Synthesis and characterization of long-chain ω-functionalized alkyl cobaloxime complexes

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Received 29 April 1996

Abstract

Two new series of cobaloxime complexes of formulae $[Co(Hdmg)_2\{(CH_2)_nI\}(py)]$ (Hdmg = the monoanion of dimethylglyoxime, py = pyridine and $n = 5, 6, 8, 9$ or 10) and $[Co(Hdmg)_2\{(CH_2)_3OC(O)C_6H_4R\}(py)]$ ($R = H, o-, m-$ or $p-OCH_3, p-OC_7H_{15}$ or $p-OC_9H_{19}$) have been synthesized and fully characterized. The former series provides versatile precursor species for a wide range of polymethylene homo- and heteronuclear complexes, while the latter series confirms that, under mild conditions, elaboration from an ω-hydroxyl group can be achieved to generate stable metal complexes.

Keywords: Cobalt; Cobaloxime; Dimethylglyoxime; Long-chain alkyl; ω-Functionalized

1. Introduction

Increasing interest in organometallic chemistry is being focused on synthetic manipulations of the functional group in ω-functionalized alkyl complexes of transition metals with general formula $[ML_x\{(CH_2)_nY\}]$ (ML_x = a transition metal and its associated ligands; Y = an organic functional group, e.g. a halogen or hydroxyl group); for a review see Ref. [1]. The complexes in which Y is a halogen have been shown to be precursors for homo- and heteronuclear complexes [2–4], as well as precursors for building up large dendritic macromolecules by extension from the ω functionality [5]. Purely from an organic perspective, many possibilities exist for functional group interconversions of the groups in question, but, in an organometallic system, severe chemical and thermal restrictions are imposed by the metal and its surrounding ligands. Hence, only by careful choice of the reaction conditions can these interconversions be accomplished.

The bis(dimethylglyoximato)cobalt(III) system, generally referred to as a cobaloxime, has been the subject of intense study as a model for vitamin B_{12} chemistry [6]. We now report on the synthesis and properties of two new series of cobaloxime complexes of general formulae $[Co(Hdmg)_2\{(CH_2)_nI\}(py)]$ (Hdmg = the monoanion of dimethylglyoxime, py = pyridine and n

$= 5, 6, 8, 9$ or 10) and $[Co(Hdmg)_2\{(CH_2)_3OC(O)-C_6H_4R\}(py)]$ ($R = H, o-, m-$ or $p-OCH_3, p-OC_7H_{15}$ or $p-OC_9H_{19}$). [1] The former provides a versatile precursor species for a wide range of polymethylene homo- and heteronuclear complexes, whereas the latter series represents an example of extension from an ω-hydroxyl functionality by ester formation.

We have previously reported on a new class of heterobimetallic cobaloxime complexes, of which $[Co]\{CH_2C_6H_4-\eta^6-Cr(CO)_3\}$ was structurally characterized [7], and we recently reported the crystal structure of the longest chain n-alkyl organometallic compound yet to be structurally characterized, $[Co]\{(CH_2)_{13}CH_3\}$ [8]. The present investigation was prompted by the desire to generate cobaloxime complexes that might exhibit mesomorphic phases. In the event, liquid-crystalline properties were not observed for the new complexes reported here.

2. Experimental

2.1. General procedures

All commercial reagents were used as supplied. [Co]Cl was prepared by a published method [9]. The

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reactions were carried out using standard Schlenk-tube techniques and a dry nitrogen atmosphere, but purification of the products was carried out in air. Except for methanol, which was saturated with nitrogen for 10 min prior to use, solvents used as reaction media were dried and distilled under nitrogen according to standard methods. Melting points were recorded on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town microanalytical laboratory using a Carlo Erba EA1108 elemental analyser. IR spectra were recorded on a Perkin Elmer 983 spectrophotometer as CH_2Cl_2 solutions or as Nujol mulls between NaCl plates. The ^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on a Varian XR-200 spectrometer; the chemical shifts are reported relative to TMS ($\delta =$ 0.00 ppm) as internal reference standard.

