

Organometallic cobalt(III) complexes with tridentate imino-oximic ligands: structural, spectroscopic and electrochemical properties †

Adriano Bigotto, Alessandro Felluga, Renata Dreos, Giorgio Nardin, Lucio Randaccio,*
Giovanni Tauzher,* Silvia Peressini and Claudio Tavagnacco

Dipartimento di Scienze Chimiche, Università di Trieste, via Giorgieri 1, 34127 Trieste, Italy

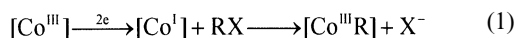
Received 1st October 2001, Accepted 11th October 2001

First published as an Advance Article on the web 28th November 2001

A series of binuclear complexes of the type $[(\mu\text{-OH})(\text{RCo}^{\text{III}}\text{L})_2]^+$ where L is the tridentate 2-(2-pyridylethyl)imino-3-butanone oximate ligand and R = Me, Et, CH_2CF_3 , CH_2Cl or Cy have been prepared and characterised. Some of their physico-chemical properties, namely the Co–R bond lengths, the $\nu_{\text{Co-Me}}$ Raman frequencies and the $E_{1/2}$ half-wave potentials of the one-electron reduction process have been determined. Comparison of these properties with those of the metalloorganic derivatives containing tetradentate ligands, such as cobaloximes, Costa model derivatives and cobalamins, suggests that in the present compounds the Co–C bond strength and the electrochemical behaviour are more influenced by electronic than by steric factors.

Introduction

Many pseudo-octahedral Co^{III} complexes with an equatorial tetradentate or bis-bidentate ligand have been found to afford stable organometallic species, formally derived by substitution of one of the axial donor groups with a σ bonded alkyl group.^{1,2} The commonly used synthetic procedure involves the oxidative addition of an alkyl halide (R–X) to the nucleophilic Co^{I} species generated by reduction of a Co^{III} precursor,³ eqn. (1).



We have reported⁴ that stable alkyl cobalt derivatives can also be obtained by this method starting from the $[\text{Co}^{\text{III}}(\text{L})_2]\text{-ClO}_4$ complex, **1**, (Scheme 1) where L is the monoanionic tridentate imino-oximate ligand 2-(2-pyridylethyl)imino-3-butanone oximate. In particular, binuclear alkyl cobalt μ -hydroxo species of the type $[(\mu\text{-OH})(\text{RCo}^{\text{III}}\text{L})_2]^+$ were obtained when Me–X or Et–X were used as alkylating agents. The overall process involves the removal of one of the two tridentate ligands present in **1**, giving a mononuclear species as precursor to the final product. However, in the presence of Bz–X the reaction proceeds in a different way (Scheme 1) leading to the formation of the mononuclear compound $[\text{BzCo}^{\text{III}}(\text{L})(\text{L}^1)]^+$, where (L^1) represents the 2-(2-pyridylethyl)amino-3-aminobutane ligand. The structural characterisation⁵ showed that, in the latter complex, the tridentate L ligand is co-ordinated to the Co atom in a way similar to that found in **1**, whereas the L^1 ligand chelates cobalt through the two amino N-donors, obtained by hydrogenation of both the imino and oxime groups originally present in the L ligand. The σ -bonded benzyl group occupies the sixth co-ordination position.

Our interest is now directed towards the chemistry of binuclear complexes, rather than mononuclear ones, since the former represent a novel category of alkyl cobalt derivatives. After their discovery, we decided to undertake a study involving, on one hand, the examination of the change in several physico-chemical properties as the R group is changed and, on the other, the definition of the cobalt–carbon bond as

compared with that present in other simple vitamin B₁₂ models such as the cobaloximes and related mononuclear complexes. Such a systematic analysis requires the availability of a large series of compounds, so that, in addition to the previously reported alkyl derivatives of the type $[(\mu\text{-OH})(\text{RCo}^{\text{III}}\text{L})_2]^+$ with R = Me (**2a**), Et (**2b**)⁴ and $[\text{BzCo}^{\text{III}}(\text{L})(\text{L}^1)]^+$ (Bz = benzyl) (**3a**),⁵ the new binuclear complexes with R = CH_2CF_3 (**2c**), CH_2Cl (**2d**) and Cy (**2e**), and the mononuclear Cy derivative (**3e**), are reported. The crystal structure of **2c** and **2e**, the FT-Raman spectrum of **2a** and the $E_{1/2}$ values of complexes **2** have been determined.

Results

Synthesis

The synthesis of the organometallic compounds follows the scheme previously described [eqn. (1)] consisting of the oxidative addition of an alkyl halide to the nucleophilic Co^{I} species generated by reduction, with NaBH_4 , of the parent Co^{III} complex. The complexes were obtained as perchlorate salts. Whereas **2d** was the exclusive product of the reaction, the compounds **2e** and **3e** were simultaneously formed and separated in approximately equal amounts by fractional crystallisation. Thus, the occurrence of a monomeric form of Cy and Bz derivatives suggests that the steric demand of the R group might be, to some extent, responsible for the preferred formation of the monomeric over the dimeric species.

