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Inorganica Chimica Acta 357 (2004) 177–184
Inorganica Chimica Acta
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Di-organocobalt complexes of macrocyclic ligands

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Received 13 June 2003; accepted 20 June 2003

Abstract

Three new di-metallorganic cobalt complexes of the type *trans*-$(Bz)_2Co(chel)$, where Bz is a benzyl group σ-bonded to cobalt atom and chel is an equatorial chelating system constituted by an amino-oximic ligand and its conjugated base, were synthesised. The protonated and the unprotonated ligands interact through an O–H···O bridge stabilising the entire structure. The complexes differ in the equatorial moiety which is derived from the following ligands: HLN-py = 3-[(2-pyridyl)ethylimino]-butan-2-one oxime), HLN-Ph = 3-[(2-phenyl)ethylimino]-butan-2-one oxime and the analogous HLN-PhCl = 3-[(2-chlorophenyl)ethylimino]-butan-2-one oxime. Two of these compounds, namely those derived from HLN-py and HLN-PhCl were structurally characterised by means X-ray diffractometry. Data reveal that each complex is characterised by the presence of two unusually long cobalt–carbon bonds which are 2.120(4) Å (mean value) in complex with HLN-py ligand and 2.119(4) Å (mean value) in complex with HLN-PhCl. These data are consistent with a strong mutual *trans*-influence exerted by one ligand on the other.

Keywords: Dialkyl; Cobalt; Complexes; Tridentate; Ligands

1. Introduction

Compounds with cobalt–carbon bonds have been known for many years [1]. The realisation that the porphyrin-like corrin ring was an important factor in the stabilisation of the cobalt–carbon bond led to the conviction that other organocobalt complexes could be prepared employing analogous tetradentate ligands. At present a number of organocobalt complexes are known [2–5] and a variety of ligands, such as dioximes [2], imino–oxime [6–9], polyamine [10,11] and Schiff bases derived from diamine and aldehydes [12,13] or chetones [14,15] have been shown to be effective in the stabilising the metal–carbon bond. Examples of di-organocobalt complexes of the type *trans*-RR′Co(chel), where chel is a tetradentate equatorial ring and R and R′ are a variety of identical or different-bonded alkyl or aryl groups, are fewer in number [16–19] and only one, namely $[(Me)_2Co(DO)(DOH)pn]^0$, has been structurally characterised [20]. It has been recognised that only a few number of ligands, namely (DO)(DOH)pn, tim and cr (Fig. 1) are capable to stabilise *trans* di-organocobalt complexes [21].

The specific properties (steric or electronic or both) conferring to the ligands this ability are difficult to be recognised. For instance cr and (DO)(DOH)pn ligands both give di-organocobalt complexes, despite of the significant differences in their structure and electronic properties (a less extensively conjugate electronic system is present in cr as compared to (DO)(DOH)pn). However the $Co(DH)_2$ complexes (DH = dimethyl glyoximate) closely related to the Co(DO)(DOH)pn complexes have been proved to give only mono-alkyl and not di-alkyl derivatives.

The most widely used method in the synthesis of di-organocobalt complexes is the reaction of Co(I) complexes with electrophiles [21] (Eqs. (1)–(4), Scheme 1). Scheme 1 shows that *trans* di-alkylcobalt complexes formation requires that nucleophilic intermediate

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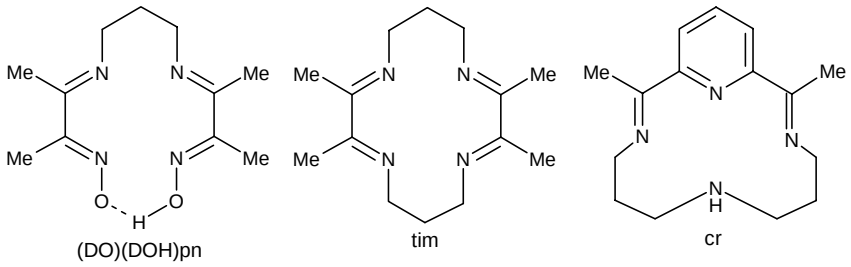
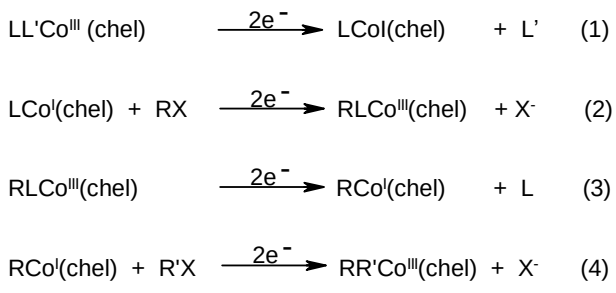
doi:10.1016/S0020-1693(03)00429-8



(DO)(DOH)pn = 3,3'-(trimethylene-diimino)bis(butan-2-oneoxime) monoanion
tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraaza-cyclotetradeca-1,3,8,10-tetra-ene
cr = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.11]-heptadeca-1-(17),2,11,13,15-pentaene

Fig. 1. Structure of chelating ligands that form di-organocobalt complexes.



