Synthesis, structure and reactivity of cobalt(III) complexes with tridentate imino- and amino-oxime ligands
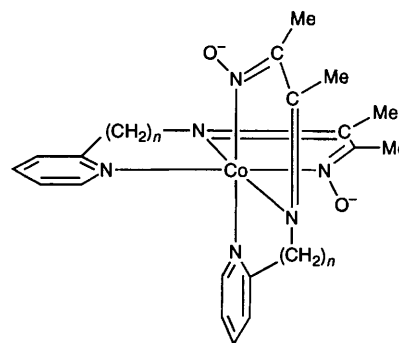
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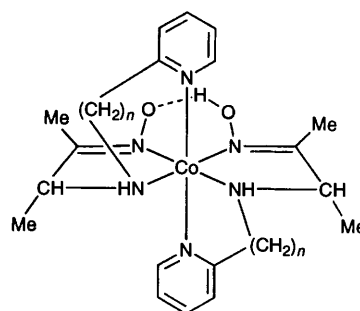
The tridentate iminooximes HL^2 and HL^1 have been prepared by condensation of biacetyl monoxime with 2-(2-aminoethyl)pyridine and 2-(aminomethyl)pyridine, respectively. They reacted with cobalt(II) ion in the presence of oxygen to give the complexes $[Co^{III}L_2]ClO_4$ ($L = L^1$ or L^2). The iminooxime may be hydrogenated in the presence of $NaBH_4$ to yield the corresponding aminooximes HL^3 and HL^4, which, on reaction with Co^{II}, formed the complexes $[Co^{III}L(HL)][ClO_4]_2$ ($L = L^3$ or L^4). All these complexes have been structurally characterized by single-crystal X-ray diffraction. The cobalt has an octahedral environment with the iminooxime ligands in *mer* configuration and the aminooxime ones in *fac* configuration. The reduction of $[Co^{III}L^2_2]ClO_4$ with $NaBH_4$ produces a nucleophilic cobalt(I) species which, on reaction with MeI, gives a stable organocobalt dinuclear complex, previously reported. On the contrary, the reduction of $[Co^{III}L^1_2]ClO_4$ involves hydrogenation of the ligand from imino- to amino-oxime, with the formation of a stable cobalt(II) species. Under these conditions, no reduction to Co^I was observed. The different reactivity is attributed to the more strained co-ordination in $[Co^{III}L^1_2]ClO_4$ with respect to that in $[Co^{III}L^2_2]ClO_4$.

The deprotonated iminooxime 3-[2-(2-pyridyl)ethylimino]-butan-2-one oximate, L^2, has been shown to act as a tridentate ligand, co-ordinating to Co^{III} through its N-donors to form the monocationic $[CoL^2_2]^+$ species.[1,2] The complex $[CoL^2_2]ClO_4$ **1** has been structurally characterized and the cobalt atom is co-ordinated to six N atoms from two tridentate ligands in a slightly distorted octahedral arrangement. Each ligand forms one five- and one six-membered chelate ring. The ligands are almost planar in a *mer* configuration around the metal.[3] Recently we have shown that this complex can be reduced to Co^I which, *via* oxidative addition with aliphatic halides, affords complexes with stable cobalt–carbon bonds.[4] The ability to stabilize cobalt in oxidation state +1 and to form alkylcobalt derivatives is typical of some strong-field tetradentate chelating agents, such as dimethylglyoximate and tetradentate Schiff-base dianions, such as N,N'-bis(salicylidene)-ethane-1,2-diaminate (salen).[5] Their cobalt complexes, the so-called vitamin B-12 models, have been widely studied in the last decades owing to their reactivity pattern being similar to that of the B-12 coenzyme.[5] Much less attention has been devoted to cobalt complexes with tridentate ligands able to form stable organocobalt derivatives, examples being limited to the above case[4] and to some derivatives of 2-amino-N-[1-(2-hydroxy)-phenylethylidene]ethylamine.[6,7]

In view of the possibility of obtaining further insight into the cobalt(I) species and their organometallic derivatives we have considered the anion L^1. Since when co-ordinated to Co it should form two five-membered rings, it was also of interest to compare its behaviour with that of L^2 which forms one five- and one six-membered ring upon co-ordination. The aminooximates

[CoL²₂]ClO₄ **1** (*n* = 2)
[CoL¹₂]ClO₄ **2** (*n* = 1)

[CoL⁴(HL⁴)][ClO₄]₂ **3** (*n* = 2)
[CoL³(HL³)][ClO₄]₂ **4** (*n* = 1)

