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Evidence of the interaction between steric and electronic influence in rhodoximes and cobaloximes. Synthesis of pyRh(DH)$_2$I and X-ray structure of pyRh(DH)$_2$Cl, pyCo(DH)$_2$Cl and pyRh(DH)$_2$I

Silvano Geremia, Renata Dreos, Lucio Randaccio* and Giovanni Tauzher
Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste (Italy)

Luciano Antolini
Dipartimento di Chimica, Università di Modena, 41100 Modena (Italy)

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Abstract

The crystal structure of pyRh(DH)$_2$Cl (I) and pyCo(DH)$_2$Cl (II) are reported together with the synthesis and the crystal structure of pyRh(DH)$_2$I (III). **I**: RhClO$_4$N$_5$C$_{13}$H$_{19}$; $a = 7.5090(8)$, $b = 8.588(1)$, $c = 14.479(2)$ Å; $\alpha = 96.45(8)$, $\beta = 87.07(8)$, $\gamma = 76.12(9)$°; triclinic $P\bar{1}$; $Z = 2$; $R = 0.022$. **II**: CoClO$_4$N$_5$C$_{13}$H$_{19}$; $a = 14.738(2)$, $b = 8.606(1)$, $c = 13.369(2)$ Å; $\beta = 96.30(1)$°, monoclinic *Cc*; $Z = 4$; $R = 0.022$. **III**: IRhO$_4$N$_5$C$_{13}$H$_{19}$; $a = 8.875(1)$, $b = 14.741(2)$, $c = 14.163(3)$ Å, $\beta = 97.47(8)$°; monoclinic $P2_1/c$; $Z = 4$; $R = 0.031$. The Rh–py distance of 2.046(1) Å in **I**, compared to that of 2.079(3) Å in **III**, indicates that I is a slightly better *trans*-influencing ligand than Cl. The difference in the M–py distances when X = Cl and i-pr is 0.18 Å for M = Rh and 0.14 Å for M = Co. This result suggests that the interaction between steric and electronic factors is reduced in rhodoximes, owing to the larger size of Rh^{III}.

Key words. Crystal structures; Rhodium complexes; Cobalt complexes; Rhodoxime complexes; Cobaloxime complexes

Introduction

Cobaloximes, LCo(DH)$_2$X where L = neutral ligand, DH = monoanion of dimethylglyoxime and X = monoanionic ligand, have been widely studied in solution and in the solid state [1, 2], since then they have been proposed as a model of the vitamin B$_{12}$ system. These studies have furnished some foundation for understanding the mechanism of the Co–C bond cleavage in the vitamin B$_{12}$ coenzyme [3]. Notwithstanding, some problems are still waiting an answer, particularly those relative to the role played by the electronic and steric properties of the ligands about Co.

Therefore, recently we have extended [4] the study to the analogous Rh derivatives of cobaloximes, pyRh(DH)$_2$X, hereinafter called rhodoximes, where the steric factors are less important. In fact, preliminary results have confirmed that the increased size of Rh, with respect to Co, partially relieves the steric hindrance between the ligands around the metal centre, as shown by the variation of the M–C distances with the increase in bulk of the axial ligand, significantly smoother in Rh than in Co complexes [4]. This observation suggests that the R *trans*-influence and *trans*-effect should be relatively greater in rhodoximes. This is supported by the variation in log of rate constants for the pseudo first-order reaction of the py displacement. In fact, log*k* varied by 5.7 units in rhodoximes and by 5.0 units in cobaloximes, on going from R = CH$_2$CF$_3$ to R = i-pr. Correspondingly, the variation in the M–py distances was 0.06 Å in the latter complexes [1] and 0.09 Å in the former [4]. It should be expected that the above difference in M–py distances are even larger for a weak σ-donating group, such as Cl.

Although non-alkyl pyCo(DH)$_2$X complexes are well known, the analogous rhodoximes are scarcely documented, since to our knowledge, only the pyRh(DH)$_2$Cl compound (**I**) has been reported [5]. We report the structural characterization of **I** and of the analogous cobaloxime, pyCo(DH)$_2$Cl (**II**). Furthermore, in the course of the attempts to synthesize perfluoromethylrhodoximes, a crystalline sample of pyRh(DH)$_2$I (**III**) complex was obtained, when CF$_3$I and py were added to the Rh^{1} species, obtained by reduction of

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*Author to whom correspondence should be addressed

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$Cl_2Rh(DH)(DH_2)$. Since there are few examples about the *trans*-influencing order between halogens in this system, synthesis and structural characterization of $pyRh(DH)_2I$ are also reported.

