DALTON
FULL PAPER

Polydentate ligand construction: preparation of oxime–imine complexes *via* intramolecular condensation reactions

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Complexes of tridentate ligands containing oxime, imine and amine donor groups have been prepared both by complexation of the preformed ligands and by condensation reactions between added dionemonoxime ligands and coordinated amine ligands. Higher yields of the bis(tridentate) complexes result from the former method, while the latter method produces other complexes that may prove synthetically useful as well. Many of the complexes have been characterised by X-ray crystallographic techniques.

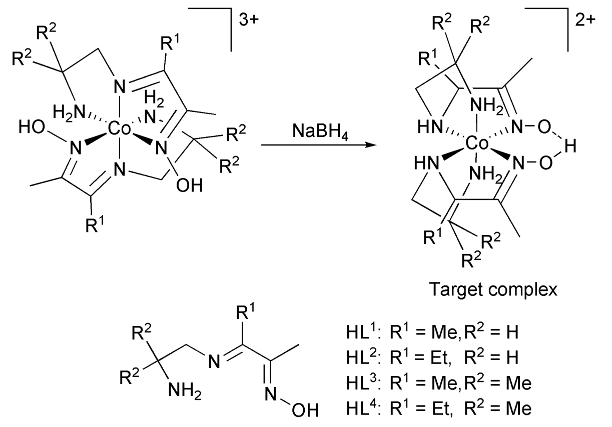
Introduction

Photochemical reactions of cobalt(III) complexes containing coordinated amino acids have been shown to produce stable Co–C–N metallacycles.[1] The stepwise mechanistic pathway for this reaction has been proposed to involve a cobalt–oxygen bond homolysis, radical decarboxylation then recombination of the resulting alkyl radical with cobalt(II) to form the Co–C bond. Metallacyclic products have also been reported from the irradiation of cobalt(III) compounds containing coordinated primary amines.[1a]

A key problem in the study of this type of reaction lies in the isolation of a stable metallacyclic product. For example, photolysis of complexes where the amino acid is substituted at the α-position gives metallacycles that have been characterised only by UV-Vis spectroscopy. Recently, substitution of a radical clock onto the amino acid backbone has been used successfully to monitor the formation and decomposition of a metallocyclic species *via* UV-Vis and NMR spectroscopy.[2] However, few Co–C–N metallocycles have been structurally characterised and the stability of those complexes can be attributed to the choice of the complex coordination sphere. Thus, complexes containing π-acceptor ligands or amino acids that are part of a polydentate framework give rise to stable metallacycles following UV irradiation.

Another series of cobalt complexes containing Co–C bonds that are well documented in the literature are the oxime-based model systems for co-enzyme B_{12}. These systems have a common feature in that the meridional ligand arrangement is completed with one or two strong intramolecular hydrogen bonds. More specifically, a B_{12} model system has been developed recently from the cobalt(III) complex of the tridentate ligand 2-(2-pyridyl-ethyl)-amino-3-butanone oxime (HL).[3] In $[Co(HL)(L)]^{3+}$ (**1**), the secondary amine and oxime nitrogen atoms of both ligands lie in the same plane as the cobalt(III) centre and the ligands are linked by an intramolecular hydrogen bond through the oxime oxygen atoms. The axial sites are occupied by the pyridine groups. The authors have also prepared a Co–C–N metallacycle from the reaction of dihaloalkyl species in a solution of the complex under strongly reducing conditions.[4]

We are interested in preparing analogous systems of the type shown in Scheme 1 from the reduction of the corresponding imine/oxime complexes. The target molecules contain primary amines in axial positions that should, based on literature reports,[1a] give rise to Co–C–N metallocycles upon irradiation with UV light. The ligands are variously substituted with ethyl and methyl groups that will act as spectroscopic handles for our intended photochemical experiments. The alkyl substitution is possible on both the amine and imine fragments of the ligands. This paper describes the synthesis and crystal structures of the imine/oxime complex precursors and a subsequent paper will deal with their reduction chemistry.



Scheme 1

Owing to the diverse coordination behaviour of ligands containing oxime groups, we have prepared the primary amine complexes both from the free ligand and *via* intramolecular condensation reactions of the corresponding cobalt(III) amine complexes. This paper is an extension of previous work on the construction of polydentate ligands that has been undertaken in the group.[5]

Experimental

Materials

Reagent grade compounds were used without further purification for all syntheses. 1,2-Diaminoethane, 1-methyl-1,3-propanediamine and Dowex 50WX2–400 ion-exchange resin were obtained from Aldrich Chem. Cobalt(II) acetate tetrahydrate and cobalt(II) chloride hexahydrate from BDH. Butanedionemonoxime was purchased from BDH and also prepared as described below. *trans*-$[Co(en)_2Cl_2]Cl$, *cis*-$[Co(en)_2(OH)(OH_2)]$-

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$(ClO_4)_2$ and *trans*-$[Co(dmen)_2Cl_2]_2ZnCl_4$ were prepared according to literature procedures.[6,7]

Measurements

The ^{13}C NMR spectra were obtained at 300 MHz on a Varian Unity-300 spectrometer at 23 °C. An internal reference was used for spectra recorded in D_2O and DCl solutions (sodium 3-trimethylsilylpropanesulfonate (TMPS), δ 0 (singlet)). UV-Vis data were recorded on a GBC 920 spectrometer. Microanalyses were performed by the University of Otago Microanalytical Service.

Ligand syntheses

Butanedionemonoxime was prepared according to a modified literature procedure:[8] Sodium nitrite (162.5 g), ethanol (71 mL) and water (550 mL) were placed in a two-necked round bottom flask. A solution of H_2SO_4 (64 mL, conc.), ethanol (71 mL) and water (490 mL) was added dropwise to the above solution, and the ethyl nitrite so produced was allowed to flow into a flask containing methylethyl ketone (192.5 mL) and HCl (10 mL, conc.). The temperature of this solution was kept below 55 °C using a salt/ice bath and by controlling the rate of ethyl nitrite production. Ammonia (approx. 9 mL) was used to neutralise this solution and it was then diluted to twice its volume with water. Ethanol was removed on a rotary evaporator with the water bath heated at 40 °C. The solution was then refrigerated overnight during which time the monoxime crystallised. A further crop is obtained after another 24 h of refrigeration. Yield: 130 g (60%).

Pentane-2,3-dione-2-oxime was prepared by the same method, but on a smaller scale, from 3-pentanone (57 ml, 0.54 mol) with all reagents scaled accordingly. Yield: 19.3 g (31%).

General procedure for amine condensations: 1,2-diaminoethane (1.2 g, 0.02 mol) or 1-methyl-1,3-propanediamine (1.53 g, 0.02 mol) was added to butanedionemonoxime (2 g, 0.02 mol) or pentane-2,3-dione-2-oxime (2.25 g, 0.02 mol) dissolved in dry THF. The solution was heated at reflux over 1 h, cooled and the solvent removed on a rotary evaporator. This would leave either a white solid or pale yellow oil that solidified on standing. The solids were washed with ether. The solids could be recrystallised from methanol, but these ligands are vulnerable to hydrolysis and this prevented satisfactory elemental analyses being obtained in some cases. The crude ligands were sufficiently pure for use in the complex syntheses.

