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Synthesis and characterization of some new cobaloximes, including the first members of a new class of heterobimetallic cobaloxime complexes. Crystal structure of [{η^6-C$_6$H$_5$CH$_2$Co(DH)$_2$(py)}Cr(CO)$_3$]

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Abstract

The mononuclear cobaloxime complex *o*-[{(py)(DH)$_2$CoCH$_2$}C$_6$H$_4$(CH$_2$Br)] (1) has been prepared by the reaction of the appropriate xylene dibromide with an equimolar amount of [Co(DH)$_2$(py)Cl] in the presence of sodium borohydride (where DH = monoanion of dimethylglyoxime). The dinuclear xylylene-bridged cobaloximes [Co(DH)$_2$(py)]$_2$[μ-(*m*- and *p*-CH$_2$C$_6$H$_4$CH$_2$)] (2, 3) were obtained similarly from the reaction of the xylene dibromides with two molar equivalents of [Co(DH)$_2$(py)Cl]. The heterobimetallic complexes [{η^6-C$_6$H$_5$CH$_2$Co(DH)$_2$(py)}Cr(CO)$_3$] (4) and [Co(DH)$_2$(py)]$_2$[μ-{(η^6-*p*-CH$_2$C$_6$H$_4$CH$_2$)Cr(CO)$_3$}] (7) were prepared from [{η^6-C$_6$H$_5$CH$_2$Cl}Cr(CO)$_3$] and [{η^6-*p*-C$_6$H$_4$(CH$_2$Cl)$_2$}Cr(CO)$_3$] (6) respectively, by similar procedures. The new compounds were characterized by standard spectroscopic methods and the structure of 4 was determined by X-ray crystallography. The Co–N(py) and Co–C bond lengths in 4 are 2.038(4) and 2.044(4) Å, respectively.

1. Introduction

Alkylcobaloximes, the generic name for complexes of the type [Co(DH)$_2$(L)R] (where L = a base such as pyridine, DH = monoanion of dimethylglyoxime and R = alkyl group), have long been the object of intense study. Much of the interest in such complexes has arisen from their relevance to the chemistry of vitamin B$_{12}$ [1–5]. As part of a systematic study of hydrocarbon-bridged transition metal complexes [6–12] we have investigated the synthesis of cobaloximes in which the hydrocarbon bridge incorporates an arene ring. We now report the synthesis of some xylylene-bridged cobaloximes and their precursors and derivatives.

We were particularly interested in preparing hetero-bimetallic complexes containing cobalt and chromium to use as heterogeneous catalyst precursors for the CO hydrogenation reaction [13]. For this purpose we had to design high yield syntheses of compounds containing the two metals of interest, *viz.*, Co and Cr, in the same

molecule and with no potential catalyst poisons; we were thus restricted to the elements C, H, N and O in our choice of ligand systems. In order to evaluate the catalytic effect of varying the metal ratios, we were also interested in preparing complexes with different Co:Cr atomic ratios. Here we report the preparation of two such complexes having Co:Cr atomic ratios of 1:1 and 2:1. Both complexes are members of a new class of compound of the type [Co(DH)$_2$(py)R], where the R group contains Cr in a (η^6-arene)Cr(CO)$_3$ unit.

2. Experimental details

All reactions were carried out by Schlenk techniques under dinitrogen with continuous stirring. Final purification of products was achieved either by recrystallization (CH$_2$Cl$_2$/hexane) or column chromatography (silica gel 70–230 mesh, Merck; hexane). The xylene dibromides, *p*-C$_6$H$_4$(CH$_2$OH)$_2$ and [Cr(CO)$_6$] were purchased from Aldrich and used as supplied. The compounds [Co(DH)$_2$(py)Cl] [14], [{η^6-C$_6$H$_5$CH$_2$OH}-Cr(CO)$_3$] [15] and [{η^6-C$_6$H$_5$CH$_2$Cl}Cr(CO)$_3$] [16] were prepared by published methods. The solvents di-n-butyl

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ether and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled prior to use. Methanol was saturated with nitrogen immediately prior to use.

IR spectra were recorded as Nujol mulls (4000–200 cm^{-1}) between NaCl or CsI plates, or in NaCl solution cells (1600–2000 cm^{-1}) on a Perkin Elmer 983 spectrophotometer. Melting points were determined with a Kofler Hotstage Microscope (Reichart-Thermovar) and are uncorrected. Microanalyses were performed in the microanalytical laboratories of the University of Cape Town. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 200 NMR spectrometer at 25°C. Unless otherwise stated, all ^1H and ^{13}C spectra were recorded in CDCl$_3$ with tetramethylsilane as an internal standard (δ 0.00 ppm). Electron impact mass spectra were obtained with a VG Micromass 16 F spectrometer operating at 70 eV.

2.1. Preparation of [o-{(py)(DH)$_2$CoCH$_2$}C$_6$H$_4$CH$_2$Br] (1)

[Co(DH)$_2$(py)Cl] (0.50 g, 1.24 mmol) was added to methanol (10 ml) and the slurry stirred for 5 min. o-C$_6$H$_4$(CH$_2$Br)$_2$ (0.34 g, 1.28 mmol) was added and the mixture stirred for a further 5 min. NaBH$_4$ (0.25 g, 6.60 mmol) was then added in portions during 10 min and the resulting orange solution stirred for a further 1 h then cooled to 0°C. The orange product was filtered off, washed with diethyl ether (5 ml), and recrystallized from CH$_2$Cl$_2$/hexane to give 1 (0.34 g, 50%) as orange crystals. M.p. 207°C (dec.). Anal. Found: C, 45.2; H, 5.0; N, 14.1. C$_{21}$H$_{27}$BrCoN$_5$O$_4$ calcd.: C, 45.6; H, 4.9; N, 12.7%.

