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The Adduct Zinc Dicyanide–Bis(2,9-dimethyl-1,10-phenanthroline) Trihydrate

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Abstract. $Zn(CN)_2.2C_{14}H_{12}N_2.3H_2O$, M_r = 588·03, monoclinic, $P2_1/c$, a = 13·8140 (4), b = 18·0104 (7), c = 12·8026 (3) Å, β = 114·836 (2)°, U = 2890·6 (1) Å^3, Z = 4, D_c = 1·351 g cm^{-3}, μ(Cu $K\alpha$) = 15·6 cm^{-1}. The structure has been refined to R = 0·037 for 4216 independent reflexions. The Zn atom exhibits a distorted tetrahedral coordination, one bidentate phenanthroline group forming an angle of 83° with the plane defined by Zn and the two cyanide ligands. The water molecules connect the free phenanthroline molecule to the N atoms of the CN ligands through hydrogen bonds. An asymmetrically bifurcated hydrogen bond has been found.

Introduction. The compound, prepared as described by Cano, Santos & Ballester (1977), has transparent colourless prismatic crystals which slowly get dull superficially. The intensities of all 4818 unique reflexions with $2 < \theta < 65°$ were measured at 22 °C with monochromatic Cu $K\alpha$ radiation (λ = 1·54178 Å) on a fully automated four-circle PW1100 diffractometer. An $\omega/2\theta$ scan technique was used for intensity measurements. There was no appreciable change in the periodically monitored standard reflexions. Absorption effects were corrected using the program *ORABS* (Schwarzenbach, 1972) and Lorentz and polarization factors were applied. 4216 data were accepted as observed on the criterion $I > 2\sigma(I)$.

Scattering factors for neutral atoms and anomalous dispersion corrections for Zn were taken from *International Tables for X-ray Crystallography* (1974). The structure was solved by direct methods with the program *MULTAN* (Main, Woolfson, Declercq & Germain, 1974). The set of phases with the highest figure of merit gave ~60% of the structure, the remaining non-hydrogen atoms being located in a difference synthesis. Anisotropic full-matrix least-squares refinement using unit weights led to a conventional R of 0·054. A difference synthesis calculated with reflexions having $\sin\theta/\lambda < 0·5$ Å^{-1} showed all H atoms as the highest peaks of the map. In order to prevent bias on ΔF *vs* F_o or $\sin\theta/\lambda$, weights were assigned as $w = 1/(a + b\sin\theta/\lambda)^2$, with coefficients calculated by the program *PESOS* (Martínez-Ripoll & Cano, 1975) to be a = 7·12, b = −17·85 for $\sin\theta/\lambda \leq$ 0·37 Å^{-1} and a = 1·01, b = −0·79 for other data. Final refinement, with isotropic temperature factors for H atoms, gave R = 0·037 and R_w = $(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ = 0·040. A final difference synthesis had no electron density greater than 0·2 e Å^{-3}. Table 1 shows the final atomic parameters.*

