Table 2. *Bond distances* (Å) *and angles* (°)

Ca–O(4)	2·425 (2)	C(12)–C(13)	1·399 (3)
Ca–O(5)	2·406 (2)	C(13)–C(14)	1·363 (3)
Ca–O(6)	2·415 (2)	C(14)–C(15)	1·444 (3)
Ca–O(7)	2·410 (2)	C(15)–C(16)	1·416 (3)
Ca–O(14)	2·412 (2)	C(15)–C(20)	1·425 (2)
Ca–O(15)	2·375 (2)	C(16)–C(17)	1·370 (3)
Ca–O(16)	2·435 (2)	C(17)–C(18)	1·419 (4)
C(1)–C(2)	1·377 (3)	C(18)–C(19)	1·345 (3)
C(1)–C(10)	1·406 (3)	C(19)–C(20)	1·438 (3)
C(2)–C(3)	1·406 (3)	C(1)–N(1)	1·393 (2)
C(3)–C(4)	1·373 (3)	C(11)–N(11)	1·413 (2)
C(4)–C(5)	1·410 (3)	C(4)–S(1)	1·769 (2)
C(5)–C(6)	1·402 (3)	C(14)–S(11)	1·752 (2)
C(5)–C(10)	1·443 (2)	S(1)–O(1)	1·442 (2)
C(6)–C(7)	1·389 (3)	S(1)–O(2)	1·464 (2)
C(7)–C(8)	1·402 (3)	S(1)–O(3)	1·473 (2)
C(8)–C(9)	1·361 (3)	S(11)–O(11)	1·430 (2)
C(9)–C(10)	1·423 (3)	S(11)–O(12)	1·428 (3)
C(11)–C(12)	1·357 (3)	S(11)–O(13)	1·475 (2)
C(11)–C(20)	1·416 (3)		

C(2)–C(1)–C(10)	119·2 (2)	C(13)–C(14)–S(11)	118·2 (1)
C(2)–C(1)–N(1)	119·3 (2)	C(15)–C(14)–S(11)	122·1 (1)
C(10)–C(1)–N(1)	121·3 (2)	C(14)–C(15)–C(16)	122·7 (2)
C(1)–C(2)–C(3)	120·9 (2)	C(14)–C(15)–C(20)	118·2 (2)
C(2)–C(3)–C(4)	120·5 (2)	C(16)–C(15)–C(20)	119·1 (2)
C(3)–C(4)–C(5)	121·1 (2)	C(15)–C(16)–C(17)	121·2 (2)
C(3)–C(4)–S(1)	117·6 (1)	C(16)–C(17)–C(18)	119·6 (2)
C(5)–C(4)–S(1)	121·3 (1)	C(17)–C(18)–C(19)	120·8 (2)
C(4)–C(5)–C(6)	123·0 (2)	C(18)–C(19)–C(20)	121·3 (2)
C(4)–C(5)–C(10)	117·4 (2)	C(11)–C(20)–C(15)	119·6 (2)
C(6)–C(5)–C(10)	119·5 (2)	C(11)–C(20)–C(19)	122·5 (2)
C(5)–C(6)–C(7)	120·0 (2)	C(15)–C(20)–C(19)	117·9 (2)
C(6)–C(7)–C(8)	120·9 (2)	C(4)–S(1)–O(1)	108·2 (1)
C(7)–C(8)–C(9)	120·5 (2)	C(4)–S(1)–O(2)	105·8 (1)
C(8)–C(9)–C(10)	121·1 (2)	C(4)–S(1)–O(3)	106·6 (1)
C(1)–C(10)–C(5)	120·5 (2)	O(1)–S(1)–O(2)	112·5 (1)
C(1)–C(10)–C(9)	121·2 (2)	O(1)–S(1)–O(3)	111·6 (1)
C(5)–C(10)–C(9)	118·2 (2)	O(2)–S(1)–O(3)	111·8 (1)
C(12)–C(11)–C(20)	120·0 (2)	C(14)–S(11)–O(11)	107·2 (1)
C(12)–C(11)–N(11)	120·1 (2)	C(14)–S(11)–O(12)	106·8 (2)
C(20)–C(11)–N(11)	119·9 (2)	C(14)–S(11)–O(13)	106·0 (1)
C(11)–C(12)–C(13)	121·4 (2)	O(11)–S(11)–O(12)	114·6 (1)
C(12)–C(13)–C(14)	121·0 (2)	O(11)–S(11)–O(13)	111·3 (1)
C(13)–C(14)–C(15)	119·7 (2)	O(12)–S(11)–O(13)	110·5 (1)

There are 19 hydrogen bonds per asymmetric unit, three originating from the amino groups with a mean N(H)···O length of 3·121 (5) Å, and sixteen originating at the water oxygens with a mean O(H)···O length of 2·838 (4) and O(H)···N length of 2·874 (4) Å. All the other bond lengths in the molecule have standard values.