A
L^1 *n* = 1
L^2 *n* = 2

B
L^3 *n* = 1
L^4 *n* = 2
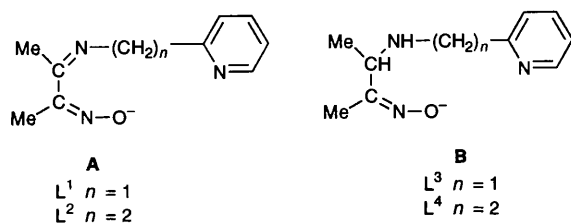
of type **B**, *i.e.* L^3 and L^4, which can be obtained by hydrogenation of the corresponding A-type compounds, can also co-ordinate to cobalt so that it is interesting to compare the structural and the chemical properties of the complexes derived from the two types. The crystal structures of complexes **2–4** were also determined, that of **1** having been previously reported.[3]

Experimental

Electronic spectra were recorded in the range 400–700 nm on a Uvikon 940 spectrometer, ^1H and ^{13}C NMR spectra on a JEOL EX-400 spectrometer (^1H at 400 MHz and ^{13}C at 100.4 MHz) from $(CD_3)_2SO$ solutions and using $SiMe_4$ as internal standard.

Syntheses of the oximes

HL^2. To a stirred solution of biacetyl monoxime (8.45 g, 83.6 mmol) in diisopropyl ether (30 cm^3) was added dropwise 2-(2-aminoethyl)pyridine (9.8 cm^3, 83.6 mmol). The mixture was refluxed for 30 min and then cooled in an ice–NaCl bath. Vigorous stirring of the solution resulted in the formation of a white precipitate which was filtered off, washed many times with pentane and dried *in vacuo*. Yield 14.7 g, 82% (Found: C, 63.4; H, 7.3; N, 20.2. $C_{11}H_{15}N_3O$ requires C, 64.4; H, 7.4; N, 20.5%). NMR: δ_H 1.89, 1.95 (6 H, s, 2CH$_3$), 3.07, 3.74 (4 H, t, 2CH$_2$), 7.20, 7.29, 7.69, 8.49 (4 H, m, C_5H_4N), 11.46 (1 H, br s, OH); δ_C 8.98, 12.91 (CH$_3$), 38.93 (CH$_2C_5H_4N$), 51.15 (CH$_2$N), 121.27, 123.39, 136.14, 148.92, 156.43 (aromatic C), 160.02 (C=NOH) and 164.00 (C=NCH$_2$).

HL^1. 2-(Aminomethyl)pyridine (10 cm^3, 97.0 mmol) was added dropwise to a stirred solution of biacetyl monoxime (9.8 g, 97.0 mmol) in diisopropyl ether (30 cm^3). The mixture was refluxed for 1 h: during this time a white precipitate was formed. After cooling to room temperature, the precipitate was filtered off, washed with water and air-dried. Yield 13.18 g, 74% (Found: C, 63.6; H, 6.9; N, 22.1. $C_{10}H_{13}N_3O$ requires C, 62.8; H, 6.9; N, 22.0%). NMR: δ_H 2.00, 2.14 (6 H, s, 2CH$_3$), 4.70 (2 H, s, CH$_2$), 7.27, 7.57, 7.79, 8.52 (4 H, m, C_5H_4N), 11.58 (1 H, br s, OH); δ_C 9.03, 13.62 (CH$_3$), 56.88 (CH$_2$), 121.63, 121.78, 136.57, 148.70, 156.36 (aromatic C), 160.13 (C=NOH) and 165.23 (C=NCH$_2$).

HL^4. Sodium tetrahydroborate (0.2 g, 5.5 mmol), dissolved in the minimum volume of water, was added to a solution of HL^2 (0.4 g, 1.9 mmol) in methanol (30 cm^3). The mixture was allowed to stand overnight at room temperature and the methanol then removed by evaporation. The residue was extracted twice with CH$_2$Cl$_2$. The product was collected as a pale yellow oil after evaporation of the solvent and used in the syntheses of the complexes without any purification. Yield 0.22 g, 56%. NMR: δ_H 1.06 (3 H, d, CH_3CH), 1.63 (3 H, s, CH$_3$C=N), 2.70, 2.83 (4 H, m, CH$_2$), 3.27 (1 H, q, CH), 3.42 (1 H, br s, NH), 7.18, 7.23, 7.67, 8.47 (4 H, m, C_5H_4N), 10.36 (1 H, s, OH); δ_C 8.16, 19.06 (CH$_3$), 37.95 (CH$_2C_5H_4N$), 46.76 (CH$_2$N), 56.39 (CH), 121.12, 122.95, 136.21, 148.81, 158.26 (aromatic C) and 160.20 (C=NOH).

