Crystal Structure of Tris-μ-[2,5-di(2-pyridyl)-3,4-diazahexa-2,4-diene]-dicobalt(II) Di[aquotrichlorozincate(II)] Tetrachlorozincate(II) Tetrahydrate: A Helical Binuclear Cobalt(II) Cation

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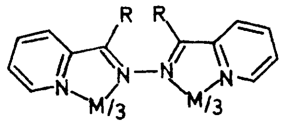
Crystals of the title compound are monoclinic, space group $P2_1/n$, a = 11·47(2), b = 26·88(4), c = 19·89(3) Å, β = 98·57(8)°, Z = 4. The structure was solved by direct methods from diffractometer data, and refined to R 0·082 for 1489 unique observed reflexions. The cation possesses approximately D_3 symmetry; the two cobalt atoms are linked by a helical arrangement of the three quadridentate ligands so that there are three Co–N–N–Co bridges, with Co · · · Co 3·81 Å. The ligands are twisted about their N–N bonds, probably a result of intraligand methyl–methyl repulsions. Each cobalt atom is co-ordinated by a trigonal prism of six nitrogen atoms, which has been twisted by 17·5° from octahedral geometry.

BINUCLEAR complex cations of the type $M_2^{II}L_3^{4+}$ (I; M = Fe, Co, or Ni) were first reported for R = H,[1,2] and more recently for R = Me.[3] In the structure suggested, the three ligands bond symmetrically to two metal ions, each metal atom being co-ordinated by three 2-aldimino-pyridine groups from one half of each ligand, as in the mononuclear complexes recently reported.[4,5] The bulk magnetic susceptibilities of such binuclear nickel(II) cations have been studied[6] to liquid nitrogen temperatures; an analysis of the data using a Heisenberg–Dirac–Van Vleck exchange Hamiltonian model indicated a Ni–Ni antiferromagnetic interaction of *ca.* 8—13 cm^{-1} for R = H. Stratton[3] has reported the room-temperature magnetic moments of $M_2^{II}(pmk)_3^{4+}$ salts [M = Fe, Co, or Ni; pmk = methyl pyridyl ketazine = 2,5-di-(2-pyridyl)-3,4-diazahexa-2,4-diene]. As part of a study of single-crystal magnetic properties of polynuclear transition-metal complexes we have determined the crystal structure of $Co_2(pmk)_3ZnCl_4(ZnCl_3,H_2O)_2,4H_2O$. Although the corresponding $Co_2(pmk)_3^{4+}$ and $Ni_2(pmk)_3^{4+}$ iodides formed excellent block-shaped crystals, both were cubic and hence unsuitable for magnetic anisotropy studies.



(I)

EXPERIMENTAL

A 0·05M-solution of the complex cation $Co_2(pmk)_3^{4+}$ was prepared by the method of Stratton,[3] and to this was added a four-fold excess of aqueous potassium chloride–zinc chloride (1 : 1), a few drops of hydrochloric acid being added to the mixture to dissolve any zinc hydroxide precipitate before it was added to the cation solution. The mixture was allowed to evaporate slowly, when dark red-brown

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[2] W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 4834.

[3] W. J. Stratton, *Inorg. Chem.*, 1970, **9**, 517.

[4] E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parkes, and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2652.

[5] E. B. Fleischer, A. E. Gabala, D. R. Swift, and P. A. Tasker, *Inorg. Chem.*, 1972, **11**, 2775.

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TABLE 1

Atom fractional co-ordinates ($\times 10^4$), and isotropic temperature factors ($Å^2 \times 10^3$)