2.2. Preparation of complexes of type $[Co]\{(CH_2)_nI\}$, 1–5

2.2.1. $[Co]\{(CH_2)_5I\}$, 1

[Co]Cl (0.50 g, 1.24 mmol) was added to nitrogen-saturated methanol (15 cm³) and the slurry was stirred for 5 min. $I(CH_2)_5I$ (0.37 cm³, 2.48 mmol) was added, followed after 5 min by sodium borohydride (0.25 g, 6.55 mmol). The mixture was subsequently stirred for a further 12 min and the resulting orange solution was cooled to 0 °C. Bright orange crystals separated, which were filtered and washed with cold methanol (3 cm³) to yield $[Co]\{(CH_2)_5I\}$, 1 (0.41 g). Water was then added to the filtrate until the solution became cloudy, and this was kept at -15 °C for 12 h to yield additional 1 (0.25 g). Both portions were combined and purified by recrystallization from CH_2Cl_2–hexane to give a 95% yield.

2.2.2. $[Co]\{(CH_2)_6I\}$, 2

[Co]Cl (0.50 g, 1.24 mmol) was added to nitrogen-saturated methanol (15 cm³) and the slurry was stirred for 5 min. $I(CH_2)_6I$ (0.41 cm³, 2.48 mmol) was added, followed after 5 min by sodium borohydride (0.25 g, 6.55 mmol). The mixture was subsequently stirred for a further 12 min and the resulting orange solution was cooled to 0 °C. Bright orange crystals separated from the solution and were filtered and washed with cold methanol (3 cm³) to yield the bimetallic complex $[Co]_2[\mu-(CH_2)_6]$ (0.10 g, 20%). Water was added to the filtrate until the solution became cloudy, and this was kept at -15 °C for 12 h to yield $[Co]\{(CH_2)_6I\}$, 2, which was purified by recrystallization from CH_2Cl_2–hexane (0.52 g, 72% yield).

2.2.3. $[Co]\{(CH_2)_nI\}$ (n = 8, 9 or 10), 3–5

The complexes $[Co]\{(CH_2)_nI\}$ (n = 8, 9 or 10), 3–5 respectively, were prepared by the method described

above for 1 using the same molar quantities of reagents and a reaction time of 15 min. The characterization data for compounds 1–5 are given in Tables 1–3.

2.3. Preparation of complexes of type $[Co]\{(CH_2)_3OC(O)C_6H_4R\}$, 6–11

A representative preparation is described since the complexes were all synthesized by the same general method.

2.3.1. Preparation of $[Co]\{(CH_2)_3OH\}$

3-Bromopropanol (340 μl, 0.517 g, 3.72 mmol) was added to a slurry of [Co]Cl (1.0 g, 2.48 mmol) in methanol (20 cm³). After stirring for 10 min, sodium borohydride (0.5 g, 13.2 mmol) was introduced portionwise and the resulting dark-green solution was stirred for a further 30 min. The solvent was then evaporated to give a dark-brown residue that yielded, after recrystallization from CH_2Cl_2–hexane, orange-brown crystals of $[Co]\{(CH_2)_3OH\}$ (0.66 g, 62%) (Found: C, 45.25; H, 6.2; N, 16.1. $C_{16}H_{26}CoN_5O_5$: Calc.: C, 45.0; H, 6.1; N, 16.4%). ^1H NMR ($CDCl_3$): δ 1.14 (m, 2H, CH_2), 1.51 (m, 2H, $CoCH_2$), 2.09 (s, 12H, CH_3 of Hdmg), 3.43 (t, 2H, CH_2O, $J_{HH} = 6.6$ Hz), 7.29 (t, 2H, m-H of py, $J_{HH} = 6.7$ Hz), 7.69 (t, 2H, p-H of py, $J_{HH} = 7.6$ Hz) and 8.54 (d, 2H, o-H of py, $J_{HH} = 4.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 12.0 (CH_3), 33.8 (CH_2), 62.6 (CH_2O), 125.2 (m-C), 137.5 (p-C), 149.4 (C=N) and 149.9 (o-C). IR ν/cm^{-1}: 1556 ($\nu(C=N)$, in CH_2Cl_2), 324 ($\nu(Co-C)$, as Nujol mull).