2-(2-Aminoethyl)imino-3-butanone oxime (HL^1): yield 1.5 g (52%).

2-(2-Aminoethyl)imino-3-pentanone oxime (HL^2): yield 2.0 g (64%).

2-(2-Amino-2-methylpropyl)imino-3-butanone oxime (HL^3): yield 2.35 g (68%). *Anal.* Required for $C_8H_{17}N_3O$: C, 56.11; H, 10.01; N, 24.54%. Found: C, 56.34; H, 9.72; N, 24.55%.

2-(2-Amino-2-methylpropyl)imino-3-pentanone oxime (HL^4): yield 2.1 g (56%).

Complex syntheses by intramolecular condensation reactions

$[Co(HL^1)(en)Cl][ZnCl_4]$ (2). $[Co(en)_2Cl_2]Cl$ (2 g, 0.007 mol) and butanedionemonoxime (0.8 g, 0.008 mol) were heated at reflux in methanol (100 mL) over 24 h. The solution was filtered while warm and the solvent removed on a rotary evaporator. The residue was dissolved in water (50 mL) and loaded onto a column of Dowex resin (14 × 5.5 cm, H^+ form). Elution with water (250 mL) and HCl (0.5 M, 250 mL) afforded one major red band that was eluted with HCl (1 M). The red band was taken to dryness using a rotary evaporator to give 1.6 g red powder (crude product). $ZnCl_2$ (0.75 g) dissolved in HCl (4 M, 20 mL) was added and the solution was taken to dryness. The residue was treated with methanol to give a red precipitate that was filtered and washed with methanol and acetone. Yield 1.7 g (49%).

^{13}C NMR (D_2O): 178.90 (C=N), 171.128 (C=NOH), 52.77, 45.71, 45.15, 44.46 (all CH_2–N), 18.99, 15.14 (both CH_3). UV-Vis (H_2O): λ_{max} 361.3, 306.9, 266.9 nm. *Anal.* Required for $C_8H_{21}Cl_5CoN_5OZn$: C, 19.03; H, 4.19; N, 13.87%. Found: C, 19.36; H, 4.23; N, 13.21%.

$[Co(HL^1)_2][ZnCl_4]Cl$ (3) and $[Co(HL^1)(H_2L^1)Cl]Cl_3$ (4). $[Co(en)_2Cl_2]Cl$ (1.25 g, 0.004 mol) and butanedionemonoxime (2 g, 0.02 mol) were heated at reflux in methanol (100 mL) over 24 h. The solution was filtered while warm and the solvent was removed on a rotary evaporator. The remaining residue was dissolved in water (50 mL) and loaded onto a column of Dowex resin (14 × 5.5 cm, H^+ form). Elution with water (250 mL), HCl (0.5 M, 250 mL) and HCl (1 M, 250 mL) separated the mixture into two major bands. The first red band was collected by elution with HCl (1 M), and the second yellow band by elution with HCl (2 M).

$[Co(HL^1)(H_2L^1)Cl]Cl_3.3H_2O$. The first red band was taken to dryness using a rotary evaporator to give a hygroscopic red solid. Water (*ca.* 10 mL) was added and the solution allowed to evaporate slowly. Dark red crystals formed which were washed with cold methanol and air dried. Yield 0.5 g (21%).

^{13}C NMR (0.1 M DCl): 187.03, 178.44 (both C=N), 170.92, 159.71 (both C=NOH), 55.12, 51.58, 47.96, 40.81 (all CH_2–N), 21.23, 21.12, 17.24, 16.86 (all CH_3). UV-Vis (H_2O): λ_{max} 310.4, 260.5 nm. *Anal.* Required for $C_{12}H_{31}Cl_4CoN_6O_4$: C, 27.50; H, 5.95; N, 16.03%. Found: C, 27.33; H, 5.95; N, 15.72%.

$[Co(HL^1)_2][ZnCl_4]Cl.H_2O$. The second yellow band was taken to dryness using a rotary evaporator to give a hygroscopic yellow solid (approximately 0.5 g) which was treated with $ZnCl_2$ (0.2 g) dissolved in HCl (4 M, 20 mL). The solution was taken to dryness using a rotary evaporator to leave a yellow solid which was triturated with ethanol, and washed with acetone and cold methanol. Yield 0.57 g (22%)

^{13}C NMR (D_2O): 181.60 (C=N), 165.92 (C=NOH), 54.97, 48.26 (both CH_2–N), 21.06, 16.587 (both CH_3). UV-Vis (H_2O): λ_{max} 351.4 (sh), 303.4, 256.0 nm. *Anal.* Required for $C_{12}H_{26}Cl_5CoN_6O_2Zn$: C, 24.51; H, 4.46; N, 14.29%. Found: C, 23.75; H, 4.43; N, 13.37%.

$[Co(HL^2)(en)Cl][ZnCl_4]$ (5) and $[Co(HL^2)(L^2)][ZnCl_4].H_2O$ (6). $[Co(en)_2Cl_2]Cl$ (1.5 g, 0.0053 mol) and pentane-2,3-dione-2-oxime (2.5 g, 0.022 mol) were heated at reflux in methanol (100 mL) over 24 h. The solution was filtered while warm and the solvent removed using a rotary evaporator. The residue was treated with water (50 mL) and loaded onto a column of Dowex resin (14 × 5.5 cm, H^+ form). Elution with water (250 mL), HCl (0.5 M, 250 mL) and HCl (1 M, 250 mL) separated the mixture into two major bands. The first red band was collected by elution with HCl (1 M) and the second yellow band collected by elution with HCl (2 M).

$[Co(HL^2)(en)Cl][ZnCl_4]$. The first red band was taken to dryness using a rotary evaporator to give a red powder (approx 0.8 g) which was dissolved in HCl (4 M, 20 mL). $ZnCl_2$ (0.35 g) was added and the solution was taken to dryness on a rotary evaporator. The remaining red solid was triturated with ethanol, washed with cold methanol and air dried. Yield 0.86 g (27%).

^{13}C NMR (D_2O): 186.70 (C=N), 160.99 (C=NOH), 53.64, 48.21, 47.62, 46.87, 27.29 (all CH_2), 16.02, 12.63 (both CH_3). UV-Vis (H_2O): λ_{max} 367.0, 308.2, 267.5. *Anal.* Required for $C_9H_{23}Cl_5CoN_5OZn$: C, 20.83; H, 4.47; N, 13.50%. Found: C, 20.32; H, 4.65; N, 12.78%.

$[Co(HL^2)(L^2)][ZnCl_4].H_2O$. The yellow band was taken to dryness using a rotary evaporator to give a hygroscopic yellow solid (approximately 0.6 g) that was then treated with $ZnCl_2$ (0.23 g) dissolved in HCl (4 M, 20 mL). The solution was taken to dryness using a rotary evaporator to leave a yellow solid which was triturated with ethanol, and washed with acetone and cold methanol. Yield 0.69 g (23%).