HL^3. This compound was prepared similarly to HL^4 as a colourless oil. Yield 64%. NMR: δ_H 1.17 (3 H, d, CH_3CH), 1.77 (3 H, s, CH$_3$C=N), 3.35 (1 H, q, CH), 3.70 (2 H, d, CH$_2$), 7.23, 7.43, 7.73, 8.51 (4 H, m, C_5H_4N) and 10.58 (1 H, s, OH); δ_C 8.5, 19.06 (CH$_3$), 52.03 (CH$_2$), 56.22 (CH), 121.87, 136.39, 148.68, 158.10 (aromatic C) and 160.13 (C=NOH).

Syntheses of the complexes

Complex **1** was prepared by a modification (see below) of the procedure previously reported;[2] **2–4** were prepared in the same way.

CAUTION: Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should only be handled in small quantities.

[CoL^2$_2$]ClO$_4$ 1. To a solution of CoCl$_2$·6H$_2$O (1.31 g, 5.5 mmol) in methanol (20 cm^3) was added dropwise a solution of HL^2 (2.26 g, 11.0 mmol) in the same solvent (30 cm^3). After stirring at room temperature for 15 min the solvent was

removed by a rotary evaporator and the residue treated with water (30 cm^3). After complete dissolution, a concentrated aqueous solution of NaClO$_4$ was added to yield the product as a red-brown precipitate. This was filtered off, washed with water and air-dried. Yield 1.65 g, 53% (Found: C, 42.4; H, 4.3; N, 14.7. $C_{20}H_{24}ClCoN_6O_6$ requires C, 44.6; H, 4.5; N, 15.6%). NMR: δ_H 1.86, 2.63 (12 H, s, 4CH$_3$), 5.66, 5.97 (4 H, q, 2CH$_2$), 7.34, 7.75, 8.00, 8.16 (8 H, m, 2C$_5H_4$N); δ_C 13.61, 18.53 (CH$_3$), 57.59 (CH$_2$), 123.59, 126.22, 141.0, 149.27, 151.37 (aromatic C), 164.34 (C=NO) and 177.93 (C=NCH$_2$).

[CoL^1$_2$]ClO$_4$ 2. Red-brown crystals. Yield 61% (Found: C, 42.4; H, 4.3; N, 14.7. $C_{20}H_{24}ClCoN_6O_6$ requires C, 44.6; H, 4.5; N, 15.6%). NMR: δ_H 1.86, 2.63 (12 H, s, 4CH$_3$), 5.66, 5.97 (4 H, q, 2CH$_2$), 7.34, 7.75, 8.00, 8.16 (8 H, m, 2C$_5H_4$N); δ_C 13.61, 18.53 (CH$_3$), 57.59 (CH$_2$), 123.59, 126.22, 141.0, 149.27, 151.37 (aromatic C), 164.34 (C=NO) and 177.93 (C=NCH$_2$).

[CoL^4(HL^4)][ClO$_4$]$_2$·H$_2$O 3. Red crystals. Yield 58% (Found: C, 37.9; H, 5.0; N, 11.9. $C_{22}H_{33}Cl_2CoN_6O_{10}$ requires C, 39.3; H, 5.0; N, 12.5%). NMR: δ_H 0.81 (6 H, d, 2CH_3CH), 2.19 (6 H, s, 2CH$_3$C=N), 3.07, 3.45, 3.73, 4.02 (8 H, m, 4CH$_2$), 6.61 (2 H, br s, 2NH), 7.49, 7.59, 7.88, 8.01 (8 H, m, 2C$_5H_4$N); δ_C 14.83, 15.19 (CH$_3$), 30.16 (CH$_2C_5H_4$N), 43.72 (CH$_2$N), 61.48 (CH), 124.92, 128.69, 140.45, 152.04, 160.40 (aromatic C) and 165.65 (C=NOH).

