Journal of Organometallic Chemistry, 346 (1988) 253–266
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis and characterisation of $\mu(\alpha,\omega)$-alkanediylcobaloximes and their haloalkyl precursors

Karol P. Finch and John R. Moss *

Department of Inorganic Chemistry, University of Cape Town, Rondebosch 7700 (South Africa)

(Received November 2nd, 1987)

Abstract

The mononuclear bromoalkyl cobaloximes of type $[Co(DH)_2py(CH_2)_nX]$ (I), where $X = Br$ ($n = 3$–7, Ia–e) or $X = I$ ($n = 3$, Ia′) have been prepared by the reaction of the chloro(pyridine)cobaloxime, $[Co(DH)_2(py)Cl]$ with 1.5 mol of dihaloalkane in the presence of sodium borohydride (where DH = monoanion of dimethylglyoxime). The dinuclear polymethylene-bridged cobaloximes of type $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_n]$ (II), where $n = 4$–6 (IIb–d), can be synthesized by the reaction of these mononuclear cobaloximes I with an equimolar quantity of the chloro(pyridine)cobaloxime in the presence of the reducing agent, $NaBH_4$. The dinuclear complexes where $n = 4$–8, (IIb–f), have also been prepared from $[Co(DH)_2pyCl]$ and the corresponding dihaloalkane in a 2/1 molar ratio in the presence of $NaBH_4$. All the cobaloximes have been fully characterised by microanalysis, NMR and IR spectroscopic techniques.

Introduction

The cobalt(III) complexes of dimethylglyoxime, $[Co(DH)_2LR]$ (where L = a base such as pyridine, DH = monoanion of dimethylglyoxime and R = an alkyl group such as (CH_3)), known commonly as the "cobaloximes", have been used extensively as models for the vitamin B_{12} complexes [1–7].

The analogies between the chemical behaviour of vitamin B_{12} and the cobaloximes have been ascribed to the similarities in the coordinating power of the sp^2-hybridized nitrogen atoms surrounding the cobalt atom in both types of compound [5]. As part of a general study of polymethylene-bridged complexes of transition metals [8–11] we were particularly interested in the synthesis of complexes of type $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_n]$. Binuclear metal complexes of general formula $L_xM\text{–}(CH_2)_n\text{–}M'Ly'$ (in which the metal centres are separated by an alkyl chain), have been proposed as possible models for the bonding of hydrocarbon

0022-328X/88/$03.50

groups at metal surfaces [8–12]. For example, Fischer and Tropsch proposed that the products of catalytic CO hydrogenation could be formed by the polymerisation of methylene groups on a metal surface. One route to binuclear polymethylene bridged compounds is via their corresponding monomeric haloalkyl complexes [8].

$$L_nM-(CH_2)_nX + Ly'M' \xrightarrow[\text{agent}]{\text{reducing}} L_xM-(CH_2)_n-M'L' \qquad (1)$$

The preparation of dinuclear polymethylene bridged cobaloximes where $n = 3$ and 4 has previously been briefly reported by Schrauzer and Windgassen [2]. However, these compounds were only partially characterised at the time. Such binuclear cobaloximes may also be considered as models for vitamin B_{12} of type $[Co(DH)_2LR]$ (L = axial base), where R incorporates not only an alkyl group but also a metal atom carrying its own ligand system.

It is noteworthy that Smith and co-workers [13] attempted the preparation of dinuclear polymethylene-bridged vitamin B_{12s} complexes. They found that such dimeric coenzyme analogues were only formed if the length of the bridging carbon chain exceeded three ($-CH_2-$) units, as predicted by Crowfoot–Hodgkin and quoted in [13]. This is probably due to steric interference of the bulky ligands in the cobalamin. The dimeric nature of these complexes appears to have been established by analysis of halogen content and by paper chromatography.

Thus, no reaction of 1,2-dibromomethane with vitamin B_{12s} was observed while dibromomethane and 1-chloro-3-bromopropane gave only halogen-containing monomers as shown in eq. 2a. However, reaction of vitamin B_{12s} with 1,4-dibromobutane yielded a "halogen-free" bridged dimer as the major product under all reaction conditions even when a large excess of dibromobutane was used (see eq. 2b).

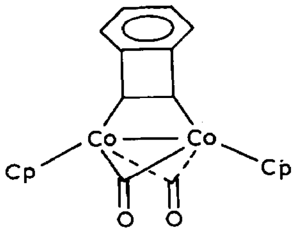
$$\begin{aligned}(Co) + X-(CH_2)_n-X \rightarrow\ & (Co)-(CH_2)_nX \qquad (2a)\\ & (\mathbf{1}, X = Br,\ n = 1,\\ & \ \mathbf{2}, X = Br, Cl,\ n = 3)\\ & (Co) = \text{vitamin } B_{12s}\end{aligned}$$

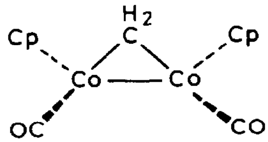
$$(Co) + X-(CH_2)_4-X \rightarrow (Co)-(CH_2)_4-(Co) + \underset{(\mathbf{3},\ X = Br)}{(Co)(CH_2)_4-X} \qquad (2b)$$

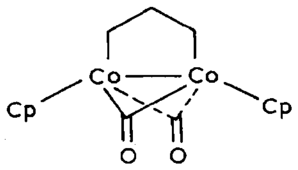
The minor product, the bromobutyl B_{12s} monomer, could be extracted and reacted further with B_{12s} to form the dimer [13]. This reaction was observed to occur even more rapidly than that with the dihaloalkane.

