

Diaqua(7,15-dihydro-7,9,13,15-tetramethylpyrido[2',1',6':12,13,14][1,2,4,7,9,10,13]-heptaazacyclopentadeca[3,4,5,6,7,8-*aklmn*][1,10]phenanthroline)cobalt(II) Bis(tetrafluoroborate) [Co(H₂O)₂(tdmmb)][BF₄]₂

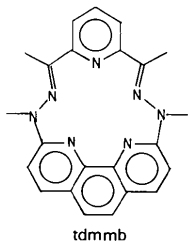
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Abstract. C₂₃H₂₅CoN₇O₂²⁺·2BF₄⁻, [Co(C₂₃H₂₁N₇)(H₂O)₂][BF₄]₂, monoclinic, *P*2₁/*c*, *a* = 14.162 (3), *b* = 11.492 (3), *c* = 16.681 (5) Å, β = 93.70 (3)°, *U* = 2709.2 Å³, *Z* = 4, *D*_c = 1.628 Mg m⁻³, μ(Mo *K*α) = 0.68 mm⁻¹; final *R* = 0.097 for 4230 unique diffractometer data. The Co^{II} atom is seven-coordinate with atoms at the vertices of a slightly distorted pentagonal bipyramid. The two water molecules occupy the axial sites. The Co atom is coplanar with the coordinated N atoms. The anions are not coordinated.

Introduction. A synthetic study of the series [M(H₂O)₂(tdmmb)][BF₄]₂ (*M* = Fe, Co, Ni) is of current interest in this laboratory. Consistent with this is a detailed study of the metal–ligand interactions within the angular-overlap model which allows resolution of these interactions into their respective σ and π components. The magnetic study is being undertaken as part of a series of investigations of pentagonal-bipyramidal systems (Gerloch, Morgenstern-Badarau & Audiere, 1979; Gerloch & Morgenstern-Badarau, 1979).



The title compound was prepared by the condensation of 2,6-diacetylpyridine with 2,9-bis(1-methylhydrazino)-1,10-phenanthroline monohydrochloride in the presence of a Co^{II} template (Ramsden, 1980). Red block-shaped crystals were grown by evaporation from water. 5552 intensities were measured for 3.0 < 2θ ≤ 55.0° on a Stoe AED four-circle diffractometer with graphite-monochromated Mo *K*α radiation, an ω–θ scan technique, and a crystal 0.50 × 0.47 × 0.39 mm. Lp corrections and a semi-empirical absorption correc-

tion based on a pseudo-ellipsoid model with 488 azimuthal scan data from 28 independent reflections were applied; transmission factors ranged from 0.968 to 0.998. The data were averaged to give 4230 unique observed reflections [*F* > 5σ(*F*)]. Cell dimensions were derived from the angular measurement of 20 strong reflections in the range 20 < 2θ < 30°.