Experimental

Synthesis

Formation of pyRh(DH)$_2$I

0.27 g (0.7 mmol) of $Cl_2Rh(DH)(DH_2)$ [6] were suspended in 120 ml of methanol containing 2 ml of pyridine and a solution of NaOH (one pellet in 10 ml) was added to dissolve the starting material. Then the unaerated solution was treated under nitrogen atmosphere with a stoichiometric amount of $NaBH_4$ dissolved in a minimum amount of water. The dark solution of the reduced complex was degassed and about 0.04 mol of the gaseous CF_3I was added to the reaction vessel. During the dissolution of the gaseous phase the solution was magnetically stirred and rapidly assumed an orange colour. The volume of the solution was reduced by a rotavapor to about 25 ml. Neutralization with 1 M $HClO_4$ led to the formation of an orange precipitate. 1 ml of pyridine and a few ml of water were added to the crude product, dissolved in acetone. By slow evaporation of the solvent the crystalline product was precipitated. It was collected by filtration and dried in the air.

Crystallographic data

Prismatic yellow $pyRh(DH)_2Cl$ (**I**), red–brown $pyCo(DH)_2Cl$ (**II**) and orange $pyRh(DH)_2I$ (**III**) crystals were selected for X-ray analysis and sealed on a glass fiber. All intensity data were collected on a CAD4 Enraf-Nonius single crystal diffractometer by the $\omega/2\theta$ scan technique. The intensities were corrected for Lorentz and polarization factors. An empirical absorption correction, based on ψ scan and secondary extinction were applied to the data. Crystal data are reported in Table 1.

Solution and refinement of the structures

The structures were solved by conventional Patterson and Fourier methods and refined through full-matrix least-squares methods. The difference Fourier map of structure **III** showed a residual peak, with a height of about 2 electrons/Å^3, located in the centre of the pyridine ligand at 2.7 Å from the Rh atom On the basis of the electron density map, this peak was attributed to an iodine atom (IB) with an occupancy factor of 0.03. Therefore the occupancy factor of I was assumed to be 0.97. All non-hydrogen atoms were treated anisotropically, and IB isotropically. In all three structures, the hydrogen atoms, located on Δ Fourier maps, were added as fixed contributions at their observed positions (B values were 1.3 times the B_{eq} of the atom to which they are attached). Least-squares refinement led to the R factors reported in Table 1. The unitary weighting scheme gave satisfactory agreement analyses. Anomalous dispersion was applied. For structure **II**, the test for crystal chirality was carried out by using the en-

TABLE 1. Crystallographic data for $pyRh(DH)_2Cl$ (**I**), $pyCo(DH)_2Cl$ (**II**) and $pyRh(DH)_2I$ (**III**) All data collected at 18 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å)

	I	**II**	**III**
Formula	$RhClO_4N_5C_{13}H_{19}$	$CoClO_4N_5C_{13}H_{19}$	$IRhO_4N_5C_{13}H_{19}$
Formula weight	447.7	403.7	539.1
a (Å)	7.5090(8)	14.738(2)	8.875(1)
b (Å)	8.588(1)	8.606(1)	14.741(2)
c (Å)	14.479(2)	13.369(2)	14.163(3)
α (°)	86.45(8)		
β (°)	87.07(8)	96.30(1)	97.47(8)
γ (°)	76.12(9)		
V (Å^3)	904.1	1685.4	1837.2
Z	2	4	4
Space group	$P\bar{1}$(No.2)	Cc (No. 9)	$P2_1/n$ (No. 14)
D_{calc} (g cm^{-3})	1.64	1.59	1.95
D_{meas} (g cm^{-3})	1.65	1.60	1.95
μ (Mo Kα) (cm^{-1})	11.0	11.3	26.0
$2\theta_{max}$ (°)	64	56	60
No. measured reflections	6670	2016	5514
No. independent reflections ($I > 3\sigma(I)$)	5987	1877	3859
$R(F_o)$	0.022	0.022	0.031
$R_w(F_o)$	0.026	0.024	0.031

antiomeric structure. The resulting residuals, after least-squares refinement, were $R = 0.026$, $R_w(F_o) = 0.029$ suggesting that the previous assignment was correct

Atomic scattering factors, anomalous dispersion terms, and programmes were taken from the Enraf-Nonius Molen package. See also 'Supplementary material'.

Atomic parameters for **I–III** are given in Tables 2–4.

