Alkylcobalt(III) Complex of a Quinquedentate Ligand. Preparation, Characterisation, and Crystal and Molecular Structure of 2,12-Di-2-pyridyl-3,7,11-triazatrideca-2,11-diene-$N^{2'},N^{2''},N^{3},N^{7},N^{11}$-(methyl)cobalt(III) Di-iodide Dihydrate

By **David A. Stotter,*** Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ
Jill Trotter,* Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB

Crystals of the title compound (I) are triclinic, space group $P\bar{1}$, $a = 15.310(6)$, $b = 10.413(2)$, $c = 8.464(2)$ Å, $\alpha = 97.34(2)$, $\beta = 103.37(3)$, $\gamma = 92.59(2)°$, $Z = 2$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to $R = 0.053$ for 2 493 unique reflections measured by diffractometer. The cobalt atom of the cation has approximately octahedral co-ordination involving a methyl group and the five nitrogen atoms of the quinquedentate ligand. The methyl group is *trans* to a pyridine nitrogen [Co–N(1) 2.05(1) Å]; the mean of the equatorial Co–N distances is 1.96(2) Å. The water of crystallisation, secondary amino-group, and iodide ions form a hydrogen-bonded array which is discussed with reference to analytical and spectroscopic data.

THE title compound (I) has been synthesised as part of a study of the properties of transition-metal complexes of quinquedentate ligands. The low-spin cobalt(II) parent compound has previously been characterised.[1]

Alkylcobalt(III) complexes of quadridentate ligands are well known, and several have been investigated by single-crystal X-ray diffraction.[2,3] However, apart from the naturally occurring corrinoids,[4] only one other

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[1] R. H. Prince and D. A. Stotter, *Inorg. Chim. Acta*, 1974, **10**, 89.

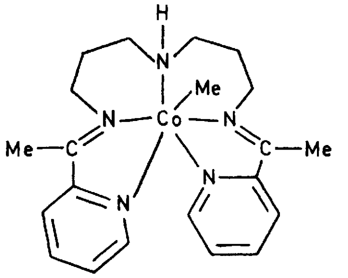
[2] D. Dodd and M. D. Johnson, *J. Organometallic Chem.*, 1973, **52**, 1.

[3] D. A. Stotter, G. M. Sheldrick, and R. Taylor, *J.C.S. Dalton*, 1975, 2124.

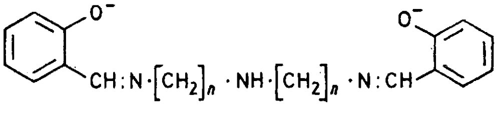
[4] R. H. Prince and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 321.

quinquedentate ligand (II) has previously been shown to form alkylcobalt(III) complexes,[5,6] and crystal structures of these compounds have not so far been published.

The di-iodide salt (I) was chosen for investigation because i.r. spectroscopy and other studies (see later) indicated the presence of hydrogen bonding involving water and the secondary amino-group of the ligand. This interaction appears to be absent in the diperchlorate salt, which may also be unsuitable for *X*-ray crystallographic study owing to disorder of the anions.[7] Hydrogen bonding of the secondary amino-group has been suggested to explain the broadness or weakness of the N–H stretching band in the i.r. spectra of copper(II) and nickel(II) complexes of (III) and related ligands,[8,9] and such an interaction has been demonstrated by crystallography[10] to occur in a cobalt(III) complex of (II) discussed later.



(I)



(II) $n = 3$

(III) $n = 2$

EXPERIMENTAL

Microanalytical, spectroscopic, and conductometric results were obtained as previously described.[11] Thermogravimetric analysis was performed by use of a DuPont 950-900. Deuterium substitution of O–H and N–H groups was carried out by recrystallisation from D_2O at pD 11.

