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Crystallographic Characterization of π-[Co(bpy)(dien)Cl]Cl$_2$.3H$_2$O

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Abstract. Bipyridyl(chloro)(diethylenetriamine)cobalt(III) dichloride trihydrate, [CoCl($C_4H_{13}N_3$)($C_{10}H_8N_2$)]Cl$_2$.3H$_2$O, $M_r = 478{\cdot}6$, monoclinic, $P2_1/c$, $a = 12{\cdot}272\,(2)$, $b = 12{\cdot}174\,(3)$, $c = 13{\cdot}497\,(2)$ Å, $\beta = 92{\cdot}24(2)°$, $V = 2015\,(1)$ Å^3, $Z = 4$, D_m(by flotation) $= 1{\cdot}58$, $D_x = 1{\cdot}58$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 13{\cdot}1$ cm^{-1}, $F(000) = 992$, $T = 295$ K, $R = 0{\cdot}040$ for 2034 unique reflections [$I > 3{\cdot}0\sigma(I)$]. The crystal structure consists of [Co(bpy)(dien)Cl]$^{2+}$ complex cations, chloride anions and three water molecules of crystallization. Two water molecules are weakly hydrogen bonded, the third appears hydrogen bonded to one of the Cl anions.

Introduction. Preparation, analysis, NMR, IR and aquation for complexes of the type [Co(bpy)(dien)X]ZnX_4 (where X = Cl, Br) were reported earlier (Gainsford & House, 1982). The mixed-ligand complex of cobalt(III) [Co(bpy)(dien)Cl]Cl$_2$.3H$_2$O was prepared, purified and crystallized. The preparation and structure determination are reported herein.

Experimental. The title compound was prepared by the following procedure: 2,2′-bipyridyl (4·69 g) in 100 ml of hot water was gradually added to CoCl$_2$.6H$_2$O (7·14 g) in 20 ml of water. Concentrated HCl was added (5·2 ml), the solution was cooled to room temperature, and air was passed through the solution for 48 h. Diethylenetriamine (dien) (3·09 g) was then added gradually and air was passed through the solution for an additional 48 h. Pink crystals were isolated by partial evaporation, addition of ethanol, and cooling (yield 5·2 g). Analysis: calculated for [Co(bpy)(dien)Cl]Cl$_2$.3H$_2$O: C, 35·1; H, 5·68; N, 14·6; Cl, 22·2; found: C, 34·8; H, 5·60; N, 14·70; Cl, 22·5%.

Table 1. *Details of the structure determination*

Crystal dimensions (mm)	0·32 × 0·16 × 0·07
Diffractometer	Nicolet *P*3F
Data collected	$+h, +k, \pm l$
Monochromator	Graphite
Scan technique	θ–2θ
Scan range (2θ), min.–max. (°)	3·0–50·0
Scan speed (° min^{-1})	Variable, 2·0–30·0
Scan range	0·8° below $K\alpha_1$ and 0·8° above $K\alpha_2$
Background	Stationary crystal–stationary counter
Background time	0·5 × (scan time)
Number of unique reflections measured	3557
Number of observed reflections	2034
Criterion	$F > 6\sigma(F)$
R, wR*	0·040, 0·050
Weight	$1/[\sigma(F)^2 + 0{\cdot}001F^2]$
Number of parameters	234
Ratio of observations to parameters	8·7

Cell dimensions were determined by least-squares fit of the setting angles of 21 reflections with 2θ in the range 20–25°.