The Co atom was located from a Patterson synthesis, and all the other non-hydrogen atoms were found from subsequent difference syntheses. The structure was refined by blocked-full-matrix least squares. The Co, N, C, and O atoms were assigned anisotropic thermal parameters. The H atoms of the coordinated water molecules were not located, but all the other H atoms were placed in idealized positions and constrained to ride 1.08 Å from the appropriate C atom; the methyl groups were refined as rigid bodies. The H atoms were assigned a common isotropic temperature factor. Both BF₄⁻ groups were severely disordered; each was treated as a B atom surrounded by two interlocking tetrahedra of F atoms. In each tetrahedron the B–F and F···F distances were fixed at 1.37 and 2.237 Å, respectively; the occupancies of the F atoms were refined as *k* and (1 – *k*). The B atoms were assigned individual isotropic and the F atoms common isotropic temperature factors. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme *w* = 5.4624/[σ²(*F*) + 0.0007|*F*_o|²] for the final stages of refinement. The final *R* = 0.097 and *R*' = ∑ *w*^{1/2}Δ/∑ *w*^{1/2}|*F*_o| = 0.111. Final atomic coordinates, and equivalent isotropic and isotropic temperature factors are given in Table 1, and bond lengths and angles in Tables 2 and 3.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35155 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$), isotropic temperature factors ($\text{\AA}^2 \times 10^3$), and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U/U _{eq}
Co(1)	7496 (1)	1132 (1)	1179 (1)	35 (1)
N(1)	8238 (4)	-56 (5)	505 (4)	46 (7)
N(2)	7999 (4)	2098 (6)	112 (3)	46 (7)
N(3)	7774 (4)	3264 (6)	33 (4)	48 (8)
N(4)	7056 (4)	2887 (5)	1214 (3)	38 (6)
N(5)	6764 (4)	1265 (5)	2242 (3)	38 (6)
N(6)	7027 (4)	-656 (5)	2512 (4)	44 (7)
N(7)	7482 (4)	-583 (5)	1798 (3)	41 (7)
C(1)	9187 (7)	-1605 (9)	-391 (6)	71 (13)
C(2)	9006 (6)	-518 (9)	-685 (6)	71 (13)
C(3)	8528 (5)	291 (8)	-231 (4)	52 (10)
C(4)	8318 (5)	1486 (8)	-458 (4)	51 (10)
C(5)	8456 (7)	1805 (11)	-1302 (5)	78 (15)
C(6)	8422 (7)	4088 (9)	-325 (6)	73 (15)
C(7)	7265 (5)	3676 (6)	679 (4)	43 (8)
C(8)	6956 (6)	4838 (7)	735 (5)	54 (10)
C(9)	6506 (6)	5187 (6)	1377 (5)	54 (10)
C(10)	6308 (5)	4366 (6)	2000 (5)	48 (9)
C(11)	6606 (5)	3221 (6)	1850 (4)	37 (7)
C(12)	5893 (6)	4618 (7)	2730 (5)	57 (11)
C(13)	5726 (6)	3773 (8)	3256 (5)	62 (12)
C(14)	6428 (5)	2330 (6)	2423 (4)	39 (8)
C(15)	6000 (5)	2604 (7)	3133 (4)	49 (9)
C(16)	5874 (6)	1631 (7)	3639 (4)	52 (10)
C(17)	6169 (6)	558 (8)	3449 (4)	53 (10)
C(18)	6635 (5)	388 (6)	2729 (4)	41 (8)
C(19)	6571 (7)	-1767 (7)	2723 (6)	70 (13)
C(20)	8034 (5)	-1389 (6)	1582 (5)	44 (8)
C(21)	8392 (7)	-2447 (7)	2022 (6)	69 (13)
C(22)	8414 (5)	-1123 (6)	784 (5)	48 (9)
C(23)	8887 (6)	-1937 (8)	339 (6)	65 (12)
O(1)	8800 (4)	1595 (5)	1877 (4)	63 (8)
O(2)	6204 (4)	695 (5)	465 (4)	62 (8)
B(1)	9722 (4)	4621 (4)	1793 (3)	58 (2)
F(11)	9852 (7)	5490 (7)	1250 (5)	123 (2)
F(12)	10376 (6)	4728 (9)	2430 (4)	123 (2)
F(13)	9825 (8)	3562 (5)	1433 (6)	123 (2)
F(14)	8830 (5)	4703 (10)	2062 (6)	123 (2)
F(11A)	9005 (7)	3820 (9)	1735 (8)	123 (2)
F(12A)	10547 (6)	4107 (11)	1590 (8)	123 (2)
F(13A)	9507 (9)	5529 (8)	1282 (6)	123 (2)
F(14A)	9833 (10)	5026 (11)	2566 (4)	123 (2)
B(2)	4018 (3)	2300 (4)	252 (2)	54 (2)
F(21)	3106 (3)	2567 (8)	410 (5)	94 (1)
F(22)	4031 (6)	1814 (7)	-496 (3)	94 (1)
F(23)	4554 (6)	3295 (6)	282 (5)	94 (1)
F(24)	4385 (6)	1528 (7)	815 (4)	94 (1)
F(21A)	4882 (4)	2712 (11)	539 (6)	94 (1)
F(22A)	3886 (8)	1201 (5)	542 (7)	94 (1)
F(23A)	3319 (6)	3018 (8)	497 (6)	94 (1)
F(24A)	3980 (7)	2270 (10)	-571 (2)	94 (1)