Scheme 1.

species of the type RCo^{I}(chel) (Eq. (3)) can be produced from $RLCo^{III}$(chel) (Eq. (3)). These generally unstable intermediates are, in the majority of cases, generated in situ. However, in two case [17] they have been isolated in an oxygen-free atmosphere.

Electrochemical studies reveal that alkyl derivatives undergo two-electron and one-electron reduction at more negatives potential than those required for the reduction of the parents non-metallorganic complexes. In addition Co^{I} alkyl derivative resulting from the electrochemical reduction are generally short living species [23,24]. This could justify the exiguous number of di-alkylcobalt up to day synthesised, since conventional reducing agents such as $NaBH_4$ could be ineffective in promoting the two-electron reduction process $RLCo^{III}(chel) \rightarrow RCo^{I}(chel)$.

We are currently interested in the problems concerning the formation and the rupture of the cobalt–carbon bond. In the past years, on the basis of Eqs. (1) and (2) in Scheme 1, we prepared some series of stable mono-alkyl organocobalt complexes starting from non-metallorganic compounds containing tridentate amino-oximic and imino-oximic ligands (Fig. 2).

The results indicated that the above ligands are effective in the stabilising the cobalt–carbon bond in the same way as the better-known tetradentate ligands [25–30]. In the present work we show that, under appropriate experimental conditions, the above-mentioned tridentate ligands are capable to stabilise also di-alkylcobalt complexes.

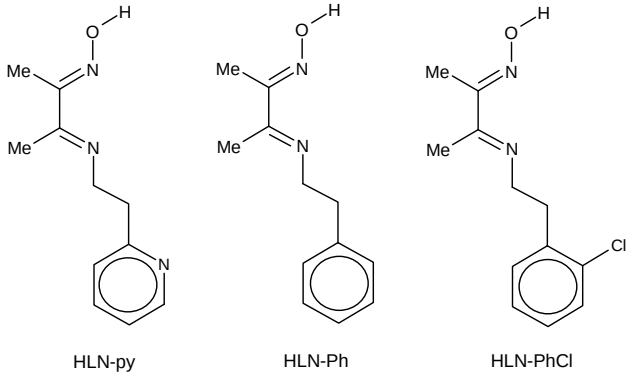


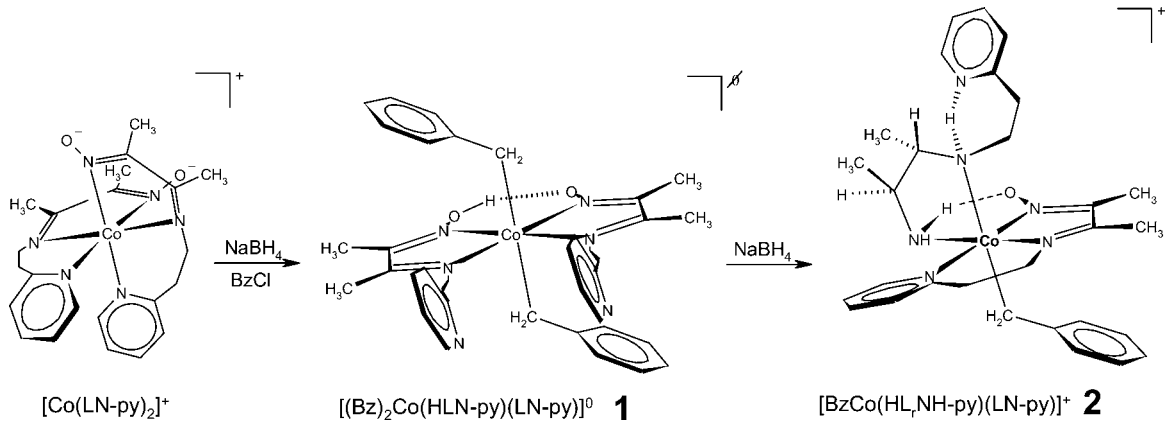
Fig. 2.

