Table 3. *Bond angles* (°) *in the* Fe_4C *group* (*present study*)

Fe(2)–Fe(1)–Fe(3)	57·59 (4)	C(1)–Fe(1)–Fe(2)	48·6 (2)
Fe(2)–Fe(4)–Fe(3)	57·29 (4)	C(1)–Fe(1)–Fe(3)	47·8 (2)
	⟨57·44⟩	C(1)–Fe(4)–Fe(2)	48·8 (2)
Fe(2)–Fe(1)–Fe(4)	46·77 (4)	C(1)–Fe(4)–Fe(3)	47·0 (2)
Fe(3)–Fe(1)–Fe(4)	47·32 (3)		⟨48·0⟩
Fe(2)–Fe(4)–Fe(1)	46·94 (3)	C(1)–Fe(2)–Fe(1)	42·6 (2)
Fe(3)–Fe(4)–Fe(1)	46·57 (3)	C(1)–Fe(2)–Fe(4)	43·7 (2)
	⟨46·90⟩	C(1)–Fe(3)–Fe(1)	42·9 (2)
Fe(1)–Fe(2)–Fe(3)	60·90 (4)	C(1)–Fe(3)–Fe(4)	43·3 (2)
Fe(4)–Fe(2)–Fe(3)	61·84 (4)		⟨43·1⟩
Fe(1)–Fe(3)–Fe(2)	61·51 (4)	C(1)–Fe(2)–Fe(3)	49·1 (2)
Fe(4)–Fe(3)–Fe(2)	60·87 (4)	C(1)–Fe(3)–Fe(2)	50·4 (2)
	⟨61·28⟩		⟨49·8⟩
Fe(1)–Fe(2)–Fe(4)	86·30 (5)	Fe(1)–C(1)–Fe(4)	176·3 (4)
Fe(1)–Fe(3)–Fe(4)	86·11 (5)		
	⟨86·21⟩	Fe(2)–C(1)–Fe(3)	80·5 (3)
		Fe(1)–C(1)–Fe(2)	88·8 (3)
		Fe(1)–C(1)–Fe(3)	89·4 (3)
		Fe(4)–C(1)–Fe(2)	87·5 (3)
		Fe(4)–C(1)–Fe(3)	89·7 (3)
			⟨88·8⟩

the neutral species. We thus conclude that the two anions are very similar, the largest differences being observed in the Fe—Fe distances.

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trans-Tetraaquabis(nicotinamide)cobalt(II) Dichloride Dihydrate

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Abstract. $[Co(H_2O)_4(C_6H_6N_2O)_2]Cl_2.2H_2O$, $C_{12}H_{20}CoN_4O_6^{2+}.2Cl^-.2H_2O$, $M_r = 482\cdot18$, monoclinic, $P2_1/n$, $a = 11\cdot0895$ (2), $b = 13\cdot2582$ (3), $c = 7\cdot1124$ (1) Å, $\beta = 101\cdot35$ (1)°, $Z = 2$, $D_c = 1\cdot562$ Mg m^{-3}, $\mu(Mo\,K\alpha) = 1\cdot140$ mm^{-1}, $F(000) = 498$, final $R = 0\cdot041$ for 2116 observed reflexions. The structure consists of *trans*-tetraaquabis(nicotinamide)cobalt(II) cations, chloride anions and water molecules forming a three-dimensional network. Hydrogen bonds are responsible for the structure building. The Co atom is at the center of a distorted octahedron with the four water molecules in equatorial positions. The nicotinamide molecules coordinate to Co through the N atoms of the pyridine rings which adopt an eclipsed configuration.

Introduction. The title compound has been used as starting material for the synthesis of a new Co complex containing nicotinamide and glutathione as ligands (Silió, 1978). This new compound presents a high biological activity as a glucose tolerance factor (GTF) and it has been postulated that its specific action is to facilitate the physiological action of insulin so that animals deprived of a GTF develop insulin-resistant diabetes (Silió, 1979).

This structural study has been undertaken in order to determine the coordination features of the nicotinamide molecules in the title compound, which would be expected to be maintained in the GTF compound.

Salmon-pink crystals were obtained from two aqueous solutions of $CoCl_2$ and nicotinamide as reported previously (Silió, 1978).

