one basal axial carbonyl in the C_{3v} arrangement replaced by the phosphine ligand.

The Rh—Rh bond lengths range from 2·692 to 2·795 (2) Å, mean value 2·734 Å, and this is in good agreement with the corresponding lengths in $[Rh_4(CO)_{12}]$ (mean value 2·732 Å) (Wei, 1969), $[Rh_4(CO)_{10}(PPh_3)_2]$ (mean value 2·729 Å), $[Rh_4(CO)_9\{P(OPh)_3\}_3]$ (mean value 2·706 Å) (Heaton *et al.*, 1981) and $[Rh_4(CO)_8\{P(OPh)_3\}_4]$ (mean value 2·720 Å) (Ciani, Garlaschelli, Manassero, Sartorelli & Albano, 1977). The three longest Rh—Rh bond lengths are those involving Rh(1), the substituted atom, showing the back-bonding effect of the phosphine ligand. The Rh—P distance is quite long at 2·394 (2) Å, but this may be expected as the aliphatic isopropyl groups make this phosphine ligand more bulky than, for example, PPh_3 {Rh—P bond lengths in $[Rh_4(CO)_{10}(PPh_3)_2]$ are 2·337 (4) and 2·341 (3) Å}.

In $[Rh_4(CO)_{10}(PPh_3)_2]$ (Heaton *et al.*, 1981), one phosphine ligand is coordinated in a basal axial position, the other in a basal equatorial position. The basal axial positioning of the phosphine ligand in the title compound indicates that this is the site of first substitution.

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Structure of Carbonatobis(histamine)cobalt(III) Chloride Monohydrate

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Abstract. Bis[4-(2-aminoethyl)imidazole-N^3,N^8]-(carbonato-O,O')cobalt(III) chloride monohydrate, $[Co(CO_3)(C_5H_9N_3)_2]Cl.H_2O$, $M_r = 394·71$, triclinic, $P\bar{1}$, $a = 9·712$ (3), $b = 15·556$ (5), $c = 7·192$ (3) Å, $\alpha = 92·24$ (3), $\beta = 128·14$ (2), $\gamma = 106·69$ (3)°, $V = 784·1$ (4) Å^3, $Z = 2$, $D_m = 1·663$ (1), $D_x = 1·672$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·339$ mm^{-1}, $F(000) = 408$, room temperature, $R = 0·030$ for 1950 observed reflections. The histamine molecules and carbonate ion each act as bidentate ligands. The imidazole rings of the histamine molecules are coordinated in *trans* positions. The short O···O distance within the bidentate carbonate ligand results in the distortion of the coordination sphere,

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the O—Co—O angle being 68·4 (1)°. The structure contains a three-dimensional network of hydrogen bonds.

Introduction. The biological significance of histamine has prompted the current interest in its complexes with transition metals. Several structures of histamine complexes have been determined so far (*e.g.* Bonnet & Jeannin, 1970; Dahan, 1976; Wojtczak, Jaskólski & Kosturkiewicz, 1983, 1985, 1987). However, none of them contain Co^{3+} as a central ion. The title compound was prepared as described by Danilczuk & Surdykowski (1986). Their investigations suggest that the imidazole rings of both histamine ligands occupy *trans* positions. The present investigation has been undertaken to determine the structure of the Co^{3+}–histamine system and verify the conclusions of previous studies.

Experimental. Crystals from water, density by flotation, 15 reflections with $22 < 2\theta < 30°$ used to obtain lattice parameters; 2141 unique reflections with $2\theta \leq 45°$ (h: $-10\rightarrow 7$, k: $-16\rightarrow 16$, l: $0\rightarrow 7$) measured on a Syntex $P2_1$ diffractometer; crystal 0·4 × 0·4 × 0·25 mm; graphite-monochromated Mo $K\alpha$ radiation; no significant intensity variation for $24\bar{4}$, 321 and $4\bar{6}\bar{4}$ check reflections monitored every 100 reflections; no absorption correction; 1950 observed reflections with $I \geq 2\sigma(I)$. Structure solved by Patterson method, $\sum w(\Delta F)^2$ minimized in full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976), two reflections ($\bar{2}5\bar{1}$ and $1\bar{2}1$) omitted because of extinction, $w = \sigma^{-2}(F)$ from counting statistics, H-atom positions from $\Delta\rho$ map and not refined, final $R = 0{\cdot}030$, $wR = 0{\cdot}039$, $S = 2{\cdot}387$, $|\Delta/\sigma|_{\max}$ in the final refinement 0·061, $\Delta\rho_{\max} = 0{\cdot}49$, $\Delta\rho_{\min} = -0{\cdot}38$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Other programs used: *ORTEP*II (Johnson, 1976), *PLUTO*78 (Motherwell & Clegg, 1978) and those described by Jaskólski (1982). RIAD-32 computer.