2.3.2. $[Co]\{(CH_2)_3OC(O)C_6H_5\}$, 6

A Schlenk tube containing a pre-cooled solution of benzoyl chloride (35 μl, 42 mg, 0.30 mmol) in CH_2Cl_2 (3 cm³) was placed in an ice-salt bath and a solution of pyridine (34 μl, 0.42 mmol) in CH_2Cl_2 (2 cm³) was added. This was followed by portionwise addition, with vigorous stirring, of the ω-hydroxyl derivative $[Co]\{(CH_2)_3OH\}$ (0.20 g, 0.47 mmol). The suspension

Table 1
Characterization data for $[Co]\{(CH_2)_nI\}$ (n = 5, 6, 8, 9 or 10)

Complex	n	Yield (%)	M.p. (°C)	Elemental analysis (%) [a]		
				C	H	N
1	5	95	164–174	38.5 (38.2)	5.3 (5.1)	12.7 (12.4)
2	6	72	154–160	39.9 (39.4)	5.6 (5.4)	12.5 (12.1)
3	8	93	148–155	41.8 (41.5)	5.9 (5.8)	11.5 (11.5)
4	9	89	139–143	42.9 (42.5)	6.1 (6.0)	12.2 (12.3)
5	10	90	85–88	43.8 (43.5)	6.3 (6.1)	11.1 (11.0)

[a] Found (Calc.).

Table 2
^{1}H NMR chemical shift data (ppm) [a] for [Co]{(CH$_2$)$_n$I} (n = 5, 6, 8, 9 or 10)

Complex	n	Pyridine			Hdmg [b]	Polymethylene chain				
		o-H (d, 2H) [c]	m-H (t, 2H)	p-H (t, 1H)	CH$_3$ (s, 12H)	CoCH$_2$ (m, 2H)	CoCH$_2$CH_2 (qn, 2H)	–CH$_2$–	CH_2CH$_2$I (qn, 2H)	CH$_2$I (t, 2H)
1	5	8.55	7.27	7.68	2.09	1.54	0.90	1.25 (qn, 2H)	1.72	3.06
2	6	8.56	7.28	7.69	2.10	1.57	0.88	1.22 (m, 4H)	1.71	3.11
3	8	8.57	7.29	7.69	2.10	1.59	0.88	1.20 (m, 8H)	1.77	3.14
4	9	8.57	7.29	7.69	2.10	1.60	0.90	1.25 (m, 10H)	1.78	3.16
5	10	8.55	7.27	7.68	2.07	1.58	0.86	1.20 (m, 12H)	1.77	3.17

[a] In CDCl$_3$ relative to TMS (δ = 0.00 ppm), s = singlet, d = doublet, t = triplet, qn = quintet, m = multiplet. [b] The oxime proton resonance (ca. 18 ppm) was only observed in concentrated solutions and is not reported. [c] (Multiplicity, integration).

was stirred and allowed to warm to room temperature. The reaction was monitored by TLC (ethyl acetate) and after 4 h the reaction appeared complete, resulting in a clear, brown solution. The solvent was evaporated to give a dark-brown residue, which was dissolved in a minimum amount of methanol. Water was then added to give a cloudy, yellow-orange suspension. After standing at 0 °C for 24 h, fine orange microcrystals precipitated out of solution and these were filtered, washed with cold water and dried. Recrystallization from CH$_2$Cl$_2$–hexane gave orange needle-shaped crystals of [Co]{(CH$_2$)$_3$OC(O)C$_6$H$_5$}, 6 (0.108 g, 68%).