Results and discussion

The metal atom has a distorted octahedral coordination in all three complexes, as shown by the ORTEP drawings for non-hydrogen atoms of **I–III**, depicted in Figs. 1–3, together with the numbering scheme. The two DH units in **I–III** are essentially coplanar, making dihedral angles of less than 3°. A comparison of the M–py distances, which are 2.046(1) Å in **I** and 2.079(3) Å in **III**, suggests that I exerts a *trans*-influence slightly greater than that of Cl. A similar trend is derived for the Co series from the pK_a values of Cl and I aquo complexes, which are 6.30 and 7.40, respectively [7]. For the *trans*-effect, the tentative order I > Cl could be in agreement with the observation that when the [ClRh(DH)$_2$I]$^-$ complex is reacted with thiourea, Cl is displaced but not I [8]. Furthermore, very strong activation by iodine occurs in [ClRh(en)$_2$I]$^+$ and [BrRh(en)$_2$I]$^+$ as deduced from the rates of replacement of Cl$^-$ and Br$^-$ [9].

TABLE 2. Fractional atomic coordinates and isotropic equivalent displacement parameters with e.s.d.s in parentheses for pyRh(DH)$_2$Cl (**I**)

Atom	x/a	y/b	z/c	B^a (Å^2)
Rh	0.06231(2)	0.24616(1)	0.25144(1)	1.920(2)
Cl	−0.11142(6)	0.51027(5)	0.24280(3)	3.174(8)
O1	−0.2656(2)	0.1375(2)	0.3056(1)	3.81(3)
O2	0.3055(2)	0.3393(2)	0.3796(1)	3.82(3)
O3	0.3913(2)	0.3522(2)	0.1969(1)	3.50(3)
O4	−0.1914(2)	0.1686(2)	0.1225(1)	3.78(3)
N1	−0.1292(2)	0.1869(2)	0.3376(1)	2.63(2)
N2	0.1504(2)	0.2852(2)	0.3727(1)	2.64(2)
N3	0.2519(2)	0.3072(2)	0.1642(1)	2.55(2)
N4	−0.0304(2)	0.2133(2)	0.1300(1)	2.57(2)
N5	0.2177(2)	0.0151(2)	0.25725(9)	2.18(2)
C1	−0.2558(3)	0.1813(4)	0.4974(2)	4.98(5)
C2	−0.1142(3)	0.2070(2)	0.4255(1)	3.09(3)
C3	0.0503(3)	0.2621(2)	0.4456(1)	3.06(3)
C4	0.0984(4)	0.2879(3)	0.5416(2)	5.03(5)
C5	0.3657(4)	0.3301(4)	0.0031(2)	5.55(6)
C6	0.2310(3)	0.2944(2)	0.0765(1)	3.10(3)
C7	0.0648(3)	0.2431(2)	0.0569(1)	2.99(3)
C8	0.0073(4)	0.2292(3)	−0.0388(2)	4.91(5)
C9	0.4001(2)	−0.0161(2)	0.2697(1)	2.93(3)
C10	0.5092(3)	−0.1702(2)	0.2685(2)	3.52(4)
C11	0.4312(3)	−0.2965(2)	0.2544(2)	3.53(4)
C12	0.2438(3)	−0.2649(2)	0.2437(1)	3.13(3)
C13	0.1416(2)	−0.1093(2)	0.2455(1)	2.61(3)

^{a}Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}\Sigma_i\Sigma_j a_i a_j \beta(i,j)$.

TABLE 3 Fractional atomic coordinates^a and isotropic equivalent displacement parameters with e.s.d.s in parentheses for pyCo(DH)$_2$Cl (**II**)

Atom	x/a	y/b	z/c	B^b (Å^2)
Co	0.5	0.78384(3)	0.5	2.25(1)
Cl	0.37900(5)	0.68589(9)	0.40628(6)	3.60(3)
O1	0.4000(2)	0.7749(4)	0.6697(2)	4.4(1)
N1	0.4219(2)	0.8605(3)	0.5925(2)	2.91(8)
C1	0.3319(3)	1.0801(6)	0.6449(4)	5.7(2)
C2	0.3917(2)	0.9996(4)	0.5766(3)	3.5(1)
C3	0.4207(2)	1.0693(4)	0.4857(3)	3.3(1)
C4	0.3902(3)	1.2261(5)	0.4462(4)	5.4(2)
N2	0.4747(2)	0.9812(3)	0.4417(2)	2.78(8)
O2	0.5089(2)	1.0245(3)	0.3577(2)	3.94(9)
O3	0.5936(2)	0.7843(3)	0.3246(2)	4.4(1)
N3	0.5758(2)	0.7062(3)	0.4065(2)	3.38(9)
C5	0.6673(3)	0.4878(7)	0.3561(4)	7.1(2)
C6	0.6098(2)	0.5682(4)	0.4243(3)	4.2(1)
C7	0.5820(3)	0.4981(4)	0.5158(4)	4.6(1)
C8	0.6121(4)	0.3429(5)	0.5536(5)	7.0(2)
N4	0.5265(2)	0.5856(3)	0.5598(2)	3.6(1)
O4	0.4911(2)	0.5407(3)	0.6428(2)	5.2(1)
N5	0.6063(1)	0.8705(2)	0.5821(2)	2.31(7)
C9	0.6724(2)	0.9441(3)	0.5387(2)	2.73(9)
C10	0.7490(2)	1.0041(4)	0.5942(2)	3.3(1)
C11	0.7582(2)	0.9896(4)	0.6974(2)	3.4(1)
C12	0.6911(2)	0.9140(4)	0.7418(2)	3.1(1)
C13	0.6157(2)	0.8573(3)	0.6831(2)	2.73(9)