	x/a	y/b	z/c	U
Co(1)	2444(5)	2637(2)	1645(3)	
Co(2)	2253(5)	3937(2)	2386(3)	
Zn(1)	7902(5)	1497(2)	2579(3)	
Cl(11)	9864(11)	1580(5)	2601(6)	
Cl(12)	6868(11)	2181(6)	2404(7)	
Cl(13)	7506(11)	1082(6)	3478(6)	
Zn(2)	7492(6)	4049(3)	4374(3)	
Cl(21)	5582(12)	4279(7)	4139(7)	
Cl(22)	8493(15)	4503(11)	3706(13)	
Cl(23)	7775(13)	3248(7)	4166(8)	
Cl(24)	8011(21)	4153(7)	5526(9)	
Zn(3)	2088(5)	1063(3)	4664(2)	
Cl(31)	2752(12)	1824(6)	4552(7)	
Cl(32)	2932(10)	419(6)	4231(6)	
Cl(33)	1824(10)	918(6)	5738(5)	
N(101)	3669(33)	4434(15)	2356(14)	44(11)
N(102)	3778(30)	3441(14)	2518(13)	35(10)
N(103)	3651(25)	2947(13)	2433(14)	26(10)
N(104)	2935(27)	2061(14)	2298(14)	36(10)
C(101)	3552(47)	4945(22)	2293(19)	72(17)
C(102)	4552(49)	5257(23)	2317(21)	97(19)
C(103)	5615(49)	5015(23)	2365(20)	90(19)
C(104)	5745(42)	4514(19)	2354(18)	50(15)
C(105)	4737(49)	4248(19)	2399(18)	51(15)
C(106)	4759(49)	3697(19)	2373(19)	57(15)
C(107)	5885(39)	3388(18)	2277(18)	56(15)
C(108)	4672(33)	2883(16)	3659(17)	39(13)
C(109)	4018(32)	2694(17)	2972(19)	38(13)
C(110)	3776(34)	2119(16)	2849(18)	26(12)
C(111)	4356(39)	1788(20)	3291(21)	66(16)
C(112)	4160(37)	1302(18)	3088(19)	53(14)
C(113)	3277(36)	1162(19)	2563(19)	60(15)
C(114)	2704(32)	1549(16)	2180(17)	29(12)
N(201)	852(25)	4399(13)	1942(16)	32(10)
N(202)	1943(27)	3776(13)	1316(13)	30(10)
N(203)	2496(29)	3318(13)	1146(14)	34(10)
N(204)	3733(28)	2552(14)	1026(14)	38(11)
C(201)	346(37)	4751(17)	2306(19)	45(14)
C(202)	−594(36)	5033(17)	1952(21)	52(14)
C(203)	−936(36)	4995(18)	1299(21)	58(16)
C(204)	−408(31)	4619(15)	922(17)	26(12)
C(205)	480(29)	4329(14)	1305(17)	7(11)
C(206)	1055(33)	3933(16)	921(17)	24(11)
C(207)	606(33)	3814(17)	202(17)	50(14)
C(208)	3602(35)	3898(19)	457(18)	55(14)
C(209)	3330(41)	3383(19)	760(21)	55(15)
C(210)	4012(38)	2948(20)	691(19)	46(14)
C(211)	4987(34)	2925(17)	288(17)	40(13)
C(212)	5611(34)	2490(16)	336(16)	34(13)
C(213)	5322(34)	2078(19)	677(18)	50(14)
C(214)	4302(39)	2091(21)	1026(19)	67(16)
N(301)	2059(24)	4028(13)	3413(13)	19(9)
N(302)	1245(27)	3334(13)	2598(16)	37(11)
N(303)	966(25)	2915(12)	2115(13)	23(9)
N(304)	958(30)	2337(15)	1057(15)	40(11)
C(301)	2421(36)	4406(18)	3799(21)	60(15)
C(302)	2135(36)	4478(19)	4437(20)	57(15)
C(303)	1457(36)	4126(18)	4686(20)	56(15)
C(304)	979(35)	3695(18)	4281(20)	53(14)
C(305)	1347(35)	3673(18)	3613(20)	41(13)
C(306)	996(35)	3242(18)	3181(21)	36(13)
C(307)	406(37)	2792(19)	3438(19)	63(15)
C(308)	−1194(38)	3158(19)	1848(18)	63(15)
C(309)	−38(32)	2844(14)	1787(16)	9(11)
C(310)	−24(45)	2470(18)	1220(20)	56(15)
C(311)	−1081(49)	2250(22)	984(23)	92(18)
C(312)	−1115(44)	1843(21)	520(21)	79(18)
C(313)	−104(47)	1736(20)	301(21)	78(17)
C(314)	972(38)	1976(18)	600(20)	53(15)
O(14)	7353(28)	1056(15)	1709(14)	109(12)
O(34)	426(20)	1094(11)	4128(10)	47(8)
O(41)	7029(29)	2079(15)	4372(14)	108(13)
O(61)	8811(34)	513(17)	1054(18)	159(16)
O(71)	5431(28)	551(14)	1376(14)	115(13)
O(81)	9456(37)	183(19)	4396(18)	189(19)

crystals formed (Found: C, 33·5; H, 3·3; Cl, 23·0; N, 11·2. Calc. for $C_{42}H_{54}Cl_{10}Co_2N_{12}O_6Zn_3$: C, 33·4; H, 3·7; Cl, 23·5; N, 11·1%).

Intensities were determined on a Stoe Stadi-2 two-circle diffractometer for two crystals (layers 0—9*kl* and *h*0—6*l*), with Mo-K_α radiation, and a graphite crystal monochromator. Data were collected in an approximately ' constant count ' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. A stationary background–ω scan–stationary background technique was employed, with variable reflexion width, and with the background-measurement time proportional to the step-measurement time. Of 4268 reflexions measured, 260 were rejected mainly because of background imbalance or because the net count was $<2\cdot5\sigma$ based on counting statistics. Interlayer scale factors were calculated from common reflexions by a linear least-squares method.[7] Averaging equivalent reflexions led to 1489 unique observed reflexions. Lorentz, polarisation, and absorption corrections were applied. Unit-cell dimensions were obtained by a least-squares fit to the diffractometer ω angle measurements.