[CoL^3(HL^3)][ClO$_4$]$_2$·H$_2$O 4. Orange crystals. Yield 42% (Found: C, 36.4; H, 4.4; N, 12.6. $C_{20}H_{31}Cl_2CoN_6O_{11}$ requires C, 36.3, H, 4.7; N, 12.7%). NMR: δ_H 0.90 (6 H, d, 2CH_3CH), 2.13 (6 H, s, 2CH$_3$C=N), 4.07 (2 H, m, 2CH), 4.60, 5.44 (4 H, m, 2CH$_2$), 6.98 (2 H, d, 2NH), 7.66, 7.84, 7.97, 8.21 (8 H, m, 2C$_5H_4$N); δ_C 14.68, 17.43 (CH$_3$), 61.68 (CH$_2$), 67.35 (CH), 124.05, 126.44, 141.27, 150.78, 163.02 (aromatic C) and 165.07 (C=NOH).

Formation of 4 from 2. Compound **2** (0.7 g, 1.3 mmol) was dissolved in methanol (150 cm^3) and the solution deareated *in vacuo*. It was then treated under a nitrogen atmosphere with NaBH$_4$ (0.34 g, 9.0 mmol), dissolved in the minimum volume of water: the colour rapidly turned from brown to red-orange. The mixture was kept under a nitrogen atmosphere and at room temperature for 10 min and then its volume was reduced to about 30 cm^3 by means of a rotary evaporator. After neutralization with 1 mol dm^{-3} HClO$_4$ and addition of aqueous concentrated NaClO$_4$, the solution was allowed to evaporate in the air. The red crystalline product was filtered off, washed with water and air-dried. Orange crystals. Yield 0.26 g, 30% (Found: C, 36.2; H, 4.6; N, 12.6%).

Crystallography

Crystal data and experimental conditions for complexes **2–4** are listed in Table 1. The densities of the crystals were determined by flotation in CHBr$_2$Cl$_2$–pentane. An Enraf-Nonius CAD4 four-circle automated diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) was employed to collect data. Cell parameters were obtained by least-squares refinement with $12 < \theta < 18°$, $T = 295$ K. Reflections were collected in the range $4 < 2\theta < 56°$ using the ω–2θ scan technique. Three standard reflections were monitored every 250 for each crystal and showed no systematic decrease in intensity. Corrections for Lorentz-polarization and ψ-scan absorption were applied.

Structure analysis and refinement. All structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques (on F) with all non-hydrogen atoms anisotropic. The H atoms were not refined but included at calculated positions in the final refinement. The Fourier-
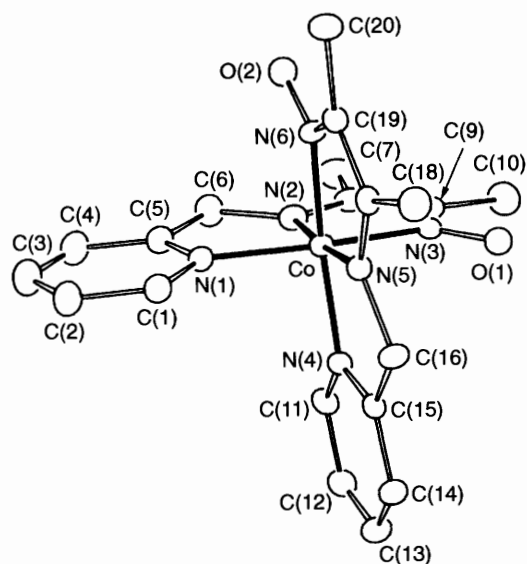
Fig. 1 An ORTEP[10] drawing and the atom numbering scheme of the cation of complex **2** (thermal ellipsoids at 20% probability)
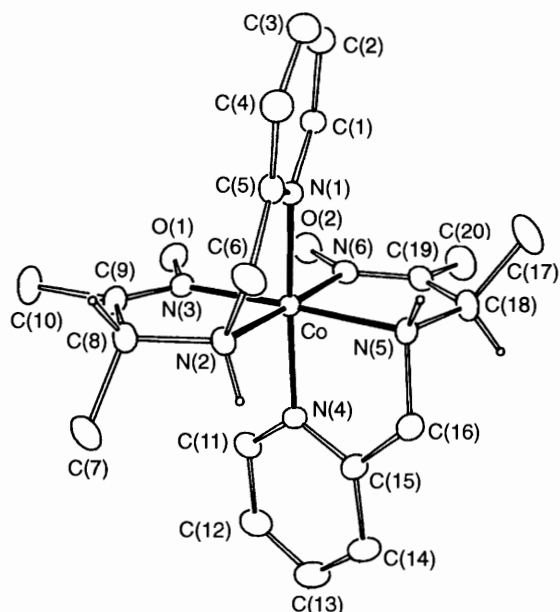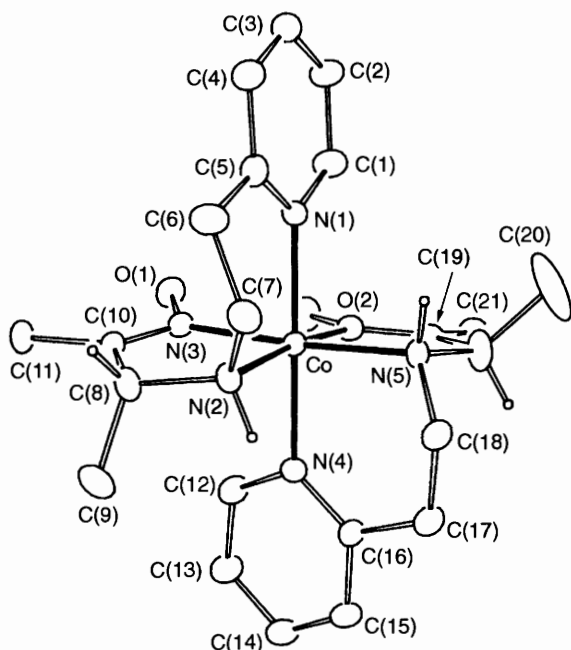