Deaerated solutions of cobalt(II) nitrate hexahydrate (1.45 g, 5 mmol) and glacial acetic acid (6 drops) in water (20 ml), 3,3′-iminobispropylamine (0.66 g, 5 mmol) in ethanol (20 ml), and 2-acetylpyridine (1.25 g, 10.3 mmol) in ethanol (20 ml) were mixed and gently heated under reflux under nitrogen for 6 h. The red-brown solution was set aside overnight. Sodium hydroxide (0.3 g) in water (5 ml) was added, and the solution cooled in an ice-bath. Excess of sodium borohydride (0.1 g, *ca.* 25 mmol) and methyl iodide (3.0 g, *ca.* 20 mmol) were introduced, and the solution warmed to room temperature and stirred in the dark under nitrogen for 1 h. Sodium iodide (0.75 g, 5 mmol) was added, the ethanol evaporated, and the solid *product* filtered off and dried *in vacuo* (1.91 g, 55%). Orange crystals of the dihydrate suitable for *X*-ray diffraction were produced by recrystallisation from water and dried in air (Found: C, 36.2; H, 4.9; N, 10.0. $C_{21}H_{34}CoI_2N_5O_2$ requires C, 36.0; H, 4.9; N, 10.0%).

A crystal *ca.* 0.04 × 0.09 × 0.17 mm was selected for data collection. Intensity measurements were made on a Philips PW 1100 four-circle *X*-ray diffractometer by use of graphite-monochromated Mo-K_α radiation and a θ—2θ scan technique. Weak reflections which gave $I_t - 2\sqrt{I_t} < I_b$ on the first scan were omitted, I_t being the intensity at the top of the reflection peak and I_b the mean of two preliminary 5-s background measurements on either side of the peak. The intensities of 2 703 reflections with $3.0 < \theta < 25.0°$ were measured in one hemisphere of reciprocal space and 2 223 reflections were omitted; in the other hemisphere 1 937 reflections were measured and 694 were omitted in the range $3.0 < \theta < 20.0°$. The background measuring time was proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan of the reflection peak. Reflections for which $I_i < 500$ counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a variable scan width [θ range (0.70 + 0.20 tan θ)°] were used. Three standard reflections measured every 3 h during data collection showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements by use of a program written for the PW 1100 diffractometer.[12] The variance of the intensity *I* was calculated as the sum of the variance due to counting statistics and $(0.03I)^2$, where the term in I^2 was introduced to allow for other sources of error.[13] *I* and σ(*I*) were corrected for Lorentz and polarisation factors and reflections for which $I < 3\sigma(I)$ were rejected. No absorption corrections were applied. Equivalent reflections were averaged to give 2 493 unique reflections.

RESULTS

Crystal Data.—$C_{21}H_{34}CoI_2N_5O_2$, $M = 701.3$, Triclinic, $a = 15.310(6)$, $b = 10.413(2)$, $c = 8.464(2)$ Å, $\alpha = 97.34(2)$, $\beta = 103.37(3)$, $\gamma = 92.59(2)°$, $U = 1\,298.12$ Å^3, $D_c = 1.79$, $Z = 2$, $D_m = 1.78$ (by flotation). Mo-K_α radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 28.74$ cm^{-1}. Space group $P\bar{1}$ assumed and confirmed by subsequent satisfactory refinement.

Structure Solution and Refinement.—The two iodide ions and the cobalt atom were located from a three-dimensional Patterson map; their positions were refined by least-squares procedures and gave *R* as 0.224. The positions of all the remaining non-hydrogen atoms were determined from a difference-Fourier synthesis. Subsequent refinement with anisotropic temperature factors for the cobalt atom and iodide ions and isotropic temperature factors for the remaining atoms gave *R* 0.054. Examination of the values of F_o and F_c indicated that a few of the strong low-angle reflections were subject to extinction and these were omitted from further refinement and from the final *R* index. A difference-Fourier map did not show any features >0.6 eÅ^{-3} or < -0.6 eÅ^{-3} apart from diffraction ripples around