RESULTS

Crystal Data.—$C_{42}H_{54}Cl_{10}Co_2N_{12}O_6Zn_3$, $M = 1509\cdot3$, Monoclinic, $a = 11\cdot47(2)$, $b = 26\cdot88(4)$, $c = 19\cdot89(3)$ Å, $\beta = 98\cdot57(8)°$, $D_m = 1\cdot69$, $Z = 4$, $D_c = 1\cdot67$, $U = 6009\cdot6$ Å^3, $F(000) = 3008$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å, $\mu(\text{Mo-}K_\alpha) = 22\cdot2$ cm^{-1}. Space group $P2_1/n$ from systematic absences: $0k0$ with k odd, $h0l$ with $h + l$ odd. All atoms occupy the four-fold general positions of the set $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. $M_2(pmk)_3I_4,xH_2O$ (M = Ni, $x = 2$), cubic, $a = 21\cdot6(1)$ Å.

Structure Solution and Refinement.—The structure was solved by multisolution Σ_2 refinement; three reflexions were used to define the origin, and a further four to generate 16 initial sign permutations. The best E map revealed all the cobalt, zinc, and chlorine atom positions, together with those of two oxygen atoms and of most of the three pmk ligands [except N(303), N(304), and C(308)—(314)]. The remaining ligand atoms and the four free water molecules were located from difference electron-density syntheses.

TABLE 2

Heavy-atom anisotropic temperature factors * ($\times 10^4$)

Co(1)	19(4)	38(5)	39(4)	−10(4)	23(3)	−5(4)
Co(2)	21(4)	27(5)	65(4)	0(4)	17(3)	1(4)
Zn(1)	51(5)	47(5)	96(5)	10(4)	−3(3)	−3(5)
Cl(11)	43(10)	53(12)	146(12)	27(10)	25(9)	10(10)
Cl(12)	69(11)	78(14)	163(13)	38(12)	61(10)	31(11)
Cl(13)	64(11)	88(13)	133(12)	25(12)	2(9)	−25(12)
Zn(2)	82(6)	82(7)	168(7)	48(6)	−47(5)	−38(6)
Cl(21)	89(13)	130(18)	133(12)	64(12)	16(10)	1(13)
Cl(22)	71(14)	376(42)	474(34)	334(34)	8(18)	−29(22)
Cl(23)	69(12)	131(18)	177(14)	24(14)	37(11)	−30(13)
Cl(24)	386(32)	86(16)	195(18)	35(14)	−204(20)	−42(20)
Zn(3)	38(4)	84(6)	70(4)	−17(4)	16(3)	16(5)
Cl(31)	60(11)	102(16)	148(13)	−17(12)	45(9)	9(12)
Cl(32)	65(10)	108(15)	71(10)	−33(9)	−3(8)	28(11)
Cl(33)	64(11)	108(15)	73(8)	−2(10)	22(7)	44(11)

* In the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)$.

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[7] A. D. Rae and A. B. Blake, *Acta Cryst.*, 1966, **20**, 586.

TABLE 3

Hydrogen atom fractional co-ordinates (Å × 10^4)

	z/a	y/b	z/c	U
H(101)	2740(47)	5090(22)	2233(19)	72(17)
H(102)	4479(49)	5628(23)	2297(21)	97(19)
H(103)	6337(49)	5228(23)	2410(20)	90(19)
H(104)	6521(42)	4350(19)	2332(18)	50(15)
H(111)	4880(39)	1882(20)	3720(21)	66(16)
H(112)	4681(37)	1037(18)	3324(19)	53(14)
H(113)	3076(36)	803(19)	2477(19)	60(15)
H(114)	2087(32)	1458(16)	1789(17)	29(12)
H(201)	639(37)	4801(17)	2800(19)	45(14)
H(202)	−1002(36)	5278(17)	2216(21)	52(14)
H(203)	−1562(36)	5222(18)	1066(21)	58(16)
H(204)	−653(31)	4568(15)	423(17)	26(12)
H(211)	5150(34)	3210(17)	−7(17)	40(13)
H(212)	6341(34)	2477(16)	118(16)	34(13)
H(213)	5810(34)	1769(19)	677(18)	50(14)
H(214)	4028(39)	1789(21)	1252(19)	67(16)
H(301)	2962(36)	4648(18)	3622(21)	60(15)
H(302)	2419(36)	4779(19)	4708(20)	57(15)
H(303)	1256(36)	4175(18)	5154(20)	56(15)
H(304)	471(35)	3437(18)	4454(20)	53(14)
H(311)	−1824(49)	2370(22)	1139(23)	92(18)
H(312)	−1858(44)	1654(21)	365(21)	79(18)
H(313)	−100(47)	1481(20)	−65(21)	78(17)
H(314)	1742(38)	1871(18)	466(20)	53(15)