Discussion. The atomic parameters and bond lengths and angles are given in Tables 1 and 2.[*] The numbering scheme is shown in Fig. 1.

In the present structure, histamine exists in the N^{τ}—H tautomeric form (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). The same tautomeric form was also found in other complexes containing bidentate histamine ligands (*e.g.* Wojtczak, Jaskólski & Kosturkiewicz, 1985, 1987). However, the monodentate histaminium ligand (Wojtczak, Jaskólski & Kosturkiewicz, 1983) as well as the histamine base (Bonnet & Ibers, 1973) exist in the N^{π}—H form.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0·48298 (6)	0·22669 (3)	0·09438 (8)	0·0205 (2)
N(1)	0·0824 (4)	−0·0330 (2)	−0·1529 (5)	0·034 (1)
C(2)	0·1411 (5)	0·0570 (2)	−0·1431 (6)	0·032 (1)
N(3)	0·3294 (4)	0·0995 (2)	0·0296 (5)	0·0257 (9)
C(4)	0·3930 (5)	0·0320 (2)	0·1355 (6)	0·028 (1)
C(5)	0·2405 (6)	−0·0494 (2)	0·0224 (7)	0·035 (1)
C(6)	0·5997 (5)	0·0550 (2)	0·3389 (7)	0·035 (1)
C(7)	0·6987 (5)	0·1504 (2)	0·5176 (6)	0·030 (1)
N(8)	0·7109 (4)	0·2262 (2)	0·4035 (5)	0·0252 (9)
N(11)	0·8182 (4)	0·4684 (2)	0·1432 (6)	0·035 (1)
C(12)	0·7344 (5)	0·3760 (2)	0·0828 (6)	0·029 (1)
N(13)	0·6326 (4)	0·3530 (2)	0·1518 (5)	0·0239 (9)
C(14)	0·6557 (5)	0·4369 (2)	0·2646 (6)	0·030 (1)
C(15)	0·7721 (6)	0·5083 (2)	0·2591 (7)	0·040 (1)
C(16)	0·5603 (6)	0·4429 (2)	0·3624 (7)	0·038 (1)
C(17)	0·5190 (5)	0·3585 (3)	0·4465 (7)	0·035 (1)
N(18)	0·3911 (4)	0·2716 (2)	0·2381 (5)	0·0272 (9)
O(1)	0·5236 (3)	0·1791 (2)	−0·1101 (4)	0·0274 (7)
O(2)	0·2856 (3)	0·2164 (2)	−0·2469 (4)	0·0278 (7)
C(21)	0·3667 (5)	0·1812 (2)	−0·3032 (6)	0·024 (1)
O(3)	0·2981 (3)	0·1512 (2)	−0·5197 (4)	0·0333 (8)
Cl	0·0328 (1)	0·35590 (7)	−0·0116 (2)	0·0367 (3)
O*W*	0·0058 (4)	0·2653 (2)	0·3684 (5)	0·046 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s in parentheses*

