Refinement of the Crystal and Molecular Structure of Tetra-aquabis-[dicyanomercury(II)]zinc(II) Nitrate Trihydrate by Neutron Diffraction

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A neutron diffraction study of the title compound has been carried out. Crystals are monoclinic, space group *C*2/*c*, with $Z = 4$ in a cell of dimensions $a = 17.587(2)$, $b = 6.659(7)$, $c = 16.144(5)$ Å, $\beta = 94.84°$. Full-matrix least-squares refinement led to *R* 0.051. The neutron diffraction results agree well with those from an earlier *X*-ray diffraction study, but in addition show the bonding of the cyanide nitrogen atoms to the zinc, enabling precise location of all hydrogen atoms. Of the seven possible hydrogen bonded interactions suggested previously, six are confirmed. The structure consists of the zinc atom octahedrally co-ordinated by four water molecules and two nearly linear $Hg(CN)_2$ groups.

A NEUTRON diffraction study of tetra-aquabis[dicyanomercury(II)]zinc(II) nitrate trihydrate has been carried out because in a previous *X*-ray determination[1] the presence of heavy atoms dominating the scattering resulted in low accuracy of positional and thermal parameters of the light atoms. Hence whether the carbon or the nitrogen atom of the cyanide is co-ordinated to mercury was not unambiguously determined by the *X*-ray method, and the hydrogen-bonding scheme for the water molecules could not be investigated satisfactorily.

EXPERIMENTAL

Crystal Data.—$[Zn(H_2O)_4\{Hg(CN)_2\}_2][NO_3]_2\cdot 3H_2O$, $M = 768.5$, Monoclinic, $a = 17.587(2)$, $b = 6.659(7)$, $c = 16.144(5)$ Å, $\beta = 94.84°$; $U = 1883.7$ Å^3, $D_m = 2.89(1)$, $Z = 4$, $D_c = 2.70$ g cm^{-3}. Space group *C*2/*c* (No. 15, C^6_{2h}).

Prismatic crystals suitable for neutron diffraction were grown by partial evaporation of an aqueous solution as prisms elongated along *c* with bounding forms (001) and (011). A well formed sample of dimensions 1.1 × 2.7 × 4.5 mm along *a*, *b*, and *c* respectively was mounted on a computer-controlled neutron diffractometer 2TANA at the HIFAR reactor, A.A.E.C. Research Establishment, Lucas Heights. Data were collected at room temperature by use of a crystal-monochromated neutron beam of wavelength $\lambda = 0.981$ Å. The monoclinic cell constants were refined by least-squares techniques from the diffractometer

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[1] C. Mahon, *Inorg. Chem.*, 1971, **10**, 1813.

setting angles observed for 30 reflections distributed in reciprocal space.

Two sets of equivalent reflections were collected by use of the ω—2θ scan technique, and analysis of these equivalents after correction for absorption yielded a unique set of 1 093 reflections on which the final analysis was based. Systematic absences confirmed the space group $C2/c$, as determined in the X-ray study.

Structure Refinement.—All the hydrogen atoms were located from a difference-Fourier synthesis based on the structure factors calculated from the atomic co-ordinates of the non-hydrogen atoms obtained from the X-ray analysis.[1] This synthesis also indicated that the carbon and nitrogen positions suggested in ref. 1 were correct. The structure was refined anisotropically, with all observed data by full-matrix least-squares with experimental weights, using the Brookhaven programme Linus. Neutron scattering lengths used were b_C 0.6626, b_N 0.949, b_O 0.575, b_{Hg} 1.266, b_{Zn} 0.570, and b_H −0.372. As there was evidence for extinction in the structure factors, an isotropic extinction correction [2] was included in the refinements.

