

Soulignons l'étroite similitude de la structure des dérivés méthylé (Colleter, Gadret & Goursolle, 1969), propylé (Colleter, Gadret & Goursolle, 1970), et butylé.

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The Crystal and Molecular Structure of Diaquobis-(*N,N*-diethylnicotinamide)-diisothiocyanatozinc

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Crystals of the title compound, $\text{Zn}(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{NCS})_2(\text{H}_2\text{O})_2$, are triclinic, space group $P\bar{1}$ with $a = 7.626$ (7), $b = 11.998$ (10), $c = 9.486$ (8) Å, $\alpha = 98.7$ (1), $\beta = 123.7$ (1), $\gamma = 97.2$ (1)°, $Z = 1$. The structure has been determined by X-ray methods from three-dimensional intensity data collected on a single crystal automated diffractometer. The structure, solved by Fourier methods and refined by least-squares, consists of discrete centrosymmetric octahedral complexes held together by hydrogen bonds $\text{O}_w\text{-H}\cdots\text{O}$ and $\text{O}_w\text{-H}\cdots\text{S}$. The organic ligands coordinate only through the pyridine nitrogen atoms; the other ligands are the water molecules and the nitrogen atoms of the isothiocyanate groups. The strongest interaction between metal and donor atoms appears to be that involving the isothiocyanate group.

Introduction

Structure analyses of complexes formed by *N,N*-diethylnicotinamide (DENA) with cadmium dithiocyanate (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972) and with manganese dithiocyanate (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973) show coordination through the pyridine nitrogen and the amide oxygen, so that the organic ligand acts as a bridge between different coordination polyhedra. Single (in the case of cadmium) and double (in the case of manganese) ribbons of bridging ligands run through the structure. In both compounds coordination is octahedral but in the cadmium complex, in which the ratio Cd:DENA is 1:1, the thiocyanate groups also act as bridges, while in the manganese derivative, in which the ratio Mn:DENA is 1:2, the thiocyanate groups are monodentate.

In the present paper the crystal structure of diaquobis-(*N,N*-diethylnicotinamide)diisothiocyanatozinc is reported. In this complex no bridges are formed and the organic ligand coordinates to metal only through the pyridine nitrogen which is the more basic point.

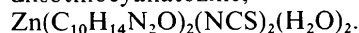
Experimental

Preparation

Crystals of $\text{Zn}(\text{DENA})_2(\text{NCS})_2(\text{H}_2\text{O})_2$ suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing zinc thiocyanate and *N,N*-diethylnicotinamide. At first, crystals of the dihydrate were formed, which, on standing in the mother liquor, decomposed into the anhydrous complex $\text{Zn}(\text{DENA})_2(\text{NCS})_2$.

Crystal data

Compound: diaquobis-(*N,N*-diethylnicotinamide)-diisothiocyanatozinc,



F.W. 574.03;

Unit cell: the parameters, determined from rotation and Weissenberg photographs and refined with data obtained on an automated single crystal diffractometer (Cu $K\alpha$, $\lambda = 1.54178$ Å), are:

$a = 7.626$ (7), $b = 11.998$ (10), $c = 9.486$ (8) Å;

$\alpha = 98.7$ (1), $\beta = 123.7$ (1), $\gamma = 97.2$ (1)°;

$V = 690.6$ Å³; $Z = 1$;

$D_x = 1.38$, $D_m = 1.39$ g cm⁻³;

$\mu(\text{Cu } K\alpha) = 29.45 \text{ cm}^{-1}$; $F(000) = 300$;
Space group: $P\bar{1}$ [$C_i(1) - \text{No. } 2$] from systematic absences and structure determination.

Intensity data

The intensities were collected on a single-crystal automated Siemens diffractometer on line with a Siemens 304/P computer with Ni-filtered Cu $K\alpha$ radiation and the ω - 2θ scan technique. A rather irregular prism of approximate dimensions $0.12 \times 0.19 \times 0.24 \text{ mm}$ was aligned with [001] along the φ axis of the diffractometer and all reflexions with $2\theta \leq 140^\circ$ were estimated. 2624 independent reflexions were measured and 2381 used in the analysis, taking as unobserved the reflexions whose intensities were less than twice their standard deviations $\{\sigma^2(I) = [\text{total counts} + (0.005 I)^2]\}$. Corrections for Lorentz and polarization factors were made in the usual way, but not for absorption. Absolute scale and mean isotropic temperature factor were obtained by Wilson's (1942) method.