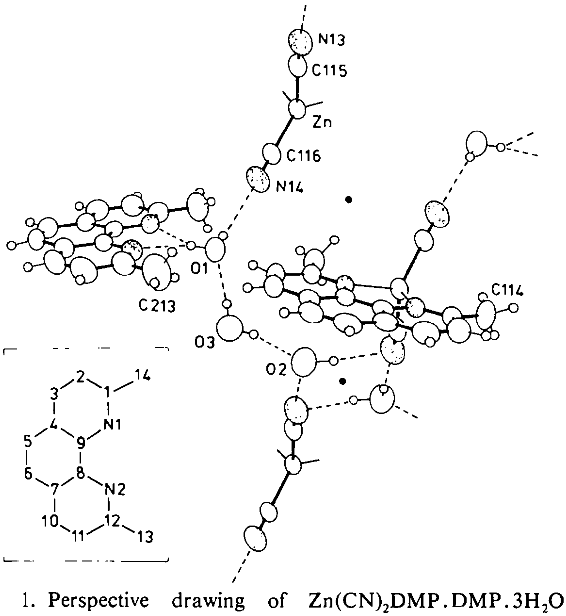

Fig. 1. Perspective drawing of $Zn(CN)_2DMP.DMP.3H_2O$. Dashed lines represent hydrogen bonds. For clarity more atoms than comprise one asymmetric unit are shown, related through the symmetry centres (dark circles). The atom labels of the DMP molecules can be obtained from the scheme in the lower left corner, adding a 1 after the chemical symbol for molecule (1) (right side) or a 2 for molecule (2) (left side). The labels of two methyl groups are shown for reference.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33618 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and, for* H *atoms, isotropic thermal parameters for* $Zn(CN)_2DMP.DMP.3H_2O$

Standard deviations are given in parentheses.

	x	*y*	*z*	*U* (Å² × 10³)
Zn	0·77866 (2)	0·39999 (1)	0·20974 (2)	
C(11)	0·8812 (2)	0·3104 (1)	0·4339 (2)	
C(12)	0·9291 (2)	0·3059 (2)	0·5557 (3)	
C(13)	0·9447 (2)	0·3680 (2)	0·6209 (2)	
C(14)	0·9125 (2)	0·4373 (2)	0·5683 (2)	
C(15)	0·9265 (2)	0·5061 (2)	0·6290 (2)	
C(16)	0·8933 (2)	0·5707 (2)	0·5736 (2)	
C(17)	0·8422 (2)	0·5734 (1)	0·4511 (2)	
C(18)	0·8278 (2)	0·5073 (1)	0·3886 (2)	
C(19)	0·8640 (2)	0·4385 (1)	0·4472 (2)	
C(110)	0·8036 (2)	0·6389 (1)	0·3872 (3)	
C(111)	0·7557 (2)	0·6362 (1)	0·2701 (3)	
C(112)	0·7439 (2)	0·5682 (1)	0·2127 (2)	
C(113)	0·6906 (3)	0·5632 (2)	0·0846 (2)	
C(114)	0·8637 (3)	0·2441 (2)	0·3591 (3)	
C(115)	0·8745 (2)	0·4000 (1)	0·1266 (2)	
C(116)	0·6366 (2)	0·3509 (1)	0·1279 (2)	
N(11)	0·8501 (1)	0·3760 (1)	0·3828 (2)	
N(12)	0·7796 (1)	0·5056 (1)	0·2713 (2)	
N(13)	0·9240 (3)	0·4057 (2)	0·0765 (3)	
N(14)	0·5574 (2)	0·3241 (2)	0·0828 (2)	
C(21)	0·5046 (2)	0·6179 (2)	0·2606 (2)	
C(22)	0·4722 (2)	0·5595 (2)	0·1806 (3)	
C(23)	0·4943 (2)	0·4890 (2)	0·2185 (3)	
C(24)	0·5496 (2)	0·4741 (1)	0·3363 (3)	
C(25)	0·5746 (3)	0·4010 (2)	0·3817 (4)	
C(26)	0·6265 (3)	0·3895 (1)	0·4944 (4)	