^{13}C NMR (D_2O): 184.67 (C=N), 162.02 (C=NOH), 53.91, 47.99, 27.17 (all CH_2), 15.83, 12.36 (both CH_3). UV-Vis (H_2O): λ_{max} 361.3 (sh), 305.3, 257.3 nm. *Anal.* Required for $C_{14}H_{31}Cl_4CoN_6O_3Zn$: C, 28.14; H, 5.23; N, 14.06%. Found: C, 28.30; H, 5.29; N, 13.82%.

$[Co(HL^3)_2][ZnCl_4]Cl$ (7) and $[Co(HL^4)_2][ZnCl_4]$ (8). $[Co(dmen)_2Cl_2]_2[ZnCl_4]$ (2 g, 0.0025 mol) and either butanedionemonoxime (2 g, 0.02 mol) or pentane-2,3-dione-2-oxime (2.25 g, 0.02 mol) were heated at reflux in methanol (100 mL) over 24 h. The solution was filtered whilst warm and the solvent was removed using a rotary evaporator. The residue was treated with water (50 mL) and loaded onto a column of Dowex resin (14 × 5.5 cm, H^+ form). In each case, the major red band was eluted with HCl (2 M), taken to dryness using a rotary evaporator and treated with $ZnCl_2$ dissolved in HCl (4 M, 30 mL). Removal of solvent yielded a powder in each case that was washed with acetone, cold ethanol and air dried.

$[Co(HL^3)_2][ZnCl_4]Cl$. Yield: 0.95 g (59%). ^{13}C NMR (D_2O): 183.63 (C=N), 164.81 (C=NOH), 66.62, 65.49 (both CH_2–N), 30.14, 28.77, 21.17, 16.65 (all CH_3). UV-Vis (H_2O): λ_{max} 305.3, 257.6 nm. *Anal.* Required for $C_{16}H_{34}Cl_5CoN_6O_2Zn$: C, 29.84; H, 5.32; N, 13.05%. Found: C, 31.01; H, 5.65; N, 13.06%.

$[Co(HL^4)(L^4)][ZnCl_4]$. Yield: 0.93 g (57%). ^{13}C NMR (D_2O): 187.24 (C=N), 163.97 (C=NOH), 66.12, 65.19, 30.16 (all CH_2), 28.81, 27.58, 16.53, 12.54 (all CH_3). *Anal.* Required for $C_{18}H_{37}Cl_4CoN_6O_2Zn$: C, 34.01; H, 5.87; N, 13.22%. Found: C, 33.21; H, 5.97; N, 12.79%.

$[Co(en)_2(bdm)][ZnCl_4]$ (9). $[Co(en)_2(OH)(OH_2)](ClO4)_2$ (1.6 g, 0.0037 mol) and butanedionemonoxime (1.9 g, 0.0185 mol) were heated at reflux in methanol (100 mL) over 24 h. The crude reaction mixture was reduced in volume to *ca.* 10 mL using a rotary evaporator, water (100 mL) was added and the solution was loaded onto a column of Dowex (14 × 5.5 cm, H^+ form). Elution with water (250 mL) and HCl (0.5 M, 250 mL) separated the mixture into two major bands. The first orange band was eluted with 1 M HCl and the second yellow band was eluted with 2 M HCl. The first orange band was taken to dryness on a rotary evaporator to give an orange residue (approximately 0.5 g). $ZnCl_2$ (0.22 g) dissolved in HCl (4 M, 20 mL) was added, and the solution was taken to dryness on a rotary evaporator. The residue was triturated with ethanol to give an orange solid that was washed with cold methanol, acetone and air dried. Yield: 0.6 g (33%). ^{13}C NMR (D_2O): δ 216.26 (C=O), 159.11 (C=NO), 47.26, 46.53, 46.29, 44.11 (all CH_2–NH_2), 27.12, 13.85 (both CH_3). UV-Vis (H_2O): λ_{max} 328.3, 264.3, 223.0 nm. *Anal.* Required for $C_8H_{22}C_{14}CoN_5O_2Zn$: C, 19.75; H, 4.56; N, 14.40%. Found: C, 20.06; H, 4.69; N, 14.31%.

Complexes from the free ligands

General procedure: To a solution of cobalt(II) chloride hexahydrate (1 equivalent) in methanol (30 mL), HL^n (2 equivalents, $n = 1$–4) dissolved in methanol (30 mL) was added. The solution was heated at reflux for 1 h and the solvent removed on a rotary evaporator. The residue was treated with water (50 mL) and loaded onto a column of Dowex (14 × 5.5 cm, H^+ form). Elution with water (250 mL), HCl (0.5 M, 250 mL) and finally HCl (2 M) afforded a single major band in each case. This band was taken to dryness using a rotary evaporator, and the corresponding complexes isolated as tetrachlorozincate salts using the methods described above.

Crystal structure determinations

The X-ray data was collected on a Siemens P4 four circle diffractometer, using a Siemens SMART 1K CCD area detector and irradiating the samples with graphite monochromated Mo-Kα (λ = 0.71073 Å) X-rays. The crystals were mounted 5.5 cm from the detector. The data were collected by the SMART program and processed with the help of SAINT to apply Lorentz and Polarisation corrections to the diffraction spots (integrated three dimensionally). SADABS was used to scale the diffraction data, apply empirical absorption corrections and to apply decay corrections if required. The structures were solved by direct methods and refined using the SHELXTL program. Hydrogen atoms were calculated at ideal positions unless otherwise stated and refined using a riding model.

Crystallographic data are shown on Table 1 and selected bond lengths and angles in Table 2.

$[Co(HL^1)(en)Cl][ZnCl_4]$ (2). Vapour diffusion of methanol into a concentrated aqueous solution of the complex yielded suitable crystals (red blocks) for X-ray diffraction.

$[Co(HL^1)_2][ZnCl_4]Cl.H_2O$ (3). Vapour diffusion of methanol into a concentrated solution of the complex in HCl (1 M) yielded crystals (red blocks) suitable for X-ray diffraction.

$[Co(HL^1)(H_2L^1)Cl]Cl_3.2H_2O$ (4). Slow evaporation of an aqueous solution of the complex yielded large red crystals of which one was cut to a suitable size for X-ray diffraction.

$[Co(HL^2)(L^2)][ZnCl_4].H_2O$ (6). Vapour diffusion of methanol into a concentrated solution of the complex in HCl (1 M) yielded crystals (orange prisms) suitable for X-ray diffraction.

$[Co(HL^3)_2][ZnCl_4]Cl.3H_2O$ (7). Vapour diffusion of methanol into a concentrated solution of $[Co(HL^3)_2][ZnCl_4]Cl$ in HCl (1 M) yielded crystals (red blocks) suitable for X-ray diffraction.