Co—N(3)	1·932 (3)	Co—N(13)	1·923 (3)
Co—N(8)	1·943 (3)	Co—N(18)	1·948 (3)
Co—O(1)	1·915 (2)	N(11)—C(12)	1·327 (5)
Co—O(2)	1·925 (2)	C(12)—N(13)	1·330 (4)
N(1)—C(2)	1·332 (5)	N(13)—C(14)	1·392 (4)
C(2)—N(3)	1·327 (4)	C(14)—C(15)	1·361 (5)
N(3)—C(4)	1·385 (4)	C(15)—N(11)	1·364 (5)
C(4)—C(5)	1·346 (5)	C(14)—C(16)	1·487 (5)
C(5)—N(1)	1·368 (5)	C(16)—C(17)	1·520 (5)
C(4)—C(6)	1·489 (5)	C(17)—N(18)	1·481 (4)
C(6)—C(7)	1·511 (5)	O(1)—C(21)	1·292 (4)
C(7)—N(8)	1·481 (4)	O(2)—C(21)	1·307 (4)
		C(21)—O(3)	1·253 (4)
N(8)—Co—N(3)	93·2 (1)	O(1)—Co—N(8)	96·0 (1)
N(13)—Co—N(3)	178·8 (1)	O(1)—Co—N(13)	90·9 (1)
N(13)—Co—N(8)	87·8 (1)	O(1)—Co—N(18)	168·2 (1)
N(18)—Co—N(3)	89·3 (1)	O(2)—Co—N(3)	87·6 (1)
N(18)—Co—N(8)	95·7 (1)	O(2)—Co—N(8)	164·3 (1)
N(18)—Co—N(13)	91·2 (1)	O(2)—Co—N(13)	91·3 (1)
O(1)—Co—N(3)	88·5 (1)	O(2)—Co—N(18)	100·0 (1)
		O(2)—Co—O(1)	68·4 (1)
C(2)—N(3)—Co	126·2 (2)	C(14)—N(13)—Co	129·0 (2)
C(4)—N(3)—Co	127·3 (2)	C(17)—N(18)—Co	119·5 (2)
C(7)—N(8)—Co	120·6 (2)	C(21)—O(1)—Co	90·1 (2)
C(12)—N(13)—Co	124·7 (2)	C(21)—O(2)—Co	89·2 (2)
C(5)—N(1)—C(2)	107·5 (3)	C(15)—N(11)—C(12)	108·5 (3)
N(1)—C(2)—N(3)	110·7 (3)	N(11)—C(12)—N(13)	110·5 (3)
C(2)—N(3)—C(4)	106·3 (3)	C(12)—N(13)—C(14)	106·3 (3)
N(3)—C(4)—C(5)	108·3 (3)	N(13)—C(14)—C(15)	107·9 (3)
C(4)—C(5)—N(1)	107·3 (3)	C(14)—C(15)—N(11)	106·8 (3)
N(3)—C(4)—C(6)	121·1 (3)	N(13)—C(14)—C(16)	123·9 (3)
C(5)—C(4)—C(6)	130·6 (3)	C(15)—C(14)—C(16)	128·1 (3)
C(4)—C(6)—C(7)	111·5 (3)	C(14)—C(16)—C(17)	113·2 (3)
C(6)—C(7)—N(8)	111·3 (3)	C(16)—C(17)—N(18)	110·5 (3)
		O(1)—C(21)—O(2)	112·2 (3)
		O(1)—C(21)—O(3)	124·0 (3)
		O(2)—C(21)—O(3)	123·8 (3)

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52375 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths and angles in the imidazole rings are similar to those found in other histamine complexes (Wojtczak *et al.*, 1987, and references cited therein) as well as in the histidine–Co^{3+} complex (Throup, 1977).

Both imidazole rings are planar within experimental error $[\sum(\Delta/\sigma)^2 = 0{\cdot}118$ and $1{\cdot}981]$.

Bond lengths and angles in the side chains are similar to those found in other histamine complexes (*e.g.* Wojtczak *et al.*, 1983, 1987). However, the C(14)—C(16)—C(17) angle [113·2 (3)°] is larger than the corresponding C(4)—C(6)—C(7) angle [111·5 (3)°].

The side-chain conformation of the histamine ligands is synclinal, the C(4)—C(6)—C(7)—N(8) and C(5)—C(4)—C(6)—C(7) torsion angles being −69·4 (4), −140·8 (6)° and −60·4 (4), −153·6 (5)° for the two ligands, respectively.