### 2.3.3. [Co]{(CH$_2$)$_3$OC(O)C$_6$H$_4$R}, 7–11

Using the above method with other acyl chlorides, as indicated, the series of cobaloxime complexes 7–11 was generated: o-CH$_3$OC$_6$H$_4$COCl gave 7, m-CH$_3$OC$_6$H$_4$COCl gave 8, p-CH$_3$OC$_6$H$_4$COCl gave 9, p-CH$_3$(CH$_2$)$_6$OC$_6$H$_4$COCl gave 10 and p-CH$_3$(CH$_2$)$_8$OC$_6$H$_4$COCl gave 11. Characterization data for compounds 6–11 are given in Tables 4–6.

3. Results and discussion

3.1. Complexes of type [Co]{(CH$_2$)$_n$I} (n = 5, 6, 8, 9 or 10), 1–5

Finch and Moss [10] have prepared mononuclear bromoalkyl cobaloxime complexes of the general type

[Co]{(CH$_2$)$_n$Br} by reacting the chloro(pyridine)-cobaloxime complex, [Co]Cl, with 1.5 molar equivalents of dibromoalkane in the presence of sodium borohydride. Using this procedure, we have now prepared a series of new mononuclear iodoalkyl cobaloxime complexes, [Co]{(CH$_2$)$_n$I} (n = 5, 6, 8, 9 or 10), by reacting [Co]Cl with two molar equivalents of diiodoalkane in the presence of excess sodium borohydride (Eq. (1)).

$$[Co]Cl + I(CH_2)_nI \xrightarrow[MeOH]{NaBH_4} [Co]\{(CH_2)_nI\} \qquad (1)$$
$$n = 5(1), 6(2), 8(3), 9(4) \text{ or } 10(5)$$
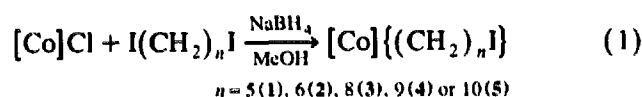
We envisage that these ω-functionalized alkyl complexes could be useful precursors to heterobimetallic complexes by reaction of the CH$_2$–I bond. It is interesting to note that in the reaction of [Co]Cl with two molar equivalents of I(CH$_2$)$_6$I both the mononuclear iodoalkyl cobaloxime, [Co]{(CH$_2$)$_6$I}, and the dinuclear, polymethylene-bridged cobaloxime, [Co]$_2$[μ-(CH$_2$)$_6$], were obtained. However, when [Co]Cl was reacted with five molar equivalents of I(CH$_2$)$_6$I only the mononuclear iodoalkyl cobaloxime was obtained, in 95% yield.

Complexes 1–5 were isolated as stable, orange, crystalline solids in yields of 72–95%. All the complexes are slightly light sensitive; however, they can be stored in air for several months when protected from light. In solution, exposed to air, they decompose within a few hours.

The complexes were fully characterized by melting point, microanalysis (Table 1) and ^{1}H (Table 2) and ^{13}C

Table 3
^{13}C NMR chemical shift data (ppm) [a] for [Co]{(CH$_2$)$_n$I} (n = 5, 6, 8, 9 or 10)

Complex	n	Pyridine			Hdmg		Polymethylene chain									
		o-C	m-C	p-C	CH$_3$	C=N	CoC$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$
1	5	149.9	125.1	137.3	11.9	149.0	33.1	29.3	31.3	33.2	7.3					
2	6	150.0	125.1	137.4	12.0	149.1	30.3	29.5	30.3	26.8	33.7	7.5				
3	8	149.9	125.0	137.3	11.9	148.9	30.5	30.4	30.5	30.6 [b]	29.1 [b]	28.4 [b]	33.5	7.5		
4	9	149.9	125.0	137.2	11.9	148.9	30.5	30.4	30.5	30.5 [b]	29.3 [b]	29.1 [b]	28.4 [b]	33.5	7.3	
5	10	150.0	125.0	137.3	12.0	149.0	30.5	30.4	30.5	30.8	29.7 [b]	29.5 [b]	29.5 [b]	28.5 [b]	33.6	7.3