$[Co(en)_2(bdm)][ZnCl_4]$ (9). Vapour diffusion of acetone into an aqueous solution of $[Co(en)_2(bdm)][ZnCl_4]$ yielded crystals (orange plates) suitable for X-ray diffraction.

CCDC reference numbers 188183–188188.

See http://www.rsc.org/suppdata/dt/b2/b205956h/ for crystallographic data in CIF or other electronic format.

Results and discussion

The cobalt–amine/imine/oxime complexes (**2**–**8**), reported here have been prepared for the first time. A complex closely related to **3**, the $[Co(L^1)_2]^+$ complex cation (where both oxime groups are deprotonated), has been reported previously, but without X-ray structural characterisation.[9] A series of related cobalt(III) complexes containing tridentate N-substituted oxime ligands have also been prepared, again without structural characterisation or reference to the stereochemistry found at the coordinated secondary amine.[10] Previous work with these ligands has been focused mainly on their complexes with other transition metals, such as the iron(II) species[11] or the nickel(II)/nickel(IV) complexes and their redox activity.[12,13] To our knowledge, no previous syntheses have been attempted from intramolecular condensation of the bis(1,2-diaminoethane) complexes, however, a trimetallic copper(II) complex has been prepared from the 'one-pot' reaction of 1,2-diaminoethane, butanedionemonoxime and copper(II) acetate.[14]

We have used two methods for preparing cobalt complexes of tridentate oxime ligands; firstly from the reaction of keto-oximes with diamine-containing complexes such as *trans*-$[Co(en)_2Cl_2]Cl$, and secondly from the reaction of $CoCl_2.6H_2O$ and the free ligand. In general, the reactions involving the preformed tridentate ligands gave only the product complexes containing two tridentate ligands, while the complexation–condensation reactions often gave more than one product. Many of the resulting complexes have been characterised by X-ray crystallographic techniques.

Table 1 Crystallographic data

	$[Co(HL^1)(en)Cl]ZnCl_4$	$[Co(HL^1)_2][ZnCl_4]Cl.H_2O$	$[Co(HL^1)(H_2L^1)Cl]Cl_3.2H_2O$	$[Co(en)_2(bdm)]ZnCl_4$	$[Co(HL^2)(L^2)]ZnCl_4.H_2O$	$[Co(HL^3)_2](ZnCl_4)Cl.3H_2O$
Formula	$C_8H_{21}Cl_5CoN_5OZn$	$C_{12}H_{28}Cl_5CoN_6O_3Zn$	$C_{12}H_{31}Cl_4CoN_6O_4$	$C_8H_{22}C_{14}CoN_5OZn$	$C_{14}H_{31}Cl_4CoN_6O_3Zn$	$C_{16}H_{40}Cl_5CoN_6O_5Zn$
M	504.85	605.95	524.16	486.41	597.55	698.09
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pca*2(1)	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	16.375(3)	8.229(2)	14.137(5)	10.006(4)	13.598(5)	10.144(3)
b/Å	8.3790(17)	20.348(6)	11.532(4)	10.967(4)	11.705(4)	10.782(3)
c/Å	13.418(4)	14.258(4)	14.020(5)	16.506(6)	15.371(5)	14.234(4)
a/°					90	106.538(4)
β/°		99.293(4)	96.683(4)	92.348(5)	107.312(6)	93.305(5)
χ/°					90	96.088(4)
V/Å^3	1841.0(7)	2356.0(12)	2270.2(14)	1809.7(12)	2335.6(14)	1477.6(8)
Z	4	4	4	4	4	2
T/K	163(2)	163(2)	163(2)	163(2)	163(2)	163(2)
μ/mm^{-1}	2.932	2.314	1.256	2.840	2.223	1.861
Reflections	12820	30869	28940	22618	23123	19196
Independent	3718	4801	4609	3682	4793	5939
Observed	3681	3496	3501	3081	4012	4449
Parameters refined	193	259	250	192	278	317
$R\ [I > 2\sigma(I)]$	0.017	0.064	0.023	0.040	0.027	0.033
$R_w\ [I > 2\sigma(I)]$	0.044	0.171	0.054	0.119	0.071	0.075

Table 2 selected bond lengths and angles (Å and °)

	$[Co(HL^1)_2]^{3+}$	$[Co(L^2)(HL^2)]^{2+}$	$[Co(HL^3)_2]^{3+}$
Co–N(1)	1.925(4)	1.9098(18)	1.960(2)
Co–N(2)	1.881(4)	1.8669(19)	1.897(2)
Co–N(3)	1.963(5)	1.9873(18)	1.964(2)
Co–N(4)	1.937(4)	1.9184(18)	1.957(2)
Co–N(5)	1.886(4)	1.8792(19)	1.898(2)
Co–N(6)	1.962(5)	1.9583(19)	1.952(3)
N(1)–Co–N(3)	165.97(18)	167.18(8)	163.68(10)
N(4)–Co–N(6)	165.61(19)	165.32(8)	162.91(10)
N(2)–Co–N(5)	177.51(18)	176.52(8)	172.83(10)
N(1)–Co–N(2)	80.91(18)	82.36(8)	80.37(10)
N(2)–Co–N(3)	85.19(19)	84.89(8)	83.97(10)
N(4)–Co–N(5)	80.22(19)	80.75(7)	79.96(10)
N(5)–Co–N(6)	85.49(19)	84.89(8)	84.13(10)

Condensation reactions

Our initial studies revealed that reaction of *trans*-$[Co(en)_2Cl_2]Cl$ with two molar equivalents of butanedionemonoxime or pentane-2,3-dione-2-oxime over 24 hours produced the singly condensed complex cations (**2**, **5**) and the desired bis-oxime complex cations (**3**, **6**) in similar yields. Subsequently we found that the use of one molar equivalent of the oxime produces the singly condensed products as the major component. When five equivalents of the oxime are used over the same time period, the principal products are those resulting from two condensation reactions having occurred.

Use of *cis*-$[Co(en)_2Cl_2]Cl$ as the complex starting material yielded similar results to those seen for the *trans* isomer, which is consistent with the chemistry observed in coordination–condensation reactions of such complexes with keto acids.[5b] Similar chemistry is observed when *trans*-$[Co(dmen)_2Cl_2]Cl$ is employed as the starting material.

