Inorganica Chimica Acta, *91* (1984) 33–38

Crystal Structure of Dichloro Bis(1-methylcytosine)zinc(II)

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Received June 14, 1983

The title compound belongs to the triclinic space group $P\bar{1}$, with a = 7.318(2), b = 7.453(1), c = 13.733(2) Å, α = 100.31(1), β = 103.96(2), γ = 91.54(2)°, Z = 4 molecules per unit cell. The crystal contains individual $ZnCl_2(1\text{-methylcytosine})_2$ molecules, in which the zinc atom has a distorted tetrahedral $ZnCl_2N_2$ coordination. The cytosine molecule acts as a monodentate ligand via *N(3), and the adjacent carbonyl oxygen is not significantly involved in binding. Each amino group forms one intramolecular hydrogen bond with a chlorine atom. Intermolecular interactions include stacking of the cytosine rings and hydrogen bonding from the amino groups to carbonyl oxygens or chlorine atoms. In spite of the fact that Zn^{2+} is a Lewis acid harder than Cd^{2+} and Hg^{2+}, chelating interaction of zinc with the nearby carbonyl group is less pronounced than in the similar compounds of the heavier elements.*

Introduction

In previous reports from this laboratory [1, 2], $HgCl_2$ and $CdCl_2$ were shown to form addition compounds with 1-methylcytosine (MeCy) in which metal coordination took place with the heterocyclic N(3) site. However, the metal-oxygen distances to the adjacent carbonyl group were indicative of some bonding, especially in the case of $CdCl_2(MeCy)_2$ [2]. From ^{13}C NMR and Raman difference spectra of DMSO solutions containing $Zn(NO_3)_2$, Marzilli and coworkers [3] concluded that Zn^{2+} interacts with N(3) or O(2), and they proposed a tautomeric equilibrium between these two monodentate forms. From ^{15}N NMR spectroscopy, Buchanan and Stothers [4] found that the N(3) signal was the most affected by the presence of Zn^{2+} ions, in agreement with metal bonding in the region of N(3). Increasing participation of O(2) in coordination along the series Hg < Cd < Zn would be consistent with increasing metal hardness. This property of Zn clearly shows in its preference to coordinate to phosphate oxygens instead of sites on the base in complexes with ATP and CMP [5]. This prompted us to prepared the MeCy adduct of $ZnCl_2$ and to compare its crystal structure with those of the chlorides of the heavier elements of this group. In the other zinc-cytosine compound, for which a crystallographic study was reported, the metal was not coordinated to the cytosine ligand [6].

Experimental Section

Preparation

The complex was obtained by dissolving 1-methylcytosine (Vega) and $ZnCl_2$ (2:1 ratio) in warm water. Slow evaporation at room temperature yielded colorless crystals of the compound. *Anal.* Calcd. for $C_{10}H_{14}Cl_2N_6O_2Zn$: C, 31.07; H, 3.65; N, 21.74; Cl, 18.34. Found: C, 31.16; H, 3.54; N, 21.62; Cl, 18.51.

Crystal Data

$C_{10}H_{14}Cl_2N_6O_2Zn$ fw = 386.54
Triclinic, space group $P\bar{1}$, a = 7.318(2), b = 7.453(1), c = 13.733(2) Å, α = 100.31(1), β = 103.96(2), γ = 91.54(2)°, V = 713.2 Å^3, Z = 2, D_{cal} = 1.799 g cm^{-3}. $\lambda(MoK\bar{\alpha})$ = 0.71069 Å (graphite monochromator), t = 23 °C, $\mu(MoK\alpha)$ = 21.5 cm^{-1}.

Crystallographic Measurements

A set of precession and cone axis photographs failed to reveal Laue symmetry higher than $\bar{1}$, which leaves P1 and $P\bar{1}$ as possible space groups. Cell reduction clearly indicated that the parameters were not metrically close to those of any lattice with higher symmetry. The crystal was transferred to a CAD-4 diffractometer. The automatic indexation procedure, based on 25 reflections randomly distributed in the reciprocal sphere and centered several times, yielded the cell previously found from films. The parameters reported above were obtained by least-squares fit on the setting angles for the 25 reflections.