[a] In CDCl$_3$ relative to TMS (δ = 0.00 ppm). [b] Assignments of these peaks are ambiguous as the peaks overlap.

Table 4
Characterization data for [Co]((CH$_2$)$_3$OC(O)C$_6$H$_4$R)

Complex	R group	Yield [a] (%)	M.p. (°C)	IR data (cm^{-1}) [b]			Elemental analysis (%) [c]		
				C=N	C=O	Co–C	C	H	N
6	H	68	150–154	1557(m)	1715(s)	324(w)	49.8 (50.2)	5.5 (5.6)	12.0 [d] (12.2)
7	*o*-OCH$_3$	72	158–161	1555(m)	1715(s)	325(w)	51.0 (51.3)	5.7 (5.7)	12.3 (12.5)
8	*m*-OCH$_3$	75	156–160	1555(m)	1710(s)	325(w)	50.95 (51.3)	5.8 (5.7)	12.3 (12.5)
9	*p*-OCH$_3$	70	150–155	1556(m)	1712(s)	324(w)	51.1 (51.3)	5.8 (5.7)	12.4 (12.5)
10	*p*-OC$_7$H$_{15}$	74	152–156	1556(m)	1709(s)	324(w)	55.5 (55.8)	6.85 (6.9)	10.7 (10.85)
11	*p*-OC$_9$H$_{19}$	70	115–125	1555(m)	1710(s)	325(w)	56.8 (57.05)	7.0 (7.2)	10.35 (10.4)

[a] Based on the reaction of the hydroxypropyl(pyridine)cobaloxime with the respective acyl chloride. [b] In CH$_2$Cl$_2$ except for ν(Co–C), which was obtained as a Nujol mull between polyethylene sheets; m = medium, s = strong, w = weak. [c] Found (Calc.). [d] Crystallized with 1/2 mol CH$_2$Cl$_2$.

(Table 3) NMR spectroscopy. The ^{1}H and ^{13}C NMR and IR data and melting point for [Co]$_2$[μ-(CH$_2$)$_6$] correspond to the reported values [10]. All the mononuclear cobaloxime complexes melt below 174°C (see Table 1) and, as expected, the melting points decrease with increasing alkyl chain length. A similar trend has been observed for the complexes [Co]((CH$_2$)$_n$Br) [10] and [Fe(η^5-C$_5$H$_5$)(CO)$_2$]$_2$[μ-(CH$_2$)$_n$] [11].

3.1.1. IR spectra

Owing to the complex nature of the IR spectra of cobaloximes in general, only the more prominent bands which could be assigned with a degree of certainty, as determined by Rutherford and Thornton [12], are considered. The band at ca. 1558 cm^{-1} in all of the complexes is assigned to the C=N stretch, while all bands arising from ν metal–ligand stretch occur below

600 cm^{-1}. The band at 517 cm^{-1} is assigned to ν(Co–N) of the dimethylglyoximato ligand, while the band at 450 cm^{-1} is assigned to the pyridine ν(Co–N) vibration. The IR spectrum of the chloro(pyridine)cobaloxime complex, [Co]Cl, serves as a reference for determining the presence of a newly formed Co–C bond. On reaction of [Co]Cl with the diiodoalkane, the fairly strong band at 380 cm^{-1} due to ν(Co–Cl) disappears and a new, weak band appears at 321 cm^{-1}. This band is assigned to ν(Co–C), in agreement with earlier assignments [13]. None of the values reported above changed significantly on changing the length of the alkyl chain.