TABLE 4

Distances (Å)

(*a*) Ligand bond lengths

N(101)–C(101)	1·38(6)	C(204)–C(205)	1·41(4)
N(101)–C(105)	1·31(5)	C(205)–C(206)	1·52(5)
N(102)–N(103)	1·34(4)	C(206)–C(207)	1·48(4)
N(102)–C(106)	1·39(5)	C(208)–C(209)	1·56(6)
N(103)–C(109)	1·29(4)	C(210)–C(209)	1·42(6)
N(104)–C(110)	1·36(4)	C(210)–C(211)	1·47(5)
N(104)–C(114)	1·42(5)	C(211)–C(212)	1·37(5)
C(101)–C(102)	1·41(6)	C(212)–C(213)	1·37(5)
C(102)–C(103)	1·37(6)	C(213)–C(214)	1·45(5)
C(103)–C(104)	1·36(7)	N(301)–C(305)	1·35(5)
C(104)–C(105)	1·37(6)	N(301)–C(301)	1·30(5)
C(105)–C(106)	1·48(6)	N(302)–C(306)	1·26(4)
C(106)–C(107)	1·57(6)	N(302)–N(303)	1·49(4)
C(108)–C(109)	1·54(5)	N(303)–C(309)	1·25(4)
C(110)–C(109)	1·58(6)	N(304)–C(310)	1·27(5)
C(110)–C(111)	1·35(5)	N(304)–C(314)	1·33(5)
C(111)–C(112)	1·37(6)	C(301)–C(302)	1·37(4)
C(112)–C(113)	1·39(5)	C(302)–C(303)	1·36(5)
C(113)–C(114)	1·39(5)	C(303)–C(304)	1·47(5)
N(201)–C(201)	1·37(5)	C(304)–C(305)	1·45(4)
N(201)–C(205)	1·29(3)	C(305)–C(306)	1·46(5)
N(202)–C(206)	1·26(4)	C(306)–C(307)	1·51(6)
N(202)–N(203)	1·45(4)	C(308)–C(309)	1·59(5)
N(203)–C(209)	1·32(4)	C(310)–C(309)	1·51(5)
N(204)–C(210)	1·32(5)	C(310)–C(311)	1·37(6)
N(204)–C(214)	1·40(5)	C(311)–C(312)	1·43(6)
C(201)–C(202)	1·42(5)	C(312)–C(313)	1·33(5)
C(202)–C(203)	1·30(4)	C(313)–C(314)	1·44(6)
C(203)–C(204)	1·44(5)		

(*b*) Cobalt–nitrogen bond lengths

Co(1)–N(103)	2·10(3)	N(101)–Co(2)	2·11(4)
Co(1)–N(203)	2·09(4)	N(201)–Co(2)	2·12(3)
Co(1)–N(303)	2·18(3)	N(301)–Co(2)	2·10(3)
N(104)–Co(1)	2·04(4)	N(102)–Co(2)	2·18(3)
N(204)–Co(1)	2·07(4)	N(202)–Co(2)	2·15(3)
N(304)–Co(1)	2·08(4)	N(302)–Co(2)	2·07(4)

(*c*) Anion bond lengths

Zn(1)–Cl(11)	2·25(2)	Zn(2)–Cl(23)	2·22(2)
Zn(1)–Cl(12)	2·19(2)	Zn(2)–Cl(24)	2·30(2)
Zn(1)–Cl(13)	2·21(2)	Zn(3)–Cl(31)	2·20(2)
Zn(1)–O(14)	2·11(4)	Zn(3)–Cl(32)	2·22(2)
Zn(2)–Cl(21)	2·26(2)	Zn(3)–Cl(33)	2·24(1)
Zn(2)–Cl(22)	2·24(2)	Zn(3)–O(34)	2·04(2)

The structure was refined by full-matrix least-squares, in the final cycles with anisotropic temperature factors for the cobalt, zinc, and chlorine atoms, and isotropic temperature factors for the light atoms. The hydrogen atoms attached to the pyridine rings were inserted in calculated positions, and the refinement completed with the constraint that the C···H vectors remained constant in magnitude and direction, although the carbon atoms were free to move. The hydrogen-atom temperature factors were constrained to be equal to those of the carbon atoms to which they were attached. We were not successful in locating the methyl-group hydrogens or the hydrogen atoms of the water molecules. In the final cycles of refinement a total of 367 parameters were varied independently, with a weighting scheme $w = \Sigma[\sigma^2(N) + 0{\cdot}001N^2]^{-1}/(50{\cdot}79 + |F_o| + 0{\cdot}00374F_o^2)$, where N is the net peak count, and the summation is over equivalent reflexions. Complex neutral atom scattering factors were employed for all atoms.[8,9] The final value of R' [$= \Sigma w|F_o - F_c|/\Sigma w|F_o|$] was 0·082, with a corresponding unweighted R index of 0·082. An analysis of variance is listed with the structure factors (see later), and atom co-ordinates and temperature factors in Tables 1—3. The resulting bond lengths and angles are given in Tables 4 and 5; the standard deviations were estimated by use of the full covariance matrix, and include contributions from the estimated errors in the cell constants. Shortest non-bonded distances are given in Table 6. Observed and calculated structure factors are listed in Supplementary