In the singly condensed complex cation of $[Co(HL^1)(en)Cl][ZnCl_4]$ (**2**), the cobalt(III) ion lies at the centre of a distorted octahedron and has a N_5Cl coordination sphere (Fig. 1). The

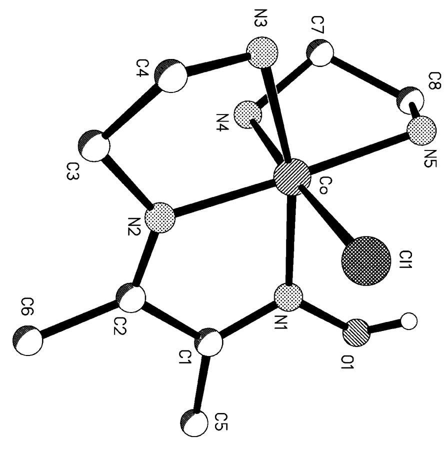


Fig. 1 The $[Co(en)(HL^1)Cl]^{2+}$ complex cation. Most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co–N(1), 1.9136(19); Co–N(2), 1.8767(17); Co–N(3), 1.961(2); Co–N(4), 1.9589(17); Co–N(5), 1.9613(17); Co–Cl(1), 2.2407(6); N(2)–Co–N(1), 80.63(8); N(2)–Co–N(5), 176.35(7); N(2)–Co–N(3), 84.93(8); N(1)–Co–N(3), 165.44(7); N(4)–Co–Cl(1), 175.25(5).

coordinated Cl(5) was found to be *trans* to N(4) of the coordinated 1,2-ethanediamine. HL^1 coordinates in a tridentate manner through oxime, imine and amine nitrogen atoms and the shortest metal ligand contact in the complex is 1.88 Å for the N(2) imine nitrogen atom. The required bite angle from imine and oxime coordination causes the greatest deviation from a regular octahedron, with N(1)–Co–N(3) being 165.4°. The oxime proton was located crystallographically.

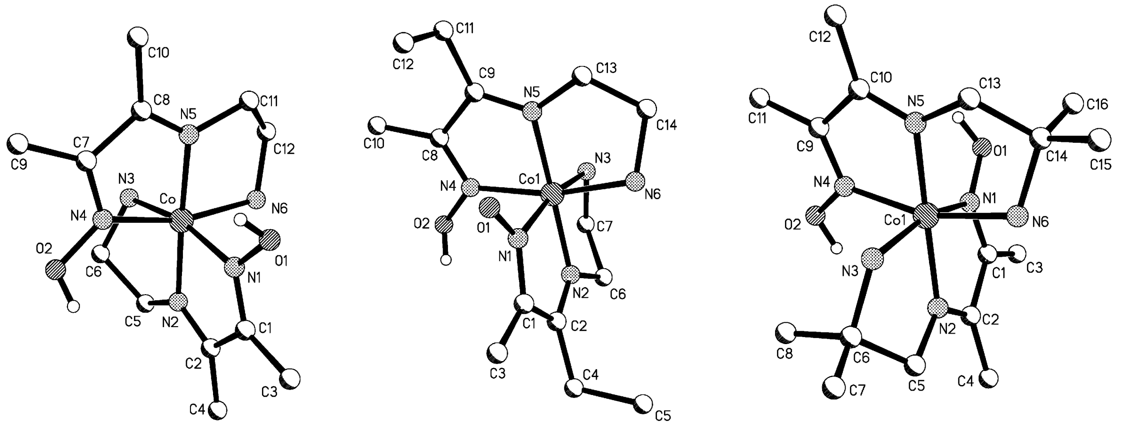


Fig. 2 Crystal structures of the complex cations $[Co(HL^1)_2]^{3+}$, $[Co(HL^2)(L^2)]^{2+}$ and $[Co(HL^3)_2]^{3+}$. Most hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 2.

Three products from double condensation reactions have been characterised by crystallographic methods: $[Co(HL^1)_2][ZnCl_4]Cl.H_2O$ (**3**), $[Co(HL^2)(L^2)][ZnCl_4].H_2O$ (**6**), and $[Co(HL^3)_2][ZnCl_4]Cl.3H_2O$ (**7**) (Fig. 2). All three complexes have a distorted octahedral cobalt(III) centre that is coordinated by two ligands, each binding to the metal in a tridentate manner, through oxime, imine and amine nitrogen atoms to give an N_6 coordination sphere. $[Co(HL^1)_2][ZnCl_4]Cl.H_2O$ (**3**) and $[Co(HL^3)_2][ZnCl_4]Cl.3H_2O$ (**7**) have triply charged cations, with both oxime oxygen atoms in each complex being protonated. $[Co(HL^2)(L^2)][ZnCl_4].H_2O$ (**6**) has a doubly charged complex cation in which one of the oxime oxygen atoms is deprotonated. The respective Co–N(imine) and Co–N(amine) bond lengths in the complexes are similar across the three complexes, with the shortest Co–N bonds being Co–N(imine) (1.8793(19) to 1.897(3) Å) and longest being Co–N(amine) (1.948(3) to 1.9874(18) Å). There is slightly more variation in the Co–N(oxime) bond lengths, from 1.9098(18) Å in the L^2 ligand of $[Co(HL^2)(L^2)]^{2+}$, where the oxime oxygen is deprotonated, to 1.961(3) Å in $[Co(HL^3)_2]^{3+}$, where the ligand is protonated.

The N(amine)–Co–N(oxime) bond angles range from 162.9 to 167.2° showing considerable distortion from the 180° angles expected in a regular octahedron. A more extreme distortion is seen in $[Co(HL^3)_2]^{3+}$ where N(5)–Co(1)–N(1) is pulled 15.5° from the regular 90°. The Co–N distances and N–Co–N bond angles observed in these structures are comparable to those in the related complex, $[Co(L)_2]ClO_4$ (HL = 3-[2-(2-pyridyl)methylimino]-butan-2-one oxime).[3]

In all three crystal structures, the protonated oxime groups (the protons were located crystallographically) are involved in long range interactions in the lattice with either chloride ions or oxygen atoms from waters of crystallisation. The deprotonated oxime moiety in $[Co(HL^2)(L^2)]^{2+}$ exhibits an oxime C–N double bond which is longer (1.322(3) *cf.* 1.294(3) Å) and a significantly shorter N–O(oxime) bond (1.273(2) *cf.* 1.380(2) Å) than in the protonated ligand. Together with the shorter Co–N bond for this ligand, this is consistent with the presence of electron delocalisation through these bonds. This effect is also reflected in the C(oxime)–N–O bond angle which is 123.3° in the deprotonated ligand *cf.* 115.0° in the protonated ligand. A similar trend was observed in the related nickel(II) and nickel(IV) species, $[Ni(HL^1)_2]^{2+}$ and $[Ni(L^1)_2]^{2+}$, that contain protonated and deprotonated ligands respectively.[15,16]

The isolation of materials in which only a single coordination–condensation reaction had occurred offered the prospect that we may be able to prepare mixed ligand systems. Unfortunately, submission of the singly condensed complex cation, $[Co(HL^1)(en)Cl][ZnCl_4]$ (**2**), to reaction with different monoximes lead only to the formation of mixtures of complexes that could not be separated easily. Similar reactions with $[Co(HL^2)(en)Cl][ZnCl_4]$ (**5**) also failed. We speculate that the isolation of significant amounts of the singly condensed complex from the original condensation reaction may be related to difficulty of bringing a second oxime donor, which is rather hindered, into the coordination sphere. Indeed, we believe that the singly condensed complex is actually rather unreactive (see below). The conditions that are required to induce reaction of this complex may be sufficiently harsh to result in ligand exchange and the formation of mixtures when different oxime ligands are present.

