

SHORT STRUCTURAL PAPERS

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Acta Cryst. (1975). **B31**, 2683

Dichlorobis-(4-methylpyridine)cobalt(II)

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(Received 17 May 1975; accepted 21 May 1975)

Abstract. $\text{CoCl}_2(\text{NC}_5\text{H}_4\text{CH}_3)_2$, monoclinic, $P2_1/n$, $a=5.70$ (1), $b=10.16$ (1), $c=24.36$ (2) Å, $\beta=92.4$ (1)°, $Z=4$, $D_c=1.49$ g cm⁻³. Cl-Co-Cl=121, N-Co-N=107°; Co is tetrahedrally coordinated. The molecular packing differs from that of the ZnCl_2 and ZnBr_2 analogues.

Introduction. Previous work (Gill, Nyholm, Barclay, Christie & Pauling, 1961; Graddon & Watson, 1965) has shown that in the crystalline state 4-substituted-pyridine complexes of CoCl_2 , $[\text{CoCl}_2(4\text{-Rpy})_2]$, can exist either as molecules with Co tetrahedrally coordinated or as polymeric CoCl_2 chains with Co in a pseudo-octahedral environment. In several cases, the tetrahedrally coordinated compounds are isostructural with the analogous ZnCl_2 compounds (Admiraal & Gafner, 1968; Erasmus, 1967), while the structure of the polymeric pseudo-octahedral form is closely related to that of the analogous complex of CuCl_2 (Dunitz, 1957; Laing & Horsfield, 1968, 1969).

It seemed that the stereochemistry of the CoCl_2 compounds was dictated solely by the size and shape of the 4-substituent on the pyridine ring, so a series of 4-substituted pyridine complexes of CoCl_2 and CuCl_2 was prepared to test this proposition (Carr, 1970). Under certain conditions it was possible to prepare the 4-methylpyridine complex of CoCl_2 in the violet pseudo-octahedral form, but within hours the material changed to the blue tetrahedral form whose structure is reported here.

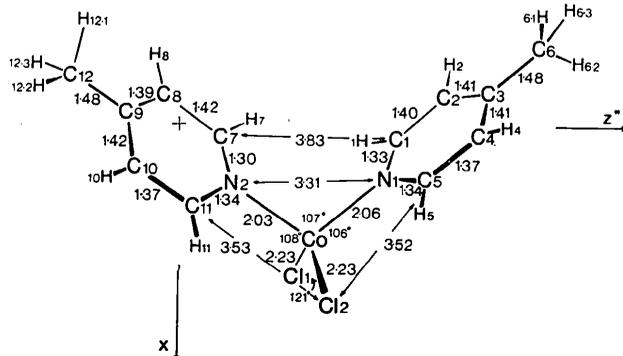


Fig. 1. The numbering system and selected bond distances and angles.

$\text{CoCl}_2(4\text{-methylpyridine})_2$ forms deep-blue needles from ethanol, monoclinic, space group $P2_1/n$ uniquely determined from the systematic absences. Data were collected with Ni-filtered $\text{Cu K}\alpha$ radiation by the multiple-film equi-inclination Weissenberg method for layers $0kl$ to $4kl$. The Co and Cl atoms were located from a Patterson map and the lighter atoms from the subsequent Fourier map. The H atoms were clearly defined in a difference map; they were therefore included in the structure-factor calculations but their parameters

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$)

Estimated standard deviations are in parentheses. The expression for the thermal parameters is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	x/a	y/b	z/c
Co	4401 (4)	1856 (2)	1115 (1)
Cl(1)	5676 (7)	-205 (3)	1010 (1)
Cl(2)	6899 (6)	3520 (3)	1263 (1)
N(1)	2252 (17)	1825 (10)	1778 (4)
N(2)	2361 (17)	2325 (10)	438 (4)
C(1)	852 (22)	797 (12)	1847 (5)
C(2)	-790 (23)	737 (13)	2256 (5)
C(3)	-828 (21)	1807 (13)	2625 (5)
C(4)	643 (22)	2890 (13)	2528 (5)
C(5)	2171 (25)	2871 (13)	2110 (5)
C(6)	-2527 (24)	1848 (13)	3068 (5)
C(7)	481 (20)	1713 (13)	322 (5)
C(8)	-1088 (23)	1996 (15)	-129 (5)
C(9)	-570 (22)	3065 (14)	-462 (5)
C(10)	1560 (23)	3739 (14)	-332 (5)
C(11)	2951 (24)	3322 (15)	108 (5)
C(12)	-2094 (26)	3469 (16)	-938 (5)

