0.10702(8)	0.79813(8)	0.15389(6)	3.18(2)
O(1)	0.2299(4)	0.5003(3)	0.7696(3)	4.0(1)	0.2659(3)	0.7918(3)	0.2155(3)	3.7(1)
O(2)	0.0704(4)	0.4864(3)	0.6037(3)	4.1(1)	0.1280(4)	0.8082(3)	0.0421(3)	4.2(1)
N(1)	0.3959(4)	0.5079(4)	0.6883(4)	4.1(1)	0.0712(4)	0.7854(4)	0.2642(3)	3.8(1)
N(2)	0.2439(4)	0.5085(4)	0.5310(3)	3.9(1)	−0.0571(4)	0.8100(4)	0.1024(4)	4.1(1)
C(1)	0.2794(8)	0.5472(6)	0.9149(5)	6.5(3)	0.4335(6)	0.7446(6)	0.3148(5)	5.3(2)
C(2)	0.3118(6)	0.5262(5)	0.8352(4)	4.4(2)	0.3109(5)	0.7620(5)	0.2925(4)	3.7(1)
C(3)	0.4190(6)	0.5343(6)	0.8378(5)	5.2(2)	0.2541(6)	0.7471(5)	0.3508(4)	4.3(2)
C(4)	0.4620(5)	0.5188(5)	0.7681(5)	4.7(2)	0.1399(5)	0.7594(5)	0.3377(4)	3.8(1)
C(5)	0.5875(6)	0.5118(7)	0.7895(6)	6.3(2)	0.1005(7)	0.7408(7)	0.4152(5)	6.2(2)
C(6)	0.4400(6)	0.4865(6)	0.6177(5)	5.5(2)	−0.0481(6)	0.7954(7)	0.2554(5)	6.3(2)
C(7)	0.3596(6)	0.5190(7)	0.5327(5)	5.9(2)	−0.1114(7)	0.8281(7)	0.1674(6)	6.3(2)
C(8)	0.1857(8)	0.5250(7)	0.3723(5)	6.7(2)	−0.2394(7)	0.8175(6)	−0.0122(6)	6.0(2)
C(9)	0.1615(6)	0.5133(5)	0.4581(4)	4.6(2)	−0.1136(6)	0.8059(4)	0.0194(5)	4.1(2)
C(10)	0.0491(6)	0.5064(6)	0.4544(4)	4.8(2)	−0.0615(6)	0.7935(5)	−0.0443(5)	4.5(2)
C(11)	0.0102(6)	0.4944(5)	0.5225(5)	4.5(2)	0.0498(6)	0.7959(5)	−0.0312(4)	4.5(2)
C(12)	−0.1142(7)	0.4875(7)	0.5079(6)	6.7(3)	0.0935(8)	0.7884(7)	−0.1078(5)	6.6(3)
N(3)	0.2136(5)	0.6306(4)	0.6551(3)	3.8(1)	0.1024(4)	0.6695(4)	0.1386(3)	3.6(1)
C(31)	0.1162(7)	0.6616(6)	0.6561(6)	5.6(2)	0.1919(6)	0.6308(5)	0.1290(5)	4.4(2)
C(32)	0.1007(7)	0.7465(6)	0.6639(6)	7.0(3)	0.2007(7)	0.5459(5)	0.1268(5)	5.5(2)
C(33)	0.1859(9)	0.7994(6)	0.6702(6)	7.3(3)	0.1139(7)	0.4984(6)	0.1334(5)	5.6(2)
C(34)	0.2854(8)	0.7687(6)	0.6696(6)	6.4(2)	0.0216(7)	0.5373(5)	0.1408(5)	5.6(2)
C(35)	0.2968(7)	0.6842(5)	0.6614(5)	4.9(2)	0.0185(6)	0.6227(5)	0.1431(5)	4.7(2)
N(4)	0.2489(4)	0.3720(4)	0.6512(4)	3.9(1)	0.1162(5)	0.9281(4)	0.1694(3)	3.8(1)
C(41)	0.3037(6)	0.3315(5)	0.7240(5)	4.5(2)	0.1498(8)	0.9637(5)	0.2467(5)	5.8(2)
C(42)	0.3144(7)	0.2457(6)	0.7278(6)	6.0(2)	0.1549(8)	1.0488(5)	0.2596(5)	5.8(2)
C(43)	0.2704(8)	0.2003(6)	0.6553(6)	6.9(2)	0.1245(7)	1.0997(5)	0.1882(6)	5.9(2)
C(44)	0.2149(8)	0.2409(6)	0.5788(6)	6.5(2)	0.0939(9)	1.0647(6)	0.1098(6)	7.1(3)
C(45)	0.2066(6)	0.3268(5)	0.5800(5)	5.0(2)	0.0900(8)	0.9790(6)	0.1023(5)	6.2(2)
Zn	0.34678(7)	1.02814(6)	0.87215(5)	4.27(2)	0.65086(7)	0.75548(6)	0.65574(6)	4.61(2)
Cl(1)	0.2920(2)	1.1061(2)	0.9651(2)	6.99(6)	0.5934(3)	0.6623(2)	0.5516(2)	8.29(8)
Cl(2)	0.5049(2)	1.0758(2)	0.8526(1)	5.70(5)	0.6119(2)	0.7263(2)	0.7759(2)	7.65(7)
Cl(3)	0.2091(2)	1.0113(2)	0.7468(1)	6.98(6)	0.8243(2)	0.8008(2)	0.6781(2)	8.82(8)
N(5)	0.3876(5)	0.9145(4)	0.9283(4)	3.9(1)	0.5487(5)	0.8591(4)	0.6140(4)	4.2(1)
C(51)	0.3658(7)	0.8937(5)	1.0005(5)	5.0(2)	0.4692(6)	0.8616(6)	0.5369(5)	5.2(2)
C(52)	0.3949(8)	0.8186(6)	1.0406(5)	6.3(2)	0.3967(7)	0.9259(7)	0.5099(6)	6.5(2)
C(53)	0.4474(7)	0.7615(6)	1.0060(6)	6.3(2)	0.4036(7)	0.9898(7)	0.5645(6)	7.0(2)
C(54)	0.4699(7)	0.7817(6)	0.9305(6)	6.6(3)	0.4835(8)	0.9884(6)	0.6458(6)	6.6(2)
C(55)	0.4403(7)	0.8596(6)	0.8956(5)	5.3(2)	0.5528(7)	0.9226(6)	0.6668(5)	5.5(2)