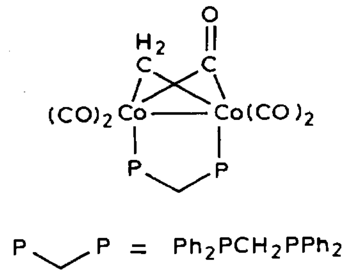
With the exception of the dinuclear polymethylene-bridged cobaloximes prepared by Schrauzer (with $n = 3,4$) [2] and the vitamin B_{12s} dimer ($n = 4$) prepared by Smith et al. [13], no other binuclear complexes of cobalt without a metal–metal bond are known. However, dicobalt methylene and polymethylene-bridged complexes containing cobalt–cobalt bonds and ligands such as cyclopentadienyl and carbon monoxide [9,14] and bis(diphenylphosphino)methane [18] are known. Some examples are shown below.

We now report the syntheses of mononuclear haloalkylcobalt complexes $[Co(DH)_2py(CH_2)_nX]$ (where $X = Br$, $n = 3–7$ (Ia–e) and $X = I$, $n = 3$ (Ia′)) and the subsequent conversion of some of these products to the dinuclear complexes $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_n]$ (where $n = 4–6$, IIb–d). The compounds of type II, where









$n = 4$–8 (IIb–f) have been prepared from [Co(DH)$_2$pyCl] and dihaloalkane in the presence of NaBH$_4$.

Experimental

All reactions were carried out in Schlenk tubes under nitrogen with continuous stirring. All products were recrystallised from CH$_2$Cl$_2$/hexane (unless stated otherwise) and dried under vacuum. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ (unless otherwise stated) on a Varian VXR200 NMR instrument and the solvent peak was used as reference (shifts are relative to tetramethylsilane). [Co(DH)$_2$pyCl] was prepared by a published method [3].

IR spectra were recorded as Nujol mulls between CsI plates on a Perkin–Elmer 983 Spectrophotometer (4000–200 cm^{-1}). Melting points were determined with a Kofler Hotstage Microscope (Reichert Thermovar) and are uncorrected.

Microanalyses were performed in the microanalytical laboratory at the University of Cape Town. Halogen analyses were performed at the CSIR.

Vaporimetric molecular weight determinations in CH$_2$Cl$_2$ were carried out by Pascher Mikroanalytisches Laboratorium. Fast Atom Bombardment (FAB) mass spectra were recorded by R. McQueen at the University of Cambridge, England.

1. Preparation of haloalkyl cobaloximes, [Co(DH)$_2$py(CH$_2$)$_n$X] (Ia–Ie)

[Co(DH)$_2$py(CH$_2$)$_3$Br] (Ia). [Co(DH)$_2$pyCl] (0.500 g, 1.24 mmol) was added to 10 ml of nitrogen-saturated methanol, the slurry was stirred for 5 min, and Br(CH$_2$)$_3$Br (0.19 ml, 1.86 mmol) then added, followed after 5 min by NaBH$_4$ (0.252 g, 6.66 mmol). The mixture was subsequently stirred for a further 5 min and the resulting orange solution cooled to 0 °C. The solution was set aside at −15 °C and the bright orange crystals that separated were filtered off and washed with 3 ml

methanol to give 0.382 g (55%) of Ia. The product was recrystallised from CH_2Cl_2/hexane.

[Co(DH)$_2$py(CH$_2$)$_4$Br] (Ib). Ib was prepared by the method described above for Ia with the following quantities of reagents and a reaction time of 6 min after the final addition. [Co(DH)$_2$pyCl], (0.502 g, 1.24 mmol); Br(CH$_2$)$_4$Br, (0.22 ml, 0.401 g, 1.86 mmol); $NaBH_4$, (0.251 g, 6.64 mmol). Orange crystals of Ib (0.351 g, 54%) were recovered before recrystallisation from CH_2Cl_2/hexane.

[Co(DH)$_2$py(CH$_2$)$_5$Br] (Ic). [Co(DH)$_2$pyCl] (0.500 g, 1.24 mmol) was added to 10 ml of nitrogen-saturated methanol, the slurry stirred for 5 min and Br(CH$_2$)$_5$Br (0.25 ml, 1.86 mmol) then added, followed after 5 min by $NaBH_4$ (0.252 g, 6.66 mmol). The mixture was stirred for a further 8 min then cooled to 0 ° C, and the insoluble brown-grey precipitate filtered off. The filtrate was diluted with 10–20 ml of distilled water and cooled to -15 ° C. The resulting orange crystals were filtered off to give 0.266 g (41%) of Ic. The product was further purified by recrystallisation from CH_2Cl_2/hexane.

[Co(DH)$_2$py(CH$_2$)$_6$Br] (Id). Id was prepared by the method described for Ic above, with the following quantities of reagents and a reaction time of 17 min after the final addition. [Co(DH)$_2$pyCl], (0.500 g, 1.24 mmol); Br(CH$_2$)$_6$Br, (0.28 ml, 0.453 g, 1.86 mmol); $NaBH_4$, (0.250 g, 6.55 mmol). After filtering off the brown-grey solid residue, the filtrate was diluted with about 25 ml of distilled water and set aside at -15 ° C. The resulting orange crystals were filtered off to give 0.486 g (74%) of Id. The product was further purified by recrystallisation from CH_2Cl_2/hexane.