A prismatic crystal of dimensions $0.25 \times 0.30 \times 0.35$ mm was used to collect the data on a PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 3114 reflexions, up to $\theta = 30°$, were measured in the $\omega/2\theta$ scan mode. Of these, 998 were considered as unobserved by the criterion $I < 2\sigma(I)$ and not taken into account in the structure determination and refinement. Systematic absences were $h0l$ for $h + l$ odd and $0k0$ for k odd, leading to the space group $P2_1/n$. No absorption correction was applied.

Scattering factors for neutral atoms, including the anomalous-dispersion factors, were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by Patterson and Fourier syntheses. The Co atom was located at the origin because of the cell-content requirements. With this, the Patterson map was solved for the Cl atom. A Fourier synthesis was used to determine the positions of the remaining non-H atoms. After anisotropic least-squares

refinement ($R = 0.055$), the H atoms were easily located on a difference synthesis calculated for reflexions with $\sin \theta/\lambda < 0.5$ Å⁻¹. Final refinements, with fixed isotropic temperature factors for H atoms, gave $R = 0.041$ for observed reflexions only. Unit weight was applied to every reflexion, giving rise to a flat dependence of $\langle w\Delta^2 F \rangle$ versus either $\langle F_o \rangle$ or $\langle \sin \theta/\lambda \rangle$. Final atomic parameters are listed in Table 1.*

Discussion. As can be seen in Fig. 1, the structure consists of *trans*-tetraaquabis(nicotinamide)cobalt(II) cations and chloride anions, held together by hydrogen bonds through H(12) and H(21) of the coordinated water molecules and H(7) of the amide group. This linkage is enhanced by additional hydrogen bonds involving a water molecule, O(4), not coordinated to Co, which connects the chloride anions with O(3) and N(2) of the amide group. O(3) forms one further bond

Table 1. *Final atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H, $\times 10^5$ *for* Cl) *and isotropic thermal parameters* ($\times 10^4$, $\times 10^3$ *for* H) *with e.s.d.'s in parentheses*

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

|	x	y	z	U_{eq} (Å²)
Co	0	0	0	218 (2)
Cl	23376 (8)	−10575 (8)	−42490 (14)	383 (3)
O(1)	481 (3)	−1219 (2)	−1556 (5)	397 (9)
O(2)	57 (3)	−934 (2)	2381 (4)	405 (9)
O(3)	4426 (2)	−1996 (2)	2065 (4)	369 (9)
O(4)	−1710 (3)	−2159 (3)	3543 (6)	417 (9)
N(1)	1932 (2)	333 (2)	876 (4)	241 (8)
N(2)	6009 (3)	−965 (3)	3144 (6)	386 (10)
C(1)	2344 (3)	1286 (3)	1075 (5)	286 (10)
C(2)	3566 (3)	1524 (3)	1719 (7)	365 (12)
C(3)	4411 (3)	755 (3)	2168 (6)	329 (11)
C(4)	4014 (3)	−239 (2)	1951 (5)	227 (9)
C(5)	4843 (3)	−1132 (3)	2397 (5)	250 (9)
C(6)	2760 (3)	−410 (3)	1309 (5)	236 (9)
H(1)	167 (4)	190 (4)	77 (6)	32
H(2)	390 (5)	219 (4)	190 (8)	32
H(3)	522 (3)	93 (3)	261 (5)	32
H(6)	249 (4)	−110 (3)	105 (6)	32
H(7)	625 (4)	−41 (4)	332 (7)	32
H(8)	640 (4)	−147 (4)	343 (7)	32
H(11)	12 (5)	−167 (4)	−200 (7)	32
H(12)	84 (5)	−112 (4)	−228 (8)	32
H(21)	63 (4)	−98 (4)	322 (7)	32
H(22)	−46 (4)	−124 (3)	272 (6)	32
H(41)	−130 (5)	−242 (4)	453 (8)	32
H(42)	−183 (5)	−251 (4)	290 (8)	32
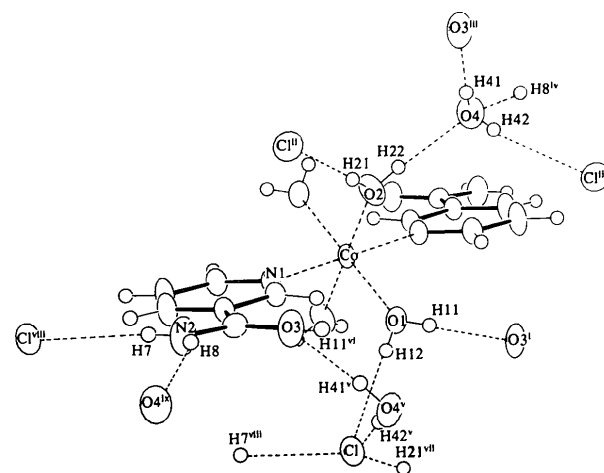
Fig. 1. Projection of the structure in the plane defined by O(1), O(2) and N(1) (*ORTEP*, Johnson, 1965), showing all the hydrogen bonds present in the crystal.