C(27)	0·6622 (2)	0·4508 (2)	0·5756 (3)	
C(28)	0·6395 (2)	0·5243 (1)	0·5343 (3)	
C(29)	0·5808 (2)	0·5359 (1)	0·4116 (2)	
C(210)	0·7190 (3)	0·4429 (2)	0·6946 (4)	
C(211)	0·7501 (3)	0·5032 (2)	0·7654 (3)	
C(212)	0·7239 (3)	0·5745 (2)	0·7166 (3)	
C(213)	0·7576 (4)	0·6426 (3)	0·7910 (3)	
C(214)	0·4803 (3)	0·6964 (2)	0·2212 (3)	
N(21)	0·5576 (2)	0·6063 (1)	0·3731 (2)	
N(22)	0·6707 (2)	0·5843 (1)	0·6049 (2)	
O(1)	0·3461 (2)	0·2432 (1)	0·9619 (2)	
O(2)	0·9587 (2)	0·5805 (1)	0·0711 (2)	
O(3)	0·8734 (2)	0·7741 (2)	0·6052 (3)	
H(12)	0·947 (2)	0·259 (2)	0·591 (3)	57 (9)
H(13)	0·976 (2)	0·366 (1)	0·703 (2)	47 (8)
H(15)	0·954 (2)	0·504 (1)	0·706 (2)	35 (7)
H(16)	0·901 (2)	0·617 (1)	0·611 (2)	44 (7)
H(110)	0·814 (2)	0·687 (1)	0·426 (2)	43 (8)
H(111)	0·729 (2)	0·679 (2)	0·227 (3)	49 (9)
H(22)	0·429 (3)	0·569 (2)	0·095 (3)	75 (12)
H(23)	0·474 (3)	0·449 (2)	0·166 (3)	63 (10)
H(25)	0·548 (3)	0·361 (2)	0·321 (3)	60 (10)
H(26)	0·650 (3)	0·342 (2)	0·536 (3)	74 (11)
H(210)	0·737 (3)	0·394 (2)	0·724 (3)	73 (12)
H(211)	0·792 (2)	0·504 (1)	0·849 (2)	39 (7)
H(1131)	0·639 (4)	0·525 (3)	0·066 (4)	102 (17)
H(1132)	0·738 (4)	0·551 (3)	0·055 (4)	100 (16)
H(1133)	0·666 (3)	0·601 (2)	0·056 (4)	82 (13)
H(1141)	0·867 (3)	0·197 (2)	0·402 (3)	86 (13)
H(1142)	0·915 (6)	0·238 (4)	0·345 (6)	99 (25)
H(1143)	0·788 (4)	0·242 (3)	0·288 (5)	107 (18)
H(2131)	0·710 (6)	0·663 (4)	0·802 (6)	100 (23)
H(2132)	0·769 (4)	0·677 (3)	0·757 (4)	105 (16)
H(2133)	0·804 (4)	0·638 (3)	0·872 (5)	104 (17)
H(2141)	0·537 (8)	0·714 (5)	0·199 (8)	108 (38)
H(2142)	0·485 (4)	0·728 (3)	0·276 (5)	103 (18)
H(2143)	0·425 (6)	0·698 (4)	0·156 (6)	103 (25)
H1(01)	0·357 (3)	0·197 (2)	0·970 (3)	70 (11)
H2(01)	0·392 (3)	0·262 (2)	1·001 (4)	75 (13)
H1(02)	0·953 (4)	0·522 (3)	0·065 (5)	97 (19)
H2(02)	0·980 (6)	0·582 (4)	0·010 (7)	98 (28)
H1(03)	0·804 (3)	0·770 (2)	0·575 (3)	73 (12)
H2(03)	0·892 (4)	0·821 (3)	0·599 (5)	91 (19)