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the iodide ions. Only a few concentrations of electron density in expected hydrogen-atom positions could be located on a difference map, and no allowance was therefore made for hydrogen atom contributions in the final least-squares refinement. This converged at R 0.053, R' 0.051 $\{R' = \Sigma w^{\frac{1}{2}}[F_o - F_c]/\Sigma w^{\frac{1}{2}}|F_o|\}$ for 140 independent parameters; the reflections were weighted as $w = 1/\sigma^2(F_o)$. Final atomic co-ordinates and thermal parameters are given in Tables 1, bond lengths and angles in Table 2. Final structure factors are listed in Supplementary Publication No. SUP 21949 (16 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates (× 10^4) and isotropic temperature factors (Å^2 × 10^3)

	x/a	y/b	z/c	U
Co	7 666(1)	3 758(1)	6 833(2)	*
N(1)	6 582(5)	3 037(8)	4 976(10)	33(2)
C(2)	6 149(7)	3 631(10)	3 729(13)	36(3)
C(3)	5 559(8)	2 912(11)	2 316(15)	49(3)
C(4)	5 442(8)	1 580(12)	2 209(15)	57(4)
C(5)	5 881(7)	959(11)	3 503(15)	49(3)
C(6)	6 453(7)	1 729(10)	4 872(13)	34(3)
C(7)	6 921(7)	1 234(10)	6 356(13)	38(3)
N(8)	7 505(5)	2 022(8)	7 368(11)	36(2)
C(9)	7 861(7)	1 727(10)	9 047(14)	44(3)
C(10)	7 244(7)	2 339(11)	10 092(14)	48(3)
C(11)	7 224(7)	3 818(11)	10 154(14)	47(3)
N(12)	6 925(5)	4 234(8)	8 457(10)	35(2)
C(13)	6 783(7)	5 660(11)	8 833(14)	48(3)
C(14)	6 505(7)	6 240(11)	7 211(14)	49(3)
C(15)	7 305(7)	6 578(10)	6 486(13)	40(3)
N(16)	7 737(5)	5 393(7)	6 006(10)	33(2)
C(17)	8 203(7)	5 431(10)	4 925(14)	42(3)
C(18)	8 613(7)	4 236(10)	4 510(13)	39(3)
C(19)	9 166(8)	4 057(11)	3 410(15)	52(3)
C(20)	9 493(8)	2 861(12)	3 125(16)	62(4)
C(21)	9 284(9)	1 879(12)	3 919(17)	64(4)
C(22)	8 737(8)	2 109(11)	5 031(15)	50(3)
N(23)	8 411(5)	3 267(8)	5 311(11)	39(2)
C(24)	8 846(7)	4 384(10)	8 476(14)	42(3)
C(25)	6 677(8)	−134(12)	6 594(16)	63(4)
C(26)	8 312(8)	6 627(12)	4 100(15)	58(4)
I(1)	4 610(1)	2 943(1)	7 492(1)	*
I(2)	8 909(1)	1 780(1)	9 160(1)	*
O(1)	972(6)	419(9)	2 748(12)	85(3)
O(2)	3 207(8)	938(11)	9 392(15)	124(4)

* Anisotropic temperature factors (Å^2 × 10^4) in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	294(8)	328(9)	335(9)	77(7)	105(7)	45(7)
I(1)	436(5)	514(5)	506(6)	86(4)	32(4)	−25(4)
I(2)	794(7)	799(8)	853(8)	204(6)	210(6)	−158(6)

All computations were performed by use of the programs SHELX.[14] Scattering factors and anomalous dispersion corrections for cobalt and iodine were taken from refs. 15 and 16.

Thermogravimetric Analysis.—(I) showed a slow weight loss of 5.0% between 60 and 130 °C (calc. for two water molecules 5.1%).

I.r. spectra.—Functional group frequencies (cm^{-1}): ν(O–H), 3 430br; ν(O–D), 2 570, ν_D/ν_H 0.75; ν(N–H), 3 085; ν(N–D), 2 310, ν_D/ν_H 0.75; δ(O–H), 1 636; δ(O–D), 1 205, δ_D/δ_H 0.74; ν(C=N), 1 612; pyridine bands I and II (ref. 17), 1 591, 1 565. ν(C=N) is weak, as was observed in the spectrum of the cobalt(II) parent complex,[1] and another exocyclic C=N stretch may be masked by band I of the pyridine ring.

Conductances.—In water (213 S cm^2 mol^{-1}) and nitromethane (144 S cm^2 mol^{-1}), values were as expected for a 2 : 1 electrolyte.