There is a vacant site in the structure, which, taken along with the Ca^{2+} ion, corresponds to the two Na^+ ions in a double-size unit cell. This vacant site is surrounded by six O atoms, O(1), O(2), O(11), O(14),

O(15') (screw-axis related) and O(17), which form a distorted octahedron. The centre of this is near (0·249, 0·302, 0·845) and the distances between this point and the O atoms lie between 2·59 and 2·67 Å. This polyhedron shares two of its corners with the neighbouring Ca coordinated polyhedra. The radius of this polyhedron is greater than the radii of either the Na or the Ca polyhedra presumably because of its neutral state.

The pentagonal bipyramid around the Ca^{2+} ion is disposed so that O(5) and O(15) lie at the apices, with the angle O(5)–Ca–O(15) 162·6 (1)°. The equatorial atoms are O(4), O(6), O(14), O(7) and O(16), subtending angles at Ca of, in order, 72·0 (1), 80·0 (1), 77·5 (1), 74·2 (1) and 68·1 (1)°, total 371·8° compared with 360° to be expected if these five atoms were exactly co-planar. The eighth water oxygen O(17), is 5·18 Å from Ca, outside the sphere of coordination.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1970). NRC crystallographic programs for the IBM-360 system. National Research Council, Ottawa, Canada.

BROWN, C. J. & CORBRIDGE, D. E. C. (1966). *Acta Cryst.* 21, 485–494.

COHEN, G. H. & HOARD, J. L. (1966). *J. Am. Chem. Soc.* 88, 3228–3234.

COOK, W. J. & BUGG, C. E. (1976). *Acta Cryst.* B32, 656–659.

CORBRIDGE, D. E. C., BROWN, C. J. & WALLWORK, S. C. (1966). *Acta Cryst.* 20, 698–699.

CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* 10, 504–508.

DAHAN, F. (1975). *Acta Cryst.* B31, 423–426.

DICKENS, B., BROWN, W. E., KRUGER, G. J. & STEWART, J. M. (1973). *Acta Cryst.* B29, 2046–2056.

FERRARIS, G. (1969). *Acta Cryst.* B25, 1544–1550.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

LI, C. T. & CAUGHLAN, C. N. (1965). *Acta Cryst.* 19, 637–645.

MacLENNAN, G. & BEEVERS, C. A. (1955). *Acta Cryst.* 8, 579–583.

PERLOFF, A. (1972). *Acta Cryst.* B28, 2183–2191.

THOMPSON, H. B. & BARTELL, L. S. (1968). *Inorg. Chem.* 7, 488–491.

TRUEBLOOD, K. N., HORN, P. & LUZZATI, V. (1961). *Acta Cryst.* 14, 965–982.

WEST, C. D. (1934). *Z. Kristallogr. Teil A*, 88, 198–204.

WEST, C. D. (1935). *Z. Kristallogr. Teil A*, 91, 480–493.

The Structure of (2,2'-Bipyridine)dichlorozinc(II), $Zn(C_{10}H_8N_2)Cl_2$

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Abstract. $M_r = 292·5$, triclinic, $P\bar{1}$, $a = 8·922$ (1), $b = 9·054$ (1), $c = 7·587$ (1) Å, $\alpha = 93·94$ (1), $\beta = 94·61$ (1), $\gamma = 111·30$ (1)°, $V = 566·1$ (1) Å^3, $Z = 2$, $D_m = 1·70$ (1), $D_x = 1·716$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0·71069$ Å, $\mu = 2·50$ mm^{-1}, $F(000) = 292$, 292 K, $R = 0·0274$, $R_{wF} = 0·0305$ for 1643 unique observed

reflections. The lattice consists of mononuclear units with a ZnN_2Cl_2 kernel. The coordination is similar to that in the 1,10-phenanthroline compound.