2. Results and discussion

2.1. Syntheses

In a preceding report we described the synthesis and structural characterisation of the new benzylcobalt complex $[BzCo^{III}(LN\text{-}py)(L_rNH\text{-}py)]ClO4$ (**2**) (L_rNH-py = 3-[(2-pyridyl) ethylamino]-butan-2-amino, HLN-py = 3-[(2-pyridyl)ethylimino]-butan-2-one oxime). Complex **2** (Scheme 2) was obtained directly from the non-metallorganic *mer*-$[Co^{III}(LN\text{-}py)_2]ClO_4$ complex (LN-py is the conjugated base derived from HLN-py) by reduction with $NaBH_4$ and successive addition of BzCl under nitrogen atmosphere. The process involves the oxidative addition of the benzyl halide to the in situ generated Co^{I} species. In addition a profound change in the nature and in configuration of the chelating system of the starting complex occurs. In fact one of tridentate imino/oximic ligand (HLN-py) undergoes reduction both at level of oximic function and imine function generating the di-amino ligand (L_rNH-py), which chelates Co in one axial and one equatorial position through its amino donors. The unchanged LN-py tridentate ligand co-ordinates Co in a *mer* configuration, whereas the σ-bonded benzyl group occupies the remaining axial position.

In the present work present we shown that, under slightly modified experimental conditions (see Section 4)



Scheme 2.

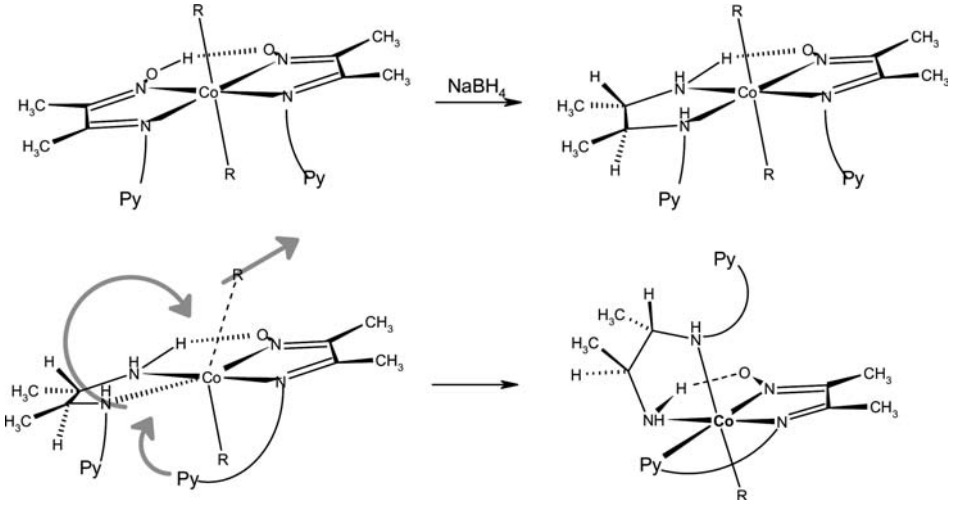
with respect to those above described [27], alkylation of the *mer*-$[Co^{III}(LN\text{-}py)_2]ClO_4$ complex gives the di-benzyl *fac*-$[(Bz)_2Co^{III}(HLN\text{-}py)(LN\text{-}py)]^0$ (**1**). The reaction involves the rearrangement of the amino-oximic ligands of the starting complex to form an equatorial chelating system stabilised by the presence of a O···H–O bridge. Complex **1** precipitated from the reaction mixture in a few minutes after the addition of the benzyl halide and was collected by filtration. By prolonging the reaction time, the product re-dissolved and a successive reaction takes place leading to a mono-benzyl derivative, which was identified, by means elemental analysis and ^1H NMR as complex **2** so far prepared and characterised [27]. This complex was also obtained by further reduction with $NaBH_4$ of a sample of the di-benzyl derivative **1** dissolved in methanol. Therefore complex **1** is intermediate in the synthesis of **2** from *mer*-$[Co^{III}(LN\text{-}py)_2]ClO_4$ as depicted in Scheme 2.

The conversion of di-benzyl derivative **1** to mono-benzyl derivative **2** involves not only the loss of a benzyl group from **2** but also the reduction of both the imino and oxime functions of one ligand to amino groups which chelates the cobalt atom trough its $-NH_2$ donors. A possible mechanism for this reaction is depicted in Scheme 3.

Reaction with MeI, instead of the expected di-methylcobalt complex gives the mono-methyl $[MeCo^{III}(LN\text{-}py)(L_rNH\text{-}py)]^+$ (**3**), homologous of **2**. On the analogy of that observed in the reaction with BzCl, it could be suggested that also the reaction with MeI involves a di-alkyl intermediate, which precedes the formation of **3** (Scheme 3). The failure in the obtaining the di-methyl derivative may be due to its intrinsic lability.

Attempts of synthesising other di-alkyl complexes in addition to the di-benzyl derivative using alkylating agents such as $ClCH_2I$, EtI and CF_3CH_2I, were unsuccessful.