2.2. Preparation of [Co(DH)$_2$(py)]$_2$[μ-(p-CH$_2$C$_6$H$_4$CH$_2$)] (2)

[Co(DH)$_2$(py)Cl] (1.00 g, 2.48 mmol) was added to nitrogen-saturated methanol (15 ml) and the slurry stirred for 5 min. p-C$_6$H$_4$(CH$_2$Br)$_2$ (0.34 g, 1.28 mmol) was then added and the mixture stirred for a further 5 min. NaBH$_4$ (0.5 g, 13.2 mmol) was then added in portions during 5 min and the resulting orange solution was stirred for a further 1 h. The crude product was filtered off and recrystallized from CH$_2$Cl$_2$/hexane to give 2 as orange crystals (1.70 g, 79%). M.p. 180°C (dec.). Anal. Found: C, 48.4; H, 5.1; N, 16.5. C$_{34}$H$_{46}$Co$_2$N$_{10}$O$_8$ calcd.: C, 48.6; H, 5.5; N, 16.6%.

2.3. Preparation of [Co(DH)$_2$(py)]$_2$(μ-(m-CH$_2$C$_6$H$_4$CH$_2$)] (3)

This was prepared by the method described above for 2 from the following reagents: [Co(DH)$_2$(py)Cl] (2.00 g, 4.96 mmol); m-C$_6$H$_4$(CH$_2$Br)$_2$ (0.68 g, 2.56 mmol); NaBH$_4$ (1.0 g, 26 mmol). Complex 3 (1.78 g,

44%) was obtained as orange crystals, which were recrystallized from CH$_2$Cl$_2$/hexane. M.p. 200°C (dec.). Anal. Found: C, 48.6; H, 5.4; N, 13.3. C$_{34}$H$_{46}$Co$_2$N$_{10}$O$_8$ calcd.: C, 48.6; H, 5.5; N, 16.6%.

2.4. Preparation of [{η^6-C$_6$H$_5$CH$_2$Co(DH)$_2$(py)}Cr(CO)$_3$] (4)

A slurry of [Co(DH)$_2$(py)Cl] (8.83 g, 21.86 mmol) with methanol (90 ml) was stirred for 5 min and [{η^6-C$_6$H$_5$CH$_2$Cl}Cr(CO)$_3$] (5.74 g, 21.86 mmol) was then added. The mixture was stirred for 5 min and NaBH$_4$ (1.65 g, 43.72 mmol) was then added in portions during 25 min and the resulting orange solution stirred for a further 1 h. The solution was kept at −15°C for 20 h. The orange crystalline product was filtered off, washed with cold hexane (3 × 3 ml) and recrystallized from CH$_2$Cl$_2$/hexane to give 4 as orange crystals in 70% (9.20 g) yield. M.p. 210°C (dec.). IR (CH$_2$Cl$_2$): ν(CO) 1958vs, 1878s cm^{-1}. Anal. Found: C, 46.2; H, 4.1; N, 11.7. C$_{23}$H$_{26}$CoCrN$_5$O$_7$ calcd.: C, 46.4; H, 4.4; N, 11.8%.

2.5. Preparation of [{η^6-pC$_6$H$_4$(CH$_2$OH)$_2$}Cr(CO)$_3$] (5)

A mixture of p-C$_6$H$_4$(CH$_2$OH)$_2$ (4.0 g, 28.9 mmol), [Cr(CO)$_6$] (6.40 g, 28.9 mmol), di-n-butyl ether (190 ml) and THF (16 ml) was refluxed for 26 h then cooled in an ice bath. The resulting yellow crystals were filtered off. Column chromatography followed by recrystallization from CH$_2$Cl$_2$/hexane afforded 5 (7.00 g, 90%) as bright yellow crystals. M.p. 108–109°C. IR (CH$_2$Cl$_2$): ν(CO) 1967vs, 1889s cm^{-1}; ^1H NMR (acetone-d$_6$): δ 5.70 (s, 4H, Ar) 4.40 (s, 4H, CH$_2$) 4.61 (s, 2H, OH); ^{13}C NMR (acetone-d$_6$): δ 113.2 (C^{tert}) 93.4 (Ar) 62.9 (CH$_2$) 234.4 (Cr–CO); the mass spectrum showed a molecular ion peak at m/e 274 as well as peaks at 246 (M$^+$ − CO), 218 (M$^+$ − 2CO), 190 (M$^+$ − 3CO). Anal. Found: C, 48.4; H, 3.6. C$_{11}$H$_{10}$CrO$_5$ calcd.: C, 48.2; H, 3.7%.

2.6. Preparation of [{η^6-p-C$_6$H$_4$(CH$_2$Cl)$_2$}Cr(CO)$_3$] (6)

A benzene (80 ml) solution of compound 5 (3.50 g, 12.8 mmol) was shaken with concentrated HCl (125 ml) for 15 min in a separatory funnel. The organic layer was separated, washed with distilled water (2 × 80 ml), and dried over MgSO$_4$. The solution was filtered through a pad of silica gel and the solvent evaporated. The residue was recrystallized from CH$_2$Cl$_2$/hexane to yield yellow crystals of 6 (3.20 g, 80%). M.p. 77–79°C. IR (CH$_2$Cl$_2$): ν(CO) 1978vs, 1901s cm^{-1}; ^1H NMR: δ 5.85 (s, 4H, Ar) 4.54 (s, 4H, CH$_2$); ^{13}C NMR: δ 107.9 (C^{tert}) 94.8 (Ar) 45.2 (CH$_2$) 233.0 (Cr–CO); the mass spectrum showed a molecular ion peak at m/e 311 as well as peaks at 283 (M$^+$ − CO), 255 (M$^+$ − 2CO), 227

$(M^+ - 3CO)$. Anal. Found: C, 42.1; H, 2.5. $C_{11}H_8Cl_2CrO_3$ calcd.: C, 42.4; H, 2.6%.