Discussion. The analysis shows that the cation (Fig. 1) is isostructural with the Fe^{II} (Bishop, Lewis, O'Donoghue, Raithby & Ramsden, 1978) and Ni^{II} (Lewis, Raithby & Ramsden, 1980) analogues. The cation exhibits the uncommon pentagonal-bipyramidal coordination geometry for Co^{II} with two water molecules occupying the two axial positions. The Co and seven N atoms are coplanar [maximum deviation 0.01 (1) Å],

Table 2. Bond lengths (Å)

N(1)—Co(1)	2.095 (6)	C(3)—N(1)	1.378 (10)
N(2)—Co(1)	2.252 (6)	C(22)—N(1)	1.330 (10)
N(4)—Co(1)	2.113 (5)	N(3)—N(2)	1.382 (9)
N(5)—Co(1)	2.116 (5)	C(4)—N(2)	1.289 (10)
N(7)—Co(1)	2.226 (6)	C(6)—N(3)	1.471 (12)
O(1)—Co(1)	2.184 (6)	C(7)—N(3)	1.417 (9)
O(2)—Co(1)	2.177 (5)	C(7)—N(4)	1.318 (9)
C(2)—C(1)	1.361 (14)	C(11)—N(4)	1.329 (9)
C(23)—C(1)	1.369 (13)	C(14)—N(5)	1.355 (9)
C(3)—C(2)	1.401 (13)	C(18)—N(5)	1.314 (9)
C(4)—C(3)	1.450 (12)	N(7)—N(6)	1.393 (8)
C(5)—C(4)	1.480 (11)	C(18)—N(6)	1.380 (9)
C(8)—C(7)	1.410 (10)	C(19)—N(6)	1.483 (10)
C(9)—C(8)	1.343 (12)	C(20)—N(7)	1.279 (9)
C(10)—C(9)	1.444 (11)	C(17)—C(16)	1.346 (12)
C(11)—C(10)	1.409 (9)	C(18)—C(17)	1.421 (10)
C(12)—C(10)	1.415 (12)	C(21)—C(20)	1.492 (11)
C(14)—C(11)	1.434 (9)	C(22)—C(20)	1.498 (11)
C(13)—C(12)	1.339 (12)	C(23)—C(22)	1.393 (12)
C(15)—C(13)	1.417 (12)	C(15)—C(14)	1.401 (10)
C(16)—C(15)	1.420 (11)	F(11)—B(1)	1.369 (9)
F(21)—B(2)	1.369 (6)	F(12)—B(1)	1.370 (9)
F(22)—B(2)	1.369 (7)	F(13)—B(1)	1.369 (9)
F(23)—B(2)	1.371 (8)	F(14)—B(1)	1.371 (9)
F(24)—B(2)	1.371 (8)	F(11A)—B(1)	1.369 (11)
F(21A)—B(2)	1.369 (8)	F(12A)—B(1)	1.371 (11)
F(22A)—B(2)	1.370 (8)	F(13A)—B(1)	1.370 (11)
F(23A)—B(2)	1.370 (10)	F(14A)—B(1)	1.370 (9)
F(24A)—B(2)	1.370 (5)		

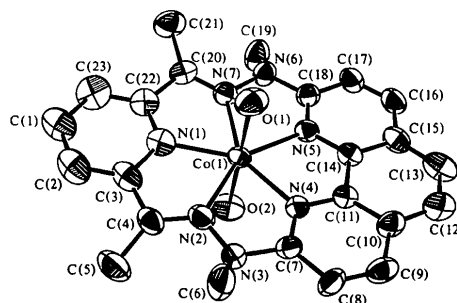


Fig. 1. An ORTEP plot (Johnson, 1965) of the cation, showing the atom labelling and 50% probability ellipsoids for the anisotropic atoms.

and the planar pyridine and phenanthroline groups make angles of 6.7 (1) and 4.2 (1)°, respectively, with this CoN₇ unit. The largest deviations from the macrocycle plane are observed in the positions of the substituent methyl C atoms. The intramolecular contacts, C(5)⋯C(6) 3.092 (12) and C(19)⋯C(21) 3.003 (11) Å, between these adjacent methyl C atoms are considerably shorter than the sum of the van der Waals radii and the macrocycle twists slightly to prevent even shorter interactions; the N atoms to which the methyl groups are bonded show small deviations from planar sp² hybridization.