Other Salts.—When the dihydrate (I) was set aside for 12 h *in vacuo* the crystals began to crumble, and analysis of two independently prepared samples of the product indicated the formation of a monohydrate [Found: C, 37.1(2); H, 4.6(2); N, 10.5(3). $C_{21}H_{32}CoI_2N_5O$ requires C, 36.9; H, 4.7; N, 10.3%]. The ν(O–H) band in the i.r. spectrum was still present but markedly reduced in intensity, in agreement with this formulation.

TABLE 2

Molecular geometry

(*a*) Intramolecular bond lengths (Å)

Co–N(1)	2.04(1)	C(9)–C(10)	1.54(2)
Co–N(8)	1.94(1)	C(10)–C(11)	1.54(2)
Co–N(12)	2.00(1)	C(11)–N(12)	1.53(1)
Co–N(16)	1.93(1)	N(12)–C(13)	1.52(1)
Co–N(23)	1.95(1)	C(13)–C(14)	1.55(2)
Co–C(24)	2.03(1)	C(14)–C(15)	1.54(1)
N(1)–C(2)	1.35(1)	C(15)–N(16)	1.48(1)
N(1)–C(6)	1.36(1)	N(16)–C(17)	1.29(1)
C(2)–C(3)	1.42(1)	C(17)–C(26)	1.52(2)
C(3)–C(4)	1.38(2)	C(17)–C(18)	1.46(1)
C(4)–C(5)	1.40(2)	C(18)–C(19)	1.40(2)
C(5)–C(6)	1.41(1)	C(19)–C(20)	1.38(2)
C(6)–C(7)	1.46(1)	C(20)–C(21)	1.36(2)
C(7)–C(25)	1.51(2)	C(21)–C(22)	1.40(2)
C(7)–N(8)	1.27(1)	C(22)–N(23)	1.34(1)
N(8)–C(9)	1.48(1)	N(23)–C(18)	1.35(1)

(*b*) Bond angles (°)

N(1)–Co–N(8)	80.2(3)	C(7)–N(8)–Co	117.3(7)
N(1)–Co–N(12)	94.3(3)	C(7)–N(8)–C(9)	119.7(9)
N(1)–Co–N(16)	92.7(3)	Co–N(8)–C(9)	121.0(7)
N(1)–Co–N(23)	87.0(3)	N(8)–C(9)–C(10)	106.2(8)
N(8)–Co–N(12)	84.0(3)	C(9)–C(10)–C(11)	114.0(9)
N(8)–Co–N(23)	94.8(4)	C(10)–C(11)–N(12)	112.9(9)
N(8)–Co–C(24)	99.7(4)	C(11)–N(12)–C(13)	103.4(8)
N(12)–Co–N(16)	99.4(3)	C(11)–N(12)–Co	117.7(6)
N(12)–Co–C(24)	93.3(4)	Co–N(12)–C(13)	116.9(6)
N(16)–Co–N(23)	82.0(4)	N(12)–C(13)–C(14)	109.9(9)
N(16)–Co–C(24)	87.0(4)	C(13)–C(14)–C(15)	113.2(9)
N(23)–Co–C(24)	85.4(4)	C(14)–C(15)–N(16)	111.3(8)
N(1)–Co–C(24)	172.4(4)	C(15)–N(16)–Co	126.3(7)
N(8)–Co–N(16)	172.3(4)	C(15)–N(16)–C(17)	118.1(9)
N(12)–Co–N(23)	178.1(3)	Co–N(16)–C(17)	115.6(7)
Co–N(1)–C(2)	128.0(7)	N(16)–C(17)–C(18)	115.4(10)
Co–N(1)–C(6)	111.0(6)	N(16)–C(17)–C(26)	122.9(10)
C(2)–N(1)–C(6)	119.2(9)	C(18)–C(17)–C(26)	121.6(10)
N(1)–C(2)–C(3)	121.1(9)	C(17)–C(18)–N(23)	113.1(10)
C(2)–C(3)–C(4)	119.3(11)	C(17)–C(18)–C(19)	125.8(10)
C(3)–C(4)–C(5)	119.9(11)	N(23)–C(18)–C(19)	121.1(10)
C(4)–C(5)–C(6)	117.9(10)	C(18)–C(19)–C(20)	119.0(11)
C(5)–C(6)–N(1)	122.5(10)	C(19)–C(20)–C(21)	120.1(13)
C(5)–C(6)–C(7)	124.5(10)	C(20)–C(21)–C(22)	118.9(12)
N(1)–C(6)–C(7)	113.0(9)	C(21)–C(22)–N(23)	121.6(11)
C(6)–C(7)–N(8)	115.9(9)	C(22)–N(23)–Co	126.8(8)
C(6)–C(7)–C(25)	119.1(9)	C(22)–N(23)–C(18)	119.3(10)
C(25)–C(7)–N(8)	124.9(10)	Co–N(23)–C(18)	113.8(7)