[Co(DH)$_2$py(CH$_2$)$_7$Br] (Ie). Ie was prepared by the method described for Ic, with the following quantities of reagents and a reaction time of 20 min after the final addition. [Co(DH)$_2$pyCl], (0.496 g, 1.23 mmol); Br(CH$_2$)$_7$Br, (0.31 ml, 0.475 g, 1.84 mmol); $NaBH_4$, (0.248 g, 6.55 mmol). The solution was cooled to 0 ° C and an insoluble grey solid filtered off. The filtrate was diluted with 25 ml distilled water and the product allowed to crystallise out at -15 ° C. The orange crystals were recrystallised from CH_2Cl_2/hexane to give 0.387 g (58%) of Ie.

[Co(DH)$_2$py(CH$_2$)$_3$I] (Ia′). [Co(DH)$_2$pyCl] (0.676 g, 1.67 mmol) was added to 22 ml of nitrogen-saturated methanol, the slurry stirred for 10 min and I(CH$_2$)$_3$I (0.08 ml, 0.67 mmol) then added, followed by $NaBH_4$ (0.331 g, 8.45 mmol). The solution immediately turned dark green in colour and then rapidly became bright orange. Stirring under N_2 was continued for 10 min and the bright orange crystals were then filtered off to give 0.596 g (78%) of Ia′. The product was recrystallised from CH_2Cl_2/hexane.

Note: The mononuclear [Co(DH)$_2$py(CH$_2$)$_3$I] formed even though a 2.5/1 molar ratio of [Co(DH)$_2$pyCl] to I(CH$_2$)$_3$ I was used.

2. Preparation of the dinuclear polymethylene-bridged cobaloximes, [Co(DH)$_2$py]$_2$[μ-(CH$_2$)$_n$] (IIb–IId, n = 4–8)

Method A. By reaction of the mononuclear haloalkyl cobaloximes (Ib–Id) with [Co(DH)$_2$pyCl]

[Co(DH)$_2$py]$_2$[μ-(CH$_2$)$_4$] (IIb). [Co(DH)$_2$pyCl] (0.081 g, 0.20 mmol) was added to 10 ml of nitrogen-saturated methanol and the slurry stirred for 5 min. [Co(DH)$_2$py(CH$_2$)$_4$Br] (0.101 g, 0.20 mmol) was then added, followed after 5 min

by $NaBH_4$ (0.067 g, 1.78 mmol). The brown solution immediately turned dark green. Stirring was continued for a further 30 min, during which the solution became bright orange in colour. Addition of ca. 2 ml of water produced a precipitate of orange crystals and the solution was kept at 0°C to give further crystals. Orange crystals of IIb (0.15 g, 95%) were filtered off and recrystallised from CH_2Cl_2/hexane.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_5]$ (IIc). IIc was prepared by the method described above for IIb with the following quantities of reagents and a reaction time of 30 min after the final addition. $[Co(DH)_2pyCl]$, (0.081 g, 0.20 mmol); $[Co(DH)_2py(CH_2)_5Br]$, (0.104 g, 0.20 mmol); $NaBH_4$, (0.068 g, 1.8 mmol). About 20 ml of distilled water were added to precipitate orange crystals and the solution cooled to 0°C. A yield of 0.102 g (63%) of IIc was obtained. The product was further purified by recrystallisation from CH_2Cl_2/hexane.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_6]$ (IId). IId was prepared by the method described above for IIb with the following quantities of reagents and a reaction time of 1.5 h after the final addition. $[Co(DH)_2pyCl]$, (0.081 g, 0.20 mmol); $[Co(DH)_2py(CH_2)_6Br]$, (0.107 g, 0.20 mmol); $NaBH_4$, (0.072 g, 1.90 mmol). About 25 ml of distilled water were added to precipitate the orange product and the solution kept at 0°C overnight. 0.105 g (65%) of orange crystals of IId were isolated by filtration and the product recrystallised from CH_2Cl_2/hexane.

Method B. By reaction of $[Co(DH)_2pyCl]$ with $Br(CH_2)_nBr$ in a 2/1 molar ratio ($n = 4$–8)

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_4]$ (IIb). $[Co(DH)_2pyCl]$ (1.002 g, 2.48 mmol) were added to 15 ml of nitrogen-saturated methanol, the brown slurry was stirred for 5 min, and $Br(CH_2)_4Br$ (0.15 ml, 1.28 mmol) then added followed after 5 min by $NaBH_4$ (0.500 g, 13.2 mmol). The solution immediately turned dark and gradually became bright orange as stirring was continued. The mixture was stirred for 20 min after the final addition of $NaBH_4$. A few ml of distilled water were added to initiate crystallisation, and the orange solution kept overnight at 0°C. The orange product was filtered off and washed with petroleum ether (b.p. 30–60°C) to give 0.884 g (90%) of IIb as orange prisms. The product was recrystallised from absolute ethanol.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_5]$ (IIc). IIc was prepared by the method described above for IIb with the following quantities of reagents. $[Co(DH)_2pyCl]$, (0.874 g, 2.16 mmol); $Br(CH_2)_5Br$, (0.15 ml, 0.255 g, 1.11 mmol); $NaBH_4$, (0.474 g, 12.5 mmol). This gave 0.781 g (90%) of IIc as orange crystals, which were recrystallised three times from CH_2Cl_2/hexane. The crystals were dried under vacuum at 70°C for 4 h in order to remove CH_2Cl_2 of crystallisation shown to be present in the ^1H NMR spectrum of IIc.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_6]$ (IId). IId was prepared by the method described above for IIb but with the following quantities of reagents. $[Co(DH)_2pyCl]$, (0.901 g, 2.23 mmol); $Br(CH_2)_6Br$, (0.17 ml, 0.271 g, 1.11 mmol); $NaBH_4$, (0.504 g, 13.3 mmol). This gave 0.709 g (77%) of IId as fine orange crystals, which were recrystallised three times from CH_2Cl_2/hexane and dried under vacuum at 70°C for 4 h. The ^1H NMR spectrum of IId showed a singlet at δ 5.38 ppm indicative of CH_2Cl_2 of crystallisation. Microanalytical results confirm that about 0.5 mol CH_2Cl_2 is present as solvent of crystallisation.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_7]$ (IIe). IIe was prepared by the method described above for IIb but with the following quantities of reagents. $[Co(DH)_2pyCl]$, (0.965

g, 2.39 mmol); $Br(CH_2)_7Br$, (0.20 ml, 0.306 g, 1.19 mmol); $NaBH_4$, (0.503 g, 13.3 mmol). This gave 0.853 g (86%) of IIe as orange plates. The product was recrystallised from absolute ethanol and dried under vacuum.