3.1.2. NMR spectra

The proton resonances of the polymethylene chain for complexes 1–5 (Table 2) were assigned by reference

Table 5
^{1}H NMR spectral data for [Co]((CH$_2$)$_3$OC(O)C$_6$H$_4$R)

Complex	Pyridine			Hdmg [a]	Functionalized alkyl group							
	o-H (d, 2H) [b]	*m*-H (t, 2H)	*p*-H (t, 1H)	CH$_3$ (s, 12H)	CoCH$_2$ (m, 2H)	–CH$_2$– (m, 2H)	CH$_2$O (t, 2H)	ArH (m, 4H)	ArOCH$_3$ (s, 3H)	ArOCH$_2$ (t, 2H)	–CH$_2$– (m)	CH$_3$ (t, 3H)
6	8.58 [c] (4.8) [d]	7.31 (6.8)	7.71 (7.6)	2.13	1.56	1.39	4.14 (6.6)	7.4, 8.0 [c]				
7	8.58 (4.8)	7.30 (6.8)	7.69 (7.5)	2.12	1.59	1.37	4.12 (6.5)	6.9, 7.7	3.88			
8	8.59 (4.8)	7.32 (7.0)	7.72 (7.3)	2.14	1.59	1.39	4.14 (6.6)	7.1, 7.6	3.86			
9	8.57 (4.9)	7.31 (6.9)	7.71 (7.5)	2.12	1.79	1.53	4.10 (6.6)	7.9, 6.9	3.85			
10	8.58 (5.0)	7.31 (6.4)	7.71 (7.7)	2.13	1.79	1.56	4.09 (6.6)	7.9, 6.9 [f] (8.7)		3.99 (6.5)	1.29 [g]	0.89 (7.0)
11	8.57 (5.0)	7.29 (6.5)	7.69 (7.7)	2.12	1.77	1.54	4.08 (6.5)	7.9, 6.9 [f] (8.8)		3.97 (6.6)	1.27 [h]	0.86 (7.0)

[a] The oxime proton resonance (ca. 18 ppm) was only observed in concentrated solutions and is not reported. [b] (Multiplicity, integration). [c] Chemical shift relative to TMS (CDCl$_3$, δ = 0.00 ppm), s = singlet, d = doublet, t = triplet, m = multiplet. [d] $^3J_{HH}$ values (Hz). [e] Integrates for 5H. [f] AA'XX' spin system. [g] Integrates for 10H. [h] Integrates for 14H.

Table 6
^{13}C NMR chemical shift data (ppm) [a] for [Co]{(CH$_2$)$_3$OC(O)C$_6$H$_4$R}

Complex	Pyridine			Hdmg		Functionalized alkyl group [b]							
	o-C	m-C	p-C	CH$_3$	C=N	–CH$_2$–	CH$_2$O	C=O	ArC	ArOCH$_3$	ArOCH$_2$	–CH$_2$–	CH$_3$
6	150.0	125.2	137.5	12.0	149.4	29.4	63.3	166.5	132.6, 130.7, 129.5, 128.2				
7	150.0	125.2	137.5	12.0	149.3	29.5	64.3	159.0	133.0, 131.5, 120.0, 112.0	56.0			
8	150.0	125.0	137.5	12.0	149.4	29.4	64.4	159.5	129.2, 122.0, 119.2, 113.9	55.4			
9	150.0	125.1	137.5	12.0	149.3	29.5	64.1	166.0	162.8, 131.5, 122.8, 113.9	55.9			
10	150.0	125.2	137.5	12.0	149.3	29.5	64.0	166.4	162.7, 131.5, 122.9, 113.9		68.2	31.7, 29.1, 29.0, 25.9, 22.6	14.1
11	150.0	125.2	137.5	12.1	149.4	29.5	64.0	166.4	162.7, 131.5, 122.9, 113.9		68.2	31.8, 29.5, 29.4, 29.2, 29.1, 26.0, 22.7	14.1