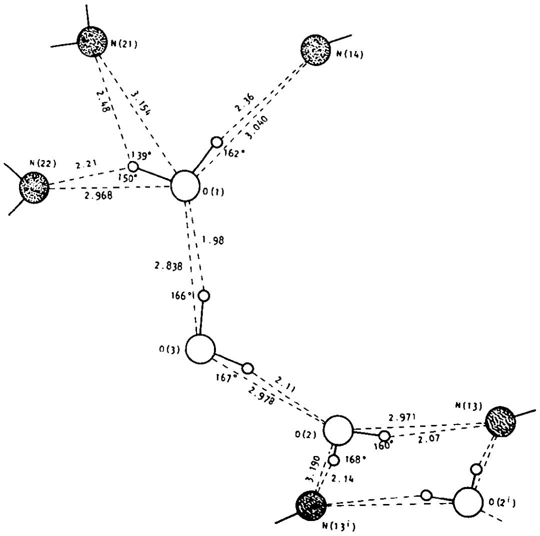

Fig. 2. Schematic drawing showing the geometrical features of the hydrogen-bond network.

Discussion. Cano, Santos & Ballester (1977) reported the preparation, chemical analysis and an infrared study of the hydrated adduct of zinc dicyanide and 2,9-dimethyl-1,10-phenanthroline (DMP), corresponding to the formula $Zn(CN)_2.2DMP.H_2O$.* That study is not conclusive about the coordination around the metal atom. The present investigation has established unequivocally that this compound has the formula $Zn(CN)_2DMP.DMP.3H_2O$. The infrared spectrum of the present compound is identical to that reported for the monohydrate.*

Fig. 1 (Johnson, 1965) shows the geometry of the adduct and the atom labelling. Table 2 shows the bond lengths and angles with their e.s.d.'s. The Zn atom has distorted tetrahedral coordination, one bidentate phenanthroline group [molecule (1), right side of Fig. 1] making an angle of 83° with the plane defined by the Zn atom and the two cyanide ligands. Both DMP molecules are almost planar with an average deviation of 0·015 Å and a maximum deviation of 0·034 Å. The three water molecules form a hydrogen-bonded bridge

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* This compound is formulated as $Zn(CN)_2.2DMP.5H_2O$ in Table II of Cano, Santos & Ballester (1977).

Table 2. *Bond lengths* (Å) *and bond angles* (°) *in* $Zn(CN)_2DMP.DMP.3H_2O$

Standard deviations

	σ (Å)	σ (°)		σ (Å)	σ (°)		σ (Å)	σ (°)
Involving H atoms	0·050	4·00	Involving Zn atoms	0·003	0·10	Involving other atoms	0·004	0·20

	Molecule (1) (*X* = 1)	Molecule (2) (*X* = 2)
Zn–C(*X*15)	2·018	
–C(*X*16)	2·001	
–N(*X*1)	2·058	
–N(*X*2)	2·056	
C(*X*1)–C(*X*2)	1·416	1·403
–C(*X*14)	1·486	1·491
–N(*X*1)	1·331	1·330
C(*X*2)–C(*X*3)	1·357	1·349
–H(*X*2)	0·94	1·016
C(*X*3)–C(*X*4)	1·400	1·400
–H(*X*3)	0·95	0·94
C(*X*4)–C(*X*5)	1·432	1·421
–C(*X*9)	1·407	1·417
C(*X*5)–C(*X*6)	1·338	1·330
–H(*X*5)	0·90	1·02
C(*X*6)–C(*X*7)	1·425	1·454
–H(*X*6)	0·95	0·98
C(*X*7)–C(*X*8)	1·401	1·410
–C(*X*10)	1·407	1·397
C(*X*15)–Zn–C(*X*16)	116·1	
C(*X*15)–Zn–N(*X*1)	116·4	
C(*X*15)–Zn–N(*X*2)	107·6	
C(*X*16)–Zn–N(*X*2)	117·2	
C(*X*16)–Zn–N(*X*1)	113·1	
N(*X*1)–Zn–N(*X*2)	81·9	
N(*X*1)–C(*X*1)–C(*X*14)	117·7	117·3
C(*X*2)–C(*X*1)–C(*X*14)	122·5	120·4
C(*X*2)–C(*X*1)–N(*X*1)	119·8	122·4
C(*X*1)–C(*X*2)–C(*X*3)	120·7	119·2
C(*X*1)–C(*X*2)–H(*X*2)	119	122
C(*X*3)–C(*X*2)–H(*X*2)	120	119
C(*X*2)–C(*X*3)–C(*X*4)	120·2	120·5
C(*X*2)–C(*X*3)–H(*X*3)	122	120
C(*X*4)–C(*X*3)–H(*X*3)	118	119·3
C(*X*3)–C(*X*4)–C(*X*5)	124·6	123·2
C(*X*3)–C(*X*4)–C(*X*9)	116·8	117·0
C(*X*5)–C(*X*4)–C(*X*9)	118·6	119·8
C(*X*4)–C(*X*5)–C(*X*6)	121·8	121·1
C(*X*4)–C(*X*5)–H(*X*5)	117	114
C(*X*6)–C(*X*5)–H(*X*5)	121	125
C(*X*5)–C(*X*6)–C(*X*7)	120·9	121·6
C(*X*5)–C(*X*6)–H(*X*6)	124	129
C(*X*7)–C(*X*6)–H(*X*6)	115	109
C(*X*6)–C(*X*7)–C(*X*10)	124·1	124·7
C(*X*6)–C(*X*7)–C(*X*8)	119·1	119·2
C(*X*8)–C(*X*7)–C(*X*10)	116·9	116·1
C(*X*7)–C(*X*8)–C(*X*9)	120·2	118·6
C(*X*7)–C(*X*8)–N(*X*2)	122·3	122·6
C(*X*9)–C(*X*8)–N(*X*2)	117·5	118·8