TABLE 1

Final atomic co-ordinates and thermal parameters * ($\times 10^4$)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.500 00(0)	0.500 00(0)	0.500 00(0)	18(1)	84(5)	21(2)	−5(2)	5(1)	1(3)
Hg	0.341 91(5)	0.868 78(11)	0.085 47(7)	20(0)	108(2)	28(1)	−12(1)	3(0)	7(1)
C(1)	0.396 71(9)	0.122 98(20)	0.054 52(13)	20(1)	97(3)	27(1)	−12(1)	4(1)	7(2)
C(2)	0.282 75(10)	0.612 61(21)	0.102 62(15)	22(1)	108(4)	46(1)	−16(1)	6(1)	7(2)
N(1)	0.428 98(7)	0.263 70(16)	0.036 89(10)	22(0)	120(3)	31(1)	−13(1)	5(1)	8(1)
N(2)	0.249 56(8)	0.468 59(19)	0.111 81(14)	34(1)	144(3)	95(1)	−29(1)	14(1)	8(2)
N(3)	0.398 22(7)	0.003 57(18)	0.282 95(9)	28(0)	151(3)	24(1)	−4(1)	2(1)	−5(1)
O(1)	0.500 00(0)	0.427 20(45)	0.250 00(0)	36(1)	128(7)	28(2)	0(0)	4(2)	0(0)
O(2)	0.404 99(12)	0.654 78(34)	−0.056 54(16)	19(1)	121(5)	25(2)	0(2)	−0(1)	10(3)
O(3)	0.485 68(12)	0.659 37(32)	0.110 35(18)	22(1)	111(5)	16(2)	−10(2)	2(1)	−9(2)
O(4)	0.209 09(16)	0.057 40(41)	0.141 05(27)	27(1)	146(6)	52(2)	−9(2)	4(1)	−19(3)
O(5)	0.437 38(23)	0.011 93(50)	0.351 52(35)	40(1)	169(7)	27(3)	20(3)	−14(2)	−24(4)
O(6)	0.372 41(24)	0.160 50(53)	0.249 03(30)	42(2)	189(8)	35(3)	3(3)	−10(2)	25(4)
O(7)	0.385 81(25)	0.837 75(54)	0.249 15(28)	59(2)	191(9)	25(2)	−18(3)	1(2)	−19(4)
H(1)	0.455 55(26)	0.340 13(59)	0.251 88(33)	51(2)	224(10)	51(3)	−25(3)	10(2)	11(5)
H(2A)	0.083 97(21)	0.734 28(57)	0.092 37(29)	32(1)	155(8)	38(3)	−2(3)	0(2)	14(4)
H(2B)	0.134 13(21)	0.926 61(48)	0.087 01(29)	24(1)	168(7)	40(3)	−8(3)	−1(2)	−6(4)
H(3A)	0.488 71(24)	0.580 52(54)	0.159 71(34)	35(2)	175(8)	29(3)	0(3)	2(2)	2(4)
H(3B)	0.019 07(21)	0.278 16(48)	0.122 73(28)	34(1)	161(7)	38(2)	−22(3)	3(2)	10(4)
H(4A)	0.216 39(25)	0.198 95(62)	0.131 18(39)	45(2)	156(10)	93(4)	−10(3)	1(2)	−29(5)
H(4B)	0.212 19(52)	0.044 69(121)	0.198 11(52)	108(5)	513(26)	54(5)	−43(8)	8(4)	−48(9)

* The temperature is of the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

Refined atomic parameters are listed in Table 1; final values for the squared structure amplitudes are deposited in Supplementary Publication No. SUP 21387 (10 pp., 1 microfiche).*

The final unweighted and weighted R values based on F^2 are:

$R(F_o^2) = \Sigma||F_o^2| - |F_c^2||/\Sigma|F_o^2| = 0.062$, and $R'(F_o^2) = [\Sigma\omega(F_o^2| - |F_c^2|)^2/\Sigma\omega|F_o^4|]^{\frac{1}{2}} = 0.061$; the conventional R value is 0.051.

DISCUSSION

The Molecular Structure.—The unit cell is illustrated in Figure 1 and the asymmetric unit in Figure 2. The molecule is nearly linear with the maximum deviation from linearity occurring in the Zn-N(1)-C(1) angle of 172.7(2)°. This may result from weak interaction of the nitrogen atom with atoms H(2A) and H(3B) with closest approaches of 2.803(4) and 2.820(5) Å. The $Hg(CN)_2$ ligands are nearly linear. The C(1)-Hg-C(2) angle [173.5(2)°] compares with that [174.1(12)°] from the X-ray study and from a neutron diffraction study [175.0(2)°] of $Hg(CN)_2$.[3] The decrease in angle for the zinc compound may be related to a weak interaction of the atom O(4) which has a closest approach of 2.862(3) to the mercury atom. As indicated by the X-ray structure, the zinc atom has a nearly regular octahedral environment. Bond distances and angles are given in Tables 2 and 3.