TABLE 5

Angles (°)

(*a*) Cation ligand bond angles

N(102)–C(105)–C(104)	149(4)	C(207)–C(206)–N(202)	131(4)
N(102)–C(106)–C(105)	118(5)	C(208)–C(209)–C(210)	123(5)
N(103)–C(109)–C(110)	111(4)	C(208)–C(209)–N(203)	123(5)
C(102)–C(101)–N(101)	121(5)	C(209)–N(203)–N(202)	114(4)
C(103)–C(102)–C(101)	115(6)	C(209)–C(210)–N(204)	116(4)
C(104)–C(103)–C(102)	125(6)	C(209)–C(210)–C(211)	124(5)
C(104)–C(105)–N(101)	126(5)	C(211)–C(210)–N(204)	120(5)
C(105)–N(101)–C(101)	117(5)	C(212)–C(211)–C(210)	115(4)
C(105)–C(104)–C(103)	115(5)	C(213)–C(212)–C(211)	124(5)
C(106)–N(102)–N(103)	123(4)	C(213)–C(214)–N(204)	116(5)
C(106)–C(105)–N(101)	113(6)	C(214)–C(213)–C(212)	119(5)
C(106)–C(105)–C(104)	120(6)	C(214)–N(204)–C(210)	124(4)
C(107)–C(106)–N(102)	118(4)		
C(107)–C(106)–C(105)	123(5)	N(302)–C(305)–C(304)	151(4)
C(108)–C(109)–N(103)	128(4)	N(302)–C(306)–C(305)	108(5)
C(108)–C(109)–C(110)	121(4)	N(303)–C(309)–C(310)	112(4)
C(109)–N(103)–N(102)	114(3)	C(302)–C(301)–N(301)	124(5)
C(109)–C(110)–N(104)	109(4)	C(303)–C(302)–C(301)	118(5)
C(109)–C(110)–C(111)	119(4)	C(304)–C(303)–C(302)	122(4)
C(111)–C(110)–N(104)	132(5)	C(304)–C(305)–N(301)	121(4)
C(112)–C(111)–C(110)	113(4)	C(305)–N(301)–C(301)	122(4)
C(113)–C(112)–C(111)	123(5)	C(305)–C(304)–C(303)	113(5)
C(113)–C(114)–N(104)	125(4)	C(306)–N(302)–N(303)	113(4)
C(114)–N(104)–C(110)	110(4)	C(306)–C(305)–N(301)	121(4)
C(114)–C(113)–C(112)	116(5)	C(306)–C(305)–C(304)	119(5)
		C(307)–C(306)–C(305)	122(4)
N(202)–C(205)–C(204)	148(3)	C(309)–N(303)–N(302)	123(3)
N(202)–C(206)–C(205)	107(3)	C(307)–C(306)–N(302)	130(4)
N(203)–C(209)–C(210)	114(5)	C(308)–C(309)–C(310)	121(4)
C(202)–C(201)–N(201)	117(4)	C(308)–C(309)–N(303)	126(4)
C(203)–C(202)–C(201)	123(5)	C(309)–C(310)–N(304)	119(5)
C(204)–C(203)–C(202)	119(4)	C(309)–C(310)–C(311)	116(5)
C(204)–C(205)–N(201)	124(4)	C(311)–C(310)–N(304)	124(5)
C(205)–C(204)–C(203)	115(4)	C(312)–C(311)–C(310)	119(6)
C(205)–N(201)–C(201)	121(4)	C(313)–C(312)–C(311)	116(6)
C(206)–N(202)–N(203)	119(3)	C(313)–C(314)–N(304)	121(5)
C(206)–C(205)–N(201)	119(4)	C(314)–N(304)–C(310)	119(4)
C(206)–C(205)–C(204)	117(3)	C(314)–C(313)–C(312)	120(5)
C(207)–C(206)–C(205)	122(4)		

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[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

TABLE 5 (*Continued*)