Two other di-benzyl derivatives have been obtained using both the 3-[(2-phenyl)ethylimino]-butan-2-one oxime bidentate ligand (HLN-Ph) and the analogous 3-[(2-chlorophenyl)ethylimino]-butan-2-one oxime ligand (HLN-PhCl) in place of HLN-py. Reaction of these



Scheme 3.

ligands with $CoCl_2 \cdot 6H_2O$ gave only amorphous unidentified material instead of the expected non-metall-organic precursors of di-organocobalt complexes. However, a mixture of $CoCl_2 \cdot 6H_2O$ and of the appropriate ligand in a 1:2 ratio in methanol, under nitrogen atmosphere, treated with $NaBH_4$ and BzCl produced the di-benzyl derivatives $[(Bz)_2(HLN\text{-}PhCl)(LN\text{-}PhCl)]^0$ (**4**) and $[(Bz)_2(HLN\text{-}Ph)(LN\text{-}Ph)]^0$ (**5**), respectively. Suitable crystals for X-ray analysis were obtained in the case of complex **4**.

2.2. Structures of complexes *1*, *3* and *4*

If the orientation of the pendant aromatic moieties is excluded, the molecular structure of **1** and **4** are very similar as it appears from the comparison of their corresponding ORTEP drawings reported in Figs. 3 and 4, respectively.

Both molecules have an approximate C_2 symmetry, the twofold axis passing through the Co and the $O1 \cdots O2$ midpoint. The co-ordination geometries of Co in **1** and **4** differ only slightly, as shown in Table 1. The two *trans* Co–C bonds are equal within the experimental errors, averaging to 2.120(4) and 2.119(4) Å in **1** and **4**, respectively. They are significantly longer by about 0.07 Å than the Co–CH_2–Ph distances found in the mono-benzyl derivative [27] (2.044(5) Å), in $[Bz(H_2O)Co\{(DO)(DOH)pn\}]^+$ (2.052(2) Å) [5] and in $BzCo(DH)_2Py$ (2.056(3) Å) [3]. However, a value of 2.128(8) Å in a less accurate structure (refined with reflection parameters about **4**) of $BzCo(DH)_2$(pyrrolidine) was reported [31]. The lengthening of Co–C bond in di-alkyl derivatives with respect to mono-alkyl ones, was also observed for the Co–Me distances in $(Me)_2Co[(DO)(DOH)pn]$ (mean value 2.047 Å) [20] when compared with those

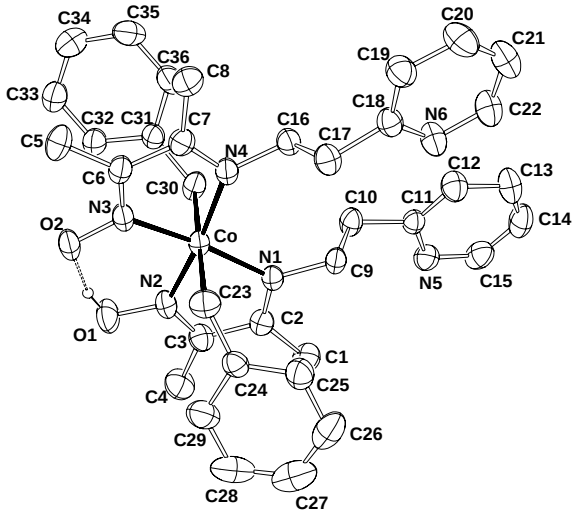


Fig. 3. An ORTEP view of the complex $Bz_2Co(HLN\text{-}py)(LN\text{-}py)$ (**1**) with the atom numbering scheme.

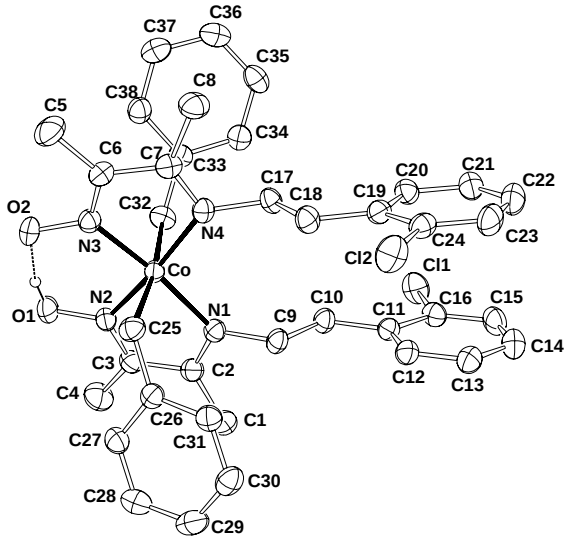


Fig. 4. An ORTEP view of the complex $Bz_2Co(HLN\text{-}PhCl)(LN\text{-}PhCl)$ (**4**) with the atom numbering scheme.

reported for some mono-methyl derivatives [3] $[MeLCo\{(DO)(DOH)pn\}]^+$ ($L = H_2O$, aniline, pyridine and 1-methylimidazole) which range from 1.991(4) to 2.003(3) Å. The lengthening observed in *trans* di-alkyl complexes can be attributed to the strong mutual *trans*-influence exerted by one alkyl group on the other. It is interesting to observe that the ideally tetrahedral Co–CH_2–Ph angle is significantly opened (Table 1) to relieve the steric interaction between the benzyl group and the equatorial moiety.