The data were collected following the procedure described elsewhere [7]. A total of 2508 hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$ reflections within a sphere limited by 2θ = 50° was collected. The fluctuations of the three standard reflections during data collection was within ±1%. Orientation was checked periodically by centering three reflections. No crystal recentering was necessary during the collection. A set of 2057 reflections were retained for structure resolution and

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refinement on the basis of the criterion $I \geqslant 3\sigma(I)$. The data were corrected for absorption (Gaussian integration, grid 8 X 8 X 8, transmission range 0.55–0.67), polarization and the Lorentz effect.

Structure Resolution

The centric $P\bar{1}$ space group was used first; this choice was subsequently confirmed by successful refinement. The Zn atoms were positioned from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located from a difference Fourier (ΔF) synthesis phased on zinc. Isotropic refinement led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.079$ and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2} = 0.087$. The hydrogen atoms were all visible in the next ΔF map. They were introduced into the structure and isotropically refined, whereas the nonhydrogen atoms were refined anisotropically. The agreement factors at convergence were $R = 0.025$ and $R_w = 0.033$. The goodness-of-fit ratio was 1.31. The final ΔF map was essentially featureless, with a general background within ±0.20 e $Å^{-3}$, and a few peaks in the range ±(0.20–0.45) e $Å^{-3}$ near Zn or Cl.

TABLE I. Refined Fractional Coordinates (X 10^4, Zn, Cl X 10^5, H X 10^3).

Atom	X	Y	Z
Zn	47889(4)	20287(4)	24104(2)
Cl(1)	22603(9)	3144(9)	25009(5)
Cl(2)	71953(10)	5295(10)	31901(5)
O(12)	1940(3)	2860(3)	742(1)
O(22)	7896(2)	4942(3)	3305(2)
N(11)	3285(3)	2936(3)	−576(2)
N(13)	5033(3)	2275(3)	985(2)
N(14)	8165(3)	1698(3)	1196(2)
N(21)	6817(3)	6887(3)	4472(2)
N(23)	4767(3)	4658(3)	3208(2)
N(24)	1572(3)	4669(3)	3010(2)
C(11)	1474(4)	3320(4)	−1216(2)
C(12)	3348(3)	2695(3)	401(2)
C(14)	6579(3)	2127(3)	617(2)
C(15)	6485(4)	2404(4)	−384(2)
C(16)	4843(4)	2780(4)	−945(2)
C(21)	8734(4)	7695(4)	4962(2)
C(22)	6550(3)	5474(3)	3641(2)
C(24)	3280(3)	5392(3)	3507(2)
C(25)	3561(4)	6877(4)	4343(2)
C(26)	5327(4)	7556(3)	4804(2)
H(15)	753(4)	229(4)	−58(3)
H(16)	468(4)	287(3)	−158(2)
H(25)	254(4)	744(4)	452(2)
H(26)	565(4)	852(4)	543(2)
H(111)	93(4)	425(4)	−83(3)
H(112)	69(5)	227(5)	−143(3)
H(113)	167(4)	354(4)	−183(3)
H(141)	819(4)	139(4)	175(2)
H(142)	918(5)	161(4)	98(3)
H(211)	950(4)	684(4)	519(2)
H(212)	919(5)	841(5)	446(3)
H(213)	870(4)	866(4)	553(3)
H(241)	62(4)	501(4)	314(2)
H(242)	132(4)	383(4)	254(2)

The refined coordinates are listed in Table I. Tables of temperature factors and of structure factors amplitudes are available upon request.

The scattering curves were taken from Cromer and Waber [8], except for hydrogen [9]. The f′ and f″ contributions to anomalous dispersion of Zn and Cl were taken into account [8].

Structure and Discussion

The crystal contains individual $ZnCl_2(MeCy)_2$ molecules (Fig. 1). Interatomic distances and bond angles are listed in Table II.

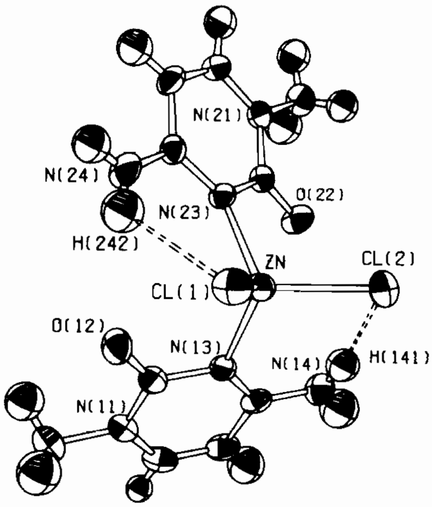

Fig. 1. Stereoview of the $ZnCl_2(MeCy)_2$ molecule. The ellipsoids correspond to 50% probability. Dashed sticks correspond to hydrogen bonds.