2.7. Preparation of [Co(DH)₂(py)]₂[μ-{(η⁶-p-CH₂C₆H₄CH₂)Cr(CO)₃}] (7)

2.7. Preparation of $[Co(DH)_2(py)]_2[\mu-\{(\eta^6-p-CH_2C_6H_4CH_2)Cr(CO)_3\}]$ (7)

Compound 7 was prepared by method (i) described above for 2a from the following reagents: [Co(DH)₂(py)Cl] (7.82 g, 19.36 mmol); 6 (3.01 g, 9.68 mmol); NaBH₄ (3.78 g, 26.4 mmol). The reaction mixture was stirred for 1 h after the last portion of NaBH₄ had been added then kept at −15°C for 20 h. The product was filtered off, washed with distilled water (5 ml) and diethyl ether (5 ml), then recrystallized from CH_2Cl_2/hexane to give 7 as orange crystals in 77% yield. M.p. 165°C (dec.). IR (CH_2Cl_2): ν(CO) 1947vs, 1870s cm^{-1}. Anal. Found: C, 45.4; H, 4.6; N, 14.4. $C_{37}H_{46}Co_2CrN_{10}O_{11}$ calcd.: C, 45.5; H, 4.7; N, 14.4%.

2.8. X-ray crystallography

2.8. X-ray crystallography

Orange crystals of 4 were grown from a CH_2Cl_2/hexane mixture kept in the dark at 25°C for 3 days. The crystals are triclinic, $P\bar{1}$, $a = 8.437(2)$, $b = 12.202(2)$, $c = 13.235(2)$ Å, $\alpha = 71.17(1)$, $\beta = 83.44(1)$, $\rho = 83.01(1)°$, $V = 1275.9(4)$ Å^3, $Z = 2$, $D_X = 1.55$ Mg m^{-3}, $F(000) = 612$, λ(Mo Kα) = 0.71069 Å, $\mu = 1.11$ mm^{-1}, room temperature.

A crystal with dimensions 0.13 × 0.25 × 0.25 mm was used. Lattice parameters were determined by least-squares fitting of the setting angles of 24 reflections $17° \geq \theta \geq 16°$ automatically centred on a CAD4 diffractometer. Intensities were collected with graphite-monochromated Mo Kα radiation, $\omega/2\theta$ scan mode, scan width $(0.85 + 0.35 \tan \theta)°$, aperture setting 4 mm, range of reflections $25 \geq \theta \geq 1°$, 4698 reflections measured of which 4006 were unique, $R_{int} = 0.016$, 3271 $[F_o > 4\sigma(F_o)]$ used in refinement, index range $h - 10/10$, $k - 14/14$, l 0/15. Three intensity control reflections $(-1\ 3\ 10, 6\ 5\ 1, -2\ 9\ 3)$ monitored after every hour of data collection showed no significant decay. Data were corrected for background, scan speed and Lorentz and polarization factors; empirical absorption correction was applied [17], transmission factors 0.87 to 0.99. The structure was solved by Patterson and Fourier methods.
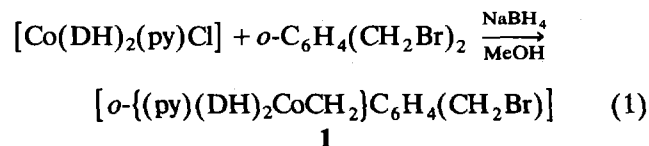
Least-squares anisotropic refinement (based on F) of positions of non-hydrogen atoms, isotropic refinement of all hydrogen atom positions constrained to idealized positions with C–H = 0.96 Å (except the hydrogen atom positions in the –NOH groups which were allowed to refine freely) gave final $R = 0.042$, $wR = 0.045$, $W = 1/[\sigma^2(F_o) + 0.00024(F_o^2)]$, $S = 2.70$, Δ/σ(max.) < 0.001, residual electron density +0.53 $\geq$ $\Delta\rho \geq -0.47$ e Å^{-3}. Complex neutral atom scattering factors were taken from [18] for the hydrogen atoms

and from [19] for all the other atom types; dispersion corrections were taken from [20]. The large librational amplitudes of the carbonyl atoms are in agreement with the appearance of a difference map from which no evidence of statistical disorder was found at any stage of the refinement. The following computer programs were used: SHELX76 [21]; SHELX86 [22]; PLUTO89 [23] and PARST [24]. All calculations were performed at the computer centre of the University of Cape Town on a Vax 8550 computer.
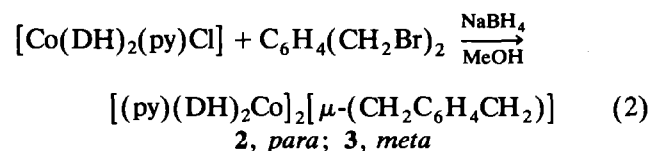
Lists of observed and calculated structure factors, and tables of hydrogen atom coordinates and anisotropic thermal parameters are available from the authors

3. Results and discussion

The compounds 1 were prepared by the reaction of [Co(DH)₂(py)Cl] with an equimolar amount of the appropriate xylene dibromide (eqn. (1)). A similar procedure was described by Finch and Moss [11] for the synthesis of the haloalkyl cobaloximes [Co(DH)₂(py){(CH₂)ₙX}].