Structure determination and refinement

The whole structure (except for the hydrogen atoms) was solved from a three-dimensional Fourier map, obtained with the phases determined by putting the zinc atom on the centre of symmetry. Refinement was carried out by the block-diagonal least-squares method, initially with isotropic, then with anisotropic thermal parameters. The hydrogen atoms were located from a difference synthesis. Further least-squares cycles were computed including the hydrogen atoms with isotropic thermal parameters. The weighting scheme was $1/w = (A + BF_0)^2$ with $A = 0.52$ and $B = 0.04942$, determined by plotting ΔF against $|F_0|$. The final R was 0.064 (observed reflexions only). Atomic scattering factors were taken from Cromer & Mann (1968) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for hydrogen atoms.

Table 1. Final fractional atomic coordinates ($\times 10^4$) with *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>
Zn	0	0	0
N(1)	2832 (6)	977 (3)	435 (4)
C(1)	4412 (5)	1661 (3)	981 (4)
S(1)	6637 (2)	2639 (1)	1781 (2)
O _w	-935 (4)	1584 (2)	194 (3)
N(2)	1626 (4)	329 (2)	2816 (3)
C(2)	2891 (5)	1390 (3)	3921 (4)
C(3)	3915 (5)	1636 (3)	5709 (4)
C(4)	3660 (6)	749 (3)	6420 (4)
C(5)	2363 (6)	-341 (3)	5283 (5)
C(6)	1377 (5)	-516 (3)	3513 (4)
C(7)	5468 (5)	2800 (3)	6915 (4)
O	7445 (4)	2856 (2)	7852 (3)
N(3)	4687 (5)	3727 (2)	6971 (4)
C(8)	6249 (7)	4838 (3)	8269 (5)
C(9)	7224 (11)	5536 (5)	7564 (9)
C(10)	2364 (6)	3706 (3)	5963 (5)
C(11)	1464 (10)	3653 (6)	7011 (9)
H(1)	3021 (68)	1975 (37)	3370 (54)
H(2)	4504 (84)	912 (47)	7710 (65)
H(3)	2289 (90)	-990 (49)	5745 (72)
H(4)	456 (68)	-1233 (37)	2729 (55)
H(5)	5476 (72)	5339 (39)	8627 (57)
H(6)	7539 (92)	4661 (49)	9429 (72)
H(7)	8181 (132)	6330 (68)	8522 (101)
H(8)	5922 (102)	5739 (55)	6412 (80)
H(9)	7987 (117)	5016 (64)	7102 (92)
H(10)	2163 (94)	4475 (51)	5528 (76)
H(11)	1572 (82)	2974 (43)	4901 (65)
H(12)	-131 (128)	3523 (68)	6304 (101)
H(13)	2332 (117)	4362 (63)	8066 (93)
H(14)	1650 (134)	2939 (74)	7393 (107)
H(15)	-1513 (81)	1982 (44)	-689 (64)
H(16)	-1923 (84)	1559 (46)	509 (69)

All the calculations were performed on the CDC 6600 Computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), with the programs written by Immirzi (1967).

Table 2. Thermal parameters with *e.s.d.*'s

The anisotropic thermal parameters are in the form: $\exp[-0.25(h^2a^{*2}B_{11} + \dots + 2klb^*c^*B_{23})]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	2.492 (21)	2.227 (20)	2.589 (21)	0.255 (16)	1.085 (18)	0.165 (16)
N(1)	3.223 (127)	3.841 (144)	3.362 (130)	0.119 (110)	1.808 (113)	0.426 (112)
C(1)	2.126 (115)	2.651 (127)	2.889 (127)	0.278 (97)	1.453 (105)	0.394 (102)
S(1)	3.175 (40)	3.010 (39)	6.923 (63)	-0.236 (32)	3.212 (44)	0.019 (39)
O _w	3.556 (109)	2.534 (96)	3.459 (105)	1.463 (83)	1.795 (92)	0.758 (81)
N(2)	2.413 (101)	1.650 (92)	2.248 (95)	0.282 (77)	1.085 (84)	0.148 (75)
C(2)	2.438 (118)	1.612 (105)	2.144 (108)	0.307 (89)	0.904 (97)	0.146 (85)
C(3)	1.947 (107)	1.663 (103)	2.312 (111)	0.442 (84)	0.886 (94)	0.133 (86)
C(4)	2.996 (136)	2.597 (128)	2.433 (124)	0.349 (105)	1.174 (111)	0.580 (102)
C(5)	3.346 (146)	2.282 (125)	3.071 (137)	0.210 (107)	1.403 (122)	0.947 (107)
C(6)	2.661 (126)	1.777 (111)	2.895 (127)	0.309 (95)	1.301 (110)	0.359 (96)
C(7)	2.372 (117)	1.863 (107)	1.997 (107)	0.419 (90)	0.818 (96)	0.207 (86)
O	2.285 (90)	2.460 (94)	3.270 (103)	0.437 (74)	0.631 (81)	0.416 (79)
N(3)	2.717 (113)	1.690 (97)	2.715 (109)	0.469 (84)	0.960 (94)	-0.399 (81)
C(8)	3.972 (176)	2.357 (140)	3.554 (160)	0.038 (125)	1.267 (141)	-1.119 (118)
C(9)	6.598 (309)	3.208 (193)	7.014 (313)	-1.404 (196)	2.862 (266)	-0.157 (198)
C(10)	2.971 (144)	3.329 (155)	3.583 (155)	1.294 (122)	1.473 (128)	0.218 (122)
C(11)	4.753 (238)	7.856 (352)	6.621 (299)	0.543 (231)	3.795 (237)	0.174 (256)