The cytosine ligand is bound to zinc *via* the usual N(3) position [10]. The Zn–N distances (2.048(2) and 2.069(2) Å) compare well with those observed for $ZnCl_2L_2$ adducts with a number of pyridine derivatives (Table III) and for zinc complexes with adenine [11, 22] and related compounds [12]. In contrast with the corresponding complexes of $HgCl_2$ [1] and $CdCl_2$ [2], the present zinc complex shows no clear evidence for significant metal-oxygen bonding with the adjacent carbonyl oxygen. The Zn–O(2) distances (2.873(2) and 2.971(2) Å) are ~0.9 Å greater than those found in $ZnCl_2$ addition compounds with oxygen donors (Table III). This distance is near or slightly above the sum of the van der Waals radii (Zn = 1.4, O = 1.5 Å) [13]. The Zn–N(3)–C angles differ by 17.3° (ligand 1) and 13.4° (ligand 2), but this in itself is not a clear proof

TABLE II. Interatomic Distances and Bond Angles.

Distances (Å)			
Zn–Cl(1)	2.261(1)	Zn–N(23)	2.069(2)
Zn–Cl(2)	2.263(1)	Zn–O(12)	2.873(2)
Zn–N(13)	2.048(2)	Zn–O(22)	2.971(2)
N(11)–C(12)	1.375(3)	N(21)–C(22)	1.379(3)
N(11)–C(11)	1.469(4)	N(21)–C(21)	1.462(3)
N(11)–C(16)	1.355(4)	N(21)–C(26)	1.354(3)
C(12)–O(12)	1.231(3)	C(22)–O(22)	1.231(3)
C(12)–N(13)	1.377(3)	C(22)–N(23)	1.371(3)
N(13)–C(14)	1.345(3)	N(23)–C(24)	1.349(3)
C(14)–C(15)	1.412(4)	C(24)–C(25)	1.416(4)
C(14)–N(14)	1.322(3)	C(24)–N(24)	1.319(3)
C(15)–C(16)	1.328(4)	C(25)–C(26)	1.335(4)
C(15)–H(15)	0.87(3)	C(25)–H(25)	0.93(3)
C(16)–H(16)	0.87(3)	C(26)–H(26)	0.99(3)
C(11)–H(111)	0.95(3)	C(21)–H(211)	0.91(3)
C(11)–H(112)	0.92(4)	C(21)–H(212)	1.05(3)
C(11)–H(113)	0.93(3)	C(21)–H(213)	0.97(3)
N(14)–H(141)	0.83(3)	N(24)–H(241)	0.80(3)
N(14)–H(142)	0.86(3)	N(24)–H(242)	0.80(3)
Angles (°)			
Cl(1)–Zn–Cl(2)	101.25(3)	Cl(2)–Zn–N(13)	110.61(6)
Cl(1)–Zn–N(13)	117.31(6)	Cl(2)–Zn–N(23)	112.02(6)
Cl(1)–Zn–N(23)	109.28(6)	N(13)–Zn–N(23)	106.46(8)
Zn–N(13)–C(12)	110.8(2)	Zn–N(23)–C(22)	112.5(2)
Zn–N(13)–C(14)	128.1(2)	Zn–N(23)–C(24)	125.9(2)
C(12)–N(13)–C(14)	121.1(2)	C(22)–N(23)–C(24)	119.8(2)
N(13)–C(14)–C(15)	119.9(2)	N(23)–C(24)–C(25)	120.5(2)
N(13)–C(14)–N(14)	119.3(2)	N(23)–C(24)–N(24)	118.1(2)
C(15)–C(14)–N(14)	120.8(2)	C(25)–C(24)–N(24)	121.3(2)
C(14)–C(15)–C(16)	118.4(3)	C(24)–C(25)–C(26)	118.2(3)
C(15)–C(16)–N(11)	121.9(3)	C(25)–C(26)–N(21)	121.5(3)
C(14)–C(15)–H(15)	116(2)	C(24)–C(25)–H(25)	121(2)
C(16)–C(15)–H(15)	126(2)	C(26)–C(25)–H(25)	121(2)
C(15)–C(16)–H(16)	122(2)	C(25)–C(26)–H(26)	123(2)
N(11)–C(16)–H(16)	116(2)	N(21)–C(26)–H(26)	115(2)
C(16)–N(11)–C(12)	120.7(2)	C(26)–N(21)–C(22)	120.7(2)
C(16)–N(11)–C(11)	121.0(2)	C(26)–N(21)–C(21)	120.7(2)
C(12)–N(11)–C(11)	118.3(2)	C(22)–N(21)–C(21)	118.6(2)
N(11)–C(12)–N(13)	118.0(2)	N(21)–C(22)–N(23)	118.8(2)
N(11)–C(12)–O(12)	120.8(2)	N(21)–C(22)–O(22)	120.4(2)
N(13)–C(12)–O(12)	121.2(2)	N(23)–C(22)–O(22)	120.8(2)
C(14)–N(14)–H(141)	121(2)	C(24)–N(24)–H(241)	125(2)
C(14)–N(14)–H(142)	121(2)	C(24)–N(24)–H(242)	126(2)
H(141)–N(14)–H(142)	117(3)	H(241)–N(24)–H(242)	109(3)
N(11)–C(11)–H(111)	109(2)	N(21)–C(21)–H(211)	111(2)
N(11)–C(11)–H(112)	109(2)	N(21)–C(21)–H(212)	109(2)
N(11)–C(11)–H(113)	108(2)	N(21)–C(21)–H(213)	109(2)
H(111)–C(11)–H(112)	111(3)	H(211)–C(21)–H(212)	116(3)
H(111)–C(11)–H(113)	117(3)	H(211)–C(21)–H(213)	110(3)
H(112)–C(11)–H(113)	102(3)	H(212)–C(21)–H(213)	103(3)