	Molecule (1) (*X* = 1)	Molecule (2) (*X* = 2)
C(*X*8)–C(*X*9)	1·426	1·449
–N(*X*2)	1·363	1·359
C(*X*9)–N(*X*1)	1·360	1·349
C(*X*10)–C(*X*11)	1·362	1·362
–H(*X*10)	0·98	0·95
C(*X*11)–C(*X*12)	1·402	1·407
–H(*X*11)	0·93	0·98
C(*X*12)–C(*X*13)	1·493	1·503
–N(*X*2)	1·330	1·316
C(*X*13)–H(*X*131)	0·96	0·82
–H(*X*132)	0·92	0·80
–H(*X*133)	0·78	0·96
C(*X*14)–H(*X*141)	0·99	0·99
–H(*X*142)	0·81	0·90
–H(*X*143)	1·06	0·86
C(*X*15)–N(*X*3)	1·122	
C(*X*16)–N(*X*4)	1·110	
C(*X*4)–C(*X*9)–N(*X*1)	122·4	122·2
C(*X*8)–C(*X*9)–N(*X*1)	118·1	118·1
C(*X*4)–C(*X*9)–C(*X*8)	119·5	119·7
C(*X*7)–C(*X*10)–C(*X*11)	120·1	121·3
C(*X*7)–C(*X*10)–H(*X*10)	120	117
C(*X*11)–C(*X*10)–H(*X*10)	119	121
C(*X*10)–C(*X*11)–C(*X*12)	120·2	118·8
C(*X*10)–C(*X*11)–H(*X*11)	121	128
C(*X*12)–C(*X*11)–H(*X*11)	119	113
C(*X*11)–C(*X*12)–C(*X*13)	121·6	120·7
N(*X*2)–C(*X*12)–C(*X*13)	117·6	117·5
N(*X*2)–C(*X*12)–C(*X*11)	120·8	121·8
H(*X*131)–C(*X*13)–C(*X*12)	107	114
H(*X*131)–C(*X*13)–H(*X*132)	108	96
H(*X*132)–C(*X*13)–H(*X*133)	106	117
H(*X*131)–C(*X*13)–H(*X*133)	113	94
C(*X*12)–C(*X*13)–H(*X*133)	112	120
C(*X*12)–C(*X*13)–H(*X*132)	111	111
C(*X*1)–C(*X*14)–H(*X*141)	111	108
C(*X*1)–C(*X*14)–H(*X*142)	109	114
C(*X*1)–C(*X*14)–H(*X*143)	115	109
H(*X*141)–C(*X*14)–H(*X*142)	100	103
H(*X*141)–C(*X*14)–H(*X*143)	104	102
H(*X*142)–C(*X*14)–H(*X*143)	116	119
N(*X*3)–C(*X*15)–Zn	174·0	
N(*X*4)–C(*X*16)–Zn	179·4	
H1(01)–O(1)–H2(01)	110	
H1(02)–O(2)–H2(02)	90	
H1(03)–O(3)–H2(03)	110	

connecting the N atoms of the cyanide ligands and molecule (2) of DMP, which is attached to the water molecule O(1) through an asymmetrically bifurcated hydrogen bond (Rich & Davidson, 1968). The geometrical features of the hydrogen-bond network are shown in Table 3 and Fig. 2.