Introduction. Earlier papers from this laboratory reported the direct electrochemical synthesis of organometallic halides of zinc and cadmium, which are readily stabilized as adducts with neutral bidentate donor ligands (Habeeb, Osman & Tuck, 1976; Habeeb & Tuck, 1978; Habeeb, Osman & Tuck, 1980). The method can also be used to obtain derivatives of substituted phenyl halides YC_6H_4MX ($Y = CN$, NO_2; $M = Zn$, Cd; $X = Cl$, Br, I) (Said & Tuck, 1982). Attempts to produce compounds in which $Y = CH_3CO$ did not yield the desired compound; amongst the mixture of reaction products were crystals of bpyZnCl$_2$ (bpy = 2,2'-bipyridine). The crystal structure determination was undertaken initially in order to characterize the crystals, since spectroscopic and analytical results were inconclusive. The work was taken to a complete refinement in order to allow comparisons with earlier studies of $ZnCl_2N_2$ species.

Experimental. Synthesis by electrochemical oxidation of anodic zinc in solution of acetonitrile (50 ml), 4-chloroacetophenone (5 ml), 2,2'-bipyridine (0·5 g) and tetraethylammonium chloride (30 mg). The solids which deposited after 2 h were washed with diethyl ether and dried. A crystal of the title compound was selected from this mixture of products.

Pale pink crystal, D_m by flotation (CCl_4/CH_3I), $0·39 \times 0·19 \times 0·15$ mm, Syntex $P2_1$ diffractometer, highly orientated graphite monochromator, data collected and processed as described earlier (Khan, Steevensz, Tuck, Noltes & Corfield, 1980; Khan, Peppe & Tuck, 1983); cell parameters from 15 reflections, $17 \le 2\theta \le 26°$, no change in intensities of three monitor reflections during data collection, space group $P\bar{1}$ used, later assumed correct because of successful refinement, 2166 reflections ($2\theta_{max} = 50°$, $\pm h$, $\pm k$, l) 1643 $[I > 3\sigma(I)]$ unique, Lorentz, polarization, analytical absorption corrections, minimum and maximum 1·31 and 1·81; position of Zn and Cl atoms from sharpened Patterson synthesis, positions of remaining non-H determined from difference Fourier map, anisotropic full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized, 136 parameters, $R = 0·0345$; difference map at this stage showed peaks for all H atoms, H atoms included in subsequent refinement with isotropic temperature factors, 168 parameters, $R = 0·027$ for 1643 reflections, $R_{wF} = 0·030$; in final two cycles of refinement $(\Delta/\sigma)_{max} = 0·1$, final difference map had no features of chemical significance, largest peak 0·3 e Å^{-3}, $S = 0·76$, $w = 1/[\sigma^2(F) + 0·002F^2]$; scattering factors for non-H atoms, including anomalous

dispersion for Zn, Cl, from Ibers & Hamilton (1974), for H from Stewart, Davidson & Simpson (1965); programs included *SHELX* (Sheldrick, 1977), *XANADU* (Roberts & Sheldrick, 1975), *ORTEP* (Johnson, 1965), *ABSORB* (Templeton & Templeton, 1973).

Discussion. The positional and thermal parameters are given in Table 1, and interatomic distances and angles are listed in Table 2.* Fig. 1 shows the molecule, with the atomic numbering scheme.

The Zn—Cl bond distances of 2·210 (1) and 2·198 (1) Å are close to those reported for phenZnCl$_2$ (phen = 1,10-phenanthroline) [2·207 (3), 2·198 (3)] (Reimann, Block & Perloff, 1966); the Cl—Zn—Cl angle [117·1 (1)°] is slightly larger than in the 1,10-phenanthroline adduct [114·7 (1)°]. Zinc–chlorine bond distances in tetrahedral $ZnCl_2L_2$ compounds (L = monodentate nitrogen donor) have been reviewed by Steffen & Palenik (1977). The range of values (2·20–2·30 Å) shows that the Zn—Cl bonds in complexes with bidentate donors are not significantly different from those with pyridine or substituted pyridines, or in the five-coordinate dichloro(2,2:6',2''-terpyridine)zinc (Einstein & Penfold, 1966).

The Zn—N distances are again similar to those in phenZnCl$_2$ [bpy 2·064 (2), 2·053 (2) Å; phen 2·072 (7), 2·050 (7) Å]. The bite angles of 80·3 (1)° (bpy) and 80·4 (3)° (phen) are essentially identical, despite differences in the structure of these ligands. Other zinc–2,2'-bipyridine adducts whose structures have been determined are noted in Table 3, which shows that the present results are in close agreement with those of other authors. Table 3 shows a monotonic inverse dependence of Zn—N bond length and N—Zn—N bond angle. Zinc–nitrogen distances in $ZnCl_2L_2$ complexes with monodentate nitrogen donors (Steffen & Palenik, 1977) are on average slightly shorter than those in complexes with 2,2'-bipyridine.