$$[Co(DH)_2(py)Cl] + o\text{-}C_6H_4(CH_2Br)_2 \xrightarrow[\text{MeOH}]{\text{NaBH}_4}$$

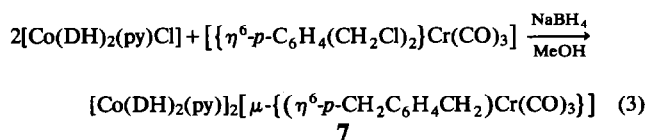$$[o\text{-}\{(py)(DH)_2CoCH_2\}C_6H_4(CH_2Br)] \qquad (1)$$
$$\mathbf{1}$$

The compounds 2 and 3 were prepared directly by the reaction of the appropriate xylene dibromides with two molar equivalents of [Co(DH)₂(py)Cl] in the presence of sodium borohydride (eqn. (2)).

$$[Co(DH)_2(py)Cl] + C_6H_4(CH_2Br)_2 \xrightarrow[\text{MeOH}]{\text{NaBH}_4}$$

$$[(py)(DH)_2Co]_2[\mu\text{-}(CH_2C_6H_4CH_2)] \qquad (2)$$
$$\mathbf{2}, para; \ \mathbf{3}, meta$$

The (arene)tricarbonyl chromium complex 5 was prepared by the thermal reaction between [Cr(CO)₆] and the free arene. This method is well documented and has been used to synthesize many $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes [25–28]. Compound 5 was converted into the corresponding dichloride 6 by treatment with hydrochloric acid.

The novel heterobimetallic complexes 4 and 7 were prepared by similar procedures to those described above for the synthesis of 1 and 2. Thus the reaction of $[\{\eta^6\text{-}C_6H_5CH_2Cl\}Cr(CO)_3]$ with [Co(DH)₂(py)Cl] afforded complex 4, while that of 6 with two molar equivalents of [Co(DH)₂(py)Cl] afforded 7 (eqn. (3)). Attempts to prepare complexes 4 and 7 by thermal reaction of [Cr(CO)₆] with the arene complexes [Co(DH)₂(py){CH₂C₆H₅}] and 2 were unsuccessful, re-

sulting only in decomposition of the starting complexes. So far as we are aware, complexes **4** and **7** represent the first examples of a cobaloxime that incorporates an $[(\eta^6\text{-arene})Cr(CO)_3]$ unit.

$$2[Co(DH)_2(py)Cl] + [\{\eta^6\text{-}p\text{-}C_6H_4(CH_2Cl)_2\}Cr(CO)_3] \xrightarrow[\text{MeOH}]{\text{NaBH}_4}$$

$$[Co(DH)_2(py)]_2[\mu\text{-}\{(\eta^6\text{-}p\text{-}CH_2C_6H_4CH_2)Cr(CO)_3\}] \quad (3)$$
$$\mathbf{7}$$

3.1. Characterization of the new complexes

The cobaloxime complexes **1–4** and **7** are air-stable, orange, crystalline solids and were isolated in moderate to good yields. They were characterized by elemental analysis and ^1H NMR (Table 1), ^{13}C NMR (Table 2) and IR spectroscopy. Complex **4** was also characterized by a single-crystal X-ray study (see below). Considerable attention has been given [29–32] to the IR spectra of cobaloximes which, although complex in nature are characteristic for complexes of this type, and complete band assignments have been made. The IR spectra (Nujol mull, $4000 - 200\ cm^{-1}$) of the new cobaloxime complexes (see supplementary material available from authors) have been assigned by reference to recent studies [33,34]. The solution IR spectra of the complexes **4–7** show two strong $\nu(CO)$ bands in the region $1850 - 2000\ cm^{-1}$ characteristic of (arene)tricarbonyl chromium complexes [35–37]. The ^1H NMR spectra of the cobaloxime complexes **1** and **2** are similar except that the mononuclear complex has a characteristic singlet at δ 4.37 ppm assigned to the CH_2Br protons. The signals from the arene protons of the heterobimetallic complexes **4** and **7** are shifted to lower frequency than those of **1** and **2** by approximately 1.5 ppm, while those from their methylene protons are shifted to lower

frequency by 0.5 ppm. This effect is attributed to the coordination of the $Cr(CO)_3$ group to the arene ring.

The ^{13}C NMR spectra of the cobaloxime complexes are similar. Complexes **4** and **7** each show a single ^{13}C resonance near 230 ppm arising from the three carbonyl ligands bonded to chromium. The equivalence of the CO ligands at 25°C indicates that rotation about the $Cr\text{-}Ph_{centroid}$ vector is rapid. The ^{13}C resonances of the basal and axial ligands were assigned with reference to published values for the free ligands [38] and those for known cobaloxime complexes [11,39].

