

dicular to the P–Pt–P moiety. Selected bond lengths and angles are given in Table 2. Values of 115.9 (10), 115.6 (10) and 116.4 (9)° are found for \angle PC(11)–C(14), \angle PC(21)C(22) and \angle PC(31)C(34) respectively. All these angles involve a C atom pointing away from the Pt. The mean value for the remaining \angle PCC angles is 107.9 (9)°.

This work was supported by the Natural Sciences and Engineering Research Council of Canada. The compound was prepared by A. B. Goel and W. O. Ogini.

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Acta Cryst. (1979). B35, 3062–3065

Structure of Aquachlorobis[*N*-(2-pyridylmethylene)aniline]cobalt(II) Nitrate Monohydrate

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(Received 30 July 1979; accepted 18 September 1979)

Abstract. $[\text{Co}(\text{C}_{12}\text{H}_{10}\text{N}_2)_2\text{Cl}(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$, $\text{C}_{24}\text{H}_{22}\text{ClCoN}_4\text{O}^+ \cdot \text{NO}_3^- \cdot \text{H}_2\text{O}$, $M_r = 556.38$, triclinic, $P1$, $a = 9.977$ (1), $b = 14.171$ (3), $c = 9.185$ (1) Å, $\alpha = 103.68$ (1), $\beta = 89.12$ (1), $\gamma = 98.27$ (1)°, $V = 1248.4$ (2) Å³, $Z = 2$, $D_c = 1.48$ Mg m⁻³. Final $R = 0.051$ for 1958 observed reflexions. The Co atom presents distorted octahedral coordination. The free water molecule connects the NO₃ group to the Cl atom and to the coordinated water molecule through hydrogen bonds.

Introduction. The crystals were provided by the Departamento de Química Analítica of the University of Granada (Spain). An orange prismatic single crystal was used to collect the intensities of 3455 reflexions up to $\theta = 25^\circ$ at 295 K on a PW 1100 four-circle diffractometer. An $\omega/2\theta$ scan technique and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) were used.

Two reflexions were monitored periodically and showed no crystal decomposition. The intensities were corrected for Lorentz and polarization effects and 1958 of them were considered as observed by the criterion $I > 2\sigma(I)$. The absorption effects ($\mu = 0.813$ mm⁻¹) were not corrected. Scattering factors for neutral atoms and anomalous-dispersion corrections for Co and Cl were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The best E map revealed ~20% of the non-hydrogen atoms. The remaining non-hydrogen atoms appeared in successive Fourier syntheses. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.060$. A difference synthesis calculated with those reflexions within $\sin \theta/\lambda < 0.5$ Å⁻¹ showed all H atoms. In order to prevent bias on ΔF vs F_o or $\sin \theta/\lambda$, the last steps of the refinement were carried out with weights w

= $w_1 w_2$, where $w_1 = 1/(a + b|F_o|)^2$ and $w_2 = 1/(c + d \sin \theta/\lambda)$, with coefficients shown in Table 1 and calculated by PESOS (Martinez-Ripoll & Cano, 1975).

After refinement with isotropic temperature factors for the H atoms, the final $R = 0.051$ and $R_w = 0.042$, where $R = (\sum w\Delta^2 F / \sum w|F_o|^2)^{1/2}$. A final difference

synthesis had no electron density $>0.35 \text{ e } \text{Å}^{-3}$. Table 2 shows the final atomic parameters.*

Discussion. Capitan, Iglesia, Salinas & Capitan-Vallvey (1977) reported the synthesis, chemical analysis and thermal properties of a compound with the formula [Co(pa)₂(H₂O)(NO₃)]NO₃·H₂O [pa = *N*-(2-pyridylmethylene)aniline]. Later, Capitan, Salinas & Capitan-Vallvey (1978) reported an infrared study of the above compound and proposed an octahedral

Table 1. Coefficients for the weighting scheme

	<i>a</i>	<i>b</i>
$ F_o < 5.4$	2.14	0.03
$5.4 < F_o < 9.4$	3.11	-0.14
$9.4 < F_o < 16.0$	2.02	-0.07
$16.0 < F_o < 23.0$	0.96	0.00
$23.0 < F_o $	0.68	0.01
	<i>c</i>	<i>d</i>
$\sin \theta/\lambda < 0.25 \text{ Å}^{-1}$	13.19	-50.76
$0.25 \text{ Å}^{-1} < \sin \theta/\lambda$	0.16	1.25