* The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

A crystal of [Co(bpy)(dien)Cl]Cl$_2$.3H$_2$O was mounted and aligned on a Nicolet *P*3F automated diffractometer. Information regarding data collection and structure determination is given in Table 1. Four standard reflections measured during data collection showed only statistical fluctuations in intensity. ψ scans carried out to estimate the effect of absorption indicated that correction was unnecessary. The location of the Co atom was determined from a Patterson map, the locations of other atoms were determined from phases generated using the Co position. Calculations were carried out using the *SHELX*76 library of computer programs (Sheldrick, 1976). Atomic scattering factors were those of *SHELX*76. Fixed contributions for all H atoms were included in final cycles of refinement. Water oxygen O(3) was found to be disordered between two sites; refinement was carried out using half-occupancy atoms at both sites with isotropic thermal parameters. All other non-hydrogen atoms of the structure were refined with anisotropic thermal parameters. The largest shift on the final cycle of refinement had a shift/e.s.d. value of 0·003, and the largest residual electron density was in the vicinity of

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Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2\times 10^3$)

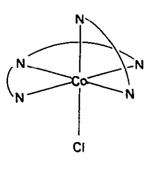
Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(U_{iso})$
Co(1)	2467 (1)	2975 (1)	2776 (1)	29 (1)
Cl(1)	3208 (1)	3070 (1)	1269 (1)	40 (1)
Cl(2)	2038 (1)	5062 (1)	5582 (1)	51 (1)
Cl(3)	1412 (1)	6039 (1)	1002 (1)	50 (1)
O(1)	1109 (3)	650 (3)	4191 (3)	54 (1)
O(2)	1873 (4)	7244 (4)	4306 (3)	80 (2)
O(3*A*)	2666 (6)	6378 (7)	7726 (5)	125 (3)*
O(3*B*)	2098 (43)	6743 (47)	7223 (39)	113 (17)*
N(1)	3670 (3)	2090 (4)	3312 (3)	38 (1)
N(2)	3421 (3)	4183 (3)	3193 (3)	34 (1)
N(3)	1590 (3)	1706 (3)	2333 (3)	34 (1)
N(4)	1226 (3)	3850 (3)	2303 (3)	33 (1)
N(5)	1783 (3)	2987 (3)	4057 (3)	33 (1)
C(1)	3713 (4)	987 (4)	3372 (4)	45 (2)
C(2)	4625 (5)	448 (6)	3748 (4)	59 (2)
C(3)	5510 (5)	1035 (7)	4067 (4)	68 (3)
C(4)	5469 (5)	2153 (6)	4021 (4)	57 (2)
C(5)	4545 (4)	2671 (5)	3646 (4)	39 (2)
C(6)	4410 (4)	3846 (5)	3559 (4)	41 (2)
C(7)	5206 (4)	4607 (5)	3823 (4)	52 (2)
C(8)	4998 (5)	5709 (6)	3741 (4)	57 (2)
C(9)	3999 (5)	6051 (5)	3380 (4)	48 (2)
C(10)	3232 (4)	5260 (4)	3108 (4)	44 (2)
C(11)	501 (4)	2024 (4)	1907 (4)	37 (2)
C(12)	571 (4)	3189 (4)	1563 (4)	39 (2)
C(13)	600 (4)	4233 (4)	3164 (4)	39 (2)
C(14)	641 (4)	3371 (4)	3964 (4)	40 (2)

* U_{iso}.

Cl(3) with a value of 0·2 e Å^{-3}. The final GOF value was 1·03. Atomic coordinates are given in Table 2.*

Discussion. Four geometric isomers exist for the Co(bpy)(dien)Cl^{2+} cation. Two are conformational isomers of structure (I) which arise from different configurations of the proton on the secondary N of the dien ligand, either towards (ψ isomer) or away from the chloro ligand (κ isomer). The other two isomers, with the dien ligand occupying facial sites of the octahedron, are related by differences in the disposition of the secondary dien nitrogen, either *trans* (ε isomer; II) or *cis* (π isomer; III) to the chloro ligand. The crystal used in the present investigation was found to contain the π isomer shown in Fig. 1. Bond distances and angles are given in Table 3. Three of the four possible isomers have been isolated for Co(en)(dien)Cl^{2+} and characterized structurally (Gainsford, House & Robinson, 1971; Johnston & Freeman, 1975). Features of π-Co(bpy)(dien)Cl^{2+} are similar to those of π-Co(en)(dien)Cl^{2+}. Co—N distances in the bipyridine complex are significantly shorter than values found in the ethylenediamine analogue. Lengths to the two bpy nitrogens, N(1) and N(2), are 1·944 (4) and 1·949 (4) Å compared with values of 1·960 (7) and 1·971 (7) Å to the two en nitrogens. Lengths to the three dien N atoms in Co(bpy)(dien)Cl^{2+} are 1·946 (4),