When dimethyl sulphate was employed as methylating agent in the preparation, a low yield (*ca.* 10%) of the anhydrous *diperchlorate* salt of the complex was obtained by addition of sodium perchlorate to the reaction mixture.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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The remainder of the cobalt(II) complex was recovered unmethylated as the known [1] perchlorate salt. The former compound may be prepared in almost quantitative yield by addition of perchloric acid or sodium perchlorate to an aqueous solution of (I) (Found: C, 41.2; H, 5.0; N, 11.4. $C_{21}H_{30}Cl_2CoN_5O_8$ requires C, 41.4; H, 4.8; N, 11.5%). ν(N–H) in the i.r. spectrum of this salt occurs at 3 203 cm^{-1}. Small crystals were grown from ethanol–water, but these gave very weak precession photographs which may be indicative of perchlorate disorder. Since this salt is anhydrous it was employed to obtain the ligand n.m.r. spectrum of the complex: τ(CD_3CN) 1.1—2.8 (8 H, m, pyridines), 7.16 (3 H, s, CH_3), 7.33 (3 H, s, CH_3), 7.69 (3 H, s, CH_3–Co), 5.5—8.0 (12 H, m, methylene chains).

DISCUSSION

The cobalt atom of the cation has approximately octahedral co-ordination; the five nitrogen atoms of the quinquedentate ligand are arranged in an approximately square-pyramidal manner and a methyl group completes the six-co-ordination. One pyridine nitrogen is co-ordinated in an axial position and the other equatorially; this is consistent with the solution n.m.r. spectrum which shows two distinct iminomethyl resonances and a complicated series of aromatic peaks.

The general arrangement of the ligand around the metal is similar to that found in the crystal structure of its copper(II) complex,[18] although a study of stereomodels [19] suggested that this mode of co-ordination would be unfavourable because of the twist required in the ligand at N(8). The *trans*-influence of a σ-bonded carbon atom [20] can be seen by comparing the Co–N(1) bond length [2.04(1) Å] with the mean of the equatorial Co–N distances [1.96(2) Å].

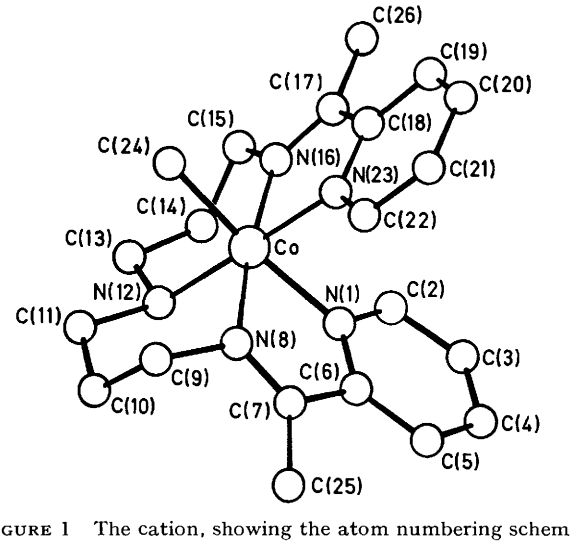

FIGURE 1 The cation, showing the atom numbering scheme employed

Both the six-membered chelate rings are in the chair conformation puckered away from the methyl-cobalt bond (Figure 1). There is some evidence from i.r. [21] and structural [10,22] studies that metal–secondary-nitrogen bonds common to two six-membered chelate rings are weak, and the differences between the Co–N(12) bond length [2.00(1) Å] and the other three equatorial Co–N distances [1.93(1), 1.94(1), and 1.95(1) Å] may be due to cumulative strain in the six-membered chelate rings. N(12) is also involved in a hydrogen-bonded array (see later).