Table 3. Bond angles (°)

N(2)—Co(1)—N(1)	72.6 (2)	C(3)—N(1)—Co(1)	118.6 (5)
N(4)—Co(1)—N(1)	142.7 (2)	C(22)—N(1)—Co(1)	120.1 (5)
N(4)—Co(1)—N(2)	70.1 (2)	C(22)—N(1)—C(3)	121.3 (7)
N(5)—Co(1)—N(1)	141.9 (2)	N(3)—N(2)—Co(1)	118.1 (4)
N(5)—Co(1)—N(2)	145.5 (2)	C(4)—N(2)—Co(1)	117.3 (5)
N(5)—Co(1)—N(4)	75.4 (2)	C(4)—N(2)—N(3)	123.3 (6)
N(7)—Co(1)—N(1)	72.0 (2)	C(6)—N(3)—N(2)	121.1 (6)
N(7)—Co(1)—N(2)	144.6 (2)	C(7)—N(3)—N(2)	112.1 (5)
N(7)—Co(1)—N(4)	145.2 (2)	C(7)—N(3)—C(6)	117.1 (6)
N(7)—Co(1)—N(5)	69.9 (2)	C(7)—N(4)—Co(1)	124.0 (5)
O(1)—Co(1)—N(1)	90.5 (2)	C(11)—N(4)—Co(1)	117.0 (4)
O(1)—Co(1)—N(2)	90.1 (2)	C(11)—N(4)—C(7)	118.8 (6)
O(1)—Co(1)—N(4)	89.6 (2)	C(14)—N(5)—Co(1)	116.7 (4)
O(1)—Co(1)—N(5)	88.8 (2)	C(18)—N(5)—Co(1)	123.9 (4)
O(1)—Co(1)—N(7)	90.1 (2)	C(18)—N(5)—C(14)	119.4 (6)
O(2)—Co(1)—N(1)	89.4 (2)	C(18)—N(6)—N(7)	112.8 (5)
O(2)—Co(1)—N(2)	88.8 (2)	C(19)—N(6)—N(7)	119.2 (6)
O(2)—Co(1)—N(4)	89.8 (2)	C(19)—N(6)—C(18)	119.8 (6)
O(2)—Co(1)—N(5)	92.0 (2)	N(6)—N(7)—Co(1)	117.9 (4)
O(2)—Co(1)—N(7)	91.0 (2)	C(20)—N(7)—Co(1)	119.1 (5)
O(2)—Co(1)—O(1)	178.8 (2)	C(20)—N(7)—N(6)	121.5 (6)
C(23)—C(1)—C(2)	121.0 (9)	C(13)—C(12)—C(10)	121.1 (7)
C(3)—C(2)—C(1)	120.0 (9)	C(15)—C(13)—C(12)	122.0 (8)
C(2)—C(3)—N(1)	118.2 (8)	C(11)—C(14)—N(5)	114.7 (6)
C(4)—C(3)—N(1)	116.0 (7)	C(15)—C(14)—N(5)	124.7 (6)
C(4)—C(3)—C(2)	125.8 (7)	C(15)—C(14)—C(11)	120.5 (6)
C(3)—C(4)—N(2)	113.6 (7)	C(18)—C(15)—C(13)	118.2 (7)
C(5)—C(4)—N(2)	129.9 (9)	C(16)—C(15)—C(13)	127.9 (7)
C(5)—C(4)—C(3)	116.5 (8)	C(16)—C(15)—C(14)	113.8 (7)
N(4)—C(7)—N(3)	115.6 (6)	C(17)—C(16)—C(15)	121.9 (7)
C(8)—C(7)—N(3)	122.8 (7)	C(18)—C(17)—C(16)	119.6 (7)
C(8)—C(7)—N(4)	121.5 (7)	N(6)—C(18)—N(5)	115.5 (6)
C(9)—C(8)—C(7)	120.1 (7)	C(17)—C(18)—N(5)	120.5 (7)
C(10)—C(9)—C(8)	120.2 (7)	C(17)—C(18)—N(6)	123.9 (7)
C(11)—C(10)—C(9)	114.1 (7)	C(21)—C(20)—N(7)	130.2 (7)
C(12)—C(10)—C(9)	126.6 (7)	C(22)—C(20)—N(7)	111.3 (6)
C(12)—C(10)—C(11)	119.3 (7)	C(22)—C(20)—C(21)	118.3 (7)
C(10)—C(11)—N(4)	125.2 (6)	C(20)—C(22)—N(1)	115.5 (6)
C(14)—C(11)—N(4)	116.1 (6)	C(23)—C(22)—N(1)	121.1 (7)
C(14)—C(11)—C(10)	118.7 (6)	C(23)—C(22)—C(20)	123.3 (7)
C(22)—C(23)—C(1)	118.4 (8)	F(12)—B(1)—F(11)	109.6 (7)
F(22)—B(2)—F(21)	109.6 (5)	F(13)—B(1)—F(11)	109.6 (6)
F(23)—B(2)—F(21)	109.5 (6)	F(13)—B(1)—F(12)	109.6 (7)
F(23)—B(2)—F(22)	109.5 (6)	F(14)—B(1)—F(11)	109.4 (7)
F(24)—B(2)—F(21)	109.5 (6)	F(14)—B(1)—F(12)	109.4 (6)
F(24)—B(2)—F(22)	109.5 (5)	F(14)—B(1)—F(13)	109.4 (7)
F(24)—B(2)—F(23)	109.3 (5)	F(12A)—B(1)—F(11A)	109.4 (7)
F(22A)—B(2)—F(21A)	109.6 (7)	F(13A)—B(1)—F(11A)	109.5 (8)
F(23A)—B(2)—F(21A)	109.5 (6)	F(13A)—B(1)—F(12A)	109.4 (8)
F(23A)—B(2)—F(22A)	109.4 (7)	F(14A)—B(1)—F(11A)	109.5 (8)
F(24A)—B(2)—F(21A)	109.5 (6)	F(14A)—B(1)—F(12A)	109.4 (8)
F(24A)—B(2)—F(22A)	109.4 (7)	F(14A)—B(1)—F(13A)	109.5 (7)
F(24A)—B(2)—F(23A)	109.4 (7)		