Table 2 (*cont.*)

	<i>B</i>
H(1)	3.33 (83)
H(2)	5.11 (112)
H(3)	6.02 (130)
H(4)	3.39 (84)
H(5)	3.76 (90)
H(6)	6.02 (128)
H(7)	10.37 (224)
H(8)	7.44 (157)
H(9)	8.85 (186)
H(10)	6.28 (133)
H(11)	4.77 (106)
H(12)	10.56 (228)
H(13)	8.89 (186)
H(14)	10.80 (230)
H(15)	4.93 (110)
H(16)	5.42 (118)

The final positional and thermal parameters are reported in Tables 1 and 2.*

Discussion

The crystal structure of diaquobis-(*N,N*-diethylnicotinamide)diisothiocyanatozinc consists of discrete octahedral complexes held together by hydrogen bonds involving the water molecules: $O_w-H \cdots O$ and $O_w-H \cdots S$ (Fig. 1). The whole complex is represented in Fig. 2. The coordination polyhedra are centrosymmetric, so their corners are occupied in *trans* positions by pairs of pyridine N atoms, of isothiocyanate N atoms and of water O atoms. The organic ligand is bound to the zinc atom *via* one donor atom, N(2), the amide O atom not being involved in coordination. This contrasts with the structures of the cadmium and manganese complexes of the same ligand (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972 and 1973). The Zn-N(2) = 2.171 Å bond distance agrees with the distances found in other octahedral Zn-complexes such as hydrazine complexes (2.163–2.177, 2.179–2.206, 2.17 Å, Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a*, *b*, *c*), bis-(*N*-nicotinato)tetraquozinc (2.142 Å, Biagini Cingi, Domiano, Guastini, Musatti & Nardelli, 1971), bis-(*N*-isonicotinato)tetraquozinc (2.144 Å, Biagini Cingi, Gaetani Manfredotti, Guastini, Musatti & Nardelli, 1971). The bond involving the isothiocyanate group, Zn-N(1) = 2.107 Å, is shorter than that found in bis(hydrazine)diisothiocyanatozinc (2.186 Å, Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a*). The zinc-water bond, Zn-O_w = 2.129 Å can be compared with the bond lengths found in the hexaaquozinc cation (Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967) which range from 2.064 to 2.130 Å, suggesting that the bond in the present compound is

* A list of observed and calculated structure factors is available from the authors on request and has also been deposited with the National Lending Library, England as Supplementary Publication No. SUP 30148. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

rather weak. Even longer bonds however have been found (2.157 Å, Biagini Cingi, Gaetani Manfredotti, Guastini, Musatti & Nardelli, 1971; 2.14 Å, van Niekerk, Schoening & Talbot, 1953; 2.18, Lumme, Lundgren & Mark, 1969). On the whole, the set of bond lengths (Table 3) around zinc indicates that the bond involving the isothiocyanate anion is the strongest, probably as a consequence of the anionic character of the ligand.