Fig. 2 An ORTEP drawing and the atom numbering scheme for one of the two crystallographically independent cations of complex **3**. Details as in Fig. 1

Fig. 3 An ORTEP drawing and the atom numbering scheme of the cation of complex **4**. Details as in Fig. 1

difference map did not reveal chemically significant residual electron density. The programs used on a VAX 2000 computer and sources of scattering factor data are given in refs. 8 and 9.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/234.

Results and Discussion

The compounds HL^1 and HL^2 were prepared starting from biacetyl monoxime and the appropriate aminopyridine following the usual procedure for the syntheses of Schiff bases; HL^3 and HL^4 were prepared by treating the above compounds with $NaBH_4$ in methanol. The reactions involve hydrogenation of the $=C=NCH_2$ imino groups to $=CHNHCH_2$ amino groups.

Syntheses

Complexes **1–4** were prepared by addition of $CoCl_2 \cdot 6H_2O$ to a solution of the appropriate oxime at room temperature and in the presence of atmospheric oxygen. All were precipitated as perchlorate salts by addition of concentrated $NaClO_4$ solutions to the reaction mixture. Complex **4** can be also obtained by treating a methanol solution of **2** with $NaBH_4$ under a nitrogen atmosphere followed by exposure to the air. The mechanism of this reaction will be presented and discussed below. Attempts to synthetize **3** from **1** by applying the above procedure failed.
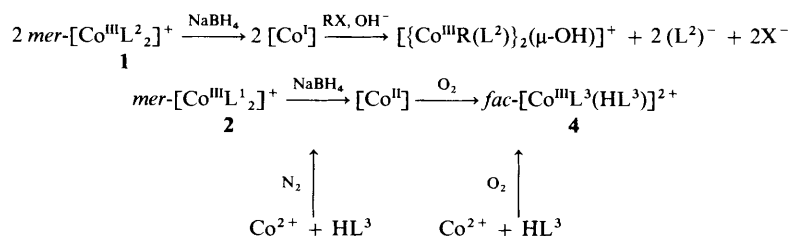
Crystal structures of complexes 2–4

The crystal structure of complex **2** consists of discrete $[CoL^1{}_2]^+$ cations and perchlorate anions. The atomic numbering scheme of the cation is shown in Fig. 1. Each tridentate ligand, in a *mer* configuration and planar within $\pm 0.143(8)$ and $\pm 0.111(7)$ Å respectively, co-ordinates Co through its N-donors in a way similar to that reported for the analogous $[CoL^2{}_2]^+$ cation.[3] The mean Co–N distances and N–Co–N angles in the five-membered rings, involving the N (oxime) and N (imine) atoms, are comparable in **1** and **2** [Co–N_{ox} 1.915(4), 1.906(5) Å; N_{ox}–Co–N_{im} 82.0(2), 82.3(2)° in **1** and **2** respectively]. On the contrary, the mean Co–N distances and N–Co–N angles in the rings containing N (imine) and N (pyridine) atoms are significantly different in **1** and **2** [Co–N_{py} 2.037(4), 1.954(4) Å; N_{py}–Co–N_{im} 93.7(2), 83.8(2)° for **1** and **2**, respectively]. The decrease in these distances and angles from complex **1** to **2** should be ascribed to the steric constraint imposed by the closure of the five-membered ring, containing an N_{py} atom in **2**.