The four equatorial Co–N distances are very similar in **1** and **4** (Table 1). The two oximic Co–N_2 and Co–N_3 are short and the two iminic Co–N_1 and Co–N_4 are long, with differences of about 0.1 Å. The crystal of **3** are built up by $[MeCo(L_rNH\text{-}py)(LN\text{-}py)]^+$ cations, ClO_4^- anions and crystallisation water molecules, the latter in a ratio Co/H_2O of 1:2. The ORTEP drawing of the mono-methyl cation of **3** is given in Fig. 5 and its overall structure is similar to that found for the mono-benzyl analogue [27].

On the analogy of mono-benzyl derivative **2**, compound **3** can be considered as derived from a hypothetical di-methyl complex by loss of one methyl group and reduction of one tridentate imino-oximic ligand (HLN-py) to the di-amino ligand (LrNH-py). The LN-py tridentate ligand equatorially coordinates Co in a *mer* configuration, whereas the σ-bonded methyl group occupies the remaining axial position. The two L_rNH-py and LN-py ligands interact through a relatively strong H-bond of 2.755 Å between O_1 and N_3 (Fig. 5) which should be compared with that of 2.724(5) Å found in **2**. A part the different σ-bonded alkyl group, the only other significant difference between **3** and **2** lies in the uncoordinated pyridyl group of the L_rNH-py, which in **2** is anchored by an intramolecular H-bond of 2.915(5) Å

Table 1
Selected bond lengths and angles for complexes $Bz_2Co(HLN\text{-}py)(LN\text{-}py)$ (**1**), $BzCo(LN\text{-}py)(L_rNH\text{-}py)ClO_4$ (**2**), $MeCo(LN\text{-}py)(L_rNH\text{-}py)ClO_4$ (**3**) and $Bz_2Co(HLN\text{-}PhCl)(LN\text{-}PhCl)$ (**4**)

	1	4	3	2
$Co–C_{ax}$	2.124(4), 2.116(4)	2.119(4), 2.119(4)	1.998(8)	2.044(5)
$Co–N_1$	1.988(3)	1.966(3)	1.893(5)	1.909(4)
$Co–N_2$	1.875(3)	1.878(3)	1.904(5)	1.871(5)
$Co–N_3$	1.882(3)	1.877(3)	1.952(6)	1.961(4)
$Co–N_4$	1.977(3)	1.972(3)	2.032(5)	2.014(5)
$Co–N_5$			2.160(5)	2.135(4)
$C_{ax}–Co–C_{ax}$	178.7(2)	172.3(2)		
$Co–CH_2–Ph$	116.8(3), 114.6(3)	118.2(2), 118.5(2)		118.8(4)

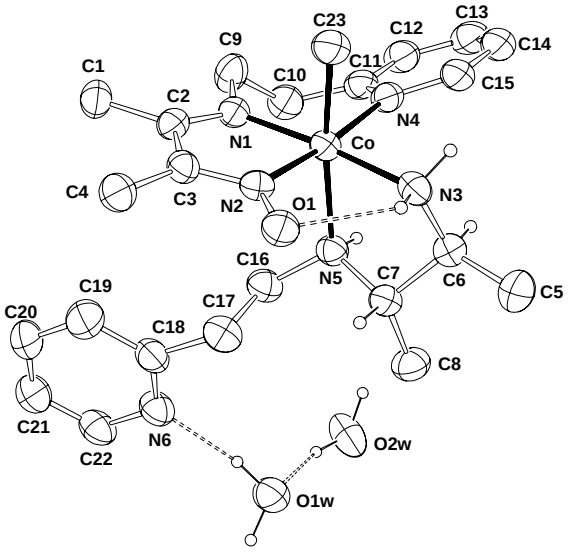


Fig. 5. An ORTEP view of the complex cation $[MeCo(LN\text{-}py)(L_rNH\text{-}py)]^+$ (**3**) with the atom numbering scheme.

between the pyridyl N atom and the axially co-ordinated amino group. In **3** the pyridyl N6 atom is not involved in the intramolecular H-bond, being H-bonded (2.825 Å) to the water molecule QW1.

The co-ordination distances are given in Table 1, where are compared with those found in **2**. Chemically equivalent distances are similar, whereas, as expected, the Co–C bond in **3** is shorter than in **2**, by about 0.05 Å as a consequence of the bulk of the methyl group smaller than that of the benzyl one. However, it falls in the range of other Co–Me distances [5]. As compared to the Co–N distances, the axial $Co–N_5$ distance in both **2** and **3** is lengthened because of the strong *trans* influence of the alkyl group as compared to the $Co–N_3$ one.