Structures

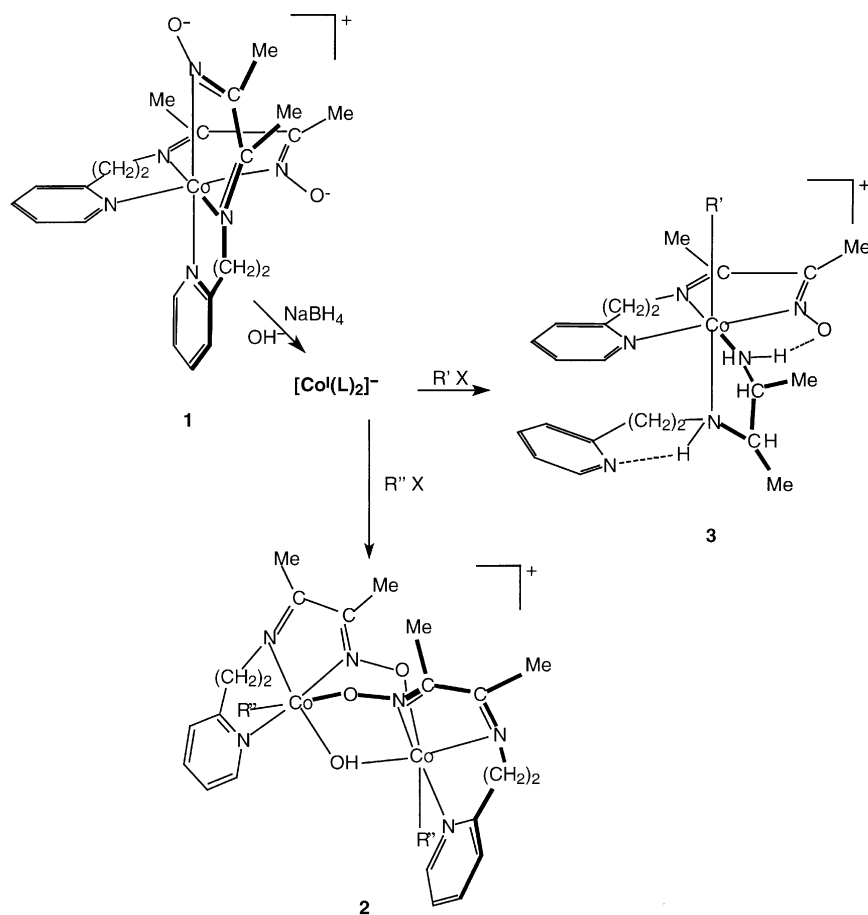
The crystals of **2c** and **2e** are built up by $[(\mu\text{-OH})(\text{RCo}^{\text{III}}\text{L})_2]^+$ cations [R = CH_2CF_3 (**2c**), Cy (**2e**)] and perchlorate anions. In **2e** MeOH solvent molecules are also present. The ORTEP drawings of **2c** and **2e** are depicted in Fig. 1.

If the alkyl group is excluded, the cations of **2a**, **2c**, and **2e** have a very similar geometry, with an approximate C_2 symmetry, the two-fold axis passing through the hydroxo oxygen atom and the midpoint of the two cobalt ions. The L ligand occupies three equatorial positions in a *mer* arrangement, the fourth being occupied by the bridging OH^- group. The alkyl group and the oxime O atom of the L ligand, co-ordinated to the other Co centre, occupy the axial positions. Thus, the imino-oxime ligand acts as a bridging tetradentate ligand.

† Electronic supplementary information (ESI) available: Raman spectra of **2a** and deuterated **2a**. See <http://www.rsc.org/suppdata/dt/b1/b109282k/>

Table 1 Selected bond lengths [\AA] and angles [$^\circ$] for CoL_2 , **2a**, **2c** and **2e**

	2a				
	CoL_2	Molecule 1	Molecule 2	2c	2e
$\text{Co} \cdots \text{Co}$	—	3.056(1)	3.057(1)	3.071(1)	3.080(1)
$\text{Co}-\text{OH}$	—	1.915(3)	1.904(3)	1.922(2)	1.927(4)
$\text{Co}-\text{C}$	—	1.911(3)	1.909(4)	1.919(2)	1.907(4)
$\text{Co}-\text{O}_{\text{ox}}$	—	1.966(5)	1.983(5)	1.997(3)	2.013(7)
$\text{Co}-\text{N}_{\text{py}}$	2.032(4)	1.975(5)	1.973(5)	1.962(3)	1.965(5)
$\text{Co}-\text{N}_{\text{im}}$	2.043(4)	1.969(4)	1.970(5)	1.978(3)	1.971(5)
$\text{Co}-\text{N}_{\text{ox}}$	1.929(4)	1.885(4)	1.879(4)	1.906(3)	1.891(5)
$\text{Co}-\text{N}_{\text{ox}}$	1.927(4)	1.895(4)	1.887(5)	1.897(3)	1.887(6)
$\text{Co}-\text{N}_{\text{ox}}$	1.913(4)	1.874(5)	1.872(5)	1.880(3)	1.871(5)
$\text{Co}-\text{N}_{\text{ox}}$	1.918(4)	1.862(4)	1.871(5)	1.873(3)	1.868(5)
$\text{N}-\text{O}_{\text{ox}}$	1.268(5)	1.326(5)	1.319(5)	1.332(3)	1.317(6)
$\text{N}-\text{O}_{\text{ox}}$	1.265(5)	1.316(5)	1.321(4)	1.322(3)	1.324(6)
$\text{N}_{\text{py}}-\text{Co}-\text{N}_{\text{im}}$	93.3, 94.1(2)	95.1, 95.0(2)	95.9, 96.1(2)	95.8, 95.6(1)	96.5, 96.5(3)
$\text{N}_{\text{im}}-\text{Co}-\text{N}_{\text{ox}}$	82.2, 81.8(2)	81.4, 81.8(2)	81.4, 81.8(2)	81.5, 81.3(1)	81.6, 82.1(3)
$\text{N}_{\text{py}}-\text{Co}-\text{N}_{\text{ox}}$	174.5, 175.2(2)	176.5, 176.3(2)	177.3, 177.3(2)	176.4, 176.2(1)	176.7, 176.0(2)
$\text{Co}-\text{C}-\text{C}$	—	—	121.9, 125.9(3)	121.8, 124.8(3)	116.2, 117.6(5)
$\text{N}_{\text{im}}\text{CoN}_{\text{py}}\text{C}_{\text{py}}$	150.1, 149.1	152.0, 146.4	150.3, 153.2	154.3, 153.9(3)	156.8, 159.1(5)
$\text{N}_{\text{ox}}\text{CoCC}$	—	—	—	113.9, 133.9(4)	137.0, 121.9(7)
d_{Co}	—	0.01(O2)	0.04(O1)	0.04, 0.03(C)	0.08(C), 0.07(C)