3.2. The crystal and molecular structure of 4

The structure of **4** is, as far as we know, the first structure determined for a heterobimetallic cobaloxime complex. Final atomic parameters are listed in Table 3. Selected molecular parameters are given in Table 4. The general features of the molecular structure are consistent with those proposed from spectroscopic data. The cobalt atom exhibits pseudo-octahedral geometry and is bonded in the equatorial plane to two mono-deprotonated dimethylglyoxime ligands which are hydrogen bonded to each other. The four nitrogen donor atoms are coplanar within ± 0.0006 Å. The axial sites are occupied by pyridine and benzylchromiumtricarbonyl. A view of the molecule is given in Fig. 1. The chromium to cobalt distance is 5.246(1) Å. The atoms of the pyridine ligand are coplanar within ± 0.008 Å with the plane almost bisecting the line between the hydrogen bonded oxygen atoms of the dioximato group, as is usual for cobaloximes containing pyridine [40]. The atom H(92) is equidistant from O(21) and O(31), 2.670(5) Å, and both C(92)–H(92) $\cdots$ O angles are 128.9(5)°. The atom H(96) is equidistant from O(11) and O(41), 2.700(7) Å, the C(96)–H(96) $\cdots$ O angles

TABLE 1. ^1H NMR data [a] for the complexes (recorded in $CDCl_3$)

Complex	Pyridine			Dimethylglyoxime		Arene	Other	
	o-H	m-H	p-H	O–H $\cdots$ O	CH_3		Co–CH_2	CH_2Br
	d (2H)	t (2H)	t (1H)	bs (2H)	s (12H)		s (2H)	s (2H)
1	8.47	7.22	7.63	18.34	1.89	7.10 (t, 2H) 6.77 (m, 2H)	2.91	4.37br
4	8.45	7.25	7.70	18.82	2.00	5.05 (m, 5H)	2.25	
	d (4H)	t (4H)	t (2H)	bs (4H)	s (24H)		s (4H)	
2	8.52	7.27	7.65	18.20	1.90	6.62 (s, 4H)	2.74	
3	8.46	7.18	7.59	18.20	1.85	6.79 (d, 2H) 6.62 (t, 1H) 6.25 (s, 1H)	2.70 (s, 4H)	
7	8.48	7.28	7.70	18.10	2.21	4.85	2.21	

[a] Chemical shifts (δ ppm) are relative to TMS.

TABLE 2. ^{13}C NMR data [a] for the cobaloxime complexes (recorded in CDCl$_3$)

Complex	Pyridine			Dimethylglyoxime		Arene		
	o-C	m-C	p-C	CH$_3$	C=N	Co–CH$_2$		
1	150.1	125.3	137.6	11.85	b	b	144.0	61.26 (CH$_2$Br)
				12.01			140.1	
							130.2	
							129.8	
							126.0	
							127.8	
2	150.3	125.1	137.3	11.81	149.2	32.5 [c]	143.4	
							128.0	
3	150.3	125.0	137.2	11.86	149.2	31.5 [c]	145.9	
							128.0	
							126.9	
							125.6	
4 [d]	150.0	125.4	137.8	12.2	149.9	b	119.3	
							93.3	
							92.5	
							90.1	
7	150.0	125.2	137.6	12.4	149.9	30.9	115.9	
							95.7	

[a] Chemical shifts (δ ppm) are relative to TMS. [b] Not assigned. [c] Very weak signal. [d] Signals due to Cr–CO at 234.0(4) and 234.9 ppm (7) also seen.

being 127.0(5) and 127.9(5)° respectively. The bulky CH$_2$X ligand {X = (η^6-C$_6$H$_5$)Cr(CO)$_3$} occupies the remaining axial position. The angle C(8)–Co–N(1), 93.2(2)°, is significantly larger than 90°, whereas the angle at the trans nitrogen atom, C(8)–Co–N(3), 85.9(2)°, is significantly less than 90°. The remaining C–Co–N$_{eq}$ and the C–Co–N$_{ax}$ angles are all close to 90°. The CH$_2$X group is positioned almost directly above the Co–N(1) bond [τ for N(1)–Co–C(8)–C(81) is −16.9(9)°]. The situation where the CH$_2$X group is located above the Co–N bond for which the C–Co–N angle is the largest has often been found in related structures [32]. The cobalt atom is displaced from the plane containing the oxime nitrogen atoms by a distance, d, of 0.015(1) Å, towards the pyridine ligand. The bending angle, α, between the two halves of the dioximato group is 2.7(2)°, and the bending is away from the pyridine ligand. Corresponding values for d, 0.037 Å, and α, (4.9°), in trans-benzylbis(dimethylglyoximato)(pyridine)cobalt(III) (4a) [40], are higher than those for compound 4, suggesting that the steric requirements of the arene in the latter compound with respect to the π-system of the dioximato ligands are lower. It has been shown that the Co–C distance in cobaloximes containing the CH$_2$X group is mainly determined by the bulk of the CH$_2$X group [41]. Further it has been argued that the Co–C bond length, 2.065(4) Å, as well as the Co–C–C$_{Ar}$ angle, 116.7(2)°, in compound 4a are mainly determined by localized π–π interactions between the DH ligand and the benzyl group [40]. On the basis of the foregoing, the

Co–C(8) bond length of 2.044(4) Å reflects the decreased spatial requirement for the π–π interaction in compound 4 relative to that in compound 4a as the large value of the Co–C(8)–C(81) angle, 115.4(3)°, and the short C(8)–C(81) bond length, 1.472(7) Å, (1.474(5) Å in 4a) are the same as in compound 4a. The Co–N$_{ax}$ bond length reflects the σ-donor power of the CH$_2$X group [41]. The Co–N$_{ax}$ bond distance of 2.038(4) Å is shorter than that of 2.056(4) Å for compound 4a, indicating that the (η^6-benzyl)Cr(CO)$_3$ group is a weaker σ-donor than the benzyl group.

Looking at the (arene)Cr(CO)$_3$ fragment of compound 4, we note that the preferred geometry for monosubstituted (η^6-arene)Cr(CO)$_3$ molecules is eclipsed, with the syn-eclipsed conformation being adopted for electron-donating substituents and the anti-eclipsed conformation exhibited for electron-withdrawing substituents [42]. In compound 4 there is a nearly syn-eclipsed conformation with respect to the atoms C(81), C(83) and C(85), with an average displacement of 11.7(5)°. The displacement from a fully syn-eclipsed conformation in the compound [(η^6-C$_6$H$_5$Me)Cr(CO)$_3$] is 2.2° [43].