[a]The temperature factor is given in the form of the isotropic equivalent displacement parameter defined as: (4/3) $[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

B by about 0.05 Å, whereas the mean Zn–Cl distance in A is longer by about 0.03 Å. Correspondingly, in A the mean values of the N–Zn–Cl and Cl–Zn–Cl angles are wider and narrower, respectively, than the analogous values in B.

The different geometries in the two anions could be due to the diverse hybridization [19] of Zn originated by intra- and/or intermolecular steric interaction. The orientation of the pyridine ligands, with respect to the $ZnCl_3$ moiety, appears to be slightly but significantly different in the two anions (Fig. 3), probably due to crystal packing forces. In the B anion, one α-carbon atom of the pyridine ligand is practically eclipsed with respect to a Cl atom, and the Zn atom lies significantly out of the pyridine plane (Fig. 3). However, the two Zn–N(py) bond lengths are shorter than those observed in the structure of [V(salen)py_2][$ZnCl_3py$] (2.13(1) Å) where the metal atom lies 0.144(2) Å out of the planar pyridine ring [14]. Interestingly, the mean value of the Zn–N(py) distance in $ZnCl_2py_2$ (2.049(3) Å) [20] is close to the Zn–N(py) bond length observed in the less stressed anion A.

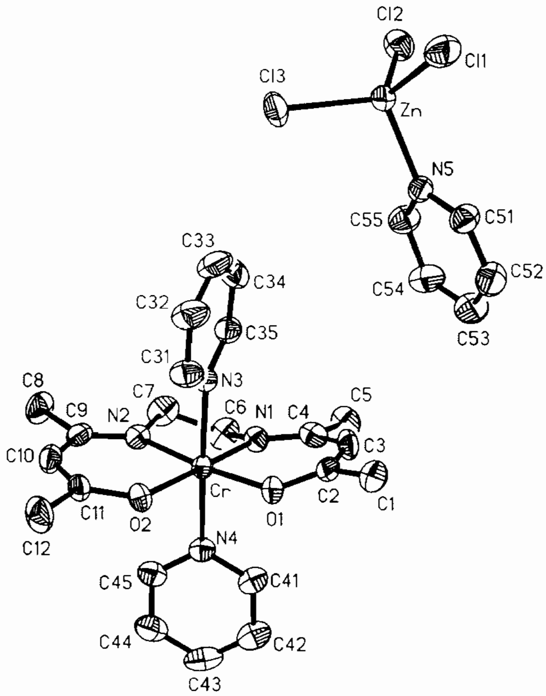

Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for the non-hydrogen atoms of [Cr(acacen)py$_2$][ZnCl$_3$py] for the crystallographically independent unit A. The same scheme applies also for the B unit.