$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_8]$ (IIf). IIf was prepared by the method described above for IIb but with the following quantities of reagents. $[Co(DH)_2pyCl]$, (0.972 g, 2.41 mmol); $Br(CH_2)_8Br$, (0.20 ml, 0.292 g, 1.07 mmol); $NaBH_4$, (0.478 g, 12.6 mmol). This gave 0.766 g (75%) of mustard-coloured crystalline IIf. The product was recrystallised three times from CH_2Cl_2/hexane and dried under vacuum.

Results and discussion

Synthesis of the compounds

We have investigated the reactions of $[Co(DH)_2pyCl]$ with α,ω-dihaloalkanes in the presence of sodium borohydride. When a 1/1.5 molar ratio of chloro(pyridine)cobaloxime to dibromo- or diiodoalkane was used, the mononuclear haloalkyl complexes I could be isolated in generally good yields (40–80%).

$$[Co(DH)_2pyCl] + 3/2X(CH_2)_nX \xrightarrow[NaBH_4]{MeOH} [Co(DH)_2py(CH_2)_nX] \qquad (3)$$

	n	X
Ia	3	Br
Ib	4	Br
Ic	5	Br
Id	6	Br
Ie	7	Br
Ia′	3	I

The mononuclear haloalkyl cobaloximes I were prepared by the route shown in eq. 3 for X = Br, n = 3–7 (Ia–Ie) and X = I, n = 3 (Ia′), and fully characterised by melting point, microanalysis (Table 1), and ^1H NMR (Table 3) and ^{13}C NMR (Table 5) spectroscopy. In addition, molecular weight measurements confirmed the mononuclear nature of the compounds in representative cases (see Table 7). All the

Table 1

Microanalysis, yield and melting point data for $[Co(DH)_2py(CH_2)_nX]$

Compound	n	X	M.p. (°C)	Yield (%)	Analysis (Found (calc.) (%))			
					C	H	N	Br
Ia	3	Br	173–180	55	(39.19)	(5.15)	(14.29)	(16.30)
					39.10	5.10	14.20	19.43
Ia′	3	I	175–177	78	(35.76)	(4.70)	(13.04)	(23.62) [a]
					35.80	4.60	13.00	25.10
Ib	4	Br	160–165	51	(40.48)	(5.41)	(13.89)	(15.84)
					40.60	5.40	13.80	17.85
Ic	5	Br	162–173	41	(41.71)	(5.61)	(13.51)	(15.41)
					41.50	5.50	13.50	17.11
Id	6	Br	155–166	74	(42.86)	(5.88)	(13.16)	(15.01)
					42.90	5.80	13.30	16.36
Ie	7	Br	145–153	58	(43.96)	(6.10)	(12.82)	(14.62)
					44.10	6.00	12.80	14.65

[a] %I.

characterisation data are consistent with the view that these complexes are members of a new series of mononuclear haloalkyl cobaloximes I.

We also investigated the reactions of these haloalkyl compounds, $[\mathrm{Co(DH)_2py(CH_2)}_n\mathrm{Br}]$, with $[\mathrm{Co(DH)_2pyCl}]$ in the presence of sodium borohydride. This reaction was found to yield the dinuclear polymethylene-bridged cobaloximes II shown in eq. 4.

$$[\mathrm{Co(DH)_2py(CH_2)}_n\mathrm{X}] + [\mathrm{Co(DH)_2pyCl}] \xrightarrow{\mathrm{MeOH/NaBH_4}} [\mathrm{py(DH)_2Co(CH_2)}_n\mathrm{Co(DH)_2py}] \quad (4)$$

(IIb, $n = 4$;
IIc, $n = 5$;
IId, $n = 6$)

This reaction is similar to a preparation described for $[\mathrm{CpFe(CO)_2}]_2[\mu\text{-}(\mathrm{CH_2})_n]$ (where Cp = η^5-C_5H_5) [8]. Schrauzer and Windgassen [2] have described a "one-pot" synthesis of the dinuclear cobaloximes, $[\mathrm{Co(DH)_2py}]_2[\mu\text{-}(\mathrm{CH_2})_n]$ (where $n = 3$ and 4), using a 1/1 molar ratio of $CoCl_2 \cdot 6H_2O$ to $\mathrm{Br(CH_2)}_n\mathrm{Br}$, but only scant characterisation data for these complexes were reported. In particular, no mention was made of molecular weight measurements. We have repeated this "one-pot" synthesis and found that the method described by Schrauzer and Windgassen [2] gives only the mononuclear bromoalkyl complex, (Ia), on reaction of $CoCl_2 \cdot 6H_2O$ with $\mathrm{Br(CH_2)_3Br}$. When we carried out a similar procedure with $\mathrm{Br(CH_2)_5Br}$, we isolated a mixture of the mononuclear bromopentyl complex, (Ic), and the dinuclear pentanediyl complex, (IIc).