for Zn–O bonding, since the nearby amino hydrogen is expected to induce some displacement of the metal toward O(2) [2]. For the Cd and the Hg compounds, metal–oxygen binding was more likely: firstly, the angles at N(3) differed to a greater extent (30–36°, Cd; 24°, Hg); secondly, the M–O distances (2.78, 2.68 Å, Cd; 2.84 Å, Hg) were markedly shorter than the sum of the van der Waals radii (3.1 Å, Cd; 3.0 Å, Hg) [13].

The Zn–Cl distances (2.261(1) and 2.263(1) Å) lie at the higher limit of the range observed for a variety of $ZnCl_2L_2$ adducts (Table III) and the Cl–Zn–Cl

TABLE III. Distances (Å) and Angles (deg) around Zn in ZnCl$_2$L$_2$ Compounds.

N-donors	Zn–Cl		Cl–Zn–Cl	Zn–L		L–Zn–L	Ref.
CH$_3$CN	2.186[a]	2.180	130.6	1.953	1.953	100.9	33
4-CN-Pyridine	2.207(2)	2.218(2)	125.7(1)	2.059(5)	2.069(6)	105.0(2)	16
4-Acetyl-Pyridine	2.216(3)	2.206(3)	123.6(1)	2.061(9)	2.042(9)	109.0(4)	16
4-Me-Pyridine	2.211(2)	2.204(2)	121.8(1)	2.046(5)	2.042(5)	100.6(2)	17
Pyridine	2.215(2)	2.228(2)	120.9(1)	2.046(5)	2.052(6)	106.3(2)	18
2,9-Me$_2$-Phenanthroline	2.204(3)	2.219(3)	120.3(1)	2.059(11)	2.074(9)	81.5(3)[b]	19
Me$_4$-Ethylenediamine	2.204(4)	2.213(4)	119.4(2)	2.107(8)	2.057(9)	87.9(4)[b]	20
4-Vinyl-Pyridine	2.214(2)	2.204(2)	118.7(1)	2.054(5)	2.040(5)	101.9(2)	16
1-Me-Tetrazole	2.198(5)	2.206(5)	118.4(2)	2.04(1)	2.06(1)	98.9(3)	21
9-Me-Adenine	2.234(1)	2.219(1)	118.3(2)	2.068(2)	2.040(2)	105.2(2)	22
Phenanthroline	2.207(3)	2.198(3)	114.7(1)	2.050(7)	2.072(7)	80.4(3)[b]	23
Imidazole	2.258(3)	2.239(3)	111.5(1)	1.995(11)	2.020(11)	105.2(5)	24
Acetone-thiosemicarbazone	2.203(2)	2.252(2)	110.0(1)	2.116(4)	2.303(2)(S)	85.2(1)[b]	25
1-Me-Cytosine	2.261(1)	2.263(1)	101.25(3)	2.048(2)	2.069(2)	106.46(8)	This work
O-donors							
Antipyrine	2.249(2)	2.243(4)	117.6(1)	1.997(4)	2.019(6)	97.4(2)	26
Ph$_3$PO	2.204(2)	2.204(2)	116.4(1)	1.984(5)	1.984(5)	96.8(3)	27
Me$_2$NC(O)Me	2.209(4)	2.220(3)	115.7(1)	1.964(7)	1.975(8)	90.5(3)	28
2,6-Lutidine-oxide	2.246(4)	2.246(4)	114.8(2)	2.01(1)	2.01(1)	94.7(4)	29
S-donors							
MeC(S)NH$_2$	2.279(1)	2.252(1)	109.8(1)	2.358(2)	2.338(2)	101.0(1)	30
(NH$_2$)$_2$CS	2.31(1)	2.32(1)	107.3(2)	2.35(1)	2.35(1)	111.5(2)	31