The Co—N(pyridine) and Co—N(hydrazone) bond lengths in the title compound are respectively shorter and longer than the 2.194 (3) and 2.197 (2) Å in [Co(dapbh)(H₂O)(NO₃)]NO₃ [dapbh = 2,6-diacetylpyridinebis(benzoic acid hydrazone)] (Giordano, Palenik, Palenik & Sullivan, 1979) where the Co—O lengths are shorter at 2.135 (2) and 2.142 (2) Å. A comparison of the N—N distances in the two compounds shows that bond lengths are slightly shorter in the benzoic acid complex [1.376 (4) and 1.365 (4) Å] where the constraint of planarity on the ligand is less severe.

Table 4. M—N bond lengths (Å) in the Fe and Ni macrocycle complexes

	Fe	Ni
M—N(1)	2.100 (9)	2.117 (6)
M—N(2)	2.242 (8)	2.313 (6)
M—N(4)	2.126 (7)	2.095 (5)
M—N(5)	2.112 (8)	2.081 (5)
M—N(7)	2.276 (8)	2.276 (5)

A comparison of the structures of the Fe^{II}, Co^{II} and Ni^{II} complexes shows no significant variation in the bond parameters of the macrocycle ligands. The cavity at the centre of the ligand is essentially the same in all three cases. The M—N lengths tend to increase from Fe to Ni as the size of the +2 ion decreases. However, as the metal ion becomes smaller it appears that there is room for it to rattle around inside the cavity, and a shorter bond is formed between the metal and the phenanthroline N atoms. The Co complex is intermediate in this series, and M—N bond-length data for the Fe^{II} (Bishop, Lewis, O'Donoghue, Raithby & Ramsden, 1978) and Ni^{II} (Lewis, Raithby & Ramsden, 1980) analogues are presented in Table 4.

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