Table 2. Atomic positional parameters ($\times 10^4$; for Co, Cl $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
Co	35098 (7)	66845 (5)	37967 (9)
Cl	33098 (15)	51202 (9)	20336 (17)
O(1)	5568 (4)	6925 (5)	4564 (6)
N(11)	4334 (4)	7426 (3)	2121 (5)
C(11)	4474 (5)	8419 (4)	2551 (7)
C(12)	5151 (6)	9006 (6)	1692 (9)
C(13)	5715 (7)	8586 (5)	381 (9)
C(14)	5580 (6)	7580 (5)	-63 (8)
C(15)	4892 (6)	7034 (5)	824 (7)
C(16)	3869 (5)	8810 (5)	3961 (7)
N(12)	3428 (4)	8243 (3)	4807 (5)
C(17)	2784 (5)	8614 (3)	6175 (6)
C(18)	1792 (7)	9209 (4)	6210 (10)
C(19)	1122 (7)	9543 (5)	7513 (10)
C(110)	1487 (8)	9318 (5)	8783 (14)
C(111)	2491 (8)	8741 (6)	8748 (12)
C(112)	3134 (7)	8374 (4)	7467 (8)
N(21)	2911 (4)	6032 (3)	5650 (5)
C(21)	1564 (6)	5983 (3)	5940 (6)
C(22)	969 (8)	5576 (4)	7069 (7)
C(23)	1776 (8)	5191 (5)	7911 (10)
C(24)	3136 (8)	5232 (5)	7611 (8)
C(25)	3649 (8)	5654 (4)	6492 (8)
C(26)	757 (6)	6374 (4)	4970 (7)
N(22)	1328 (4)	6676 (3)	3869 (5)
C(27)	544 (5)	7049 (3)	2910 (8)
C(28)	891 (6)	6916 (4)	1439 (9)
C(29)	171 (7)	7266 (5)	459 (12)
C(210)	-930 (7)	7758 (5)	973 (13)
C(211)	-1254 (8)	7880 (5)	2445 (12)
C(212)	-542 (6)	7546 (5)	3426 (12)
N(1)	7325 (7)	8989 (5)	6827 (9)
O(2)	6726 (7)	8810 (4)	5702 (10)
O(3)	7732 (7)	8361 (5)	7380 (7)
O(4)	7696 (7)	9863 (5)	7479 (7)
O(5)	7578 (5)	6378 (5)	6041 (7)

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34769 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å)

	E.s.d.'s		σ (Å)	
Involving Co atoms			0.004	
Involving H atoms			0.07	
Involving other atoms			0.01	

	Molecule 1 <i>x</i> = 1	Molecule 2 <i>x</i> = 2	Molecule 1 <i>x</i> = 1	Molecule 2 <i>x</i> = 2	
Co-Cl	2.400		N(x2)-C(x7)	1.42	1.42
-O(1)	2.135		C(x7)-C(x8)	1.39	1.37
-N(x1)	2.151	2.160	-C(x12)	1.37	1.39
-N(x2)	2.197	2.176	C(x8)-H(x8)	0.94	0.97
C(x1)-N(x1)	1.35	1.36	-C(x9)	1.38	1.38
-C(x2)	1.38	1.39	C(x9)-H(x9)	1.08	0.94
-C(x6)	1.44	1.46	-C(x10)	1.35	1.40
C(x2)-H(x2)	0.83	0.82	C(x10)-H(x10)	0.96	1.06
-C(x3)	1.36	1.37	-C(x11)	1.38	1.36
C(x3)-H(x3)	0.99	0.92	C(x11)-H(x11)	0.80	0.87
-C(x4)	1.37	1.38	-C(x12)	1.36	1.36
C(x4)-H(x4)	0.99	0.88	C(x12)-H(x12)	1.05	0.94
-C(x5)	1.37	1.37	N(1)-O(2)	1.16	
C(x5)-N(x1)	1.34	1.32	-O(3)	1.24	
-H(x5)	0.92	0.83	-O(4)	1.25	
C(x6)-N(x2)	1.27	1.28			
-H(x6)	0.96	1.04			