(*b*) Cobalt ligand bond angles

Co(1)–N(104)–C(110)	121(3)	Co(2)–N(102)–C(105)	79(2)
Co(1)–N(104)–C(114)	127(3)	Co(2)–N(201)–C(201)	123(3)
Co(1)–N(204)–C(210)	117(3)	Co(2)–N(201)–C(205)	116(3)
Co(1)–N(204)–C(214)	118(3)	Co(2)–N(101)–C(101)	124(4)
Co(1)–N(304)–C(310)	115(4)	Co(2)–N(301)–C(305)	111(3)
Co(1)–N(304)–C(314)	125(3)	Co(2)–N(301)–C(301)	126(3)
N(103)–Co(1)–N(104)	75(1)	N(102)–Co(2)–N(101)	78(2)
N(103)–Co(1)–N(204)	92(1)	N(102)–Co(2)–N(201)	162(1)
N(103)–Co(1)–N(304)	165(1)	N(102)–Co(2)–N(301)	99(1)
N(203)–Co(1)–N(103)	87(1)	N(201)–Co(2)–N(101)	99(2)
N(203)–Co(1)–N(104)	160(1)	N(202)–Co(2)–N(101)	97(1)
N(203)–Co(1)–N(204)	75(2)	N(202)–Co(2)–N(201)	73(1)
N(203)–Co(1)–N(304)	99(1)	N(202)–Co(2)–N(301)	164(1)
N(204)–Co(1)–N(104)	98(1)	N(202)–Co(2)–N(102)	90(1)
N(303)–Co(1)–N(103)	91(1)	N(301)–Co(2)–N(101)	98(1)
N(303)–Co(1)–N(203)	89(1)	N(301)–Co(2)–N(201)	99(1)
N(303)–Co(1)–N(104)	98(1)	N(302)–Co(2)–N(101)	163(1)
N(303)–Co(1)–N(204)	163(1)	N(302)–Co(2)–N(201)	98(1)
N(303)–Co(1)–N(304)	76(2)	N(302)–Co(2)–N(301)	75(1)
N(304)–Co(1)–N(204)	103(1)	N(302)–Co(2)–N(102)	88(1)
N(304)–Co(1)–N(104)	101(1)	N(302)–Co(2)–N(202)	92(1)
N(102)–N(103)–Co(1)	122(3)	N(103)–N(102)–Co(2)	121(3)
C(109)–N(103)–Co(1)	120(3)	C(106)–N(102)–Co(2)	109(3)
N(202)–N(203)–Co(1)	126(2)	N(203)–N(202)–Co(2)	113(2)
C(209)–N(203)–Co(1)	118(3)	C(206)–N(202)–Co(2)	123(3)
N(302)–N(303)–Co(1)	115(2)	N(303)–N(302)–Co(2)	122(2)
C(309)–N(303)–Co(1)	116(3)	C(306)–N(302)–Co(2)	123(3)
Co(2)–N(101)–C(105)	118(4)		

(*c*) Anion bond angles

Cl(13)–Zn(1)–Cl(12)	112(1)	Cl(24)–Zn(2)–Cl(21)	106(1)
Cl(13)–Zn(1)–Cl(11)	111(0)	Cl(24)–Zn(2)–Cl(22)	116(1)
Cl(12)–Zn(1)–Cl(11)	116(1)	Cl(24)–Zn(2)–Cl(23)	106(1)
O(14)–Zn(1)–Cl(11)	104(1)	Cl(32)–Zn(3)–Cl(31)	120(0)
O(14)–Zn(1)–Cl(12)	105(1)	Cl(33)–Zn(3)–Cl(31)	111(1)
O(14)–Zn(1)–Cl(13)	108(1)	Cl(33)–Zn(3)–Cl(32)	111(1)
Cl(22)–Zn(2)–Cl(21)	107(1)	O(34)–Zn(3)–Cl(31)	103(1)
Cl(23)–Zn(2)–Cl(21)	113(1)	O(34)–Zn(3)–Cl(32)	105(1)
Cl(23)–Zn(2)–Cl(22)	108(1)	O(34)–Zn(3)–Cl(33)	105(1)

Publication No. SUP 20945 (10 pp., 1 microfiche).* The numbering of the atoms in the cation is shown in Figure 1.

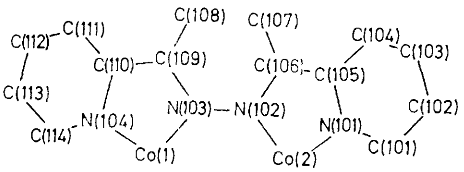

FIGURE 1 Numbering scheme for atoms in the cation. Numbering in the other two ligands (not shown) is similar, the first digit being changed to 2 or 3

DISCUSSION

The presence of a binuclear cation with three bridging quadridentate pmk ligands has been confirmed. The ligands bridge the cobalt ions in a helical manner to yield a cation of approximate D_3 symmetry. The ligand dimensions are much as expected, with a mean N–N bond length of 1·43 Å. The Co · · · Co distance is 3·81(1) Å, and the mean Co–N–N angle is 120·1°, consistent with sp^2 hybridisation for these nitrogen atoms. A stereoscopic view of the cation is presented in Figure 2. The helical arrangement can be seen in the projection of the cation perpendicular to the Co · · · Co vector (Figure 3, in which the terminal pyridine moieties have been omitted for clarity); it is probably a consequence of steric repulsion between the methyl groups on the same ligand, twisting the ligand about the N–N (single) bond. The average C · · · C distance between methyl groups on the same ligand is 3·5 Å, and the average Co–N–N–Co dihedral angle is 44° measured from the eclipsed conformation. The six bridging nitrogen atoms form a trigonal prism which has been twisted by 17·1° from the eclipsed conformation about the Co–Co vector.