On the other hand, we find that the dinuclear alkanediyl cobaloximes II, can be prepared directly using a 2/1 molar ratio of $[\mathrm{Co(DH)_2pyCl}]$ to $\mathrm{Br(CH_2)}_n\mathrm{Br}$ in the

Table 2

Microanalysis, yield and decomposition point [a] of $[\mathrm{Co(DH)_2py}]_2[\mu\text{-}\mathrm{CH_2})_n]$

Compound	n	Yield (%)	Dec.p. (°C)	Analysis (Found (calc.) (%))		
				C	H	N
IIb	4 [c]	95	215–227	(45.45)	(5.85)	(17.67)
				45.15	5.80	17.50
	4 [d]	90	202–210	(45.45)	(5.86)	(17.67)
				45.10	5.75	17.45
IIc	5 [c]	63	185–215	(46.15)	(6.01)	(17.37)
				45.40	6.00	16.90
	5 [d]	90	>195	(46.15)	(6.01)	(17.37)
				45.80	6.00	17.00
IId	6 [c]	64	>175	(46.82)	(6.15)	(17.07)
				46.40	6.00	16.50
	6 [b,d]	77	>195	(45.91)	(6.08)	(16.23)
				45.70	6.00	16.40
IIe	7 [d]	86	194–202	(47.48)	(6.29)	(16.78)
				47.30	6.30	16.50
IIf	8 [b,d]	75	190–197	(47.16)	(6.35)	(15.72)
				47.15	6.40	15.90

[a] All compounds decompose without melting. [b] Calculated values with 0.5 mol CH_2Cl_2. [c] Prepared by Method A, see Experimental. [d] Prepared by Method B, see Experimental.

Table 3

^{1}H NMR spectral data for [Co(DH)$_2$py(CH$_2$)$_n$X]; X = Br (Ia–e), X = I (Ia′) (Chemical shifts (δ(ppm)) are relative to TMS)

Compound	*n*	Pyridine			Dimethylglyoxime		Polymethylene chain				
		o-H	*m*-H	*p*-H	O–H---O	CH$_3$	Co–CH$_2$	Co–CH$_2$–*CH$_2$*	Other	–*CH$_2$*–CH$_2$X	CH$_2$–X
		d(2H)	t(2H)	t(1H)	bs(2H)	s(12H)	t	q	–	q(2H)	t(2H)
Ia	3	8.52	7.28	7.70	18.18	2.12	1.37(m, 4H)				3.17
Ia′	3	8.49	7.27	7.68	18.19	2.07	1.32(m, 4H)				2.92
Ib	4	8.56	7.31	7.72	18.26	2.12	1.52(t, 2H)	1.02(q, 2H)		1.73	3.32
Ic	5	8.56	7.26	7.68	18.19	2.10	1.51(t, 2H)	0.89(q, 2H)	1.26(q, 2H)	1.72	3.27
Id	6	8.53	7.27	7.65	18.18	2.04	1.51(t, 2H)	0.84(q, 2H)	1.21(m, 4H)	1.68	3.28
Ie	7	8.52	7.25	7.67	18.20	2.08	1.55(t, 2H)	0.85(q, 2H)	1.18(m, 6H)	1.74	3.33

Table 4

^1H NMR spectral data for $[Co(DH)_2py]_2[\mu\text{-}CH_2)_n]$; $n = 4\text{–}8$ (chemical shifts (δ(ppm)) are relative to TMS)

Compound	n	Pyridine			Dimethyl-glyoxime		Polymethylene chain		
		o-H	m-H	p-H	O–H---O	CH_3	Co–CH_2	Co–CH_2–CH_2	Other CH_2 groups
		d(4H)	t(4H)	t(2H)	bs(4H)	s(24H)	t(4H)	bm(4H)	
IIb	4	8.54	7.28	7.67	18.15	2.11	1.55	0.86	
IIc	5	8.57	7.28	7.68	18.17	2.10	1.54	0.84	1.08(bm, 2H)
IId	6	8.57	7.29	7.69	18.19	2.10	1.57	0.81	1.09(bs, 4H)
IIe	7	8.53	7.27	7.67	18.19	2.07	1.56	0.83	1.07(bs, 6H)
IIf	8	8.55	7.27	7.67	18.19	2.08	1.57	0.81	1.05(bm, 8H)

presence of sodium borohydride. Using this stoichiometry, the complexes $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_n]$ (II) (where $n = 4\text{–}8$) were obtained as the major products, (see eq. 5). The yields of these dinuclear cobaloximes II are given in Table 2.

$$2[Co(DH)_2pyCl] + Br(CH_2)_nBr \xrightarrow[NaBH_4]{MeOH} [py(DH)_2Co(CH_2)_nCo(DH)_2py] \qquad (5)$$

	n
IIb	4
IIc	5
IId	6
IIe	7
IIf	8

In contrast to Schrauzer and Windgassen [2], who stated that the dinuclear propanediyl complex $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_3]$ was obtained "with difficulty", we were unable to isolate this complex in any of our attempts to prepare it. Schrauzer and Windgassen also reported that the 1,4-butanediyl complex was formed "with ease". The fact that the 1,3-propanediyl compound is difficult to prepare may be attributed to steric factors, as in the case of the vitamin B_{12s} dimers.

This new series of dinuclear cobaloximes IIb–IIf has been characterised by microanalysis (Table 2) and ^1H NMR (Table 4) and ^{13}C NMR (Table 6) spectroscopy.