3. Concluding remarks

There are not evidences for the occurrence of di-alkyl corrinoids. However it has been observed that the reaction of (Co^I) B_{12s} with methyl iodide produces, in addition to methylcobalamin (methylcobalamin β) a small amount of the so-called methylcobalamin α, a diastereoisomer in which the methyl group replaces the 3,5-dimethyl benzimidazole in the "lower" position and water occupies the "upper" axial position [22]. Later, several other alkylcobalamins with more complicate alkyl group have been characterised both in α and in β form and facile α/β diastereomerism has been demonstrated to occur in several cases [32,33]. However evidence for di-alkyl cobaloximes has not been reported. On the other hand, since both the axial co-ordination positions can be alkylated, it is logical to ask whether B_{12} di-alkyl derivatives can exist [34]. The occurrence of synthetic di-alkyl cobalt compounds may led one to believe that analogous derivatives may be formed also in the case of vitamin B_{12}. Data of the present work support indirect evidence for a di-methyl unstable cobalt complex. This would lead to the speculation that, even in absence of any direct evidence for di-alkylcobaloximes, these species might exist, at least as short-living species.

4. Experimental

4.1. Instruments and materials

^1H NMR spectra were recorded with a JEOL EX-400 at 400 MHz from DMSO-d_6 or $CDCl_3$ solutions. Commercially available chemicals were purchased from Aldrich and used without further purification.

4.2. Syntheses

Caution. Some complexes have been isolated as perchlorate salts. Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should be handled in small quantities.

4.2.1. Preparation of $Bz_2Co(HLN\text{-}py)(LN\text{-}py)$ (**1**)

To a suspension of $[Co(LN\text{-}py)_2]ClO_4$ [35] (1 g, 1.75 mmol) in 20 ml of 96% EtOH, a drop of a $PdCl_2$ solution (prepared by addition of concentrated HCl to 1 g of

$PdCl_2$ in 20 ml of water) and some glass splinters were added. The reaction vessel was placed in an ice bath. Under nitrogen atmosphere and vigorous magnetic stirring, $NaBH_4$ (0.8 g, 21 mmol) dissolved in the minimum volume of water was added, followed by 2 ml of BzCl (17.4 mmol). The red–purple Bz_2Co(HLN-py)(LN-py) complex, which was formed, immediately precipitates. N.B.: The vigorous stirring of the reaction mixture in presence of glass fragments is necessary to induce the precipitation of the product from the over saturated solution. In absence of this care the monobenzyl complex **2** was formed (see synthesis 3.4.). The crude product was collected by filtration, washed many times with water and air-dried. Purification was made by dissolving it in a 1:1 (vol.) isopropyl ether/benzene mixture and then reducing the solution to 1/4 of the initial volume by a rotary evaporator (40 °C). The precipitate, which was formed, was filtered off and air-dried (0.30 g, yield 26%). Suitable crystals for X-ray analysis were obtained from a saturated solution of complex in pyridine after addition of isopropyl ether. *Anal.* Calcd. for $C_{36}H_{43}CoN_6O_2$: C, 66.4; H, 6.66; N, 12.9. Found: C, 66.1; H, 6.63; N, 12.7%. ^{1}H NMR (DMSO-d_6): δ 1.73 (6H, s, 2CH_3–CN–CH_2–); 1.98 (6H, s, 2CH_3–CNO); 3.10, 3.84 (8H, m, 2-CH_2–CH_2–); 3.86 (4H, d, 2CH_2–Co); 8.87 (10H, m, 2*Ph*-CH_2–Co); 7.05, 7.17, 7.54, 8.32 (8H, 2*Py*-CH_2–).

4.2.2. Preparation of $BzCo(LN\text{-}py)(L_rNH\text{-}py)ClO_4$ (**2**)

Method A. A synthetic method slightly differing from that below described has been previously reported and structure of the complex has been confirmed by X-ray analysis [27].

Method B. Complex **2** was formed as final product, by applying, the synthetic procedure for **1** (preparation 3.1.), but preventing the precipitation of **1**. If precipitate of **1** was formed it was allowed to re-dissolve to give **2**. The complex was identified from its ^{1}H NMR spectrum, which is identical to that of an authentic sample obtained by utilising Method A.