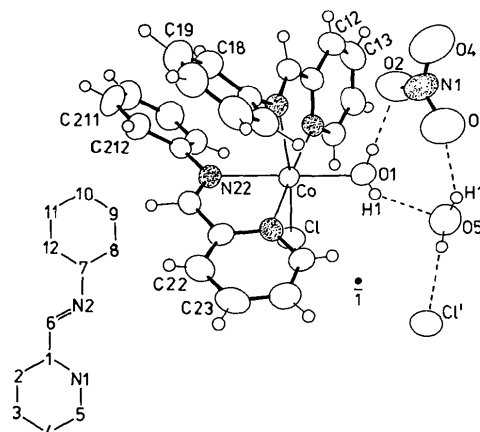


Fig. 1. Perspective drawing of [Co(pa)₂Cl(H₂O)]NO₃·H₂O. Dashed lines represent hydrogen bonds. The atom labels can be obtained from the scheme in the lower left corner, adding a 1 after the chemical symbol for molecule 1 (upper side) or a 2 for molecule 2 (lower side). The labels of several atoms are shown for reference.

Table 4. Bond angles (°) in [Co(pa)₂Cl(H₂O)]NO₃·H₂O Table 5. Atomic deviations (Å) from least-squares planes

	E.s.d.'s	σ (°)
Involving Co atoms	0.2	
Involving H atoms	4	
Involving other atoms	0.7	

Around Co atom			
N(11)—Co—N(21)	172.7	N(12)—Co—O(1)	87.8
N(11)—Co—Cl	91.4	N(22)—Co—N(21)	76.5
N(11)—Co—N(12)	75.8	N(22)—Co—Cl	92.8
N(11)—Co—N(22)	109.3	N(22)—Co—O(1)	159.2
N(11)—Co—O(1)	83.5	N(21)—Co—Cl	92.8
N(12)—Co—N(21)	101.4	N(21)—Co—O(1)	89.7
N(12)—Co—N(22)	79.9	Cl—Co—O(1)	103.5
N(12)—Co—Cl	162.0		

E.s.d.'s are in parentheses.

Plane I		Plane II	
C(17)	0.002 (6)	N(11)	0.000 (5)
C(18)	-0.013 (7)	C(11)	-0.002 (6)
C(19)	0.015 (8)	C(12)	0.004 (7)
C(110)	-0.003 (9)	C(13)	-0.002 (8)
C(111)	-0.012 (9)	C(14)	-0.001 (7)
C(112)	0.007 (7)	C(15)	0.001 (6)

Plane III		Plane IV	
C(27)	0.002 (6)	N(21)	-0.002 (5)
C(28)	0.001 (7)	C(21)	0.005 (5)
C(29)	-0.003 (8)	C(22)	-0.004 (7)
C(210)	0.001 (8)	C(23)	-0.001 (8)
C(211)	0.004 (9)	C(24)	0.003 (7)
C(212)	-0.006 (7)	C(25)	0.001 (7)

Angles between planes (°)

I and II	58.6	II and IV	73.2
I and III	5.7	III and IV	36.3

The group of atoms forming plane I deviates significantly from planarity at the 95% level.

Table 6. Hydrogen-bond distances (Å) and angles (°)

For e.s.d.'s see Tables 3 and 4.

X—H...Y	X...Y	X—H	H...Y	X—H...Y
O(1)—H1(O1)...O(5)	2.74	0.64	2.23	138
O(1)—H2(O1)...O(2)	2.72	0.84	1.90	166
O(5)—H1(O5)...O(3)	2.77	1.05	1.94	134
O(5)—H2(O5)...Cl ⁱ	3.10	0.89	2.22	171

Table 5 shows the best least-squares planes of the six-membered rings (Nardelli, Musatti, Domiano & Andreotti, 1965).

The NO₃ group is bonded to the water molecules through hydrogen bonds (Fig. 1). The free water molecule connects the NO₃ group to the Cl atom. The geometry implied in these hydrogen bonds is given in Table 6.

Most of the calculations were carried out with XRAY 70 (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on the Univac 1100/80 computer.