**Scheme 1**

These compounds appear to be the first example of organo-metallic complexes having two alkyl cobalt centres, which are stabilised by an imino-oxime ligand, both in the solid state and solution.

Equatorial co-ordination distances are very similar in **2a**, **2c** and **2e** (Table 1), with Co displaced out of the mean plane of

the four equatorial donors towards the alkyl groups in **2c** and **2e**, and towards O in **2a**. The displacement, d , increases in the order $\text{Me} < \text{CH}_2\text{CF}_3 < \text{Cy}$. As expected, the axial distances are significantly different. In fact, the $\text{Co}-\text{C}$ distance increases in the order $\text{Me} < \text{CH}_2\text{CF}_3 < \text{Cy}$, identical to the order in d , and reflects the increase in the bulk of R. The *trans* $\text{Co}-\text{O}_{\text{ox}}$ distance

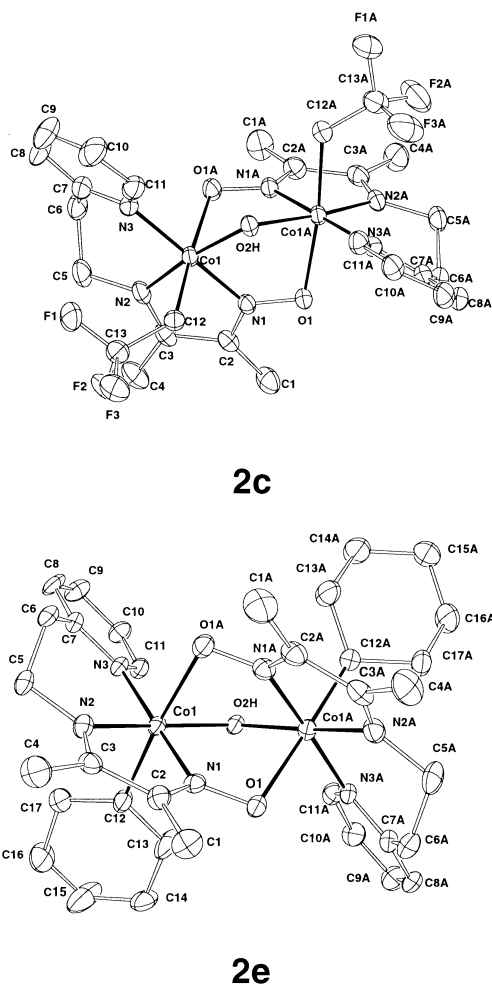


Fig. 1 ORTEP²¹ diagram with the numbering scheme for the non-hydrogen atoms for **2c** and **2e**.

increases in the order $\text{CH}_2\text{CF}_3 < \text{Me} < \text{Cy}$, and reflects the increase in the σ -donating ability of the alkyl ligand.

The Co–N_{py}, Co–N_{im}, Co–N_{ox} distances, involving the L ligand, are very similar in the three binuclear species and therefore the co-ordination geometry of the CoL unit is not influenced by the nature of the alkyl group. However, they are significantly shorter than those reported in the $[\text{Co}^{\text{III}}(\text{L})_2]^+$ parent complex and correspond to a lengthening of the N–O bond in complexes **2** (Table 1).

The L ligand deviates from planarity and this deviation may be described as due to a rotation around the Co–N_{py} bond, which brings the planar py and the 3-imine-2-butanoneoxime moieties of the L ligand out of coplanarity. The rotation can be measured by the value of the torsional angle C_{py}–N_{py}–Co–N_{im}. These values slightly increase with the bulk of the R group. The CH₂CF₃ and Cy groups lie approximately above the ethylene six-membered ring and are accommodated within the cavity formed by the two planar moieties of the L ligand.