The C—C and C—N lengths, and the corresponding angles, are identical to previously reported values within experimental error. The twist angle between the two rings is 4·3 (5)°, and the rings are planar within experimental error ($\chi^2 = 4·9$ and 12·3).

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* Lists of structure factors, anisotropic thermal parameters and interatomic distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38839 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{eq}*/U_{iso}$ ($\text{Å}^2 \times 10^3$)
Zn	0·27973 (4)	0·18156 (4)	0·23787 (4)	43·7
Cl(1)	0·1810 (1)	0·2171 (1)	−0·0256 (1)	61·0
Cl(2)	0·2104 (1)	0·2867 (1)	0·4726 (1)	61·1
N(1)	0·5225 (3)	0·2348 (3)	0·2163 (3)	41
N(2)	0·2942 (3)	−0·0349 (3)	0·2789 (3)	42
C(1)	0·6296 (4)	0·3745 (4)	0·1817 (5)	50
C(2)	0·7849 (4)	0·3947 (5)	0·1535 (5)	59
C(3)	0·8327 (4)	0·2689 (5)	0·1608 (5)	61
C(4)	0·7244 (4)	0·1235 (5)	0·1985 (5)	53
C(5)	0·4726 (5)	−0·1778 (4)	0·2894 (5)	55
C(6)	0·3498 (5)	−0·3095 (5)	0·3335 (5)	65
C(7)	0·2009 (5)	−0·3028 (4)	0·3501 (5)	62
C(8)	0·1754 (4)	−0·1637 (4)	0·3209 (4)	54
C(9)	0·5681 (3)	0·1088 (3)	0·2248 (4)	39
C(10)	0·4426 (3)	−0·0409 (3)	0·2643 (4)	39
H(1)	0·592 (4)	0·464 (4)	0·179 (5)	60 (10)
H(2)	0·858 (5)	0·495 (5)	0·130 (5)	63 (10)
H(3)	0·933 (5)	0·282 (4)	0·134 (5)	67 (11)
H(4)	0·749 (4)	0·040 (4)	0·198 (4)	41 (8)
H(5)	0·574 (5)	−0·188 (5)	0·299 (5)	77 (12)
H(6)	0·367 (4)	−0·394 (4)	0·338 (5)	53 (10)
H(7)	0·115 (5)	−0·384 (5)	0·380 (5)	75 (12)
H(8)	0·064 (4)	−0·144 (4)	0·316 (4)	53 (9)

* $U_{eq} = \frac{1}{3}\sum_{i=1}^{3}$ (r.m.s.d.)$_i^2$, r.m.s.d. values are taken from *ORTEP* output.

Fig. 1. *ORTEP* drawing of the molecule.

Table 2. *Interatomic distances (Å) and angles (°) for bpyZnCl$_2$*

Zn–Cl(1)	2·210 (1)	Zn–Cl(2)	2·198 (1)
Zn–N(1)	2·064 (2)	Zn–N(2)	2·053 (2)
N(1)–C(1)	1·338 (4)	N(2)–C(8)	1·338 (4)
N(1)–C(9)	1·347 (4)	N(2)–C(10)	1·358 (4)
C(1)–C(2)	1·368 (5)	C(7)–C(8)	1·388 (5)
C(2)–C(3)	1·357 (6)	C(6)–C(7)	1·367 (6)
C(3)–C(4)	1·386 (6)	C(5)–C(6)	1·378 (5)
C(4)–C(9)	1·384 (4)	C(5)–C(10)	1·382 (4)
C(9)–C(10)	1·479 (4)		
Cl(1)–Zn–Cl(2)	117·1 (1)	Cl(1)–Zn–N(1)	104·2 (1)
Cl(1)–Zn–N(2)	119·6 (1)	Cl(2)–Zn–N(1)	118·7 (1)
Cl(2)–Zn–N(2)	111·6 (1)	N(1)–Zn–N(2)	80·3 (1)
Zn–N(1)–C(1)	126·5 (2)	Zn–N(2)–C(8)	126·6 (2)
Zn–N(1)–C(9)	113·9 (2)	Zn–N(2)–C(10)	114·2 (2)
C(1)–N(1)–C(9)	119·4 (2)	C(8)–N(2)–C(10)	119·2 (3)
N(1)–C(1)–C(2)	122·3 (3)	N(2)–C(8)–C(7)	121·4 (3)
N(1)–C(9)–C(4)	120·4 (3)	N(2)–C(10)–C(5)	121·3 (3)
N(1)–C(9)–C(10)	116·0 (2)	N(2)–C(10)–C(9)	115·5 (2)
C(4)–C(9)–C(10)	123·6 (3)	C(5)–C(10)–C(9)	123·2 (3)
C–C–C(mean)*	119·3 (3)		