Table 3. Bond distances and angles

(a) Coordination polyhedron			
Zn-N(1)	2.107 (5) Å	N(1)-Zn-O _w	88.1 (1)°
Zn-N(2)	2.171 (4)	N(2)-Zn-N(1)	90.4 (1)
Zn-O _w	2.129 (3)	N(2)-Zn-O _w	86.9 (1)
(b) Thiocyanato anion			
N(1)-C(1)	1.151 (6) Å	N(1)-C(1)-S(1)	178.9 (4)°
C(1)-S(1)	1.623 (5)	Zn-N(1)-C(1)	164.7 (3)

The isothiocyanate group is linear; the bond lengths C-N = 1.151 and C-S = 1.623 Å agree well with values found previously in the same group and quoted by Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972.

Distances and angles in the organic molecule (Table 4) when compared with those found in other complexes do not show marked changes. The pyridine ring however is perfectly planar (Table 5) and does not show the small distortion from planarity observed in the cadmium and manganese complexes.

In the amide group the bonds radiating from carbon C(7) are planar, whereas the bonds from nitrogen N(3) are not exactly planar in accordance with what was found in the cadmium complex. The angle between the average planes through C(7) and N(3) is 2.4° (8.1° in the cadmium and 7.4° in the manganese complex). The role of interatomic repulsion between the non-bonded atoms C(2) of the pyridine ring and C(10) in determining this rotation is shown by the short distance C(2)···C(10) = 3.339 (7) Å. Also the angle between the planes through C(7) and through the pyridine ring, as determined from the rotation around the bond C(7)-C(3), does not change considerably in the different complexes (71.1° in the present

Table 4. Bond distances and angles in the organic molecule

N(2)-C(2)	1.348 (4) Å	C(2)-H(1)	0.96 (5) Å
N(2)-C(6)	1.340 (5)	C(4)-H(2)	0.99 (5)
C(2)-C(3)	1.377 (5)	C(5)-H(3)	0.96 (7)
C(3)-C(4)	1.391 (6)	C(6)-H(4)	0.92 (4)
C(4)-C(5)	1.385 (5)	C(8)-H(5)	1.04 (6)
C(5)-C(6)	1.372 (6)	C(8)-H(6)	1.07 (5)
C(3)-C(7)	1.503 (5)	C(9)-H(7)	1.05 (7)
C(7)-O	1.240 (5)	C(9)-H(8)	1.08 (6)
C(7)-N(3)	1.333 (5)	C(9)-H(9)	1.10 (10)
N(3)-C(8)	1.480 (5)	C(10)-H(10)	1.06 (7)
C(8)-C(9)	1.506 (11)	C(10)-H(11)	1.04 (5)
N(3)-C(10)	1.468 (6)	C(11)-H(12)	0.98 (8)
C(10)-C(11)	1.493 (12)	C(11)-H(13)	1.01 (6)
		C(11)-H(14)	0.98 (10)

Table 4 (cont.)

C(6)—N(2)—C(2)	117.6 (3)°	N(2)—C(6)—H(4)	118.1 (28)°
N(2)—C(2)—C(3)	123.0 (3)	N(3)—C(8)—H(5)	110.0 (29)
C(2)—C(3)—C(4)	118.8 (3)	N(3)—C(8)—H(6)	109.5 (33)
C(2)—C(3)—C(7)	121.4 (3)	C(9)—C(8)—H(5)	108.6 (29)
C(4)—C(3)—C(7)	119.5 (3)	C(9)—C(8)—H(6)	108.7 (41)
C(3)—C(4)—C(5)	118.1 (3)	H(5)—C(8)—H(6)	107.8 (44)
C(4)—C(5)—C(6)	119.7 (4)	C(8)—C(9)—H(7)	106.4 (55)
C(5)—C(6)—N(2)	122.7 (3)	C(8)—C(9)—H(8)	108.7 (46)
C(3)—C(7)—O	118.2 (3)	C(8)—C(9)—H(9)	110.8 (44)
C(3)—C(7)—N(3)	119.5 (4)	H(7)—C(9)—H(8)	106.5 (58)
N(3)—C(7)—O	122.2 (3)	H(7)—C(9)—H(9)	118.4 (76)
C(7)—N(3)—C(8)	118.0 (4)	H(8)—C(9)—H(9)	105.6 (55)
C(7)—N(3)—C(10)	124.9 (3)	N(3)—C(10)—H(10)	108.4 (42)
C(8)—N(3)—C(10)	116.9 (3)	N(3)—C(10)—H(11)	105.9 (37)
N(3)—C(8)—C(9)	112.2 (4)	C(11)—C(10)—H(10)	108.4 (42)
N(3)—C(10)—C(11)	113.1 (4)	C(11)—C(10)—H(11)	110.4 (38)
N(2)—C(2)—H(1)	115.2 (25)	H(10)—C(10)—H(11)	110.6 (43)
C(3)—C(2)—H(1)	121.8 (25)	C(10)—C(11)—H(12)	113.6 (52)
C(3)—C(4)—H(2)	118.3 (36)	C(10)—C(11)—H(13)	107.8 (56)
C(5)—C(4)—H(2)	123.4 (35)	C(10)—C(11)—H(14)	107.4 (65)
C(4)—C(5)—H(3)	119.9 (34)	H(12)—C(11)—H(13)	115.8 (74)
C(6)—C(5)—H(3)	120.0 (33)	H(12)—C(11)—H(14)	101.5 (81)
C(5)—C(6)—H(4)	119.2 (29)	H(13)—C(11)—H(14)	110.4 (65)