The oxime–imine as a didentate ligand

An unexpected species is consistently isolated from the reaction of two or more equivalents of butanedionemonoxime with $[Co(en)_2Cl_2]Cl$; the $[Co(HL^1)(H_2L^1)Cl]^{3+}$ complex cation (**4**) in which the ligand is found both as a tridentate and a didentate (Fig. 3).

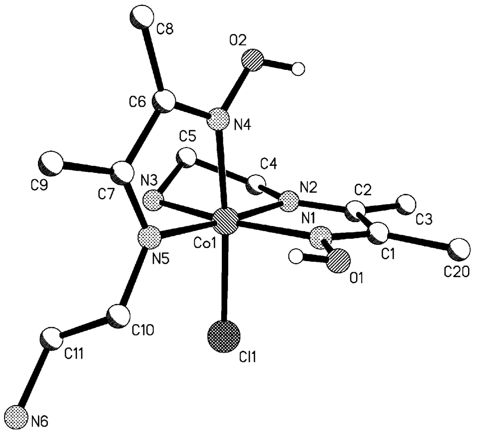
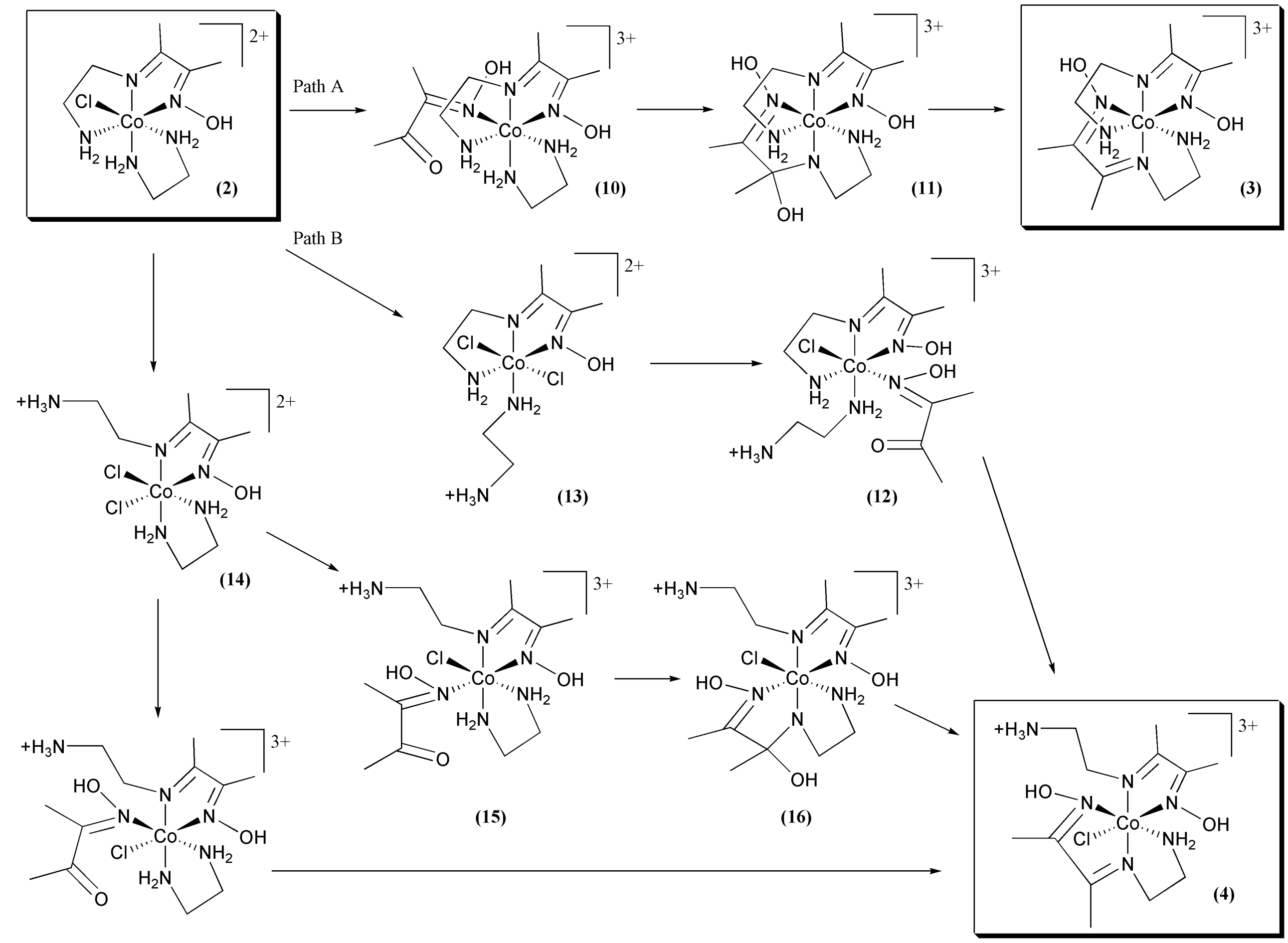


Fig. 3 The $[Co(HL^1)(H_2L^1)Cl]^{3+}$ complex cation. Most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–N(1), 1.9416(15); Co(1)–N(2), 1.8825(16); Co(1)–N(3), 1.9443(15); Co(1)–N(4), 1.9146(15); Co(1)–N(5), 1.9466(15); Co(1)–Cl(1), 2.2415(7); N(2)–Co(1)–N(1), 81.11(7); N(2)–Co(1)–N(3), 84.96(7); N(1)–Co(1)–N(3), 166.07(6); N(2)–Co(1)–N(4), 95.97(6); N(4)–Co(1)–N(5), 81.02(6); N(2)–Co(1)–N(5), 176.44(6); N(4)–Co(1)–Cl(1), 174.66(5).

The complex cation is triply charged, with the cobalt(III) ion again lying at the centre of a distorted octahedron with an N_5Cl coordination sphere. One ligand is coordinated in a tridentate manner, through oxime, imine and amine nitrogen atoms, and the other ligand is didentate, coordinating through oxime and imine nitrogen atoms only. The primary amine in the didentate ligand is protonated and pendant, thus Cl(1) completes the coordination sphere lying *trans* to oxime N(4). The pendant



Scheme 2

protonated amine group is positioned so that it would, in principle, be able to replace the chloride ligand without additional rearrangement of the coordination sphere (once the amine has been deprotonated). None of the other isomer, where the pendant is attached *trans* to chloride, was detected.

The imine N(5)–Co bond length of the didentate ligand is significantly longer than the imine N(2)–Co of the tridentate ligand (1.95 *cf.* 1.88 Å) and the Cl(1)–Co–N(4) angle is closer to 180° than that of N(1)–Co–N(3) (176.5° *cf.* 166.1°). Thus, coordination of the imine/oxime moiety as a didentate ligand releases strain and allows the complex to retain a more regular octahedral coordination sphere in comparison to the complexes in which both ligands act in a tridentate manner. Both oxime protons were located crystallographically and are involved in longer range interactions within the crystal. O(1) has a close contact of 2.55 Å to O(4) of a water molecule of crystallisation through the oxime proton. This water molecule is also close to the second water molecule of crystallisation (2.75 Å). Oxime O(2) lies 2.93 Å from Cl(2), one of the three chloride anions.