The perpendicular distance of the chromium atom from the phenyl ring is 1.723(1) Å compared with 1.72 Å in [(η^6-C$_6$H$_5$Me)Cr(CO)$_3$] [43]. The Cr–C$_{Ar}$ distances vary between 2.180(5) Å and 2.280(4) Å, the longer distances being those to the atoms nearest the methylene group. There is no systematic variation in the C$_{Ar}$–C$_{Ar}$ bond lengths. The endocyclic angles in the phenyl ring are equal, except for the ipso angle,

117.4(4) Å, which is smaller, and equal to that in $[(\eta^6\text{-}C_6H_5Me)Cr(CO)_3]$ [43]. Small variations in the (O)C–Cr–C(O) angles can be attributed to the effect of hydrogen bonding by two of the carbonyl oxygen atoms (see below).

Bond lengths and angles in the $Co(DH)_2$ moiety are normal within the precision of the structure determination. Marginal differences in the N–O and Co–N bond lengths in the Co(DH) groups could be attributed to the position of the atom H(4), which is located nearly midway between the atoms O(11) and O(41), in contrast to the atom H(2) which takes up a 'normal' intramolecular hydrogen bonding position with respect to the atoms O(21) and O(31). There is extensive intermolecular hydrogen bonding in the structure (see

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\mathring{A}^2 \times 10^3$) with esd's in parentheses for 4

Atom	x	y	z	U_{eq} [a]
Co(1)	1357.4(6)	2917.7(4)	2736.8(4)	34.5(3)
Cr(1)	3022.7(9)	−1113.7(6)	2115.0(6)	51.5(4)
N(1)	128(4)	2820(3)	1679(3)	44(1)
N(2)	−212(4)	2032(3)	3635(3)	43(1)
N(3)	2620(4)	3000(3)	3793(3)	45(2)
N(4)	2970(4)	3787(3)	1842(3)	48(1)
C(1)	−1158(5)	2268(4)	2019(4)	54(2)
C(2)	−1356(5)	1791(4)	3190(4)	50(2)
C(3)	3867(5)	3582(4)	3471(4)	51(2)
C(4)	4053(5)	4059(4)	2307(5)	56(2)
O(11)	527(5)	3288(3)	633(2)	63(1)
O(21)	−183(5)	1638(3)	4703(3)	62(2)
O(31)	2267(4)	2483(3)	4849(2)	62(2)
O(41)	2992(5)	4145(3)	758(3)	71(2)
C(11)	−2255(8)	2107(7)	1282(6)	88(3)
C(21)	−2667(7)	1080(5)	3810(6)	80(3)
C(31)	4986(7)	3719(6)	4206(6)	88(3)
C(41)	5377(8)	4788(6)	1713(7)	101(3)
C(8)	2736(5)	1408(3)	2780(4)	44(2)
C(81)	2076(4)	650(3)	2296(3)	37(2)
C(82)	1082(5)	−203(4)	2908(4)	49(2)
C(83)	414(6)	−911(4)	2449(5)	63(2)
C(84)	725(7)	−794(5)	1395(6)	77(3)
C(85)	1744(7)	19(5)	765(4)	73(3)
C(86)	2420(6)	749(4)	1205(3)	51(2)
N(91)	31(4)	4413(3)	2791(3)	38(1)
C(92)	−578(5)	4552(4)	3725(4)	48(2)
C(93)	−1465(6)	5531(4)	3813(4)	57(2)
C(94)	−1790(6)	6429(4)	2895(5)	62(2)
C(95)	−1186(6)	6311(4)	1930(4)	59(2)
C(96)	−277(5)	5301(4)	1905(4)	49(2)
C(5)	4919(9)	−933(5)	2513(8)	134(5)
C(6)	4175(7)	−1808(5)	1200(5)	82(3)
C(7)	3004(7)	−2566(5)	3100(4)	71(2)
O(5)	6150(7)	−829(5)	2724(8)	217(6)
O(6)	4886(7)	−2267(4)	618(4)	137(3)
O(7)	2940(6)	−3484(4)	3687(4)	118(2)

[a] Equivalent isotropic U calculated from anisotropic U: $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j$.