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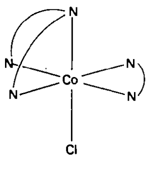

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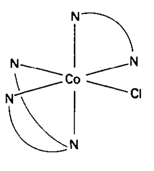

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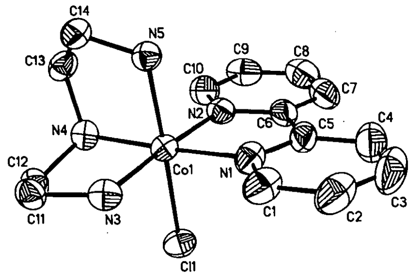

Fig. 1. View showing the π isomer of Co(bpy)(dien)Cl^{2+} and the atom-numbering scheme.

Table 3. *Bond distances* (Å) *and angles* (°)

Co(1)–Cl(1)	2·263 (2)	Co(1)–N(1)	1·944 (4)
Co(1)–N(2)	1·949 (4)	Co(1)–N(3)	1·963 (4)
Co(1)–N(4)	1·946 (4)	Co(1)–N(5)	1·951 (4)
		N(1)–C(1)	1·347 (7)
N(1)–C(5)	1·348 (6)	N(2)–C(6)	1·356 (6)
N(2)–C(10)	1·335 (7)	N(3)–C(11)	1·484 (6)
N(4)–C(12)	1·493 (6)	N(4)–C(13)	1·492 (6)
N(5)–C(14)	1·477 (6)	C(1)–C(2)	1·377 (8)
C(2)–C(3)	1·356 (9)	C(3)–C(4)	1·364 (11)
C(4)–C(5)	1·377 (8)	C(5)–C(6)	1·444 (8)
C(6)–C(7)	1·383 (8)	C(7)–C(8)	1·368 (10)
C(8)–C(9)	1·367 (8)	C(9)–C(10)	1·386 (8)
C(11)–C(12)	1·497 (7)	C(13)–C(14)	1·506 (7)

Cl(1)–Co(1)–N(1)	92·1 (1)	Cl(1)–Co(1)–N(2)	87·9 (1)
N(1)–Co(1)–N(2)	82·6 (2)	Cl(1)–Co(1)–N(3)	90·0 (1)
N(1)–Co(1)–N(3)	94·4 (2)	N(2)–Co(1)–N(3)	176·3 (2)
Cl(1)–Co(1)–N(4)	90·8 (1)	N(1)–Co(1)–N(4)	177·1 (2)
N(2)–Co(1)–N(4)	97·7 (2)	N(3)–Co(1)–N(4)	85·3 (2)
Cl(1)–Co(1)–N(5)	176·2 (1)	N(1)–Co(1)–N(5)	91·2 (2)
N(2)–Co(1)–N(5)	90·8 (2)	N(3)–Co(1)–N(5)	91·5 (2)
N(4)–Co(1)–N(5)	85·9 (2)	Co(1)–N(1)–C(1)	127·0 (3)
Co(1)–N(1)–C(5)	114·6 (3)	C(1)–N(1)–C(5)	118·3 (4)
Co(1)–N(2)–C(6)	113·3 (4)	Co(1)–N(2)–C(10)	128·0 (3)
C(6)–N(2)–C(10)	118·6 (4)	Co(1)–N(3)–C(11)	112·8 (3)
Co(1)–N(4)–C(12)	108·6 (3)	Co(1)–N(4)–C(13)	109·7 (3)
C(12)–N(4)–C(13)	114·2 (4)	Co(1)–N(5)–C(14)	111·5 (3)
N(1)–C(1)–C(2)	121·7 (5)	C(1)–C(2)–C(3)	119·7 (6)
C(2)–C(3)–C(4)	118·9 (6)	C(3)–C(4)–C(5)	120·2 (6)
N(1)–C(5)–C(4)	121·1 (5)	N(1)–C(5)–C(6)	113·9 (4)
C(4)–C(5)–C(6)	125·0 (5)	N(2)–C(6)–C(5)	115·3 (5)
N(2)–C(6)–C(7)	120·2 (5)	C(5)–C(6)–C(7)	124·4 (5)
C(6)–C(7)–C(8)	120·6 (5)	C(7)–C(8)–C(9)	119·3 (6)
C(8)–C(9)–C(10)	118·2 (6)	N(2)–C(10)–C(9)	123·1 (5)
N(3)–C(11)–C(12)	107·8 (4)	N(4)–C(12)–C(11)	109·8 (4)
N(4)–C(13)–C(14)	109·7 (4)	N(5)–C(14)–C(13)	106·7 (4)