FT-Raman spectroscopy

Raman spectroscopy is a powerful tool for the elucidation of Co–C binding in vitamin B₁₂ and its model compounds,^{6–10} provided that near IR laser excitation or cryogenic techniques are used to prevent fluorescence or photodecomposition. Raman spectra of the methyl derivative (**2a**) in saturated CH₂Cl₂ solution showed bands at 511.5, 933, 1031 and 1593 cm⁻¹. The band at 511.5 for **2a** can be ascribed to Co–C stretching, as it shifts upon deuteration of the CH₃-group to 488 cm⁻¹. Whereas the observed isotopic shift (23.5 cm⁻¹) is less than the theoretical value of 36 cm⁻¹ it lies in the range of the observed

values (20–35 cm⁻¹) for other methyl cobalt derivatives.¹⁰ Shifts smaller than the expected frequency shifts indicate that the band is not due to a pure $\nu_{\text{Co-Me}}$ mode.¹⁰

Electrochemistry

Polarography. In the range +0.4 to –2.0 V the polarograms of the binuclear compounds **2** in dmf generally show two one-electron reduction waves (I and II), except for R = CH₂Cl where only one reduction wave is observed.¹¹ As an example, the polarography of the ethyl derivative is reported in Fig. 2.

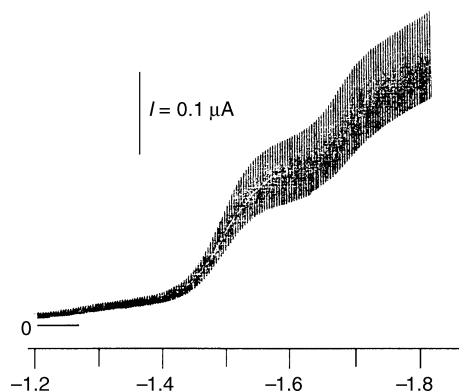


Fig. 2 Polarography of the complex **2b** with a concentration of ca. 1 mM, in dmf + teap 0.1 M at 0 °C.

The controlled potential reduction (CPR) at a potential corresponding to the plateau of the first polarographic wave (*i.e.* –1.5 V for the methyl derivative), confirms the mono-electronic character of the signal. After exhaustive electrolysis, the first wave disappears while the second remains at the same height and $E_{1/2}$. The polarographic $E_{1/2}$ values along with other electrochemical parameters are summarised in Table 2.

The reduction potential of both processes (I and II) are shifted towards more negative values when the electron donating ability of R increases. Hence, the trend of the first $E_{1/2}$ in the binuclear complexes, with exclusion of the CH₂Cl derivative,¹¹ can be rationalised in terms of changes in the electronic charge on the cobalt atom caused by the inductive effect of the R group as quantified by the σ^* Taft constants. Furthermore the strictly linear dependence of $E_{1/2}$ on σ^* values (Fig. 3) indicates that the thermodynamics of the process are

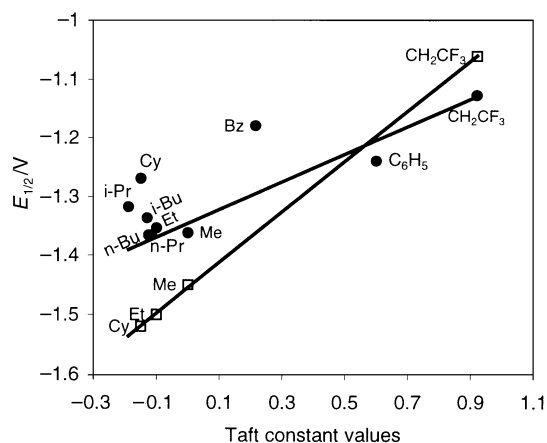


Fig. 3 Plot of $E_{1/2}$ values vs. Taft's σ^* for complexes **2** (□) and for alkyl-aquocobaloximes (●). Solvent = dmf + teap 0.1 M: $T = 25$ °C for complexes **2** and 0 °C for alkyl-aquocobaloximes.

largely dominated by the electronic influence of the R group, steric factors being much less important. Fig. 3 also reproduces the trend of $E_{1/2}$ vs. σ^* for some alkyl-aquocobaloximes.

Table 2 Summary of polarographic data (from ref. 11 unless indicated) in dmf + teap 0.1 M at 25 °C for complexes **2** and, at 0 °C, for alkyl-aquocobaloximes

R	Complexes 2 ^a		RCo(Hdmg) ₂ (H ₂ O) ^b	
	<i>E</i> _{1/2} (I)/V vs. SCE	<i>E</i> _{1/2} (II)/V vs. SCE	<i>E</i> _{1/2} /V vs. SCE	σ*
<i>i</i> -Pr	—	—	-1.318	-0.19
Cy	-1.52	-2.0	-1.27 ^c	-0.15
<i>n</i> -Bu	—	—	-1.366	-0.125
<i>i</i> -Bu	—	—	-1.337	-0.13
<i>n</i> -Pr	—	—	-1.366	-0.115
Et	-1.50	-1.65	-1.354	-0.100
Me	-1.45	-1.80	-1.362	0
Bz	—	—	-1.180	0.215
C ₆ H ₅	—	—	-1.240	0.60
CH ₂ CF ₃	-1.06	-1.40	-1.127	0.92
CH ₂ Cl	-1.26	—	-1.17 ^c	1.05

^a Ratio between polarographic limiting currents relative to waves I and II. ^b *E*_{1/2} for alkyl-aquocobaloximes relative to the first reduction polarographic wave coupled with the Co(III)/Co(II) electron transfer at 0 °C in dmf + teap 0.1 M. ^c Current work.