The bond distances are in general agreement with those found from the X-ray study and all lie within the

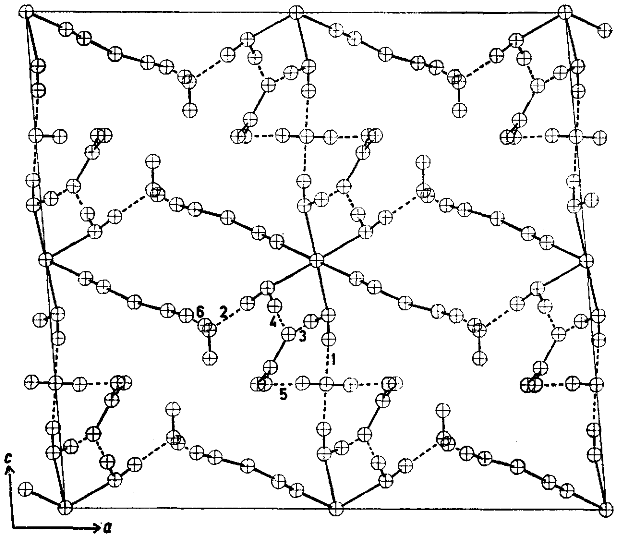

FIGURE 1 A projection of the unit cell on the ac plane. Numbers refer to the hydrogen bonds listed in Table 5

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, **1974**, Index issue.

[2] W. H. Zachariasen, *Acta Cryst.*, 1967, **23**, 558.

[3] R. C. Seccombe and C. L. Kennard, *J. Organometallic Chem.*, 1969, **18**, 243.

typical distances as described there.[1] However, the Hg–C distances are in better agreement with each other and with the neutron diffraction study [3] for $Hg(CN)_2$ in which the distance was 2.015(3) Å. The nitrate group is essentially regular and planar;[4] the small increase in bond length for two of the N–O bonds may be related to hydrogen bonding of the O(5) and O(6) atoms.

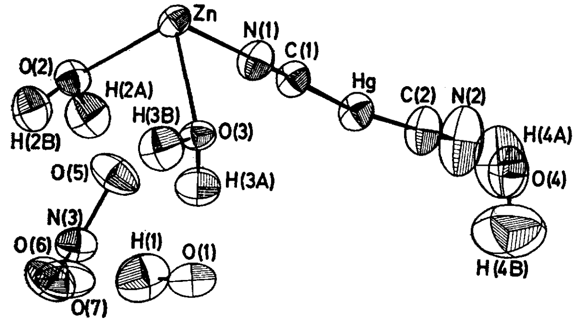

FIGURE 2 The asymmetric unit of the molecule showing thermal ellipsoids at 50% probability level

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

Atoms	Neutron	*X*-Ray *
Zn–O(2)	2.105(2)	2.12(2)
Zn–O(3)	2.107(3)	2.11(2)
Zn–N(1)	2.125(1)	2.13(2)
N(1)–C(1)	1.144(2)	1.11(4)
C(1)–Hg	2.031(2)	2.06(3)
Hg–C(2)	2.029(2)	1.97(3)
C(2)–N(2)	1.139(2)	1.18(4)
N(3)–O(5)	1.255(6)	1.23(3)
N(3)–O(6)	1.247(4)	1.26(3)
N(3)–O(7)	1.243(4)	1.29(3)
O(1)–H(1)	0.976(5)	
O(2)–H(2A)	0.968(5)	
O(2)–H(2B)	0.976(5)	
O(3)–H(3A)	0.952(6)	
O(3)–H(3B)	0.995(4)	
O(4)–H(4A)	0.966(5)	
O(4)–H(4B)	0.922(9)	

* From ref. 1.

In the asymmetric unit (Figure 2), the two water molecules co-ordinated to the zinc atom are coplanar, with no atom more than 0.01 Å of the plane. The zinc atom, which is at a centre of symmetry, lies 1.49 Å from this plane. The $Hg(CN)_2$ section of the molecule is also planar, all atoms being within 0.02 Å of the plane. Details of some planes are in Table 4.

Hydrogen Bonding and Water Molecules.—As suggested by Mahon,[1] all groups in the structure are linked by a network of hydrogen bonds. Of the seven possible hydrogen-bonded interactions suggested, we confirm six; the seventh which was reported as being an O ··· O distance of 3.08(3) Å, we have found as a distance of 3.115 Å, with O(7) ··· H(4A) [2.899(7)] and O(7) ··· H(4B) [2.784(10) Å] ruling out any hydrogen bonded interaction. This evidence for the lack of hydrogen bonding associated with the atom H(4B) is supported by the short O(4) ··· H(4B) bond length and by the atom's anisotropic thermal parameters, which indicate much greater vibrational freedom than any of the other hydrogen atoms, all of which are involved in hydrogen bonding. A view of the hydrogen bonding scheme is shown in Figure 1 and hydrogen bond distances and angles are summarized in Table 5.