Initially, our prejudice was that the pendant species **4** was likely formed from the bis(tridentate) product **3**, which is the complex we were intending to prepare *via* these condensation reactions. However, the pendant complex was not observed when the bis(tridentate) complex **3**, was prepared by the direct reaction of HL^1 with cobalt chloride, followed by a similar work-up. This implies that, if **4** is a product from reaction of **3**, the cleavage of the metal–amine bond would have to occur under the intramolecular condensation reaction conditions rather than during the isolation procedure.

Heating a methanolic solution of the isolated double condensation product, $[Co(HL^1)_2]^{3+}$ (**3**) (as the perchlorate salt) together with added chloride (three equivalents of LiCl) gave none of the pendant product. A similar reaction in which several equivalents of monoxime ligand were added as well as the LiCl again gave none of the pendant product. It appears unlikely, therefore, that the double condensation product is the precursor of the pendant complex.

An alternative possibility was that the pendant complex **4** is a precursor for the double condensation complex. However, none of the $[Co(HL^1)_2]^{3+}$ ion was detected when the pendant complex was resubmitted to the reaction conditions, either in the presence or absence of additional monoxime. We conclude therefore, that the two complexes are products from parallel reaction pathways and do not interconvert.

We have, however, confirmed that both the pendant species **4** and the double condensation product **3** can be formed from the singly condensed species **2** under the reaction conditions. Furthermore, it appears that this singly condensed intermediate is less reactive towards the coordination–condensation reaction with butanedionemonoxime than the $[Co(en)_2Cl_2]^+$ starting material.

Possible reaction mechanisms

Given that the double condensation product **3** and the pendant complex **4** appear to be formed independently from the singly condensed complex **2**, some discussion of mechanism is warranted. A number of possibilities are shown in Scheme 2. The most likely, and straight-forward mechanism for formation of the doubly condensed product involves monoxime-for-chloride ligand exchange followed by condensation between the monoxime ligand and the coordinated amine (Path A). The ligand exchange reaction appears to be rather slow, as the singly condensed complex can be isolated from the reaction mixture even after reasonably long reactions times in the presence of excess monoxime ligand. Condensation reactions between carbonyl containing ligands and coordinated amines are known to be occur readily,[5,17] so the subsequent steps are probably significantly faster than the ligand exchange reaction.

While the pendant complex **4** has been shown not to be derived from the resulting imine, it could conceivably be formed from the intermediate **10**, by cleavage of a cobalt–nitrogen bond prior to condensation, or from the carbinolamine **11**. However, the fact that condensation reactions between carbonyl containing ligands and coordinated amines and the subsequent dehydrations to give imines are both known to be relatively facile reactions[5,17] makes this seem unlikely, especially given the comparatively robust nature cobalt(III)–amine bonds.

If the cobalt–nitrogen bond cleavage reaction required for formation of the pendant complex does not occur after coordination of the monoxime ligand in place of the chloride ligand, then it must have occurred prior to that ligand exchange. The long lifetime of the singly condensed complex **2** under the reaction conditions is consistent with this proposal. Cobalt(III)–amine bonds are generally rather inert, so a long lifetime would be required for such a complex if such a cleavage reaction is to be competitive with any other reactions that it might undergo.

So which of the three cobalt–amine bonds in the single condensation product **2** is likely to be the one cleaved? If the bond to the amine *trans* to the imine of the tridentate ligand is broken, then the condensation reaction of a coordinated monoxime ligand with the remaining 1,2-ethanediamine donor would result in the pendant portion of the ligand pointing away from the chloride donor (unless there is a subsequent complete rearrangement of the coordination sphere). That is, a different complex would be formed.

Loss of the other 1,2-ethanediamine donor instead would result in the monoxime complex **12**, either directly or *via* the dichloride complex (**13**). Condensation of the carbonyl group with the coordinated amine would give the observed pendant complex. The fact that the pendant complex is only seen when there is a significant amount of chloride in the reaction mixture (*i.e.* it is not seen when $[Co(en)_2(OH)(OH_2)](ClO_4)_2$ is used as the starting material), together with the steric crowding around the oxime nitrogen atom lead us to prefer **13** as the intermediate, as the in-coming ligand would have to compete with recoordination by the cleaved amine donor atom.

The final possibility involves the bond to the amine donor in the tridentate ligand of **2** being broken. This donor could be replaced by either another chloride ion (to give **14**) or a monoxime ligand (to give **15**). However, the fact that the double condensation product (**3**), does not lose either one of the two coordinated amine donors that are very similar to that being lost in this latter pathway would have to be interpreted as circumstantial evidence against it. On this basis at least, we favour Path B, but the evidence is not strong.

The observation that the related pendant species are not observed for the corresponding reactions in which pentane-2,3-dione-2-oxime or *trans*-$[Co(dmen)_2Cl_2]_2[ZnCl_4]$ are used is presumably significant, but we can see no compelling reason why the different substitution pattern should eliminate formation of products analogous to **4**. Presumably it is related to the increased steric demand of the substituted ligands, but the details of these interactions are not clear at this time.

Butandionemonoxime as a chelating ligand

A complex with two 1,2-ethanediamine ligands and a chelated butanedionemonoxime was obtained from attempts to perform condensation reactions on $[Co(en)_2(OH)(OH_2)](ClO_4)_2$. The monoxime ligand is coordinated through the oxime nitrogen atom and the carbonyl oxygen atom (Fig. 4). This structure was identified as a possibility based on the ^{13}C NMR spectrum that was obtained, which contains four resonances that can be assigned to the amine ligands, and four that can be assigned to the monoxime ligand. The latter four included a resonance at 216.3 ppm that seemed likely to be due to a carbonyl carbon atom. The proposed structure was confirmed by X-ray crystallography. While such structures have been seen before,[18,19] it is interesting to note that the coordinated carbonyl group survives ion exchange chromatography using HCl as the eluent and subsequent evaporation to dryness. These are conditions where one might expect such a ligand to be substituted by chloride.

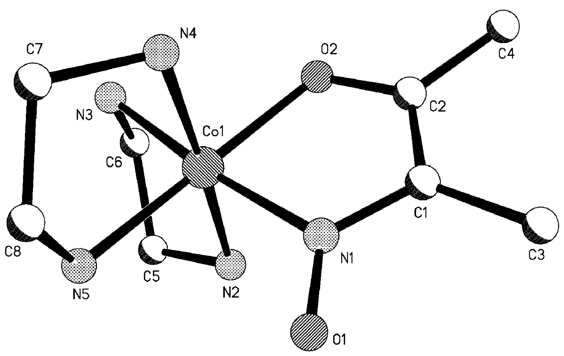


Fig. 4 The $[Co(en)_2(bdm)]^{2+}$ complex cation. Hydrogen atoms have been omitted for clarity. The oxime oxygen atom (O1) is not protonated in this structure. Selected bond lengths (Å) and angles (°): Co(1)–N(1), 1.886(4); Co(1)–O(2), 1.902(3); Co(1)–N(2), 1.949(4); Co(1)–N(3), 1.973(4); Co(1)–N(4), 1.954(4); Co(1)–N(5), 1.950(4); N(1)–Co(1)–O(2), 83.27(15); N(5)–Co(1)–N(4), 86.17(16); N(2)–Co(1)–N(3), 85.49(16); N(1)–Co(1)–N(3), 171.84(16); O(2)–Co(1)–N(5), 175.33(14); N(2)–Co(1)–N(4), 176.86(16).