TABLE 6

Selected non-bonded distances (Å)

Co(1) · · · Co(2)	3·81	N(201) · · · N(301)	3·20
N(101) · · · N(201)	3·21	N(201) · · · N(202)	2·53
N(101) · · · N(301)	3·19	N(201) · · · N(203)	3·92
N(101) · · · N(102)	2·69	N(201) · · · N(302)	3·15
N(101) · · · N(202)	3·18	N(202) · · · N(302)	3·03
N(102) · · · N(202)	3·07	N(202) · · · N(303)	3·11
N(102) · · · N(203)	2·92	N(203) · · · N(302)	3·41
N(102) · · · N(302)	2·95	N(203) · · · N(303)	3·00
N(103) · · · N(203)	2·88	N(204) · · · N(304)	3·24
N(103) · · · N(302)	3·01	N(204) · · · N(102)	3·80
N(103) · · · N(303)	3·05	N(204) · · · N(103)	3·01
N(104) · · · N(204)	3·11	N(204) · · · N(202)	3·96
N(104) · · · N(304)	3·18	N(204) · · · N(203)	2·53
N(104) · · · N(102)	3·84	N(301) · · · N(102)	3·25
N(104) · · · N(103)	2·52	N(304) · · · N(203)	3·16
N(104) · · · N(303)	3·20	N(304) · · · N(303)	2·61

Each cobalt atom is co-ordinated by three 2-aldiminomethylpyridine groups, one from each of the pmk ligands, and shows significant departures from idealised octahedral co-ordination. The mean Co–N(py) bond length is 2·09, compared to 2·13 Å for Co–N(br); the mean N–Co–N angle in the five-membered ring is 75·2, compared to 99·7 for the mean terminal N–Co–N angle and 89·3° for the N–Co–N angle involving two bridging nitrogen atoms. The five-membered chelate rings are essentially coplanar with the pyridine rings, but the

TABLE 7

Least-squares planes in the form $lX + mY + nZ = p$ (where X, Y, and Z are fractional co-ordinates and p in Å) with typical deviations for one plane. Planes include the five-membered rings about one cobalt(II) ion, the pyridine ring atoms, and methyl group carbon atom

	l	m	n	p
Plane (1)	0·1777	0·0285	0·9837	5·1030
Co(2), N(101), N(102), C(101)—(107)				
Plane (2)	0·6573	0·6724	−0·3404	7·3462
Co(2), N(201), N(202), C(201)—(207)				
Plane (3)	0·8530	−0·4772	0·2116	−1·9050
Co(2), N(301), N(302), C(301)—(307)				

Deviations (Å) of atoms from plane (2): Co(2) −0·04, N(201) −0·03, N(202) 0·15, C(201) −0·04, C(202) −0·01, C(203) 0·05, C(204) 0·05, C(205) −0·02, C(206) 0·01, C(207) −0·01

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

methyl groups are bent slightly out of this plane, consistent with the presence of significant inter-methyl repulsions. A typical least-squares plane through one of the moieties is given in Table 7. The approximately equilateral triangles formed by the three bridging and three terminal nitrogen atoms attached to the same cobalt atom have been rotated with respect to one another by 17·5° about the Co–Co vector from exact trigonal antiprism (*i.e.* approximately octahedral) geometry. The distortions from octahedral geometry may be compared with rotations in the range 10—58°, depending on the bite of the ligand, observed in analogous monomeric aldiminopyridine–metal chelates.[4,5,10]