TABLE 3

Bond angles (°), with estimated standard deviations in parentheses

N(2)–C(2)–Hg	179.6(4)	H(2A)–O(2)–H(2B)	106.9(4)
C(2)–Hg–C(1)	173.5(2)	Zn–O(3)–H(3A)	115.3(3)
Hg–C(1)–N(1)	178.5(4)	Zn–O(3)–O(1)	113.8(3)
C(1)–N(1)–Zn	172.7(2)	Zn–O(3)–H(3B)	117.5(3)
N(1)–Zn–O(3)	91.2(2)	Zn–O(3)–O(5)	92.3(2)
N(1)–Zn–O(2)	91.2(2)	H(3A)–O(3)–H(3B)	105.8(4)
Zn–O(2)–H(2B)	116.6(3)	H(4A)–O(4)–H(4B)	104.9(7)
Zn–O(2)–O(4)	119.2(4)	O(5)–N(3)–O(6)	120.2(3)
Zn–O(2)–H(2A)	116.2(3)	O(5)–N(3)–O(7)	119.3(3)
Zn–O(2)–O(5)	115.8(4)	O(6)–N(3)–O(7)	120.5(3)
O(2)–Zn–O(3)	88.4(2)		

TABLE 4

Equations of least-squares planes, in the form $Ax + By + Cz - D = 0$

Atoms in plane	*A*	*B*	*C*	*D*	χ *
Plane (1) N(3), O(5)—(7)	0.8749	0.0955	−0.4748	3.6310	0.6660
Plane (2) N(1), C(1), Hg, C(2), N(2)	0.8374	−0.5372	−0.1005	5.2674	123.3
Plane (3) O(2), O(3), H(2A), H(2B), H(3A), H(3B)	0.7783	−0.5274	−0.3407	3.6016	231.6

* $\chi^2 = \Sigma(d/\sigma)^2$, where *d* is distance of atom from relevant plane.

TABLE 5

Hydrogen-bond distances (Å) and angles (°)

Bond type	A–H ··· B–C	A ··· B	H ··· B	∠A–H ··· B	∠H ··· B–C
(1)	O(3)–H(3A) ··· O(1)–H(1)	2.728(3)	1.777(5)	176.3(4)	109.42(3)
(2)	O(2)–H(2B) ··· O(4)–H(4A)	2 724(4)	1.750(5)	175.7(4)	120.5(4)
(2)	O(2)–H(2B) ··· O(4)–H(4B)	2.724(4)	1.750(5)	175.7(4)	115.5(6)
(3)	O(3)–H(3B) ··· O(5)–N(3)	2.753(4)	1.769(5)	169.4(4)	111.3(3)
(4)	O(2)–H(2A) ··· O(5)–N(3)	2.756(5)	1.792(6)	173.6(4)	111.1(3)
(5)	O(1)–H(1) ··· O(6)–N(3)	2.861(4)	1.887(6)	175.7(5)	105.5(3)
(6)	O(4)–H(4A) ··· N(2)–C(2)	2.883(5)	1.921(4)	170.0(5)	166.9(2)

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[4] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

A generally accepted classification of hydrate water molecules based on the co-ordination of lone-pair orbitals has been suggested and modified.[5-7] Appropriate planes and bond lengths and angles for the water molecules in this structure were computed and used to classify them according to the scheme referred to by Ferraris and Franchini-Angela.[7] The classification is summarized in Table 6.

TABLE 6

Distances (Å) and angles (°) (with estimated standard deviations in parentheses), characterizing the water molecules and their environment. The meaning of the symbols is shown in ref. 6

Molecule	Class	Type	C_1	δ_1	δ_2	ε_1
H(2A)–O(2)–H(2B)	(1′)	*J*	Zn	116.6(3)	116.2(3)	45.1
H(3A)–O(3)–H(3B)	(1′)	*J*	Zn	117.5(3)	115.0(3)	45.1
H(4A)–O(4)–H(4B)	(1′)	*K*	H(2B)	114.5(5)	120.3(4)	39.6

Molecule	Class	Type	C_2	C_3	ε_2	ε_3	ε	π
H(1)–O1)–H(1)^1	(2)	*E*	H(3A)	H(3A)^1	55.4	55.4	109.9	94.1

For the three class (1′) water molecules, the water co-ordinates to only one cation along a lone-pair orbital, the cations involved in these cases being zinc and hydrogen, as indicated. For the class (2) water molecule, co-ordination takes place along the two lone-pair orbitals with two hydrogen atoms acting as cations.

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[5] R. Chidambaram, A. Sequeira, and S. K. Sikka, *J. Chem. Phys.*, 1964, **41**, 3616.

[6] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

[7] G. Ferraris and M. Franchini-Angela, *Acta Cryst.*, 1972, **B28**, 3572.