A statistical analysis* of available data for ZnCl$_3$L species (where L is a ligand with an N(sp^2)-donor atom) gives mean values of 2.239(3) Å and 112.7(5)° for the Zn–Cl distances and Cl–Zn–Cl angles, respectively. These values are reported in Table 3 together with those of related species ZnCl$_{4-n}$N(sp^2)$_n$ with $n=0$ to 3. A comparison shows that the Zn–Cl distance decreases and the Cl–Zn–Cl angle increases as the value of n increases. Steffen and Palenik have attributed this trend to electronic rather than steric factors [22]. However, our results indicate that the increase of the number of N-donor ligands provokes a deformation of the tetrahedron around the Zn atom, which can be explained in terms of different hybridizations of the metal center [19]. The s character of the Zn hybrid orbitals involved in the Zn–Cl bonds increases with the number of N-donor ligands coordinated to the metal. This change may originate from the steric repulsion due to the ligands, assuming that the N-donor ligand is less bulky than Cl. In fact, electronic arguments based on the VSEPR model would lead to a trend opposite to that observed.

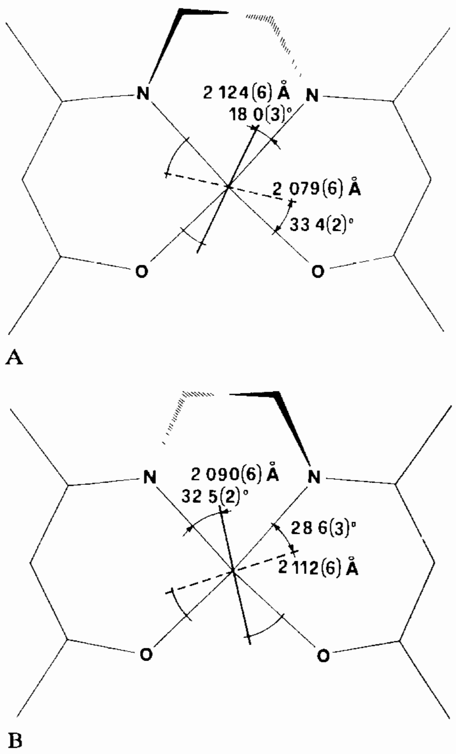

Fig. 2 Orientation of the pyridine planes with respect to the equatorial ligand acacen in the two crystallographically independent [Cr(acacen)py$_2$]$^+$ cations. Cr–py bond lengths and dihedral angles between the py plane and the coordination plane containing the two N(py) and two *trans*-bonded N and O atoms of the acacen ligand are reported.

TABLE 2. Bond lengths (Å) and angles (°) in the coordination sphere for the two crystallographically independent [ZnCl$_3$py]$^-$ anions together with the calculated average values (e.s.d.s in parentheses)

	Anion A	Anion B
Zn–N(5)	2 042(6)	2.092(6)
Zn–Cl(1)	2.241(3)	2.208(3)
Zn–Cl(2)	2.261(3)	2.213(3)
Zn–Cl(1)	2.238(2)	2.232(3)
Av. (Zn–Cl)	2.247(7)	2.218(7)
N(5)–Zn–Cl(1)	107.0(2)	106.1(2)
N(5)–Zn–Cl(2)	105.0(2)	99.7(2)
N(5)–Zn–Cl(3)	108.1(2)	105.4(2)
Av. (N–Zn–Cl)	106.7(9)	103.7(10)
Cl(1)–Zn–Cl(2)	112.5(1)	114.8(1)
Cl(1)–Zn–Cl(3)	111.4(1)	114.6(1)
Cl(2)–Zn–Cl(3)	112.4(1)	114.2(1)
Av. (Cl–Zn–Cl)	112.1(4)	114.5(2)

Supplementary material

Complete tables of full crystallographic data, bond lengths and angles, anisotropic thermal parameters,

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*The averages were calculated on data from the Cambridge Structural Database [21] CSD 4.4, version of Jan. 1991 with 86026 entries. The structures with disordered Cl atoms were omitted.