[a] In CDCl$_3$ relative to TMS ($\delta = 0.00$ ppm). [b] The solutions were too dilute to detect the α-carbon.

to reported values for the [Co]{(CH$_2$)$_n$Br} series [10]. The characteristic triplet in the region of δ 3.1 ppm was assigned to the protons of the ω-methylene unit (bonded to the iodine atom), while the α-CH$_2$ protons were found to resonate further upfield at δ ca. 1.6 ppm. The chemical shift values for both these sets of proton resonances show small, but probably not significant, trends as the length of the alkyl chain increases (see Table 2).
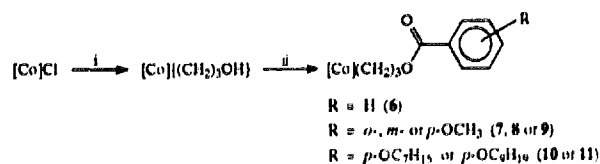
The ^{13}C NMR resonances of the pyridine and dimethylglyoximato ligands (Table 3) were assigned by reference to reported values for the free ligands [14] and other cobaloxime complexes [10,15]. The ^{13}C NMR chemical shifts for the carbon atoms of the polymethylene chain of complex 1 were assigned using HETCOR experiments. The ^{13}C NMR spectra of the remaining complexes were subsequently assigned by comparison with the assignments made for complex 1. For complexes 2–5 the assignments for some of the carbon atoms of the polymethylene chains were ambiguous as peaks were very close together. In contrast to the complexes [Co]{(CH$_2$)$_n$Br}, in which the carbon atom adjacent to the bromo group resonates at the highest chemical shift value (δ ca. 34.1 ppm) [10], in the present complexes the carbon atom adjacent to the iodo group resonates at the lowest chemical shift value (δ ca. 7.3 ppm). This decrease in chemical shift can be ascribed to the lower electronegativity of iodine compared with bromine.

3.2. Complexes of type [Co]{(CH$_2$)$_3$OC(O)C$_6$H$_4$R}, 6–11

The complexes 6–11 were prepared by firstly synthesizing the precursor alcohol [Co]{(CH$_2$)$_3$OH} from [Co]Cl and 3-bromopropanol and subsequently reacting the alcohol with the appropriate acyl chloride under basic conditions to give the desired ester (see Scheme 1).

Owing to the strong intramolecular hydrogen-bonding interactions associated with the cobaloxime system, most work-up procedures tended to involve repeated recrystallizations (as opposed to column chromatography on alumina) to obtain pure products. The complex [Co]{(CH$_2$)$_3$OH} was found to be water soluble, which provided a means of separating this compound from the hydrophobic ester: the crude product was dissolved in a minimum amount of methanol and upon the addition of water the cobaloxime ester precipitated out, while any unreacted [Co]{(CH$_2$)$_3$OH} remained dissolved in the water. Filtration of the resultant fine yellow suspension gave pure product. Recrystallization from CH$_2$Cl$_2$–hexane afforded orange needles which were relatively stable, both in the solid and in solution. Decomposition does, however, occur in solution over a few days at room temperature. All of the complexes 6–11 have been fully characterized by melting point, elemental analysis and IR spectroscopy (Table 4) and ^{1}H (Table 5) and ^{13}C (Table 6) NMR spectroscopy.

[Co]Cl ——i—→ [Co]{(CH$_2$)$_3$OH} ——ii—→ [Co]{(CH$_2$)$_3$O}

R = H (6)
R = o-, m- or p-OCH$_3$ (7, 8 or 9)
R = p-OC$_7$H$_{15}$ or p-OC$_9$H$_{19}$ (10 or 11)

Scheme 1. Reagents and conditions: (i) Br(CH$_2$)$_3$OH, NaBH$_4$, MeOH, room temperature, 30 min; (ii) RC$_6$H$_4$COCl, pyridine, CH$_2$Cl$_2$, 0–25°C, 4–6 h.