compound, 57.9° and 61.3° in the cadmium and manganese compounds, respectively). An interesting point concerns the distance between the two potential donor atoms of the organic molecule, pyridine N and amide O; this distance which is 4.52 Å in the present com-

ound and 4.56 Å in both the cadmium and manganese compounds remains practically constant, independent of the coordination.

The environment of the water molecule (Table 6) shows how O_w forms a strong, linear hydrogen bond

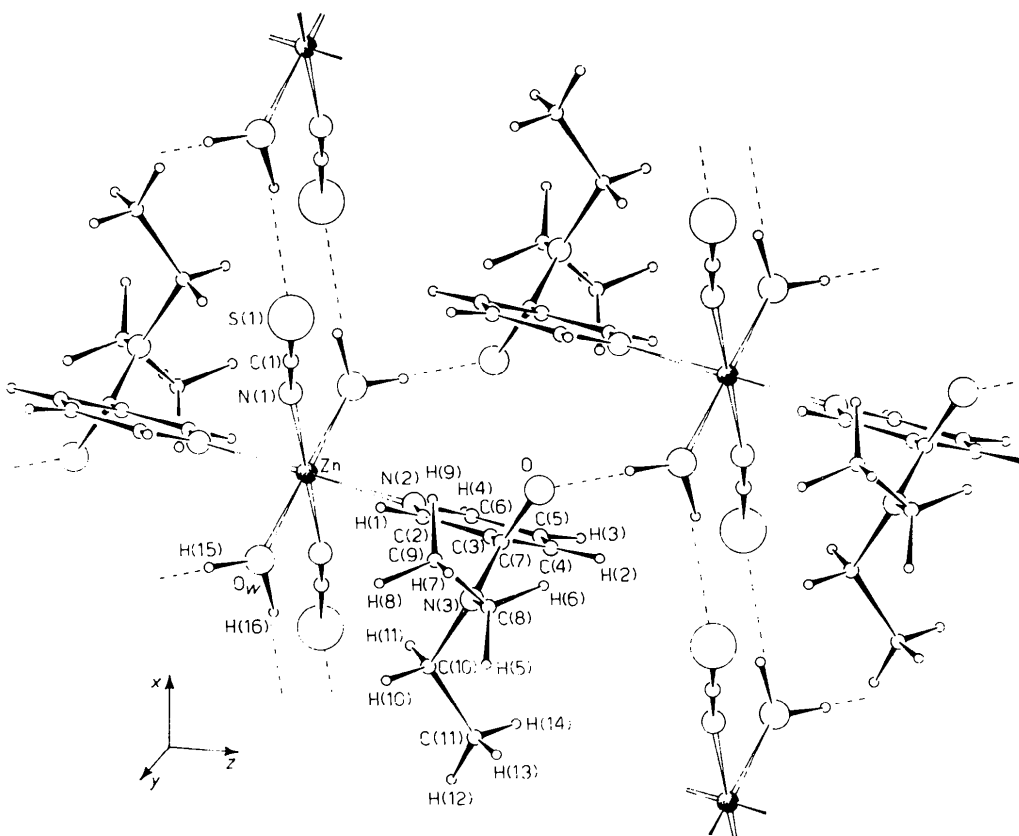


Fig. 1. Clinographic projection of the structure.