(NHEt)$_2$CS	2.277(3)	2.263(3)	106.4(1)	2.343(2)	2.337(2)	101.4(1)	32
(NHEt)$_2$CS	2.251(3)	2.274(3)	107.5(1)	2.354(2)	2.334(3)	99.7(1)	32

[a] Values taken from the Cambridge Crystallographic Data Base, National Research Council, Ottawa, Canada. Esd s not available.
[b] Angle imposed by the 'bite' of the chelating ligand.

angle is the smallest known. Inspection of Table III shows that the Zn–Cl distances are inversely correlated with the Cl–Zn–Cl angles. Thus, MeCy can be considered as a ligand with bulky substituents in α positions, which sterically force the Zn–Cl bonds together, thereby increasing the Zn–Cl distances.

The distances in the coordinated ligands lie between those reported for neutral MeCy and for the protonated form in [MeCyH]ClO$_4$, respectively [14], but they are slightly closer to those of the cationic form. For the angles, on the other hand, the pattern is somewhat closer to that of the neutral form. Significant differences are found between corresponding angles in the two ligands (*e.g.* angles at N(3) and C(4)), which undoubtedly result from different constraints imposed by packing on the two ligands.

Ideally, the MeCy molecule should be planar. The six-membered ring of ligand #1 is indeed planar with a maximum atom-to-plane distance of 0.008(3) Å (Table IV). The exocyclic groups deviate to a greater extent, but not abnormally. In contrast, ligand #2 is severely distorted toward a boat conformation (N(23) and C(26) above the remaining ring atoms). The exocyclic groups are generally more distant from the

TABLE IV. Weighted Least-squares Planes.

Ligand 1

Equation: $0.146\,x + 0.926\,y + 0.348\,z = 2.272$

Atom-to-plane Distances (Å)

N(11)*	0.002(2)	C(14)*	0.002(2)
C(12)*	−0.006(3)	C(15)*	−0.008(3)
N(13)*	0.003(2)	C(16)*	0.005(3)
C(11)	0.040(3)	N(14)	0.028(2)
O(12)	−0.027(2)	H(15)	0.01(3)
Zn	−0.0450(3)	H(16)	0.07(3)

Ligand 2

Equation: $-0.046\,x - 0.770\,y + 0.636\,z = 0.485$

Distances (Å)

N(21)*	−0.006(2)	C(24)*	0.025(3)
C(22)*	0.042(3)	C(25)*	0.012(3)
N(23)*	−0.034(2)	C(26)*	−0.020(3)
C(21)	0.010(3)	N(24)	0.071(3)
O(22)	0.134(2)	H(25)	0.12(3)
Zn	−0.7069(3)	H(26)	−0.11(3)

*Atoms used to calculate the equation.