Table 2. *Geometry of the hydrogen bonds with e.s.d.'s in parentheses*

	$X–Y$ (Å)	$X–H$ (Å)	$H \cdots Y$ (Å)	$X–H \cdots Y$ (°)
O(1)–H(11)–O(3ⁱ)	2·735 (4)	0·75 (5)	1·99 (5)	169 (5)
O(1)–H(12)–Cl	3·083 (4)	0·72 (6)	2·38 (6)	166 (5)
O(2)–H(21)–Clⁱⁱ	3·128 (3)	0·78 (4)	2·35 (4)	178 (5)
O(2)–H(22)–O(4)	2·793 (5)	0·77 (5)	2·02 (5)	175 (5)
O(4)–H(41)–O(3ⁱⁱⁱ)	2·807 (5)	0·83 (5)	1·98 (5)	170 (5)
O(4)–H(42)–Clⁱⁱⁱ	3·134 (4)	0·65 (5)	2·50 (5)	168 (7)
N(2)–H(7)–Clᵛⁱⁱⁱ	3·256 (4)	0·79 (5)	2·50 (5)	161 (4)
N(2)–H(8)–O(4ⁱˣ)	2·950 (5)	0·80 (5)	2·28 (5)	143 (5)

Symmetry code as in Table 3.

Table 3. *Bond distances (Å) and angles (°) in the coordination polyhedra around Co, Cl and O(4) with e.s.d.'s in parentheses*

Coordination around Co

Co–O(1)	2× 2·087 (3)	N(1)–O(1)	2× 2·953 (4)
Co–O(2)	2× 2·088 (3)	N(1)–O(1ˣ)	2× 3·047 (4)
Co–N(1)	2× 2·156 (3)	N(1)–O(2)	2× 3·027 (4)
O(1)–O(2)	2× 2·953 (5)	N(1)–O(2ˣ)	2× 2·976 (4)
O(1)–O(2ˣ)	2× 2·951 (4)		

O(1)–Co–O(2)	2× 90·0 (1)	N(1)–Co–O(1ˣ)	2× 91·8 (1)
O(1)–Co–O(2ˣ)	2× 90·0 (1)	N(1)–Co–O(2)	2× 91·0 (1)
N(1)–Co–O(1)	2× 88·2 (1)	N(1)–Co–O(2ˣ)	2× 89·0 (1)

Coordination around Cl

Cl–H(12)	2·38 (6)	Cl–H(7ᵛⁱⁱⁱ)	2·50 (5)
Cl–H(21ᵛⁱⁱ)	2·35 (4)	Cl–H(42ᵛ)	2·50 (5)

H(12)–Cl–H(21ᵛⁱⁱ)	84 (2)	H(21)–Cl–H(7ᵛⁱⁱⁱ)	123 (2)
H(12)–Cl–H(7ᵛⁱⁱⁱ)	110 (2)	H(21)–Cl–H(42ᵛ)	130 (2)
H(12)–Cl–H(42ᵛ)	80 (2)	H(7)–Cl–H(42ᵛ)	107 (2)

Coordination around O(4)

O(4)–H(41)	0·83 (5)	O(4)–H(8ⁱᵛ)	2·28 (5)
O(4)–H(42)	0·65 (5)	O(4)–H(22)	2·02 (5)