Fractional coordinates ($\times 10^3$) of the H atoms ($B=4.0$ Å²)

	x/z	y/b	z/c
H(1)	100	4	159
H(2)	-193	-7	230
H(4)	60	369	277
H(5)	329	364	205
H(7)	-4	90	57
H(8)	-254	146	-22
H(10)	192	451	-57
H(11)	428	387	22
H(6-1)	-350	270	310
H(6-2)	-190	160	340
H(6-3)	-390	120	290
H(12-1)	-370	380	-80
H(12-2)	-120	410	-120
H(12-3)	-240	260	-120

Table 1 (*cont.*)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	345 (8)	90 (2)	15 (0)	-34 (8)	7 (2)	5 (2)
Cl(1)	404 (15)	67 (3)	18 (1)	22 (12)	11 (5)	1 (3)
Cl(2)	365 (14)	75 (4)	17 (1)	-106 (12)	-19 (5)	18 (3)
N(1)	272 (42)	63 (10)	13 (2)	-56 (37)	-27 (13)	11 (8)
N(2)	208 (40)	78 (12)	12 (2)	-69 (34)	-21 (13)	-4 (7)
C(1)	131 (53)	47 (12)	23 (3)	-7 (37)	-26 (19)	15 (10)
C(2)	196 (53)	102 (16)	18 (3)	-71 (43)	76 (19)	-53 (11)
C(3)	217 (49)	83 (15)	16 (2)	19 (45)	-29 (16)	34 (11)
C(4)	393 (66)	59 (16)	19 (3)	79 (49)	-30 (21)	-22 (10)
C(5)	297 (53)	92 (16)	8 (2)	-8 (47)	9 (16)	-23 (9)
C(6)	459 (63)	67 (14)	10 (2)	42 (52)	17 (17)	43 (10)
C(7)	164 (49)	72 (14)	16 (2)	44 (42)	4 (16)	-13 (10)
C(8)	276 (54)	118 (18)	14 (2)	-1 (54)	12 (17)	13 (12)
C(9)	309 (56)	111 (18)	9 (2)	90 (51)	69 (17)	-19 (11)
C(10)	279 (61)	118 (19)	11 (3)	-50 (56)	1 (18)	9 (12)
C(11)	339 (54)	130 (16)	13 (2)	14 (53)	34 (16)	10 (11)
C(12)	404 (62)	159 (24)	7 (2)	7 (65)	-11 (18)	4 (12)

were not refined. The structure was refined anisotropically by block-diagonal least-squares calculations to $R=0.086$ for 1148 observed data.* All calculations were performed with a local set of programs (Laing, 1972). The atomic parameters are given in Table 1; the numbering system and some bond lengths and angles are shown in Fig. 1.

Discussion. Co is tetrahedrally coordinated; the bond lengths and angles in the molecule are normal within the observed standard deviations. The seven atoms of each of the 4-methylpyridine systems are coplanar within 0.02 Å; however in both cases Co is 0.11 Å from the mean plane of the pyridine ring. There is no obvious reason for this displacement but it is possibly due to the intramolecular repulsion between C(1) and C(7) combined with intermolecular crystal packing effects (Kitaigorodsky, 1974). A similar but larger distortion has been observed in the compound dibromo-(*N,N,N',N'*-tetramethylpyridinedicarboxamide)cobalt(II) (Du Preez, van Brecht & Laing, 1975).

Although the molecules α -[CoCl₂(4-Vpy)₂] and both α - and β -[ZnCl₂(4-Vpy)₂] retain a twofold axis of symmetry in the crystal (Admiraal & Gafner, 1968; Erasmus, 1967), [CoCl₂(4-Mepy)₂] does not. Also, the mode of packing differs from that of the geometrically similar compound [ZnBr₂(4-Mepy)₂] (Fanfani, Nunzi &

Zanazzi, 1972). The balance between enthalpy and entropy effects is not clear (Kitaigorodskii, 1961), and for this reason a study is being made of the factors which control the mode of packing in molecules of the general formula [MCl₂(4R-py)₂] where M is tetrahedrally coordinated. Preliminary work shows that [ZnCl₂(4-Mepy)₂] is isostructural with the ZnBr₂ analogue.

We thank the South African Council for Scientific and Industrial Research for generous financial support.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31138 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.