Both coordination and hydrogen bonding effect a slight deformation of the carbonate ion, the O(1)—C(21), O(2)—C(21) and O(3)—C(21) bond lengths being 1·292 (5), 1·307 (5) and 1·253 (6) Å, respectively, and the O(1)—C(21)—O(2), O(1)—C(21)—O(3) and O(2)—C(21)—O(3) angles equal to 112·2 (3), 124·4 (3) and 123·8 (4)°, respectively.

The carbonate ion is planar $[\sum(\Delta/\sigma)^2 = 0{\cdot}997]$.

The carbonate ligand is bonded to the central Co^{3+} ion *via* its O(1) and O(2) atoms, the Co—O(1) and Co—O(2) distances being 1·915 (2) and 1·925 (2) Å, respectively. This inequality seems to be caused by steric effects in the coordination sphere. Comparison of these bond lengths with those found in other Co^{3+}–CO$_3^{2-}$ systems (Niederhoffer, Martell, Rudolf & Clearfield, 1982) reveals rather weak bonding of the carbonate ligand in the present structure. As a result, the O(1)—Co—O(2) angle is 68·4 (1)° and is among the smallest in the cited review.

Each histamine ligand forms coordinate bonds *via* its N$^{\pi}$ atom of the ring and the amino group of the side chain; the Co—N(3) and Co—N(8) distances are 1·932 (3), 1·943 (3) Å and 1·923 (3), 1·948 (3) Å for the two ligands, respectively. The observed Co—N(3) bonds are similar to whereas the Co—N(8) bonds are a little longer than those found in the Co^{3+}–histidine complex (Throup, 1977).

The observed deviations of the central ion from the best planes of the rings [0·035 (1) and 0·157 (1) Å for the N(11)–C(15) and N(1)–C(5) rings respectively] as well as the differences in the C(4)—C(6)—C(7) angles and conformation of the side chains mentioned above suggest a back-bonding effect stronger for the Co—N(13) bond than for the Co—N(3) bond. This conclusion is supported by

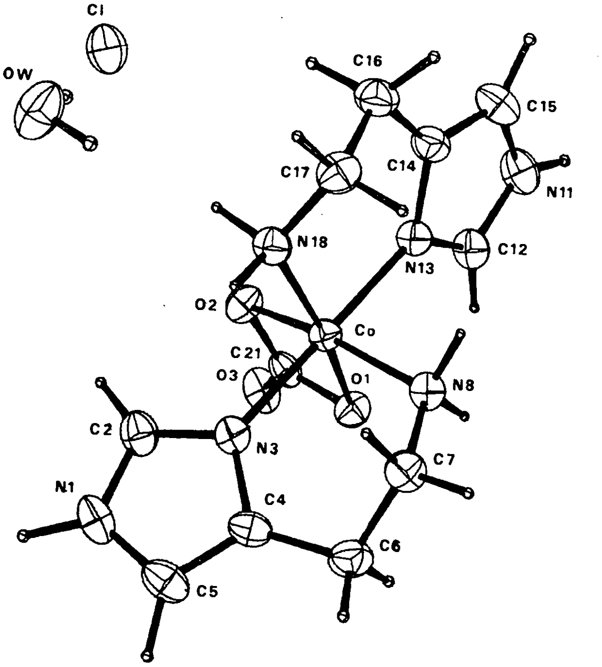

Fig. 1. A perspective view of the ions with atomic numbering scheme.