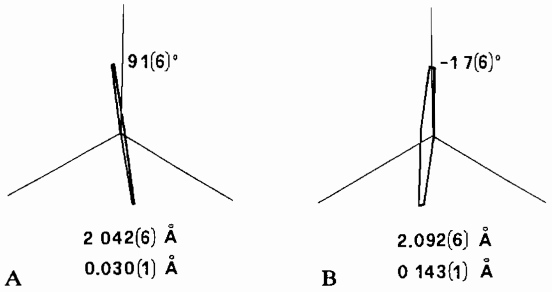

Fig. 3. Orientation of the py ligand with respect to the $ZnCl_3$ moiety, viewed along the Zn–N(5) bond, in the two crystallographically independent $[ZnCl_3py]^-$ anions. Torsional angles Cl(1)–Zn–N(5)–C(51), Zn–N(5) bond lengths, and Zn displacements out of the py plane are reported.

TABLE 3. Mean values of the Zn–Cl distances and Cl–Zn–Cl angles in tetrahedral species $ZnCl_{4-n}N(sp^2)_n$ (e.s.d.s of the mean in parentheses)

n	Species	Zn–Cl (Å)	N_{obs}[a]	Cl–Zn–Cl (°)	N_{obs}[a]
0	$[ZnCl_4]^{2-}$	2.265(1)	297	109.4(1)	448
1	$[ZnCl_3N(sp^2)]^-$	2.239(3)	33	112.7(5)	33
2	$[ZnCl_2N(sp^2)_2]$	2.216(3)	36	117.5(12)	19
3	$[ZnClN(sp^2)_3]^+$	2.170(2)	1		

[a]N_{obs} is the number of observables.

hydrogen atom coordinates (5 pages); a listing of observed and calculated structure factors (19 pages); a listing of Refcodes, Zn–Cl bond distances and Cl–Zn–Cl bond angles (from Cambridge Structural Database) for $ZnCl_{4-n}N(sp^2)_n$ species (4 pages) are available from the authors on request.

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References

1 K. Yamanouchi and S. Yamada, *Bull. Chem. Soc Jpn., 45* (1972) 2140.
2 A.E. Martell, R.L. Belford and M. Calvin, *J. Inorg. Nucl. Chem., 5* (1958) 170.
3 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals,* Pergamon, Oxford, UK, 2nd edn., 1980.
4 *CAD4 Operations Manual,* Enraf-Nonius, Delft, Netherlands, 1977.
5 W.H. Zachariasen, *Acta Crystallogr., 16* (1963) 1139.
6 MULTAN program, see ref. 10.
7 D. Rogers, *Acta Crystallogr., Sect. A, 37* (1981) 734.
8 J.A. Ibers and W.C. Hamilton, *Acta Crystallogr., 17* (1964) 781.
9 D.T. Cromer and J.T. Waber, *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Tables 2.2B and 2.3.1.
10 B.A. Frenz, The Enraf-Nonius CAD 4 SDP – a real time system for concurrent X-ray data collection and crystal structure determination, in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (eds.), *Computing in Crystallography,* Delft University Press, Delft, Netherlands, 1978, pp. 64–71.
11 K. Dey and K.C. Ray, *Inorg. Chim. Acta, 10* (1974) 139.
12 M. Macicek and F. Brezina, *Acta Univ. Palacki. Olomuc., Fac. Rerum Nat, 57* (1978) 23; *Chem. Abstr., 92* (1980) 156990h.
13 P. Coggon, A.T. McPhail, F.E. Mabbs, A. Richards and A.S. Thornley, *J. Chem. Soc. A,* (1970) 3296.
14 M. Mazzanti, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg Chem., 25* (1986) 2308.
15 L.F. Larkworthy, D.C. Povey and B. Sandell, *Inorg. Chim Acta, 83* (1984) L29.
16 K. Srinivasan and J.K. Kochi, *Inorg Chem., 24* (1985) 4671.
17 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.,* (1972) 385.
18 W.R. Scheidt, A.C. Brinegar, J.F. Kirner and C.A. Reed, *Inorg. Chem., 18* (1979) 3610.
19 H.A. Bent, *Chem Rev., 61* (1961) 275.
20 W.L. Steffen and G.J. Palenik, *Acta Crystallogr, Sect. B, 32* (1976) 298.
21 F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.B. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Roger and D.G. Watson, *Acta Crystallogr., Sect. B, 35* (1979) 2331.
22 W.L. Steffen and G.J. Palenik, *Inorg Chem., 17* (1978) 1338.