Method C. To a solution of Bz_2Co(HLN-py)(LN-py) (0.3 g, 0.46 mmol) in 50 ml of MeOH under nitrogen atmosphere and stirring, $NaBH_4$ (0.4 g, 10.5 mmol) dissolved in a minimum amount of water and a drop of $PdCl_2$ solution were added. After 30 min, the solvent was evaporated to dryness by rotary evaporator. The solid was dissolved in 10 ml of water and extracted twice with CH_2Cl_2. The organic phase was then concentrated, passed through a chromatographic column of allumine and eluted with CH_2Cl_2. Elute was treated drop wise with isopropyl ether until turbid and allowed to stand overnight. Red crystals, which were formed, were collected by filtration and air-dried (0.11 g, yield 38%). *Anal.* Calcd. for $C_{23}H_{36}CoN_6O_5Cl$: C, 48.4; H, 6.35; N, 14.7. Found: C, 48.0; H, 6.35; N, 14.8%. ^{1}H NMR (DMSO-d_6): δ 1.08 (3H, d, CH_3–CH–NH_2); 1.31 (3H, d, CH_3–CH–NH_2); 1.96 (3H, s, CH_3–CN–CH_2–); 2.50 (3H, s, CH_3–CNO); 2.20, 3.20 (10H, m, 2CH_2–CH_2–, 2C*H*–CH_3); 4.30, 4.74 (2H, dd, –NH_2); 5.27 (H, t, –NH–); 7.10 ÷ 8.81 (13H, 2*Py*-CH_2–, 2*Ph*-CH_2–).

4.2.3. Preparation of $MeCo(LN\text{-}py)(L_rNH\text{-}py)ClO_4$ (**3**)

To a suspension of $[Co(LN\text{-}py)_2]ClO_4$ (1 g, 1.75 mmol) in 20 ml of 96% EtOH, a drop of a $PdCl_2$ solution, previously prepared by addition of concentrated HCl to 1 g of $PdCl_2$ in 20 ml of water, and some glass splinters were added. The reaction vessel is placed in an ice bath. Under nitrogen atmosphere with vigorous magnetic stirring, $NaBH_4$ (0.8 g, 21 mmol), dissolved in the minimum volume of water was added followed by 1 ml of MeI (16.1 mmol). In contrast with that observed during the synthesis of **1** no precipitate was formed and the extraction with benzene does not furnished significant amount of product. To the aqueous phase a concentrated solution of $NaClO_4$ was added. Red brown crystals that were formed after a week were collected by filtration and air-dried (0.25g, yield 25%). Without any further purification the crystals were utilised for X-ray analysis. *Anal.* Calcd. for $C_{23}H_{36}CoN_6O_5Cl$: C, 48.4; H, 6.35; N, 14.7. Found: C, 48.0; H, 6.35; N, 14.8%. ^{1}H NMR (DMSO-d_6): δ 0.99 (3H, s, CH_3–Co); 1.07 (3H, d, CH_3–CH–NH–); 1.27 (3H, d, CH_3–CH–NH_2); 1.95 (3H, s, CH_3–CN–CH_2–); 2.34 (3H, s, CH_3–CNO); 2.41, 3.20 (10H, m, 2-CH_2–CH_2–, 2C*H*–CH_3); 4.41, 4.54 (2H, dd, –NH_2); 5.08 (H, t, –NH–); 7.22 ÷ 8.86 (8H, 2*Py*-CH_2–).

4.2.4. Preparation of $Bz_2Co(HLN\text{-}Ph)(LN\text{-}Ph)$ (**5**)

The starting non-organometallic complex could not been isolated. Therefore in the synthesis of di-benzyl derivative, a solution of HLN-Ph (1 g, 4.89 mmol) and $CoCl_2 \cdot 6H_2O$ (0.58 g, 2.44 mmol) in 20 ml of EtOH 96% were used. The reaction mixture was treated with $NaBH_4$ and BzCl under nitrogen and stirring. Reduction and alkylation procedures were performed as in synthesis of complex **1** (0.55 g, yield 45%). The desired complex precipitated from the reaction solution. The crude product was collected by filtration, washed many times with water and air-dried. Crystallisation was performed by addition of isopropyl ether to a saturated solution of the product in THF. Red crystals were formed allowing to stand the solution overnight. *Anal.* Calcd. for $C_{38}H_{45}CoN_4O_2$: C, 70.3; H, 6.99; N, 8.64. Found: C, 69.7; H, 7.27; N, 8.78%. ^{1}H NMR (DMSO-d_6): δ 1.73 (6H, s, 2CH_3–CN–CH_2–); 1.95 (6H, s, 2CH_3–CNO); 2.93, 3.04, 3.67, 4.06 (8H, m, 2CH_2–CH_2–); 6.44 (4H, d, 2CH_2–Co); 6.80, 7.30 (20H, 2*Ph*-CH_2–Co, 2*Ph*-CH_2–).