Cyclic voltammetry. The cyclic voltammetry of compounds **2** at relatively slow scan rates (from 20 mV s⁻¹ up to 5 V s⁻¹) on Hg or glassy carbon electrodes reveals two cathodic peaks (I, II), both of which lack the anodic counterpart. The cathodic peak currents increase proportionally to the square root of scan rate up to 5 V s⁻¹, showing the diffusion character of the process.

Peak potentials shift cathodically with increasing scan rate: this shift and the lack of anodic peaks coupled with the cathodic peaks is in agreement with an EC mechanism, *i.e.* after the one-electron transfer, a relatively fast irreversible chemical reaction occurs in the homogeneous phase. The product of this reaction can be reduced with one-electron at more negative potential.

Cobaloximes show a simpler mechanism than that of the binuclear compounds. In the former, after the first reversible one-electron transfer, a relatively slow reaction in occurs in the homogeneous phase, as shown by the fact that both the voltammetric cathodic peaks, associated with Co^{III}/Co^{II} and Co^{II}/Co^I processes respectively, show anodic counterparts even at scan rates as slow as 0.1 V s⁻¹.¹² Therefore a direct comparison of *E*_{1/2} for binuclear compounds and the corresponding alkyl-aquocobaloximes is not tenable because the mechanism associated with the electron transfer seems to be different in the two cases. However, it may be concluded that the *E*_{1/2} values of both series of compounds are dramatically influenced by the nature of the R group. A linear dependence of *E*_{1/2} vs. σ* was found for the binuclear complexes (Fig. 3), suggesting that in this case the thermodynamics of the process are largely dominated by electronic factors. A linear trend is also observed for the alkylcobaloximes containing a Co–C(primary) bond, *i.e.*: Me, Et, *n*-Pr, *n*-Bu, *i*-Bu and CH₂CF₃. An exception is the Bz derivative, which will be considered separately in the Discussion section. On the contrary remarkable deviations were observed for those complexes containing a Co–C(secondary) bond, *i.e.*: *i*-Pr and Cy derivatives (Fig. 3). The displacement of the first reduction potential towards σ* values less negative than those expected was ascribed to steric effects, lowering the energy of the electron transfer process.^{13,14} According to this, structural data^{15,16} have shown that the Co–C lengths increase in the order Co–C(primary) < Co–C(secondary) < Co–C(tertiary), suggesting that the steric interactions of the alkyl group with the Co(DH₂) moiety increase with the number of the substituents on the α carbon atom. Significant deviations from the linear trend should be expected for the *sec*-Bu and especially for the *tert*-Bu derivative having a secondary and a tertiary α carbon atom bonded to the cobalt respectively. Unfortunately data are not available for either of the latter compounds.

Table 3 Selected values of ν_{Co–Me} Raman frequencies and Co–C bond distances for some alkyl complexes^a

L	MeCo(Hdmg) ₂ L		Me[Co(do)(Hdo)pn]L ⁺	
	ν _{Co–Me} /cm ⁻¹	Co–C/Å	ν _{Co–Me} /cm ⁻¹	Co–C/Å
H ₂ O	—	1.990(5)	—	1.974(4)
1-MeIm	508	1.980(4)	503	2.001(3)
1,5,6-MeBzm	506	1.989(2)	499	2.011(3)
Py	504	1.998(5)	497	2.003(3)
Pme ₃	495	2.015(3)	487	—
PPh ₃	487	2.026(6)	—	2.018(5)
Me	—	—	455	2.047(8)

Complex 2a		Methylcobalamin	
ν _{Co–Me} /cm ⁻¹	Co–C/Å	ν _{Co–Me} /cm ⁻¹	Co–C/Å
511.5	1.974(4)	506	1.979(4)

^a dmg = dimethylglyoximate, do = diacetylmonooximate.

Discussion

Typical values of ν_{Co–Me} frequencies (which are related to the cobalt–carbon bond strength) and cobalt–carbon bond lengths for complexes **2**, methyl cobalamin and two vitamin B₁₂ models are reported in Table 3.

The order of increasing ν_{Co–Me} frequencies appears to be [(do)(Hdo)pn] < (Hdmg)₂ < Cbl < **2a**, whereas the Co–Me bond lengths follow an opposite trend: **2a** < Cbl < (Hdmg)₂ < [(do)(Hdo)pn]. Therefore complexes **2** exhibit the shortest distances and the highest ν_{Co–Me} frequencies, *i.e.* the strongest Co–Me bond, in the above series. Thus, the same order of Co–C bond strength is followed both in solution and in the solid state.