The crystal structures of complexes **3** and **4** consist of $[CoL(HL)]^{2+}$ (L = L^4 or L^3) cations, respectively, and perchlorate anions. In **3** two crystallographically independent cations A and B are present in the unit cell, but there is no significant difference in the geometry (see Table 2). The atomic numbering schemes for **3** and **4** are in Figs. 2 and 3, respectively. In both structures one protonated and one deprotonated ligand co-ordinate the Co through their N donors in a *fac* configuration in such a way that the two pyridine rings are *trans* to each other and the two O atoms make an intramolecular hydrogen bond with O ··· O distances of 2.388(7) and 2.421(6) Å in **3** and 2.387(5) Å in **4**, respectively. These distances are shorter than those reported in a large number of cobaloximes which average 2.497(4) Å.[5] This suggests a stronger bond in the

Table 1 Crystal data and experimental conditions for complexes 2–4

	2	**3**	**4**
Formula	$C_{20}H_{24}ClCoN_6O_6 \cdot 2H_2O$	$C_{22}H_{33}Cl_2CoN_6O_{10}$	$C_{20}H_{29}Cl_2CoN_6O_{10} \cdot 1.2H_2O$
M	574.84	671.38	661.34
Colour	Red-brown	Red	Orange
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
$a/\text{Å}$	8.098(1)	19.251(2)	9.031(1)
$b/\text{Å}$	18.669(4)	30.828(6)	11.641(2)
$c/\text{Å}$	17.007(2)	9.297(1)	14.217(2)
$\alpha/°$			97.23(1)
$\beta/°$	103.52(2)	96.95(3)	95.02(1)
$\gamma/°$			109.04(1)
$U/\text{Å}^3$	2500.1(8)	5476.9(9)	1388.4(7)
Z	4	8	2
$D_m/\text{Mg m}^{-3}$	1.54	1.60	1.58
$D_c/\text{Mg m}^{-3}$	1.53	1.63	1.58
$F(000)$	1192	2784	684
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	8.6	8.8	8.8
Transmission factors	0.93–1.00	0.95–1.00	0.95–1.00
Crystal dimensions/mm	$0.30 \times 0.08 \times 0.70$	$0.30 \times 0.30 \times 0.50$	$0.40 \times 0.30 \times 0.25$
No. reflections measured	7714	11 559	8381
unique (R_{int})	7492 (0.023)	11 210 (0.026)	8080 (0.016)
observed^a	3334	6133	5005
used in least squares	3334	6133	5005
No. variables	325	739	368
R^b	0.055	0.055	0.063
R'^c	0.057	0.058	0.064
Δ/σ in final cycle	0.33	0.58	0.71
$\rho_{max}/e\ \text{Å}^{-3}$	0.51	0.91	0.93

^{a} Criterion: $|F_o| > 3\sigma(|F_o|)$. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1]$

$$2\ mer\text{-}[Co^{III}L^2{}_2]^+ \xrightarrow{\ NaBH_4\ } 2\ [Co^I] \xrightarrow{\ RX,\ OH^-\ } [\{Co^{III}R(L^2)\}_2(\mu\text{-OH})]^+ + 2\ (L^2)^- + 2X^-$$
$$\mathbf{1}$$

$$mer\text{-}[Co^{III}L^1{}_2]^+ \xrightarrow{\ NaBH_4\ } [Co^{II}] \xrightarrow{\ O_2\ } fac\text{-}[Co^{III}L^3(HL^3)]^{2+}$$
$$\mathbf{2} \qquad\qquad\qquad\qquad\qquad \mathbf{4}$$

$$N_2 \uparrow \qquad\qquad O_2 \uparrow$$
$$Co^{2+} + HL^3 \qquad Co^{2+} + HL^3$$