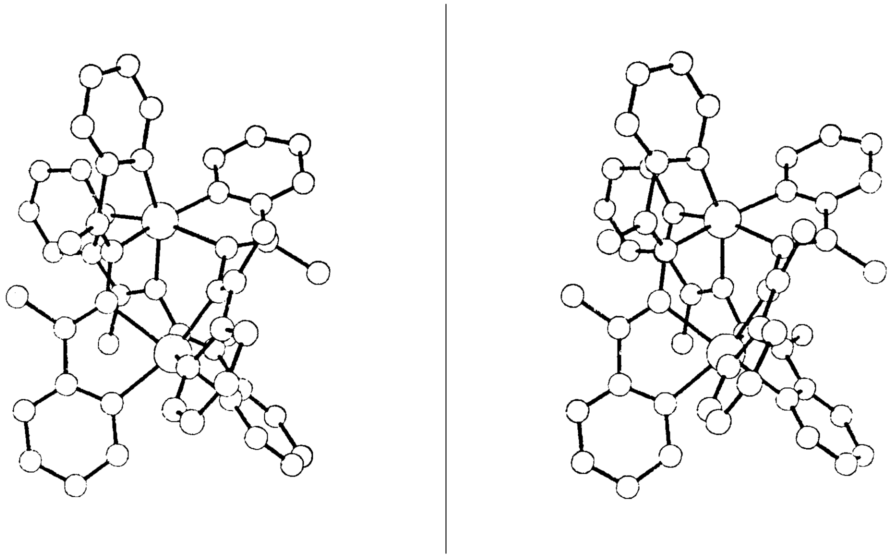

FIGURE 2 Stereoscopic view of the cation

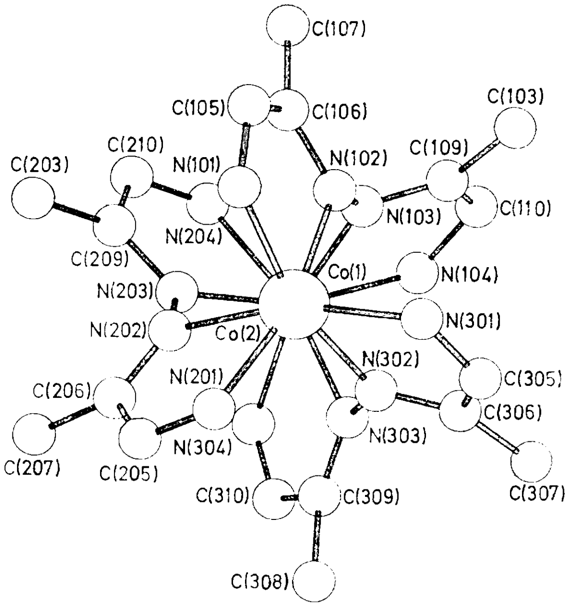

FIGURE 3 The cation viewed down the Co $\cdots$ Co vector: see text

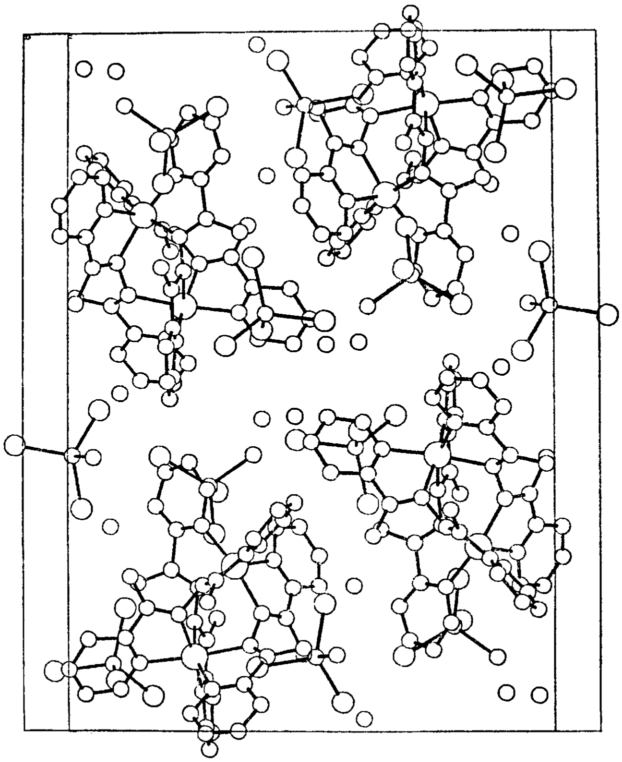

FIGURE 4 Projection of the unit cell on the *bc* plane

The bond lengths and angles in the tetrachlorozincate anion (mean Zn–Cl 2·26 Å, mean Cl–Zn–Cl 109°) agree well with those reported for other $ZnCl_4^{2-}$ ions.[11,12]

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The $[ZnCl_3(H_2O)]^-$ anions are unusual, and only two other examples of $(ZnX_3L)^-$ anions appear to be known: $[ZnBr_3(H_2O)]^-$ in $KZnBr_3,2H_2O$,[13] and $[ZnCl_3(acetone)]^-$.[14] Difference electron-density syntheses suggest that the chlorine anisotropic temperature factors may be partly compensating for some orientational disorder of the anions, which may also account for the relatively high (for diffractometer data) R index, which was significantly higher than expected from the internal consistency of equivalent reflexions. The packing of the ions is illustrated in Figure 4.

Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by Drs. S. Motherwell, P. J. Roberts, and G. M. S. We thank the Royal Commission for the Exhibition of 1851 for an Overseas Scholarship (to P. D. W. B.), and the S.R.C. for providing the diffractometer.

[3/2087 *Received, 17th July, 1973*]

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