In order to give a quantitative rationalisation of the electronic and steric influences of the R groups on the electrochemical properties (*E*_{1/2}) for both complexes **2** and cobaloximes, a simple two component model was applied, by using eqn. (2):

$$E_{1/2} = a_0 + a_1 t_1 + a_2 t_2 \quad (2)$$

where *a_i* represents the contribution of *t_i*. The *t_i* values for each R group have been derived from the multicomponent analysis of several properties of a large number of alkylcobaloximes and interpreted to be a measure of the σ-donating ability (*t*₁) and the steric bulk (*t*₂) of R.¹⁷ Then *t*₁ and *t*₂ parameters were successfully applied to analyse the intraligand coupling constants in the alkylcobaloximes¹⁸ and the structural,

Table 4 a_i values for $n = 4$ complexes **2** (R = Cy, Et, Me, CH₂CF₃) and for $n = 5$ alkylcobaloximes (R = Cy, Et, Me, CH₂CF₃, *i*-Pr). Standard deviations in parentheses; r is the correlation factor

	a_0	a_1	a_2	r	n	a_1/a_2
Complexes 2	-1.246(26)	-0.151(16)	0.086(19)	0.994	4	-1.74
R cobaloximes	-1.196(12)	-0.061(3)	0.078(9)	0.995	5	-0.78

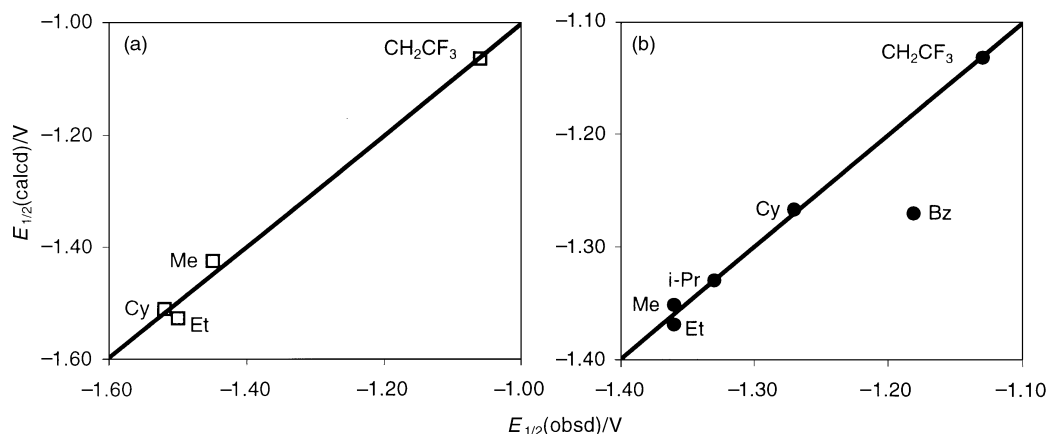


Fig. 4 (a) $E_{1/2}$ calculated vs. $E_{1/2}$ observed for the complexes **2**. (b) $E_{1/2}$ calculated vs. $E_{1/2}$ observed for the alkylcobaloximes.

spectroscopic and kinetic properties of alkylrhodoximes R–Rh–(Hdmg)₂L.¹⁹ For the R–complexes for which both the $E_{1/2}$ values and the R group t_i parameters are available the a_0 , a_1 and a_2 coefficients can be calculated using eqn. (2) (Table 4).

The t_i parameters are available for the following five R groups: Me, Et, *i*-Pr, Cy, CH₂CF₃.¹⁷ The opposite sign of a_1 and a_2 indicates that the electronic and steric factors have an opposite influence. Furthermore, the ratio a_1/a_2 of -1.74 in complexes **2** is about twice that of -0.78 in alkylcobaloximes. This indicates a larger contribution of the electronic factor with respect to the steric one in the complexes **2**. In the alkylcobaloximes series the steric factor becomes more important, in accordance with the observed deviation from linearity in the graph of $E_{1/2}$ vs. σ^* for complexes with bulky alkyl groups.

A correlation plot of $E_{1/2}$ (calcd.) vs. $E_{1/2}$ (exp.) for compounds **2** is reported in Fig. 4a. A satisfactory correlation plot may also be obtained for alkylcobaloximes with various R groups having different steric and electronic properties, if the benzyl derivative is excluded (Fig. 4b).

In fact when this complex was included a poor correlation was found ($r = 0.880$). In this regard, it is useful to re-examine the previously reported attempts to correlate the $E_{1/2}$ values for the alkyl cobaloximes with the donor properties of the R group.^{12,13} (see also Fig. 3). Less negative values of $E_{1/2}$ than those expected on the basis of σ^* of the alkyl group (this is also the case of the benzyl derivative) have been generally associated with steric factors. This interpretation was confirmed on the basis of a t_1/t_2 treatment for the majority of the alkyl groups, but not for the benzyl group. Interestingly the anomalous behaviour of this group was observed to occur not only in the cobaloxime series but also in some other related alkyl cobalt complexes.^{13,14} Hence it appears that the Co–Bz bond presents some peculiar undefined features and this puzzling question needs further investigation. The anomalous tendency of this group to give mononuclear rather than binuclear complexes with the tridentate L ligand is also remarkable.

Experimental

Spectroscopy

FT-Raman spectra were recorded on a Perkin-Elmer SYSTEM 200 instrument equipped with an In Ga Sb detector and a quartz beam splitter. Spectra were collected in a backscattering geometry from samples contained in the standard Perkin-Elmer

Raman cells. Near-IR excitation was provided by the 1.064 μ m line of a Diode-Pumped Nd–YAG laser, with powers ranging from 50 to 200 mW. The ¹H NMR spectra were recorded on a Jeol EX-400 at 400 MHz from [d₆]dmsO solution with SiMe₄ as internal standard.