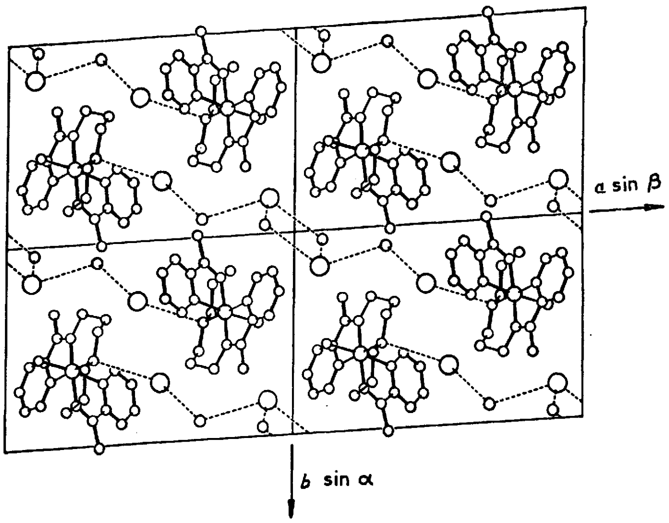

FIGURE 2 Projection of the structure down *c*, showing the molecular packing and the hydrogen-bonding interactions

The C(7)–N(8) and C(17)–N(16) bond lengths [1.27(1) and 1.29(1) Å] and the C(6)–C(7)–C(25) and C(18)–C(17)–C(26) bond angles [119.1(9) and 121.6(10)°] are comparable with the corresponding values [1.27(1) Å, and 119(1)°] in the structure of a closely related mono-imino-nickel(II) complex.[7] Thus the excess of borohydride found to be necessary in the preparation of (I) has not reduced [23] either of the imino-groups. This result is not clear from the i.r. data but was expected from the n.m.r. spectrum wherein all the methyl peaks occur as fairly sharp singlets.

The hydrogen atoms have not been located in the present structure but the short interatomic contacts involving N(12), the iodide ions, and the water of crystallisation suggest the existence of hydrogen bonding. The crystal packing in a hydrated bromide salt of a cobalt(III) complex of (II) [10] is dominated by a series of hydrogen bonds involving the water of crystallisation, the bromide anion, and the hydrogen of the secondary amino-group: relevant interatomic distances are N · · · Br 3.57(1) and Br · · · O 3.39(3) Å. Hydrogen bonding of water between chloride and nitrate ions has been observed in a macrocyclic copper(II) complex [24] [Cl · · · O 3.25(5),

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O · · · O 2.85(5) Å]. If the ionic radii of chloride, bromide, and iodide are taken [25] to be 1.70, 1.87 and 2.12 Å the mean I · · · O and I · · · N distances [3.60(8) and 3.60 Å] in (I) are seen to be compatible with the existence of a hydrogen-bonded array (Figure 2 and Table 3). This may explain (i) the different strengths of binding of the two water molecules suggested by the thermogravimetric and analytical results, (ii) the lowering [26] of the N–H stretching frequency in the iodide (3 085 cm^{-1}) as compared to that for the perchlorate (3 203 cm^{-1}) salt, and (iii) the significantly different thermal parameters of the iodide ions (Table 1). It may be noted that halide salts of the cobalt(II) complex of the analogous quinquedentate ligand formed from 2-formylpyridine all contain one molecule of water per mole.[27] The N–H stretching band is always broad and in the iodide occurs at 3 100 cm^{-1}. The results of the present structure determination strongly suggest that there may be hydrogen bonding in these complexes also.

TABLE 3

Hydrogen-bonded distances (Å)

I(1) · · · N(12)	3.60	I(2) · · · O($1^{\rm I}$)	3.49
I(1) · · · O(2)	3.69	I(2) · · · O($1^{\rm II}$)	3.51
I(2) · · · O(2)	3.66		

Roman numeral superscripts refer to the following equivalent positions relative to the asymmetric unit at x, y, z:

I $x, y, 1 + z$ II $-x, -y, z$

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