TABLE 4. Bond lengths (Å) and angles (°) for 4

Co(1)–N(1)	1.876(4)	C(1)–C(2)	1.467(7)
Co(1)–N(2)	1.870(3)	C(1)–C(11)	1.490(10)
Co(1)–N(3)	1.886(4)	C(2)–C(21)	1.489(7)
Co(1)–N(4)	1.885(3)	C(3)–C(4)	1.458(8)
Co(1)–C(8)	2.044(4)	C(3)–C(31)	1.490(10)
Co(1)–N(91)	2.038(4)	C(4)–C(41)	1.499(8)
Cr(1)–C(81)	2.280(4)	C(8)–C(81)	1.472(7)
Cr(1)–C(82)	2.222(5)	C(81)–C(82)	1.399(5)
Cr(1)–C(83)	2.194(5)	C(81)–C(86)	1.409(6)
Cr(1)–C(84)	2.195(7)	C(82)–C(83)	1.403(9)
Cr(1)–C(85)	2.180(5)	C(83)–C(84)	1.354(10)
Cr(1)–C(86)	2.229(4)	C(84)–C(85)	1.389(8)
Cr(1)–C(5)	1.800(9)	C(85)–C(86)	1.412(9)
Cr(1)–C(6)	1.822(7)	N(91)–C(92)	1.338(7)
Cr(1)–C(7)	1.830(5)	N(91)–C(96)	1.340(5)
N(1)–C(1)	1.305(6)	C(92)–C(93)	1.362(7)
N(1)–O(11)	1.336(4)	C(93)–C(94)	1.377(7)
N(2)–C(2)	1.294(7)	C(94)–C(95)	1.365(8)
N(2)–O(21)	1.339(5)	C(95)–C(96)	1.378(7)
N(3)–C(3)	1.295(6)	C(5)–O(5)	1.138(11)
N(3)–O(31)	1.350(4)	C(6)–O(6)	1.165(9)
N(4)–C(4)	1.288(7)	C(7)–O(7)	1.142(7)
N(4)–O(41)	1.357(5)		
C(8)–Co(1)–N(91)	176.2(2)	N(1)–C(1)–C(2)	112.7(4)
N(4)–Co(1)–N(91)	90.4(2)	C(2)–C(1)–C(11)	124.4(5)
N(4)–Co(1)–C(8)	90.3(2)	N(2)–C(2)–C(1)	111.8(4)
N(3)–Co(1)–N(91)	90.5(2)	C(1)–C(2)–C(21)	125.1(5)
N(3)–Co(1)–C(8)	85.9(2)	N(2)–C(2)–C(21)	123.0(5)
N(3)–Co(1)–N(4)	80.8(2)	N(3)–C(3)–C(31)	123.7(5)
N(2)–Co(1)–N(91)	90.6(2)	N(3)–C(3)–C(4)	111.7(4)
N(2)–Co(1)–C(8)	88.7(2)	C(4)–C(3)–C(31)	124.6(5)
N(2)–Co(1)–N(4)	178.9(2)	N(4)–C(4)–C(3)	113.2(4)
N(2)–Co(1)–N(3)	98.6(2)	C(3)–C(4)–C(41)	123.3(5)
N(1)–Co(1)–N(91)	90.4(2)	N(4)–C(4)–C(41)	123.5(6)
N(1)–Co(1)–C(8)	93.2(2)	Co(1)–C(8)–C(81)	115.4(3)
N(1)–Co(1)–N(4)	98.9(2)	C(8)–C(81)–C(86)	121.7(4)
N(1)–Co(1)–N(3)	179.0(2)	C(8)–C(81)–C(82)	121.0(4)
N(1)–Co(1)–N(2)	81.7(2)	C(82)–C(81)–C(86)	117.4(4)
C(6)–Cr(1)–C(7)	86.9(3)	C(81)–C(82)–C(83)	121.4(5)
C(5)–Cr(1)–C(7)	90.8(3)	C(82)–C(83)–C(84)	120.8(5)
C(5)–Cr(1)–C(6)	86.5(3)	C(83)–C(84)–C(85)	119.6(6)
Co(1)–N(1)–O(11)	122.6(3)	C(84)–C(85)–C(86)	120.7(5)
Co(1)–N(1)–C(1)	116.3(3)	C(81)–C(86)–C(85)	120.0(4)
C(1)–N(1)–O(11)	121.2(4)	Co(1)–N(91)–C(96)	122.4(3)
Co(1)–N(2)–O(21)	122.7(3)	Co(1)–N(91)–C(92)	121.0(3)
Co(1)–N(2)–C(2)	117.5(3)	C(92)–N(91)–C(96)	116.6(4)
C(2)–N(2)–O(21)	119.8(4)	C(92)–C(93)–C(94)	118.9(5)
Co(1)–N(3)–O(31)	122.6(3)	C(93)–C(94)–C(95)	118.7(5)
Co(1)–N(3)–C(3)	117.4(3)	C(94)–C(95)–C(96)	119.1(5)
C(3)–N(3)–O(31)	120.0(4)	N(91)–C(96)–C(95)	123.0(5)
Co(1)–N(4)–C(4)	116.8(4)	Cr(1)–C(5)–O(5)	176.9(8)
C(4)–N(4)–O(41)	120.5(4)	Cr(1)–C(6)–O(6)	178.6(6)
N(1)–C(1)–C(11)	122.9(5)	Cr(1)–C(7)–O(7)	176.7(5)

below) which could affect the position of the atom H(4). There are rare cases of cobaloximes with the two equatorial dimethylglyoxime ligands present as dianionic, D^{2-}, and neutral (DH_2) species [40,44]. The structure of compound 4 tends towards this unusual type, but the differences in the $Co\text{-}N_{eq}$ and N–O bond
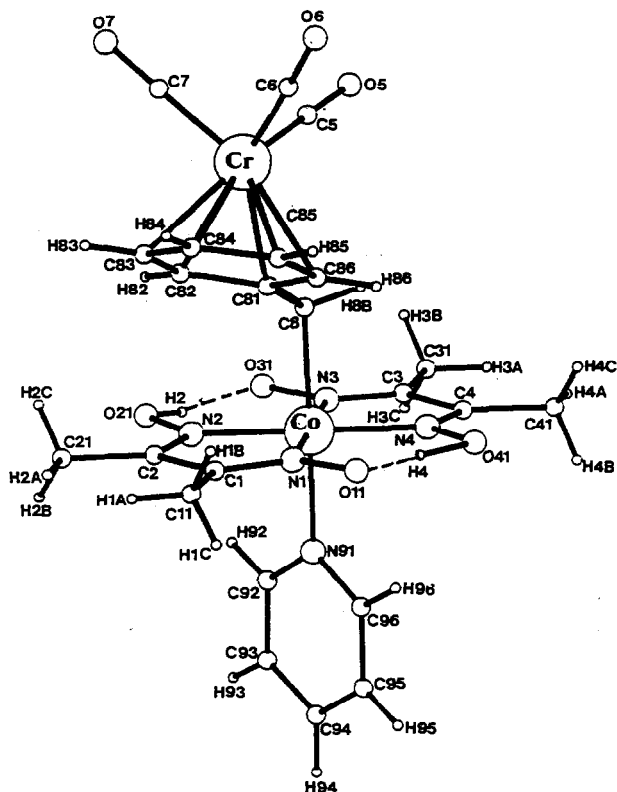
Fig. 1. A perspective view of a molecule of 4 which also shows the numbering scheme used.

lengths in the two parts are in the opposite sense to those described previously [32]; i.e. there is a small but significant shortening of the average Co–N$_{eq}$ bond length in the incipient (DH$_2$) unit, 1.873(4) versus 1.886(4) Å, and also of the average N–O bond length, 1.338(5) versus 1.354(5) Å.