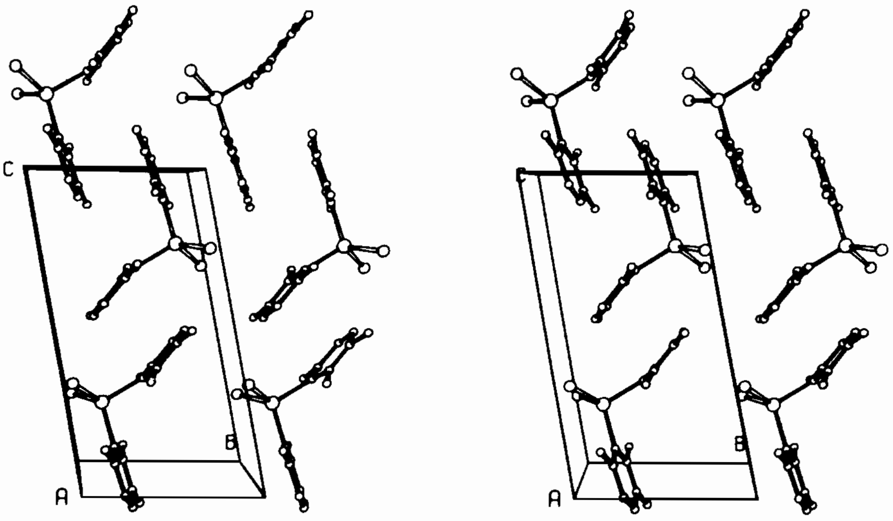

Fig. 2. Projection of the unit cell down the a^* axis. The atoms are shown as spheres of arbitrary sizes, the larger spheres corresponding to Zn atoms.

TABLE V. Geometry of the Hydrogen Bonds.

A–H...B	A–B	H–B	A–H–B
N(14)–H(141)...Cl(2)	3.243(3)	2.44(3)	162(3)
N(14)–H(142)...Cl(1)[a]	3.390(3)	2.99(3)	110(3)
N(24)–H(241)...O(22)[b]	2.823(3)	2.06(3)	160(3)
N(24)–H(242)...Cl(1)	3.274(3)	2.72(3)	128(3)

[a] 1 + x, y, z. [b] –1 + x, y, z.

plane than in ligand #1, usually on the same side as the ring atom to which they are attached. This is particularly clear for Zn and O(22), which are at 0.7069(3) and 0.134(2) Å, respectively, from the mean plane through the ring atoms.

One proton on each amino group is involved in intramolecular hydrogen bonding with chlorine (Fig. 1 and Table V). The N(14)–H(141)...Cl(2) bond is moderately strong: the N–Cl distance (3.243(3) Å) lies in the middle of the range for this type of H-bond [15], whereas the hydrogen atom is close to the N–Cl line and defines normal angles around both N(14) and Cl(2) (Table V). Although the N(24)–Cl(1) distance is not much greater (3.274(3) Å), the N(24)–H(242)...Cl(1) interaction is probably much less efficient, because the acceptor does not lie in the plane of the amino group.

A projection of the unit cell is shown in Fig. 2. Stacking of the MeCy ligands is an important factor in determining the packing pattern. Ligands of type #1 are stacked with an interplanar distance of ~3.65 Å and define infinite columns along the *b* direction, near the *ab* plane. Ligands of type #2 also participate in stacking interactions, but only by pairs, in the z = 1/2 region of the unit cell. This interaction is probably responsible for the distortions mentioned above. Successive unit cells in the *a* direction are held together by means of two types of hydrogen bonds involving the amino hydrogen atoms not used in intramolecular hydrogen-bonding. The N(14)–H(142)...Cl(1) bond is rather weak (N(14)–Cl(1) = 3.390(3) Å), but the N(24)–H(241)...O(22) interaction is definitely stronger (2.823(3) Å).

In conclusion, despite the fact that Zn^{2+} is normally considered to be harder than Cd^{2+} and Hg^{2+}, chelating interaction with the hard carbonyl oxygen in the present zinc complex seems to be less marked than in the MeCy complexes with cadmium and mercury in the solid state.

Acknowledgement

I wish to thank the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'Education du Québec for financial support. The assistance of F. Guay in X-ray camera work is acknowledged.

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