Scheme 1

oximates. However we were not able to establish a definite localization of the H atom in the oxime bridge. The formation of the hydrogen bond serves further to stabilize the *fac* arrangement of the ligands with respect to the probably less stable *mer* arrangement. The two amine methyl groups of each ligand lie on opposite sides with respect to the co-ordination plane involving the non-pyridine N-donors, pointing towards the pyridine residues. Overall the cations have approximately C_2 symmetry, the two-fold axis passing through Co and the midpoint of the oximato bridge. For both L^1 and L^2 ligands reduction occurs at the N=C double bond in the six-membered rings according to the lengthening of the $Co-N_{am}$ bonds, the averages of which are 1.986(5) and 1.975(5) in 3 and 1.985(4) Å in 4, to be compared with $Co-N_{im}$ 1.928(4) in 1 and 1.866(5) Å in 2, and the tetrahedral geometry around the nitrogen and carbon atoms (Table 2). As previously observed for 1 and 2, also in 3 and 4 the most relevant differences are detected in the rings containing the N_{py} atoms with a shortening of the average $Co-N_{py}$ bond length from 2.025(5) and 2.014(5) in 3 to 1.931(3) Å in 4 and with a narrowing of the mean $N_{am}-Co-N_{py}$ angle from 92.5(2) and 93.5(2) in 3 to 83.5(2)° in 4.

Reduction reactions: comparison between complexes 1 and 2

As previously reported,[4] complex 1 may be easily reduced by $NaBH_4$ in alkaline media. The addition of alkyl halides to the resulting nucleophilic cobalt(I) species produces organocobalt

complexes with stable metal–carbon bond.[11] This reactivity pattern parallels that observed for cobaloximes and other vitamin B-12 models.[5]

The behaviour of complex 2, when treated with $NaBH_4$, is quite different, the UV/VIS spectra suggesting the formation of a cobalt(II) species in which one of the two C=N bonds of the ligand has been hydrogenated passing from the imine to the amine form. In fact the spectrum of complex 2 after reduction ($\lambda_{max} = 477$ nm) was identified to the spectrum exhibited by a solution of $Co(NO_3)_2$ after addition of the HL^3 in a molar ratio 1:2 under a nitrogen atmosphere. Furthermore, the same spectrum was obtained upon reducing a solution of complex 4 with $NaBH_4$. Reoxidation of these solutions afforded complex 4, which was isolated as its perchlorate and identified by NMR spectra. Therefore, for complexes 1 and 2, Scheme 1 can be proposed.

The different behaviour of complexes 1 and 2 upon reduction with $NaBH_4$ can be interpreted on the basis of the structural data. In 2 the five-membered metallocycle, involving the pyridine residue (Fig. 1) appears considerably more strained than the corresponding six-membered ring in 1. Ring closure in 2 requires shortening of the $Co-N_{py}$ bond from 2.037(4) in 1 to 1.954(4) Å and decrease of the co-ordination angle $N_{im}-Co-N_{py}$ from 93.7(2) in 1 to 83.8(2)°. The steric strain in the cobalt(II) complex, larger than that in the octahedral cobalt(III) complex, owing to the increase in the ionic radius of the metal ion, should provoke opening of the five-membered chelate ring with a