Table 5. Analysis of the planarity of groups of atoms

The plane of best fit is defined by atoms with an asterisk.
X, Y, Z are orthogonal coordinates in Å†

$$\text{Equation of the plane of the pyridine ring} \\ -0.9034X + 0.4133Y - 0.1138Z = -0.0266$$

$$\Delta \cdot 10^4 \quad \sigma \cdot 10^4 \\ (\text{\AA}) \quad (\text{\AA})$$

*N(2)	-8	33	
*C(2)	-27	42	
*C(3)	45	42	
*C(4)	-23	48	
*C(5)	-28	51	
*C(6)	41	42	

$$\sum_6 (\Delta/\sigma)^2 = 3.10$$

$$\text{Equation of the plane of the carbonyl carbon [C(7)]} \\ +0.6038X + 0.3366Y - 0.7226Z = -2.9783$$

$$\Delta \cdot 10^4 \quad \sigma \cdot 10^4 \\ (\text{\AA}) \quad (\text{\AA})$$

*C(3)	-24	37	
*C(7)	67	37	
*O	-17	28	
*N(3)	-26	35	

$$\sum_4 (\Delta/\sigma)^2 = 4.62$$

$$\text{Equation of the plane of the amide nitrogen [N(3)]} \\ +0.5958X + 0.3761Y - 0.7096Z = -2.8238$$

$$\Delta \cdot 10^4 \quad \sigma \cdot 10^4 \\ (\text{\AA}) \quad (\text{\AA})$$

*C(7)	-95	37	
*N(3)	334	35	
*C(8)	-121	47	
*C(10)	-118	44	

$$\sum_4 (\Delta/\sigma)^2 = 111.48$$

† Transformation matrix from fractional to orthogonal coordinates:

$$\begin{pmatrix} a \sin \gamma & 0 & -c \sin \alpha \cos \beta^* \\ a \cos \gamma & b & c \cos \alpha \\ 0 & 0 & c \sin \alpha \sin \beta^* \end{pmatrix}$$

with the amide oxygen atom, $O_w-H \cdots O = 2.691 \text{ \AA}$ and a weak, bent hydrogen bond with S(1) of the isothiocyanate groups, $O_w-H \cdots S(1) = 3.225 \text{ \AA}$.

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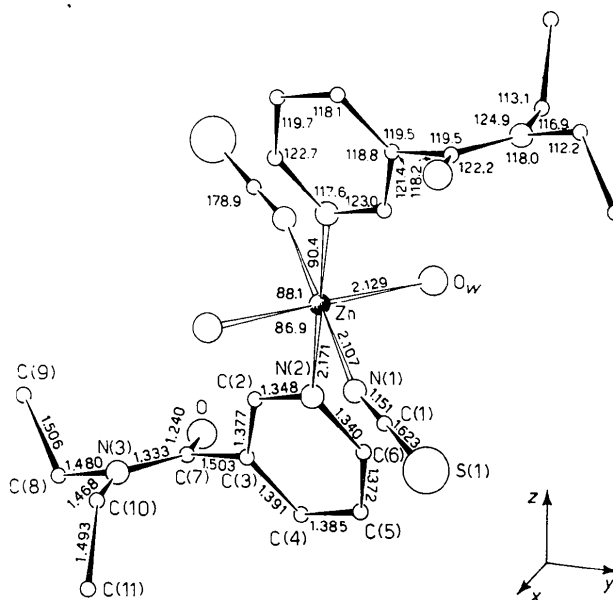


Fig. 2. Bond distances and angles in the complex.

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Table 6. Environment of the water molecule

$O_w-H(15)$	0.94 (6) Å	$H(15)-O_w-H(16)$	102.3 (54)°
$O_w-H(16)$	0.95 (8)	$Zn \cdots O_w-H(15)$	125.2 (35)
$O_w-H(15) \cdots O^i$	2.691 (5)	$Zn \cdots O_w-H(16)$	113.9 (34)
$H(15) \cdots O^i$	1.75 (6)	$Zn \cdots O_w-O^i$	129.5 (1)
$O_w-H(16) \cdots S(1^{ii})$	3.225 (5)	$Zn \cdots O_w-S(1^{ii})$	135.2 (1)
$H(16) \cdots S(1^{ii})$	2.39 (7)	$O_w-H(15) \cdots O^i$	173.3 (51)
$Zn-O_w$	2.129 (3)	$O_w-H(16) \cdots S(1^{ii})$	146.9 (47)
		$H(15)-O_w \cdots O^i$	4.4 (33)
		$H(16)-O_w \cdots S(1^{ii})$	23.9 (34)
		$O^i \cdots O_w \cdots S(1^{ii})$	88.3 (1)

Asymmetric units:

- i $-1+x, y, -1+z$
 ii $-1+x, y, z$