* E.s.d. on average value is calculated from $\sigma = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the ith and $\bar{d}$ is the mean of N measurements.

Table 3. Zn—N$_2$ *bond distances and angles in zinc–2,2′-bipyridine complexes*

	Zn–N(Å)	N–Zn–N(°)	Reference
bpyZnCl$_2$	2·064 (2), 2·053 (2)	80·3 (1)	Present work
[(bpy)$_2$Zn(ONO)]NO$_3$	2·076 (9), 2·129 (9)	77·9 (4)	Walsh, Walsh, Murphy & Hathaway (1981)
[bpyZnFe(CO)$_4$]$_2$	2·116 (2), 2·117 (2)	77·75 (8)	Neustadt, Cymbaluk, Ernst & Cagle (1980)
[bpyZn(H$_2$ATP)]$_2$.4H$_2$O*	2·13 (3), 2·14 (4), 2·20 (4), 2·09 (4)	76 (1), 78 (2)	Orioli, Cini, Donati & Mangani (1981)

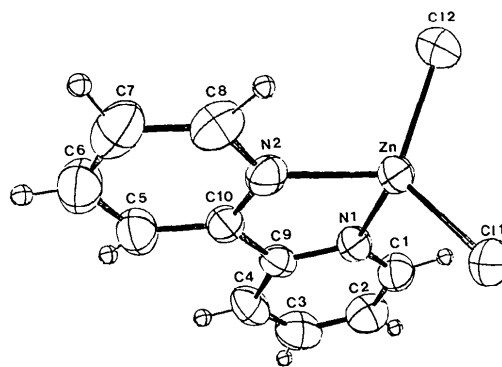* H$_2$ATP = adenosine 5′-triphosphate monoanion.

References

EINSTEIN, F. W. B. & PENFOLD, B. R. (1966). *Acta Cryst.* **20**, 924–926.

HABEEB, J. J., OSMAN, A. & TUCK, D. G. (1976). *Chem. Commun.* pp. 379–380.

HABEEB, J. J., OSMAN, A. TUCK, D. G. (1980). *J. Organomet. Chem.* **185**, 117–127.

HABEEB, J. J. & TUCK, D. G. (1978). *J. Organomet. Chem.* **146**, 213–219.

IBERS, J. A. & HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KHAN, M. A., PEPPE, C. & TUCK, D. G. (1983). *Acta Cryst.* C**39**, 1339–1342.

KHAN, M. A., STEEVENSZ, R. C., TUCK, D. G., NOLTES, J. G. & CORFIELD, P. W. R. (1980). *Inorg. Chem.* **19**, 3407–3411.

NEUSTADT, R. J., CYMBALUK, T. H., ERNST, R. D. & CAGLE, F. W. (1980). *Inorg. Chem.* **19**, 2375–2381.

ORIOLI, P., CINI, R., DONATI, D. & MANGANI, S. (1981). *J. Am. Chem. Soc.* **103**, 4446–4452.

REIMANN, C. W., BLOCK, S. & PERLOFF, A. (1966). *Inorg. Chem.* **5**, 1185–1189.

ROBERTS, P. J. & SHELDRICK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

SAID, F. F. & TUCK, D. G. (1982). *J. Organomet. Chem.* **224**, 121–124.

SHELDRICK, G. M. (1977). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

STEFFEN, W. L. & PALENIK, G. J. (1977). *Inorg. Chem.* **16**, 1119–1126.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TEMPLETON, D. & TEMPLETON, L. (1973). *ABSORB*. An analytical absorption correction program. Univ. of California, Berkeley.

WALSH, A., WALSH, B., MURPHY, B. & HATHAWAY, B. J. (1981). *Acta Cryst.* B**37**, 1512–1520.