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environment around the Co atom with two *trans* positions occupied by a NO₃ group and a water molecule. The present study has confirmed the octahedral coordination for Co, but establishes two corrections: (1) the correct formula is [Co(pa)₂Cl(H₂O)]NO₃·H₂O, (2) the coordinated water molecule is *cis* with respect to the Cl atom (assumed to be NO₃ by the above-mentioned authors).

Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Tables 3 and 4 list the bond lengths and angles.

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Acta Cryst. (1979). **B35**, 3065–3067

Bis(diethylenetriammonium) Tetrachloroplatinate(II) Tetrachloride

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(Received 4 June 1979; accepted 7 September 1979)

Abstract. [C₄H₁₆N₃]₂[PtCl₄]Cl₄, 2C₄H₁₆N₃³⁺·4Cl⁻·Cl₄Pt²⁻, monoclinic, *C*2/*c*, *Z* = 4, *a* = 21.496 (3), *b* = 6.841 (1), *c* = 15.820 (4) Å, β = 104.14 (2)°, *V* = 2256.0 (7) Å³, *D*_{calc} = 2.03, *D*_{obs} = 2.02 Mg m⁻³. The structure was determined by Patterson and electron density difference methods and refined by full-matrix least squares to *R* = 0.034, *R*_w = 0.050. The structure comprises discrete diethylenetriammonium, chloride and tetrachloroplatinate(II) ions. Bond distances are normal and NH–Cl hydrogen bonds are involved in crystal packing.

Introduction. The title compound was prepared by a modification of the method of Watt & Cude (1968). Potassium tetrachloroplatinate(II) (0.26 g) was refluxed with diethylenetriamine (0.13 g) in 1 *M* HCl (50 ml) for 4–5 hours. The solution was allowed to stand for 18 hours, when the title compound separated as red-orange crystals. (Analysis: calculated: C, 13.9; H, 4.7; N, 12.2; Cl, 41.0%; found: C, 14.0; H, 4.8; N, 12.1; Cl, 41.2%.)

A crystal, homogeneous under the polarizing microscope, was cut and ground to a cylinder of radius 0.157 mm and length 0.506 mm. Precession photographs showed the systematic absences of the space groups *C*2/*c* and *C*c. *C*2/*c* was chosen as the correct space group (see below). The cell parameters were determined by the least-squares fit of 15 well centred reflections (17° < 2θ < 25°) on a Syntex *P*2₁ diffractometer and the density was determined by flotation in a diiodomethane–carbon tetrachloride mixture, yielding *Z* = 4 for the title formula. Intensities were measured up to 2θ = 55° using a computer-controlled Syntex *P*2₁ diffractometer operated in a

2θ(counter)–θ(crystal) scan mode with a crystal monochromator and Mo *K*α radiation.

After averaging and removal of systematically absent reflections, 2374 reflections were considered significant [*I* > 3σ(*I*)] and were used for structure determination: 211 were considered unobserved and were given no weight in the structure determination unless *F*_c > *F*_o. The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Correction was made both for absorption (μ = 7.49 mm⁻¹; *A** varied from 4.618 to 6.764) and secondary extinction (Larson, 1967; *g* = 1.353 × 10⁻⁷). The stability of the experimental system was monitored by measuring two standard reflections after every 48 reflections (512, 11, 1, 2); these showed e.s.d.'s of 1.9 and 2.3% with no time variation.

The space group *C*2/*c* was chosen after obvious symmetry correlations in a Patterson map computed in *C*c and is justified by the successful solution of the structure. The chloride ions were located from an electron density difference synthesis and in further full-matrix least-squares refinement, minimizing ∑w(|*F*_o| – |*F*_c|)², the temperature factors of the Pt and Cl atoms were made anisotropic. Statistical tests (Hamilton, 1965) showed that this was significant but that the use of anisotropic temperature factors for the C and N atoms was not. Convergence was obtained with 71 variables at *R* = 0.032 (0.034) and *R*_w = 0.050 (0.050) for the observed (all) reflections. The weighting scheme applied was 1/*w* = σ_F² + (0.03*F*_o)²; the standard deviation of an observation of unit weight was 1.286. Scattering factors were taken from Cromer & Waber (1974) and correction for anomalous scattering