Table 2 Selected bond lengths (Å) and angles (°) in complexes 1–4

	1*	2	3A	3B	4
Co–N(1)	2.032(4)	1.956(5)	2.033(4)	2.045(5)	1.926(3)
Co–N(2)	1.929(4)	1.872(5)	1.991(5)	1.988(5)	1.985(4)
Co–N(3)	1.913(4)	1.903(5)	1.912(5)	1.914(5)	1.907(4)
Co–N(4)	2.043(4)	1.952(4)	2.017(5)	1.983(5)	1.935(4)
Co–N(5)	1.927(4)	1.859(5)	1.980(5)	1.961(5)	1.985(4)
Co–N(6)	1.918(4)	1.909(5)	1.911(5)	1.902(4)	1.905(4)
N(2)–C(6)		1.457(9)			1.481(6)
N(2)–C(7)	1.459(6)		1.477(8)	1.491(8)	
N(2)–C(8)	1.292(5)	1.283(8)	1.516(8)	1.500(8)	1.504(6)
N(5)–C(16)		1.473(6)			1.491(6)
N(5)–C(18)	1.470(6)	1.287(8)	1.483(8)	1.487(8)	1.506(6)
N(5)–C(19)	1.290(6)		1.507(9)	1.499(7)	
N(1)–Co–N(2)	93.3(2)	83.9(2)	94.0(2)	94.4(2)	83.6(2)
N(1)–Co–N(3)	174.5(2)	166.2(2)	85.5(2)	83.2(2)	90.9(1)
N(1)–Co–N(4)	93.1(1)	93.1(2)	176.4(2)	174.2(2)	173.1(2)
N(1)–Co–N(5)	94.7(1)	99.7(2)	90.3(2)	90.6(2)	91.4(2)
N(1)–Co–N(6)	89.8(2)	89.3(2)	92.7(2)	91.2(2)	95.0(2)
N(2)–Co–N(3)	82.2(2)	82.4(2)	82.0(2)	82.1(2)	83.0(2)
N(2)–Co–N(4)	94.3(2)	99.2(2)	89.1(2)	89.9(2)	92.7(2)
N(2)–Co–N(5)	168.0(2)	175.2(2)	99.1(2)	97.7(2)	97.7(2)
N(2)–Co–N(6)	89.3(2)	94.9(2)	173.1(2)	174.3(2)	178.4(2)
N(3)–Co–N(4)	90.5(2)	87.6(2)	93.2(2)	93.6(2)	94.5(2)
N(3)–Co–N(5)	89.2(2)	94.1(2)	175.7(2)	173.8(2)	177.7(1)
N(3)–Co–N(6)	86.9(2)	93.4(2)	96.9(2)	97.7(2)	96.3(2)
N(4)–Co–N(5)	94.1(2)	83.8(2)	91.0(2)	92.6(2)	83.3(2)
N(4)–Co–N(6)	175.2(2)	165.9(2)	84.2(2)	84.4(2)	88.8(2)
N(5)–Co–N(6)	81.8(2)	82.1(2)	82.6(2)	83.1(2)	83.1(2)
Co–N(2)–C(6)		117.9(4)			107.3(3)
Co–N(2)–C(7)	124.0(3)		115.1(4)	113.3(4)	
Co–N(2)–C(8)	113.6(3)	115.9(5)	111.2(4)	111.3(4)	111.2(3)
C(6)–N(2)–C(8)		125.8(6)			106.4(3)
C(7)–N(2)–C(8)	121.6(4)		110.1(5)	110.9(5)	
Co–N(5)–C(16)		118.1(4)			106.4(3)
Co–N(5)–C(18)	122.5(3)	116.4(3)	114.6(4)	115.5(4)	110.9(3)
Co–N(5)–C(19)	114.2(3)		111.7(4)	112.5(4)	
C(16)–N(5)–C(18)		124.6(5)			112.8(3)
C(18)–N(5)–C(19)	122.4(4)		111.2(5)	111.2(5)	

* Ref. 2.

consequent decrease in the co-ordination number of Co^{II}. The opening of the ring favours hydrogenation of the ligand in accord with a previous observation indicating that free Schiff bases are more easily reduced than co-ordinated ones.[12] The rearrangement of the ligand and subsequent oxidation of the metal ion leads to the final product 4 (Scheme 1).

The difference between the properties of complexes 1 and 2 can be also evidenced by the following experimental observations. We noted that a methanol–water solution of 1 containing 0.1 mol dm^{-3} NaOH, under an inert atmosphere, rapidly changes from orange to deep green (λ_{max} = 603 nm) and returns to orange after exposure to air. The ^{1}H NMR spectrum of the green solution, in (CD$_3$)$_2$SO saturated with solid NaOH, indicates the formation of a paramagnetic species, presumably a cobalt(II) complex. Complex 2 under the above conditions appears to be unreactive. The tendency of 1, but not of 2, to be reduced even in the absence of specific reductants, could be attributed to the effect of the steric strain in the octahedral cobalt(III) complex, which would be relieved in the cobalt(II) derivative with reduced co-ordination number. A similar tendency to autoreduction was previously observed in some cobalt complexes with substituted salicylideneimines and discussed in terms of steric strain.[13]

It is also of interest that the reduction with NaBH$_4$ of both complexes 3 and 4 leads to the formation of cobalt(II) species even in the presence of an excess of reducing agent. Thus it can be deduced that the amine ligands are ineffective in stabilizing cobalt(I) complexes. This failure can be attributed to the smaller extent of electron delocalization in the cobalt aminooximate with respect to the iminooximate. The influence of the extent of saturation of the chelate ring on the metal reduction appears evident when the behaviour of the complexes 1 and 3 upon reduction is compared: the former is easily reduced to Co^{I}, while with the latter the reduction does not proceed beyond the formation of a cobalt(II) derivative. A similar behaviour has been observed in previous studies[14] on some cobalt complexes with macrocyclic ligands, where progressive amounts of ligand unsaturation resulted in an anodic shift in the half-wave potentials of the couple Co^{II}–Co^{I}. On the other hand, the less strained six-membered chelate ring of 1 ensures a higher stability of the complexes in all the cobalt oxidation states, so that the co-ordinated L^2 ligand is not reduced and is still able to stabilize the cobalt in the oxidation state +1.

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