In addition, the molecular weights of two representative complexes have been measured by two methods (Vaporimetric determination in dichloromethane and fast atom bombardment (FAB) mass spectrometry). All the results are consistent with formulation of these complexes as the binuclear alkanediyl cobaloximes II.

Since both series of complexes, I and II, exist as orange crystalline solids, they cannot be distinguished visually. However, in addition to microanalysis, NMR and molecular weight data, it is also possible to differentiate between I and II by their thermal behaviour. Whereas all the mononuclear cobaloximes I melt below 180 °C (see Table 1), the dinuclear cobaloximes II decompose without melting above 190 °C (see Table 2). It is noteworthy that for both species the melting or decomposition temperatures decrease with increasing alkyl chain length. Such a trend has been observed for the complexes $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ [10].

Table 5

^{13}C NMR spectral data for [Co(DH)$_2$py(CH$_2$)$_n$X]; where X = Br (Ia–e), X = I (Ia′) (chemical shifts (δ(ppm)) are relative to TMS)

Compound	*n*	Pyridine			Dimethylglyoxime		Polymethylene chain						
		α-C	β-C	γ-C	CH$_3$	C=N	Co–CH$_2$	C$_\beta$	C$_\gamma$	C$_\delta$	C$_\epsilon$	C$_\eta$	CH$_2$-X
Ia	3	149.7	125.1	137.4	12.1	149.3	25.8	31.7					34.1
Ia′	3	149.7	125.1	137.4	12.2	149.3	28.3	35.2					5.2
Ib	4	149.8	125.2	137.4	12.1	149.0	29.3	28.9	33.3				33.9
Ic	5	149.7	125.1	137.2	12.0	149.1	31.0	28.8	29.9	32.4			34.2
Id	6	150.7	125.8	137.9	12.2	149.6	31.5	29.5	27.8	30.2	32.6		34.1
Ie	7[a]	150.1	124.6	137.2	12.1	148.8	31.8	30.3	27.9	28.2	30.3	32.8	34.1

[a] Only six signals observed for polymethylene chain; C$_\beta$ and C$_\epsilon$ thought to be superimposed at 30.3 ppm.

Table 6

^{13}C NMR spectral data for $[Co(DH)_2py]_2[\mu\text{-}CH_2)_n]$; where $n = 4\text{–}8$ in $CDCl_3$ (chemical shifts (δ(ppm)) are relative to TMS)

Compound	n	Pyridine			Dimethylglyoxime		Polymethylene chain			
		α-C	β-C	γ-C	CH_3	C=N	C_α	C_β	C_γ	C_δ
IIb	4 [a]	150.0	125.2	137.5	12.1	149.2	31.4	32.8		
IIc	5	149.8	125.0	137.2	12.1	149.0	32.7	31.4	30.4	
IId	6	149.8	125.0	137.2	12.1	148.9	32.4	30.7	30.5	
IIe	7	149.7	125.0	137.2	12.1	148.9	32.8	30.9	30.7	29.3
IIf	8	149.7	125.0	137.2	12.0	148.9	32.3	30.8	30.7	29.5

[a] Spectrum recorded in CD_2Cl_2.

IR spectra

Although there are some minor differences, the IR spectra of compounds I and II, are very similar. The infrared spectrum of chloro(pyridine)cobaloxime serves as a reference for determining the presence of new Co–C bonds. On reaction of the latter with a dihaloalkane, the fairly strong, sharp band at 380 cm^{-1}, due to ν(Co–Cl), disappears and a new weak band appears at about 321 cm^{-1}. Schrauzer and Windgassen [2] assigned this band to ν(Co–C). A weak band at 650 cm^{-1} in the spectra of mononuclear cobaloximes I may be from ν(C–Br). By comparison with the IR data for the alkylcobaloximes [2], the band at 1560 cm^{-1} was assigned to the C=N stretch of (DH), while the bands at 512, 455 and 420 cm^{-1} were assigned as the stretching vibrations of the Co–N(DH) and Co–N(py) bonds.

^1H NMR spectra

Together with melting point and microanalysis, ^1H NMR spectroscopy provides a very useful method of distinction between the mononuclear and dinuclear cobaloximes. Complexes of the type $[Co(DH)_2py(CH_2)_nX]$ (I) show a characteristic triplet in the region of δ 3.2 ppm (X = Br) or δ 2.9 ppm (X = I) assigned to the protons of the terminal methylene unit attached to the halogen atom. This triplet is thus absent in the spectra of the dinuclear cobaloximes, $[Co(DH)_2py]_2[\mu\text{-}(CH_2)_n]$ (II). Figures 1 and 2 show typical spectra of compounds of series I and II, respectively. The proton resonances of the dimethylglyoxime and pyridine ligands are shown, together with their assignments in Tables 3 and 4; there are no significant differences in these resonances for compounds I and II.

Table 7

Molecular weights of some representative mononuclear and dinuclear cobaloximes

Compound		Molecular weight	
		Calc.	Found
$[Co(DH)_2py(CH_2)_3Br]$	(Ia)	490	490 [a]
$[Co(DH)_2py(CH_2)_5Br]$	(Ic)	518	518 [a]
$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_4]$	(IIb)	793	793 [b]
$[Co(DH)_2py]_2[\mu\text{-}(CH_2)_7]$	(IIe)	835	830 [a]

[a] Determined by fast Atom Bombardment Mass Spectrometry at Cambridge. [b] Vaporimetric Molecular Weight Determination in CH_2Cl_2.