4.2.5. Preparation of $Bz_2Co(HLN\text{-}PhCl)(LN\text{-}PhCl)$ (**4**)

The synthetic route, and work-up followed in the above synthesis were followed also in this case. A

Table 2
Crystal data and structure refinement for **1**, **4** and **3**

	1	**4**	**3**
Formula	$C_{36}H_{43}CoN_6O_2$	$C_{38}H_{43}Cl_2CoN_4O_2$	$C_{23}H_{40}ClCoN_6O_7$
F_w	650.69	717.59	606.99
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, $P-1$	monoclinic, $P2_1/c$
a (Å)	7.603(3)	7.729(2)	14.176(3)
b (Å)	17.624(4)	12.415(2)	10.205(3)
c (Å)	24.889(5)	19.026(5)	20.325(5)
α (°)	90	87.48(2)	90
β (°)	98.13(2)	81.59(2)	98.71(3)
γ (°)	90	71.88(2)	90
V (Å^3)	3301.5(16)	1716.5(7)	2906.5(13)
Z, D_{calc} (Mg/m^3)	4, 1.309	2, 1.388	4, 1.387
ρ (mm^{-1})	0.561	0.696	0.733
Refinement method	full-matrix l.s. on F^2	full-matrix l.s. on F^2	full-matrix l.s. on F^2
Goodness-of-fit on F^2	1.014	1.029	1.070
R indices $[I > 2\sigma(I)]$[a]	$R1 = 0.0563$	$R1 = 0.0523$	$R1 = 0.0847$
	$wR2 = 0.1379$	$wR2 = 0.1395$	$wR2 = 0.2318$
R indices (all data)[a]	$R1 = 0.0985$	$R1 = 0.0699$	$R1 = 0.1181$
	$wR2 = 0.1611$	$wR2 = 0.1522$	$wR2 = 0.2710$

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o^2|^2]^{1/2}$.

solution of HLN-PhCl (1 g, 4.19 mmol) and $CoCl_2 \cdot 6H_2O$ (0.50 g, 2.09 mmol) in 20 ml of EtOH 96% (0.76 g, yield 51%) was used. Red crystals were obtained. *Anal.* Calcd for $C_{38}H_{43}Cl_2CoN_4O_2$: C, 63.6; H, 6.04; N, 7.81. Found: C, 61.6; H, 6.44; N, 7.61%. Complex was characterised by X-ray analysis.

4.2.6. Preparation of the ligand HLN-Ph

A suspension of diacethyl monoxime (8.1 g, 79.6 mmol) in 50 ml of isopropyl ether was heated to reflux with stirring. Phenyl ethylamine (10 ml, 79.6 mmol) was added drop wise and the heating is protract for 3 h. Then the solution was poured into a beaker and allowed to evaporate in air. To the concentrated solution (about 10 ml) *n*-pentane was added. The white precipitate that was formed was collected by filtration on sintered glass funnel and washed with pentane (13.8 g, yield 85%). *Anal.* Calcd. for $C_{12}H_{16}N_2O$: C, 70.5; H, 7.89; N, 13.7. Found: C, 70.2; H, 7.81; N, 13.6%. ^{1}H NMR ($CDCl_3$): δ 1.90 (3H, s, C*H*$_3$–CN–CH_2–); 2.10 (3H, d, CH_3–CNO); 3.00, 3.70 (4H, t, –CH_2–CH_2–); 7.15 ÷ 7.30 (5H, m, *Ph*-CH_2–).

4.2.7. Preparation of the ligand HLN-PhCl

The above-described method (preparation *3.6*) was followed also in this case using as reagents diacethyl monoxime (7.15 g, 70.7 mmol) and 2-(2-chloro phenyl) ethyl amine (10 ml, 70.7 mmol) (13.9 g, yield 82%). *Anal.* Calcd. for $C_{12}H_{15}N_2OCl$: C, 60.4; H, 6.33; N, 11.7. Found: C, 60.2; H, 6.10; N, 11.2%. ^{1}H NMR ($CDCl_3$): δ 1.93 (3H, s, C*H*$_3$–CN–CH_2–); 2.08 (3H, s, CH_3–CNO); 3.12, 3.71 (4H, t, –CH_2–CH_2–); 7.12 ÷ 7.37 (4H, m, Cl*Ph*–CH_2–).

4.3. X-ray crystallographic data collection and refinement of the structures

Red single needle-shaped crystals of **1**, dark red platelet of **4** and small red cubic crystals of **3** were grown as reported in Syntheses. X-ray diffraction data were collected with a Nonius DIP 1030 H system using graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Crystal data and details of structure refinement are given in Table 2.

For all the structures a total of 30 frames were collected, using XPRESS program [36], over a hemisphere of reciprocal space with rotation of 6° about the Φ-axis. A MAC Science Image Plate (diameter = 300 mm) was used and the crystal-to-plate distance was fixed at 90 mm. The determination of unit-cell parameters, integration of intensities and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite [37]. The structures were solved by direct method using SIR-92 [38] and Fourier methods and refined by the least-square method (on F^2) [39]. In the three structures, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. A suite of programs [40] was also used in the geometrical and final calculations.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 212108 (for **2**), 212109 (for **4**)

and 212110 (for **3**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to CNR (Rome) and MURST (Rome), PRIN No. MM03185591, for financial support.

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