H(22)–O(4)–H(41)	102 (4)	H(41)–O(4)–H(42)	108 (6)
H(22)–O(4)–H(42)	106 (5)	H(41)–O(4)–H(8ⁱᵛ)	123 (4)
H(22)–O(4)–H(8ⁱᵛ)	115 (2)	H(42)–O(4)–H(8ⁱᵛ)	102 (5)

Symmetry code: (i) $-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $-\frac{1}{2} + z$; (ii) $x, y, 1 + z$; (iii) $-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$; (iv) $-1 + x, y, z$; (v) $\frac{1}{2} + x$, $-\frac{1}{2} - y$, $-\frac{1}{2} + z$; (vi) $\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$; (vii) $x, y, -1 + z$; (viii) $1 - x, -y, -z$; (ix) $1 + x, y, z$; (x) $-x, -y, -z$.

with the coordinated water molecules O(1). So, hydrogen bonds are mainly responsible for the three-dimensional structure building. Their geometry is listed in Table 2.

Cl and O(4) present a very distorted tetrahedral coordination whose geometries are listed in Table 3. In the case of coordination around Cl, two of the Cl···H distances (2·50 Å) seem to be large to be considered as true H···Cl bonds. However, the H atoms involved present very short *X*–H bonds (0·65 and 0·79 Å) as a consequence of shifts produced during the least-squares refinement. In fact, their *X*–H···*Y* angles (168 and 161° respectively), as well as the O–Cl and N–Cl distances, are normal for N–H···Cl and O–H···Cl bonds (Ammon & Plastas, 1979; Mathew & Palenik, 1978; Perales, Martínez-Ripoll & Fayos, 1980).

The [Co(H₂O)₄(C₆H₆N₂O)₂]²⁺ cation is centrosymmetric with the four water molecules in the equatorial plane. Symmetry requires the two nicotinamide moieties to adopt an eclipsed configuration, as in Coᴵᴵ nicotinate tetrahydrate (Anagnostopoulos, Drew & Walton, 1969). Both compounds also present equivalent Co–O and Co–N bond lengths and angles which are listed in Table 3. The cation can be visualized in Fig. 2, including the interatomic distances and angles of the nicotinamide molecule. The pyridine ring is completely planar and almost perpendicular (90·5°) to the plane defined by the four water molecules. It is also twisted (37·8°) with respect to the plane defined by O(1), Co
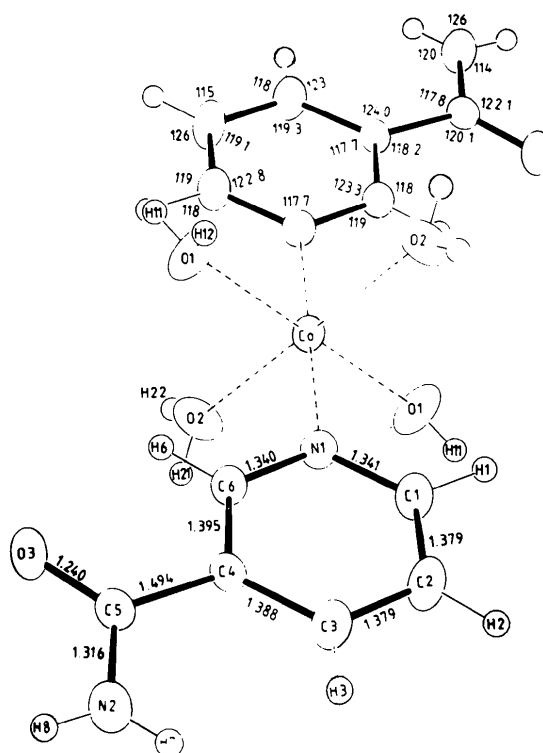
and N(1). The amide group is rotated 4·8° with respect to the ring and the C(3)–N(1)–Co angle (177·6°) deviates significantly from linearity. Hydrogen bonds and packing effects could be responsible for these results.

Fig. 2. The [Co(H₂O)₄(C₆H₆N₂O)₂]²⁺ cations projected on the O(1), O(2), N(1) plane (*ORTEP*, Johnson, 1965). Interatomic distances and angles for the nicotinamide moieties are included. E.s.d.'s are 0·005 Å and 0·03° respectively.

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