It is interesting to note that the esterification of [Co]{(CH$_2$)$_3$OH} with the acid chlorides p-CH$_3$(CH$_2$)$_n$OC$_6$H$_4$COCl (n = 6 or 8) to give 10 and 11 respectively, resulted in the disappearance of the liquid-crystal mesophases observed for the parent carboxylic acids [16], with the metal complexes melting directly to isotropic liquids. This is not surprising, since the large bulk of the equatorial (Hdmg)$_2$ system disrupts the favoured alignment of the long-chain organic groups which gives rise to the mesophase.

3.2.1. IR spectra

The IR absorption frequencies (Table 4) for the prominent bands of complexes 6–11 are similar to those of complexes 1–5 and, in addition, there is a band at ca. 1715 cm^{-1} which is assigned to the ν(C=O) stretch of the ester functionality.

3.2.2. NMR spectra

The proton NMR signals for the dimethylglyoximato system and the coordinated pyridine ligand of complexes 6–11 (Table 5) showed no significant variation in their chemical shifts when compared with the complexes 1–5, as might be expected from the overall similarity in their modes of coordination.

The ortho- and meta-substituted aromatic esters 7 and 8 give rise to the complex multiplets in the aromatic region that are expected for these types of substitution. The para-substituted esters 9–11, on the other hand, display the characteristic AA'XX' spin system and their spectra were analysed as such. Assignment of the two adjacent triplets of the two -CH$_2$O- groups in 10 and 11 was based on comparison of these signals with that of 9 (which has only one of these groups) and on the fact that the alkoxy chain resonance of -CH$_2$OC$_6$H$_4$- (δ ca. 3.99 ppm) would be expected to occur further upfield than that of -CH$_2$OC(O)- (δ ca. 4.09 ppm), since the latter is influenced by the electron-withdrawing effect of the adjacent carbonyl group.

The proton-decoupled ^{13}C chemical shift values for (Hdmg)$_2$ and the pyridine ligand (Table 6) correspond closely with those for complexes 1–5. The aromatic signals in the region δ 113–163 ppm for all the complexes are consistent with the expected formulation of the complexes, and the assignment of the two -CH$_2$O- signals for 10 and 11 was made on the same basis as for the protons attached to these carbons (see above).

4. Conclusions

We have demonstrated that ω-iodoalkylcobaloxime complexes are relatively stable and may have potential as precursors for the synthesis of homo- and heterometallic complexes, especially considering that the iodo group would be more reactive towards substitution

than other halo groups. We have also reported a mild synthetic route to the esterification of the terminal -OH group of hydroxypropyl(pyridine)cobaloxime. The results obtained confirm that, by careful choice of conditions, the reaction of [Co]{(CH$_2$)$_3$OH} with acyl chlorides occurs chemoselectively to elaborate the metallopropyloxy entity only, without perturbing the other functionalities in the molecule.

While no mesophases were observed in the present work, we envisage that the introduction of greater structural anisotropy in the form of ester-linked aromatic rings into the axial organic moieties may confer liquid-crystalline properties on the complexes. We are currently pursuing this aspect of the work, which will be published elsewhere [17]. Work is also in progress to assess the effect of introducing substituted pyridine ligands that contain anisotropic regions (e.g. the stilbazole compounds, NC$_5$H$_4$CH=CHC$_6$H$_4$OC$_n$H$_{2n+1}$), in an attempt to discover whether this type of arrangement might confer ordering phenomena on the melting of these complexes [17].

Finally, we remark that our surprising observation that the complex [Co]{(CH$_2$)$_3$OH} is water soluble could make it an interesting model for studying vitamin B$_{12}$ reactions, since studies could be performed in an aqueous environment more closely resembling that of the living organism [6].

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