Electrochemistry

All the electrochemical measurements were made in dmf (Carlo Erba) that was freshly distilled under reduced Ar pressure or from a dmf–benzene–water mixture. Tetraethylammonium perchlorate (vacuum dried at 30 °C) was used as supporting electrolyte. Polarographic and CV measures were performed using an Amel 552 Potentiostat/Galvanostat connected with an Amel 568 function generator. All measurements were made at 25 ± 0.1 °C under Ar or N₂ atmosphere in a three electrode thermostatted cell. A dropping mercury electrode was used as the working electrode for polarography. For controlled potential reduction (CPR) a Hg pool of about 12 cm³, equipped with a magnetic stir bar, was used. The potentials were measured using a saturated aqueous NaCl–calomel electrode, contained in a glass tube separated from the solution by a glass frit of medium porosity. The latter was located 1 mm from the tip of the working electrode to minimise the ohmic drop, and filled with the supporting electrode solution. The counter electrode was a Pt ring or rod directly dipped in the solution in the case of polarography or CV, but in the case of CPR it was separated from the solution by a glass frit. The peak potentials and currents were evaluated after subtraction of background current with a self-made computer program.

Crystallography

Crystal data, experimental conditions and refinement data for **2c** and **2e** are listed in Table 5. An Enraf-Nonius CAD4 four-circle automated diffractometer with graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å) was employed to collect data. Reflections were collected in the range $4 < 2\theta < 56^\circ$ using the ω – 2θ scan technique. Corrections for Lorentz-polarisation and ψ -scan absorption were applied. The structures were solved by conventional Patterson and Fourier methods and refined by the least-squares method (on F^2). The H atoms were not refined, but included at calculated positions in the final refinement. The programs used are given in ref. 20.

CCDC reference numbers 157412 and 157413.

Table 5 Crystal data and structure refinement for **2c** and **2e**

	2c	2e ·1/3MeOH
Formula	C ₂₆ H ₃₃ ClCo ₂ F ₆ N ₆ O ₇	C _{34.33} H _{52.33} ClCo ₂ N ₆ O _{7.34}
<i>M</i>	808.89	819.85
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> /K	293(2)	293(2)
<i>a</i> /Å	21.026(3)	9.765(2)
<i>b</i> /Å	11.6760(10)	20.296(3)
<i>c</i> /Å	27.547(4)	19.717(4)
β /°	103.49(2)	97.14(2)
<i>U</i> /Å ³	6576.2(15)	3877.4(13)
<i>Z</i>	8	4
μ (Mo-K α)/mm ⁻¹	1.177	0.978
Reflections measured	8086	7021
Unique reflections	7921	6817
<i>R</i> (int)	0.0261	0.0695
Reflections with <i>I</i> \geq 2 σ (<i>I</i>)	4775	3198
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0456	0.0693
<i>wR</i> (<i>F</i> ²), all data	0.1216	0.1648

See <http://www.rsc.org/suppdata/dt/b1/b109282k/> for crystallographic data in CIF or other electronic format.

Syntheses

Complexes of the type [(μ -OH)(RCo^{III}L)₂]⁺ with R = CH₂CF₃ (**2c**), CH₂Cl (**2d**) and Cy (**2e**) and the complex RCo^{III}(L)(LR)⁺ with R = Cy (**3b**) were prepared by previously described procedures.^{4,5} All complexes were obtained in the form of perchlorate salts (yields 30–40%). **CAUTION:** Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should be handled only in small quantities.

Suitable crystals for X-ray analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in methanol.

[(μ -OH)(CH₂CF₃Co^{III}L)₂]₂ClO₄ **2c**. Found: C, 37.8; H, 4.0; N, 10.1. C₂₆H₃₃ClCo₂F₆N₆O₇ requires: C, 38.6; H, 4.11; N, 10.4%. ¹H NMR: δ 2.11 (s, 6H, CH₃C=NO), 2.36 (s, 6H, CH₃C=N), 3.20, 3.30 (m, 4H, CH₂Py), 3.40, 3.97 (m, 4H, CH₂N), 7.59, 7.67, 8.05, 9.10 (m, 8H, 2C₅H₄N).

[(μ -OH)(CH₂ClCo^{III}L)₂]₂ClO₄ **2d**. Found: C, 38.4; H, 4.35; N, 10.9. C₂₄H₃₃Cl₃Co₂N₆O₇ requires: C, 38.9; H, 4.48; N, 11.3%. ¹H NMR: δ 2.10 (s, 6H, CH₃C=NO), 2.33 (s, 6H, CH₃C=N), 3.24, 3.32 (m, 4H, CH₂py), 3.45, 3.85 (m, 4H, CH₂N), 4.51 (m, 2H, CH₂Cl), 6.74, 7.56, 8.02, 8.95 (m, 8H, 2C₅H₄N).