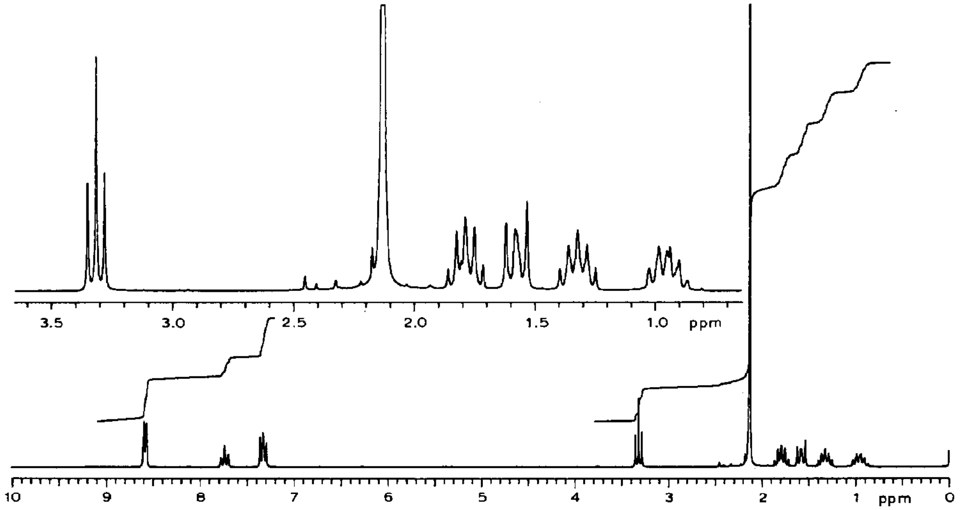


Fig. 1. ^1H NMR spectrum of [Co(DH)$_2$py(CH$_2$)$_5$Br] (Ic) in CDCl$_3$.

The signals of the protons of the polymethylene chain for series I were assigned on the basis of selective proton decoupling experiments. Assignments are given in Table 3. In contrast to the complexes [CpFe(CO)$_2$(CH$_2$)$_n$X], for which the methylene protons on the α-carbon atom resonate at the highest field [8], the protons on the carbon atom β to the cobalt atom resonate at the highest field in the spectra of the cobaloximes. The α-CH$_2$ protons were found to resonate further downfield at approximately δ 1.5 ppm. This difference may be due to the strongly electron-withdrawing nature of the axial (py) and equatorial (DH) nitrogen atoms, reducing the electron density at the cobalt atom.

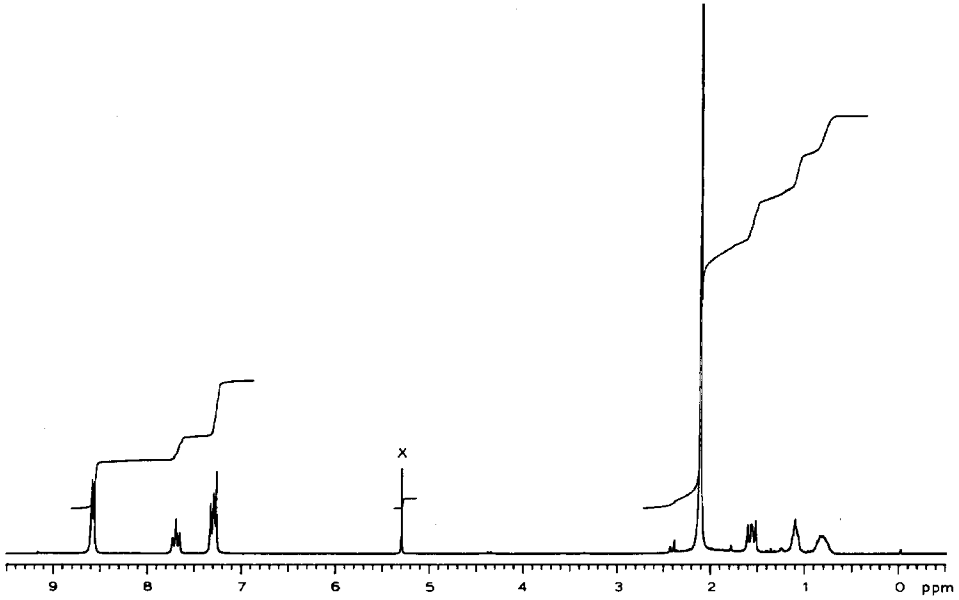


Fig. 2. ^1H NMR spectrum of [Co(DH)$_2$py]$_2$[μ-(CH$_2$)$_6$] (IId) in CDCl$_3$ (X = CH$_2$Cl$_2$).

It is interesting to note that the β-(CH_2) proton resonances for the compounds of series I, [Co(DH)$_2$py(CH_2)$_n$X] show a steady decrease in chemical shift, δ, with increasing chain length (see Table 3). This is presumably due to the increasing number of bonds between the β-(CH_2) group and the electron-withdrawing bromine atom as n increases.

The methylene resonances of series II are broader. While the Co-(CH_2) protons still occur as triplets at about δ 1.55 ppm, the protons on the carbons β to the cobalt appear as broad multiplets centred at about δ 0.85 ppm. The remaining protons in the chain appear as broad resonances at about δ 1.08 ppm. Assignments are shown in Table 4.

^{13}C NMR spectra

The ^{13}C resonances of the pyridine and dimethylglyoxime ligands in both series I and II were assigned by reference to reported values for the free ligands [19] and other cobaloximes [20]. Selective proton decoupling of the ^{13}C resonances of the $-CH_2-$ units in [Co(DH)$_2$py(CH_2)$_4$Br] (Ib) allowed assignment of the ^{13}C chemical shifts to particular carbon atoms as shown in Table 5. The spectra of other compounds of series I were subsequently assigned by comparison with the assignments made for Ib. Distinction between the pyridine α-carbon atom and the dimethylglyoxime C=N carbon, which occur very close together, was achieved by recording the proton coupled ^{13}C spectrum of [Co(DH)$_2$py(CH_2)$_4$Br]. Only the C=N carbon signal still appears as a singlet.