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* Lists of structure-factor amplitudes, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44815 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·951 (4) and 1·963 (4) Å with the longest value for the Co—N(3) bond. One of the amine protons bonded to N(3) is 2·48 Å from chloride Cl(2), perhaps contributing to the slightly longer Co—N(3) bond length. None of the other coordinated amine nitrogens interacts with other atoms in the crystal structure. Dien N lengths in Co(en)(dien)Cl^{2+} are 1·944 (7), 1·974 (7) and 1·993 (7) Å, giving an average Co—N length for this structure of 1·968 Å compared with a value of 1·950 Å for Co(bpy)(dien)Cl^{2+}. The opposite pattern appears in the difference in Co—Cl lengths for the two structures. This bond is longer for the bpy structure with a value of 2·263 (2) Å, compared with a value of 2·249 (3) Å for π-Co(en)(dien)Cl^{2+}. Both values are within the range of other Co^{III}—Cl lengths, however.

The crystal structure of the complex consists of stacks of complex cations along the crystallographic *c* axis. The stacking interactions are created by the parallel orientation of planar bipyridine ligands of adjacent cations. Separations between atoms of adjacent bipyridine ligands are greater than 4 Å. With the exception of the contact between the H atom of N(3) and Cl(2), there are no interactions between the complex cation and the chloride ions and water molecules of the unit cell. Weak hydrogen bonds appear to exist between the hydrogen of water O(1) and chloride Cl(3) and between water molecules O(2) and O(3).

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Structure of Tetracarbonyl[2-(β-diphenylphosphinoethyl)pyridine]molybdenum(0)

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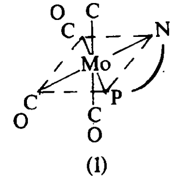
Abstract. [$Mo(CO)_4(C_{19}H_{18}NP)$], $M_r = 499·31$, monoclinic, $P2_1/n$, $a = 12·484$ (4), $b = 10·300$ (2), $c = 16·988$ (4) Å, $\beta = 96·66$ (2)°, $V = 2169·66$ Å^3, $Z = 4$, $D_x = 1·529$ g cm^{-3}; λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6·998$ cm^{-1}, $F(000) = 1008$, $R = 0·0433$ for 3133 unique reflections. The environment about the central Mo atom is a distorted octahedron; the two phenyl rings are planar, with a dihedral angle between them of 76·54°. The pyridine ring is not perfectly planar, but has two atoms out of plane.

Introduction. $Mo(CO)_6$ reacts with 2-(β-diphenylphosphinoethyl)pyridine (np) to form the substitution complex tetracarbonyl{2-(β-diphenylphosphinoethyl)pyridine}molybdenum(0) (Knebel & Angelici, 1973). Since this derivative (I) provides a convenient starting material for the synthesis of other np complexes of molybdenum, an unequivocal molecular structure provided by X-ray crystallographic data will be most beneficial to subsequent studies.



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