[(μ -OH)(CyCo^{III}L)₂]₂ClO₄ **2e**. Found: C, 49.7; H, 6.2; N, 10.5. C₃₄H₅₁ClCo₂N₆O₇ requires: C, 50.5; H, 6.35; N, 10.4%. ¹H NMR: δ 0.6–1.4 (m, 11H, C₆H₁₁ax), 1.99 (s, 6H, CH₃C=NO), 2.23 (s, 6H, CH₃C=N), 2.91, 3.14 (m, 4H, CH₂py), 3.56, 3.79 (m, 4H, CH₂N), 7.50, 7.56, 7.97, 8.98 (m, 8H, 2C₅H₄N).

CyCo^{III}(L)(L')ClO₄ **3b**. Found: C, 51.9; H, 6.8; N, 13.0. C₂₈H₄₄ClCoN₆O₅, requires: C, 52.6; H, 6.94; N, 13.1%. ¹H NMR: δ 0.6–1.5 (m, 11H, C₆H₅ax), 0.96, 1.21 (d, 6H, CH₃CH), 2.01 (s, 6H, CH₃C=NO), 2.27 (s, 6H, CH₃C=N), 2.6–3.4 (m, 2H, CH-CH₃), 3.84, 4.08 (m, 4H, CH₂py), 4.44, 4.74 (m, 4H, CH₂CN), 7.22, 7.25, 7.48, 7.56, 7.22, 8.00, 8.23, 8.62 (m, 8H, 2C₅H₄N).

[(μ -OH)(CD₃Co^{III}L)₂]₂ClO₄. Was prepared following the previously described method⁴ for complex **2a**, using CD₃I instead of CH₃I. ¹H NMR: δ 2.04 (s, 6H, CH₃C=NO), 2.23 (s, 6H, CH₃C=N), 3.17, 3.30, (m, 4H, CH₂py), 3.50–3.80 (m, 4H, CH₂N), 7.48, 7.56, 7.96, 8.85 (m, 8H, 2C₅H₄N).

[CyCo^{III}(Hdmg)₂]H₂O and [ClCH₂Co^{III}(Hdmg)₂]H₂O. Were prepared following the previously reported procedure.³

Acknowledgements

We thank Ministero della Ricerca Scientifica e Tecnologica (Roma) (PRIN 03185591) and Consiglio Nazionale delle Ricerche (CNR) for financial support.

References and notes

- L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L. G. Marzilli, *Chem. Soc. Rev.*, 1989, **18**, 225.
- N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev.*, 1985, **63**, 1 and references therein.
- B. D. Gupta and S. Roy, *Inorg. Chim. Acta*, 1988, **146**, 209 and references therein.
- R. Dreos, G. Tauzher, D. H. Trendafilova, G. Nardin and L. Randaccio, *Inorg. Chem.*, 1996, **35**, 2715.
- R. Dreos, E. Herlinger, G. Tauzher, S. Vuano, G. Nardin and L. Randaccio, *Organometallics*, 1998, **17**, 2367.
- S. Nie, L. G. Marzilli and N. Y. Yu, *J. Am. Chem. Soc.*, 1989, **111**, 9256.
- S. Dong, R. Padnakumar, R. Banerjee and T. G. Spiro, *J. Am. Chem. Soc.*, 1996, **118**, 9182.
- J. M. Pukett, Jr., M. B. Mitchell, S. Hirota and L. G. Marzilli, *Inorg. Chem.*, 1996, **35**, 4656.
- S. Nie, P. A. Marzilli, L. G. Marzilli and N. T. Yu, *J. Am. Chem. Soc.*, 1990, **112**, 6084.
- S. Hirota, S. M. Polson, J. M. Pukett, Jr., S. M. Moore, M. B. Mitchell and L. G. Marzilli, *Inorg. Chem.*, 1996, **35**, 5646.
- The different electrochemical behaviour of the CH₂Cl complex confirms that in this case the reduction path is different, so that its *E*_{1/2} value is not directly comparable with those of the other complexes.
- G. Costa, A. Puxeddu and C. Tavagnacco, *J. Organomet. Chem.*, 1985, **296**, 161.
- G. Costa, A. Puxeddu, C. Tavagnacco, G. Balducci and R. Kumar, *Gazz. Chim. Ital.*, 1986, **116**, 735.
- C. Tavagnacco, G. Balducci, G. Costa, K. Taschler and W. von Philipsborn, *Helv. Chim. Acta*, 1990, **73**, 1469.
- N. Bresciani-Pahor, L. Randaccio, E. Zangrando, M. F. Summers, J. H. Ramsden, Jr., P. A. Marzilli and L. G. Marzilli, *Organometallics*, 1985, **12**, 2086.
- N. Bresciani-Pahor, L. G. Marzilli, L. Randaccio, P. J. Toscano and E. Zangrando, *J. Chem. Soc., Chem. Commun.*, 1984, 1508.
- L. Randaccio, S. Geremia, E. Zangrando and C. Ebert, *Inorg. Chem.*, 1994, **33**, 4641.
- S. J. Moore, R. J. Lachicotte, S. T. Sullivan and L. G. Marzilli, *Inorg. Chem.*, 1999, **38**, 383.
- L. Randaccio, *Comments Inorg. Chem.*, 1999, **21**, 327 and references therein.
- (a) SHELXS-86, Program for Structure Solution: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (b) G. M. Sheldrick, SHELX-93, Program for Structure Refinement, Universität Göttingen, Germany, 1993.
- C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.