The ^{13}C chemical shifts of the chain carbons (C_α–C_η) occur between δ 27 and 34 ppm for series I, the carbon adjacent to the halogen atom being at the highest δ value. For Ia′, a dramatic shift to δ 5.2 ppm is observed for the carbon atom of the CH_2-I group. Similarly the carbon bonded to iodine in $CH_3CH_2CH_2I$ resonates at δ 9.2 ppm [19]. Similar shifts are observed for the series [CpFe(CO)$_2$(CH_2)$_n$X] on changing from X = Br to X = I [21] as a result of the lower electronegativity of iodine relative to bromine.

For the compounds of series I with shorter methylene chains (n = 3–5, X = Br), the carbon atom β to the metal is found at the lowest chemical shift (ca. δ 28.8 ppm). However, for n = 6 and n = 7, the ν-carbon shift becomes the lowest. Only six signals are observed for Ie (n = 7); we believe that the signals of C_β and C_ϵ are coincident.

The ^{13}C chemical shift of the carbon atom bonded to cobalt (C_α) shows an increase along the series [Co(DH)$_2$py(CH_2)$_n$Br] as n increases (see Table 5). This increase becomes smaller as the number of carbons in the chain increases but the reasons for this trend are as yet unknown.

For compounds of series II, fewer ^{13}C signals are observed due to the equivalence of various carbon units in the chain. Thus for IIb two resonances are observed for the polymethylene chain and for IIc, three signals are observed as would be expected. These ^{13}C chemical shifts and assignments are given in Table 6.

Finally, it must be mentioned that in the proton decoupled ^{13}C NMR spectra of both series I and II the carbon bonded to cobalt (C_α) does not produce a sharp singlet but rather a broad resonance of low intensity. This we believe is due to coupling of C_α to ^{59}Co, which has a spin of 7/2 and a natural abundance of 100%. Similar broadening of the alkyl C_α resonance has recently been observed in certain permethyl-scandocene derivatives of type [$Cp_2^\star$Sc-CH_2R] and [$Cp_2^\star$Sc(CH_2)$_n$Sc$Cp_2^\star$]

(where $Cp^{\star} = \eta^5\text{-}C_5Me_5$) and attributed to the ^{45}Sc nucleus which also has a spin of 7/2 [22,23].

The results of decomposition and reactivity studies on both of the new series of complexes will be discussed in a forthcoming publication [24].

Acknowledgements

We thank the University of Cape Town for support and Sir Jack Lewis (University of Cambridge) for the FAB mass spectra.

References

1 G.N. Schrauzer and J. Kohnle, Chem. Ber., 97 (1964) 3056.
2 G.N. Schrauzer and R.J. Windgassen, J. Amer. Chem. Soc., 88 (1966) 3738.
3 G.N. Schrauzer, Inorg. Synth., 11 (1968) 61.
4 G.N. Schrauzer and L.P. Lee, J. Amer. Chem. Soc., 92 (1970) 1551.
5 G.N. Schrauzer, Angew. Chem. Int. Ed. Engl., 15 (1976) 417.
6 E.N. Stadbauer, R.J. Holland, F.P. Lamm and G.N. Schrauzer, Bioinorg. Chem., 4 (1974) 67.
7 L.G. Marzilli, M.F. Summers, J.H. Ramsden, L. Randaccio, N. Bresciani-Pahor, E. Zangrando and P. Marzilli, Organometallics, 4 (1985) 2086.
8 J.R. Moss, J. Organomet. Chem., 231 (1982) 229.
9 J.R. Moss and L.G. Scott, Coord. Chem. Rev., 60 (1984) 171 and references therein.
10 J.R. Moss, L.G. Scott, M.E. Brown and K.J. Hindson, J. Organomet. Chem., 282 (1985) 255.
11 S.F. Mapolie, J.R. Moss and L.G. Scott, J. Organomet. Chem., 297 (1985) C1.
12 C.P. Casey and J.D. Audett, Chem. Rev., 86 (1986) 339.
13 E.L. Smith, L. Mervyn, P.E. Huggleton, D.W. Johnson and N. Straw, Ann. N.Y. Acac. Sci., 112 (1964) 565.
14 K.H. Theopold and R.G. Bergman, Organometallics, 1 (1982) 1571.
15 K.H. Theopold and R.G. Bergman, J. Amer. Chem. Soc., 103 (1981) 2489.
16 K.H. Theopold and R.G. Bergman, J. Amer. Chem. Soc., 105 (1983) 464.
17 K.H. Theopold and R.G. Bergman, J. Amer. Chem. Soc., 102 (1980) 5694.
18 R.J. Puddephatt and W.J. Laws, J. Chem. Soc., Chem. Commun., (1984) 11.
19 L.F. Johnson and W.C. Jankowski, Carbon-13 NMR Spectra: A Collection of Assigned, Coded and Indexed Spectra, John Wiley, New York, 1972.
20 N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, Coord. Chem. Rev., 63 (1985) 1.
21 H.B. Friedrich and J.R. Moss, unpublished results.
22 M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, J. Amer. Chem. Soc., 109 (1987) 203.
23 J.E. Bercaw, B.J. Burger, E. Bunel and J.R. Moss, unpublished results.
24 K.P. Finch, J.R. Moss and M.A. Rix, to be published.