The $[Co(en)_2(bdm)]^{2+}$ cation has near octahedral geometry with the cobalt(III) centre lying in an N_5O coordination sphere. The oxime proton of the coordinated butanedionemonoxime has been removed, and the N(oxime)–cobalt contact of 1.89 Å is the shortest nitrogen–metal distance. Coordination of the carbonyl oxygen affords a Co–O(2) bond length of 1.90 Å which is similar to that seen in a closely related structure.[18]

The fact that this compound was only seen when $[Co(en)_2(OH)(OH_2)](ClO_4)_2$ was employed as the starting material may be significant in terms of the mechanism by which this complex is formed. Presumably the first step in the reaction is coordination of the oxime nitrogen atom, through ligand exchange with a coordinated water molecule. The chelate would then be formed by nucleophilic attack of the coordinated hydroxide on the carbonyl group of the oxime ligand, followed by elimination of water. There is much precedent for this kind of chemistry from the study of cobalt(III) complexes with amino acid derivatives.[20] The ligand exchange alternative to this second step, in which the coordinated hydroxide would leave, probably after protonation, and be replaced by the carbonyl oxygen atom of the oxime ligand, seems less likely. If such a ligand exchange mechanism were occurring then we would have expected to see this same product in reactions where a $[Co(en)_2Cl_2]^+$ ion is employed as a starting material, because the chloride ligands are also readily exchanged.

It seems likely, therefore, that the observed product distribution results from competition between nucleophilic attack on the carbonyl group of the monoxime ligand by the deprotonated coordinated amines (leading to imine formation) and by coordinated hydroxide (leading to the chelated monoxime complex). Use of the chloride containing starting materials leaves the coordinated amines without any intramolecular competition, and only imine containing products are observed.

Conclusion

Cobalt(III) complexes of tridentate ligands containing oxime, imine and amine donor groups have been prepared by direct complexation of the free ligand and by templated intramolecular condensation reactions. The latter method results in the formation of other complexes as well, including those in which only a single coordination–condensation reaction sequence has occurred and, in one case, a complex in which a pendant complex is formed. Unless these other complexes are required for some purpose, the direct method is probably preferable for the preparation of the bis(tridentate) complexes. A complex containing a chelated butanedionemonoxime ligand has also been isolated and fully characterised, which is quite remarkable when the strongly acidic conditions used during its isolation are taken into account. The complexes have been analysed crystallographically and show considerable distortions from a regular octahedron. The ligands themselves are easily substituted to provide spectroscopic probes useful for monitoring subsequent photochemical reactions.

References

1 For reviews of early work see: (*a*) V. I. Pazlovskii and A. L. Poznyak, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 789; (*b*) J. Sykora and J. Sima, *Coord. Chem. Rev.*, 1990, **107**, 1; (*c*) V. I. Pavlovski and A. L. Poznyak, *Z. Chem.*, 1989, **29**, 6.

2 R. M. Hartshorn and S. G. Telfer, *J. Chem. Soc., Dalton Trans.*, 1999, 3565.

3 L. Catalano, R. Dreos, G. Nardin, L. Randaccion, G. Tauzher and S. Vuano, *J. Chem. Soc., Dalton Trans.*, 1996, 4269.

4 D. Dreos, A. Felluga, G. Nardin, L. Randaccio, P. Siega and G. Tauzher, *Inorg. Chem.*, 2001, **40**, 5541.

5 (*a*) J. M. W. Browne, J. Wikaira and R. M. Hartshorn, *J. Chem. Soc., Dalton Trans.*, 2001, 3513; (*b*) J. M. W. Browne, J. Wikaira, C. M. Fitchett and R. M. Hartshorn, *J. Chem. Soc., Dalton Trans.*, 2002, 2227.

6 J. Springbørg and C. E. Schäffer, *Inorg. Synth.*, 1973, **14**, 63.

7 M. Harnett, D. A. House and W. T. Robinson, *Inorg. Chim. Acta*, 1985, **102**, 87.

8 W. L. Semon and V. R. Damerell, *Organic Synthesis*, vol. II, 204.

9 G. Costa, G. Mestroni and E. de Savorgnani, *Inorg. Chim. Acta*, 1969, **3**, 323.

10 H. Tanaka, H. Kuma and S. Yamada, *Synth. React. Inorg. Met.-Org. Chem.*, 1985, **15**, 699.

11 A. N. Singh, *Ind. J. Chem.*, 1980, **19A**, 1215.

12 A. McAuley, C. J. Macdonald, L. Spencer and P. R. West, *J. Chem. Soc., Dalton Trans.*, 1988, **9**, 2279.

13 A. Dutta, S. Bhattachrya and P. Banerjee, *Polyhedron*, 1998, **17**, 2313 and references therein.

14 J. A. Bertrand, J. H. Smith and D. G. Van Der Veer, *Inorg. Chem.*, 1977, **16**, 1477.

15 J. Korvenranta, H. Saarinen and E. Näsäkkälä, *Finn. Chem. Lett.*, 1979, 81.

16 H. Saarinen, J. Korvenranta and E. Näsäkkälä, *Acta Chem. Scand.*, 1980, **A34**, 443.

17 (*a*) B. T. Golding, J. McB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc.*, 1974, **96**, 3003; (*b*) J. D. Bell, A. R. Gainsford, B. T. Golding, A. J. Herlt and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1974, 980; (*c*) A. R. Gainsford and A. M. Sargeson, *Aust. J. Chem.*, 1978, **31**, 1679; (*d*) A. R. Gainsford, R. D. Pizer, A. M. Sargeson and P. O. Whimp, *J. Am. Chem. Soc.*, 1981, **103**, 792; (*e*) L. M. Engelhardt, A. R. Gainsford, G. J. Gainsford, B. T. Golding, J. McB. Harrowfield, A. J. Herlt, A. M. Sargeson and A. H. White, *Inorg. Chem.*, 1988, **27**, 4551.

18 H. Saarinen, J. Korvenranta and E. Näsäkkälä, *Acta Crystallogr.*, 1979, **B35**, 963.

19 H. Saarinen, J. Korvenranta and E. Näsäkkälä, *Acta Chem. Scand.*, 1978, **32**, 303.

20 P. Sutton and D. A. Buckingham, *Acc. Chem. Res.*, 1987, **20**(10), 357 and references therein.