Packing is determined by van der Waals' forces and by an extensive system of hydrogen bonds; see Fig. 2. The carbonyl oxygen atom O(5) makes a weak interaction with a proton on C(21). O(6) is involved in a two centre hydrogen bond with a methyl proton on C(41)
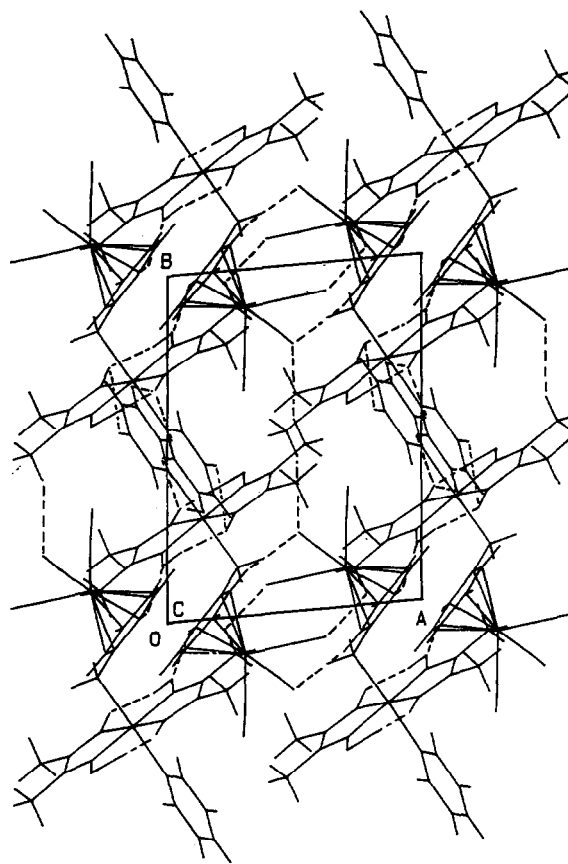

Fig. 2. Packing diagram viewed down Z0; hydrogen bonds are indicated by broken lines.

and the aromatic proton on C(86). Another aromatic proton H(82) interacts with O(21) on the (DH$_2$) group. Other hydrogen bonds to the (DH$_2$) group are all to protons on the pyridine group: O(11) takes part in a two centre bond to H(95) and H(96), and O(31) interacts weakly with H(93). The only oxygen atom in the (DH$_2$) groups which does not take part in a hydrogen

TABLE 5. Hydrogen bonding parameters (Å and °)

O(21)–H(2)	0.83(9)	O(21)···O(31) [a]	2.472(6)	O(21)–H(2)···O(31)	167(8)
O(31)···(H2)	1.66(8)				
O(41)–H(4)	1.18(8)	O(41)···O(11) [a]	2.483(6)	O(41)–H(4)···O(11)	178(8)
O(H)···H(4)	1.30(8)				
C(21)–H(2A)	0.96(1)	C(21)···O(5) [b]	3.40(1)	C(21)–H(2A)···O(5)	130.7(7)
C(41)–H(4B)	0.96(1)	C(41)···O(6) [c]	3.406(8)	C(41)–H(4B)···O(6)	151.0(7)
C(82)–H(82)	0.960(7)	C(82)···O(21) [d]	3.137(6)	C(82)–H(82)···O(21)	144.1(5)
C(86)–H(86)	0.960(6)	C(86)···O(6) [e]	3.362(7)	C(86)–H(86)···O(6)	162.2(5)
C(93)–H(93)	0.959(8)	C(93)···O(31) [f]	3.400(7)	C(93)–H(93)···O(31)	128.5(5)
C(95)–H(95)	0.960(6)	C(95)···O(11) [g]	3.259(6)	C(95)–H(95)···O(11)	123.0(5)
C(96)–H(96)	0.961(7)	C(96)···O(11) [g]	3.262(5)	C(96)–H(96)···O(11)	124.9(5)

[a] Intramolecular. [b] At $x-1$, y, z. [c] At x, $y+1$, z. [d] At $-x$, $-y$, $-z+1$. [e] At $-x+1$, $-y$, $-z$. [f] At $-x$, $-y+1$, $-z+1$.
[g] At $-x$, $-y+1$, $-z$.

bond is that with the longest N–O bond length, N(4)–O(41), and which is also bonded to the proton situated nearly mid-way between O(11) and O(41). Parameters for the hydrogen bonds are given in Table 5.

4. Conclusion

We have prepared and fully characterized two new heterobimetallic complexes of cobalt and chromium containing Co:Cr atomic ratios of 1:1 and 2:1. The crystal and molecular structure of the 1:1 complex has been determined by X-ray crystallography. These complexes have been used as precursors for heterogeneous CO hydrogenation catalysts and preliminary results show that they are active, show novel product selectivity and have good catalyst lifetime [13].

Acknowledgments

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