The magnitudes of the bond lengths on both sides of a hypothetical line passing through the mid-points of the C(15)–C(16) and C(18)–C(19) bonds suggest the existence of a non-crystallographic twofold axis for the coordinated DMP molecule. A half-normal probability plot (Abrahams & Keve, 1971), calculated from a

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

For standard deviations, see Table 2.

Bond (X–H···Y)	$X\cdots Y$	X–H	H···Y	X–H···Y
O(1)–H1(01)···N(21)*	3·154	0·84	2·48	139
O(1)–H1(01)···N(22)*	2·968	0·84	2·21	150
O(1)–H2(01)···N(14)	3·040	0·71	2·36	162
O(2)–H1(02)···N(13)	3·190	1·06	2·14	168
O(2)–H2(02)···N(13^i)	2·971	0·95	2·07	160
O(3)–H1(03)···O(1)	2·838	0·88	1·98	166
O(3)–H2(03)···O(2)	2·978	0·89	2·11	167

* Asymmetrically bifurcated.

comparison of all intramolecular distances less than 3·5 Å on both sides of this line, gave a linear array with slope $m = 1{\cdot}30$ (6) and zero intercept at $y_o = 0{\cdot}15$ (6). The values of slope and intercept could not be interpreted as significant for the existence of any bias because the data are not independent, but the linearity of the plot, and consequently the high value of the correlation coefficient of the fit ($r = 0{\cdot}98$), support the above-mentioned symmetry of the molecule. A similar comparison applied to the free DMP molecule also gives a linear array, $m = 2{\cdot}49$ (8), $y_o = 0{\cdot}25$ (8), and a correlation coefficient for the fit of $r = 0{\cdot}99$, which also confirms the existence of a twofold axis in this molecule. A comparison of both DMP molecules gives a straight line with $m = 4{\cdot}1$ (1), $y_o = -0{\cdot}6$ (1) and $r = 0{\cdot}98$, indicating their geometrical identity. The interatomic distances less than 3·5 Å obtained by averaging both DMP molecules in the present compound have also been compared with the corresponding distances in the DMP molecule of the $Zn(CN)_2$DMP adduct (Monge, Martinez-Ripoll & Garcia-Blanco, 1977). A linear array was obtained with $m = 1{\cdot}58$ (2), $y_o = 0{\cdot}06$ (2) and $r = 1{\cdot}00$. The high value of the correlation coefficient indicates the DMP molecules were identical in both adducts. The value of the zero intercept, within its standard deviation, shows no bias in either experiment. The value of the slope indicates that the calculated standard deviations for the interatomic distances of both compounds are underestimated by a factor of 1·58.

Most of the calculations were carried out using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid, for the facilities provided on the 1108 Univac computer.

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Caesium Di-μ-sulphido-bis[aquaoxalatooxomolybdate(V)] Dihydrate

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Abstract. $C_4H_8Cs_2Mo_2O_{14}S_2$, $M_r = 801{\cdot}9$, monoclinic, $P2_1/n$, $a = 12{\cdot}427$ (3), $b = 16{\cdot}197$ (2), $c = 9{\cdot}590$ (3) Å, $\beta = 109{\cdot}77$ (2)°, $Z = 4$, $D_x = 2{\cdot}933$ g cm^{-3}, $V = 1816$ (1) Å^3, μ(Mo $K\alpha$) = 55·5 cm^{-1}. The binuclear complex anion approximates C_2 symmetry, with the aqua- and μ-sulphido ligands all *cis* to the oxo ligand. There is no detectable *trans* influence of the oxo ligand, the Mo–O(oxalate) bond lengths *trans* to oxo being 2·155 (5) and 2·164 (6) Å while those *trans* to S are 2·159 (5) and 2·166 (5) Å.