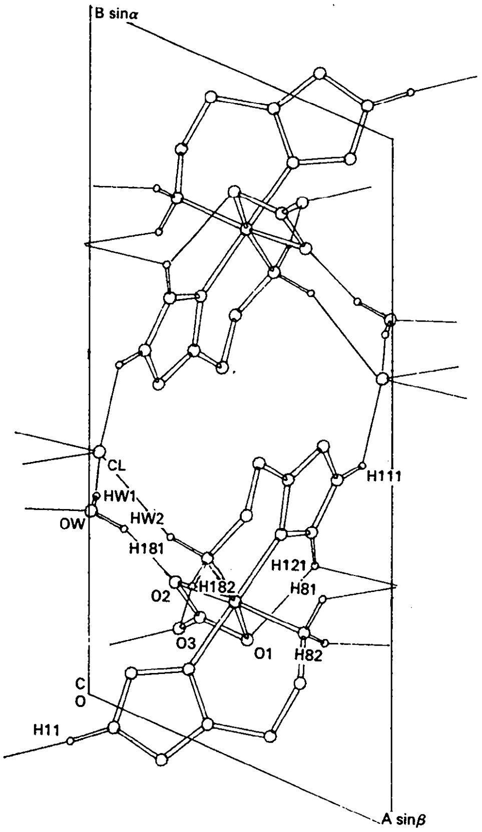

Fig. 2. Projection of the structure down the *c* axis. Hydrogen bonds are shown as single lines.

comparison of the dihedral angles between the Co, N(3), N(13), N(18) and Co, N(3), N(8), N(13) planes and the ring planes [176·8 (3), 92·9 (3)° and 110·1 (3), 164·6 (3)° for the N(11)–C(15) and N(1)–C(5) rings, respectively].

The structure contains a three-dimensional network of hydrogen bonds (Fig. 2) involving N^{τ}—H, amino, water and C(12)—H groups as donors, and water O atoms, carbonate and Cl^- anions as acceptors. The N(1)—H group forms a hydrogen bond, the N(1)···O(3) ($-x$, $-y$, $-1-z$) distance being 2·755 (4) Å. The N(8) amino group is a donor in two hydrogen bonds. With N(8)···Cl($1+x$, y, $1+z$) and N(8)···O*W*($1+x$, y, z) distances of 3·318 (4) and 2·922 (5) Å, respectively. The N(11)—H group of the second histamine ligand forms a hydrogen bond to the Cl^- ion [N(11)···Cl($1-x$, $1-y$, $-z$) = 3·175 (4) Å]. The C(12)—H group acts as a donor in a bifurcated hydrogen bond, the C(12)···O(1) and C(12)···Cl($1+x$, y, z) distances being 2·838 (5) and 3·448 (5) Å, respectively. The N(18) amino group is a donor in two hydrogen bonds, the N(18)···Cl and N(18)···O(3) (x, y, $1+z$) distances being 3·484 (5) and 2·930 (5) Å, respectively. Both water O—H groups form hydrogen bonds [O*W*···Cl = 3·240 (4) and O*W*···O(2) (x, y, $1+z$) = 2·772 (4) Å]. The Cl^- ion participates in five hydrogen bonds, and the carbonate ion is an acceptor in four such bonds, whereas the water O atom is a single-hydrogen-bond acceptor.

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Structure of *trans*-Bromodicarbonyl[*o*-phenylenebis(diphenylphosphine)]-(*p*-tolylmethylidyne)tungsten(0)

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Abstract. $[WBr(CO)_2(C_8H_7)(C_{30}H_{24}P_2)]$, $M_r = 869·39$, monoclinic, $P2_1/n$, $a = 9·505$ (5), $b = 18·333$ (4), $c = 20·775$ (8) Å, $\beta = 96·68$ (4)°, $V = 3595$ (3) Å^3, $Z = 4$, $D_x = 1·606$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0·71073$ Å), $\mu = 4·50$ mm^{-1}, $F(000) = 1704$, $T = 291$ K, final $R = 0·025$ for 4337 observed reflections and 509 variables. The W atom is in a distorted octahedral environment formed by the two P atoms of the chelating diphosphine, two mutually *cis* carbonyl groups and a bromide ligand *trans* to a methylidyne group. The W≡C—*R* ($R = C_6H_4CH_3$-4) group deviates slightly from linearity and the short W—C distance suggests a formal metal—carbon triple bond.

Introduction. Very few X-ray structure determinations have been carried out on neutral six-coordinated methylidyne complexes of tungsten(0), and the majority of them are *trans*-tetracarbonyls, having also halogens (Huttner, Lorenz & Gartzke, 1974; Neugebauer, Fischer, Dao & Schubert, 1978; Fischer, Gammel & Neugebauer, 1980) or the

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