^{a}The origin of the unit cell was arbitrarily defined by assigning the value 0.5 to the x/a and z/a fractional coordinates of the Co atom. ^{b}Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}\Sigma_i\Sigma_j a_i a_j \beta(i,j)$.

The M–L axial distances for some rhodoximes and cobaloximes are compared in Table 5. The trend illustrates well the change in the mutual influence among the axial ligands, when the metal is varied. As expected, the increase in the *trans*-influence follows the order Cl < I < CH$_2$CF$_3$ < i-pr in both the Rh and Co series. However this increase is significantly more enhanced in rhodoximes, as shown by the difference of 0.18 Å between the Rh–py bond distances when X = Cl and X = i-pr, whereas it is 0.14 between the corresponding Co–py ones. Owing to the less steric interaction between X and the equatorial moiety in rhodoximes with respect to cobaloximes, a minor extralengthening of the M–X distances, due to the bulk of X, occurs in rhodoximes [4]. Therefore, a good σ donor and bulky ligand may exert in cobaloximes a *trans*-influence less than that in rhodoximes and, consequently, the difference in the *trans* metal–py bond when X = Cl and X = i-pr, is larger in rhodoximes than in cobaloximes.

TABLE 4. Fractional atomic coordinates and isotropic equivalent displacement parameters with esds in parentheses for pyRh(DH)$_2$I (**III**)

Atom	*x/a*	*y/b*	*z/c*	B^a (Å^2)
I	0.73872(3)	0.14891(2)	0.65187(2)	4.489(6)^b
Rh	0.99902(3)	0.14306(2)	0.76588(2)	3.133(5)
O1	0.8822(4)	0.0037(3)	0.8807(3)	5.90(8)
O2	1.1492(4)	0.1119(3)	0.5985(2)	5.52(8)
O3	1.1217(4)	0.2843(3)	0.6553(3)	5.54(8)
O4	0.8459(4)	0.1735(3)	0.9326(3)	5.76(9)
N1	0.9519(4)	0.0181(3)	0.8039(3)	4.31(8)
N2	1.0848(4)	0.0708(3)	0.6670(3)	4.04(7)
N3	1.0469(4)	0.2694(3)	0.7299(3)	4.13(8)
N4	0.9108(4)	0.2145(3)	0.8642(3)	4.25(8)
N5	1.2064(4)	0.1363(2)	0.8528(2)	3.51(6)
C1	0.9770(8)	−0.1443(4)	0.7784(7)	8.6(2)
C2	0.9976(5)	−0.0473(3)	0.7534(4)	4.9(1)
C3	1.0707(5)	−0.0168(3)	0.6724(4)	4.7(1)
C4	1.1199(7)	−0.0806(4)	0.6002(5)	7.1(1)
C5	1.0199(7)	0.4322(4)	0.7597(6)	7.5(2)
C6	0.9996(5)	0.3342(3)	0.7813(4)	4.8(1)
C7	0.9241(5)	0.3026(3)	0.8597(4)	4.8(1)
C8	0.8679(7)	0.3642(5)	0.9310(5)	7.9(2)
C9	1.3355(5)	0.1474(3)	0.8162(3)	4.09(9)
C10	1.4748(5)	0.1430(4)	0.8709(4)	4.6(1)
C11	1.4821(5)	0.1268(4)	0.9656(4)	5.3(1)
C12	1.3493(6)	0.1152(5)	1.0028(4)	6.8(2)
C13	1.2137(5)	0.1199(4)	0.9436(4)	5.4(1)
IB	1.280(1)	0.1406(7)	0.8862(7)	4.2(2)^c

^{a}Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as. $\frac{4}{3}\Sigma_i\Sigma_j a_i a_j \beta(i,j)$. ^{b}Occupancy factor = 0.97. ^{c}Isotropically refined with occupancy factor = 0.03.

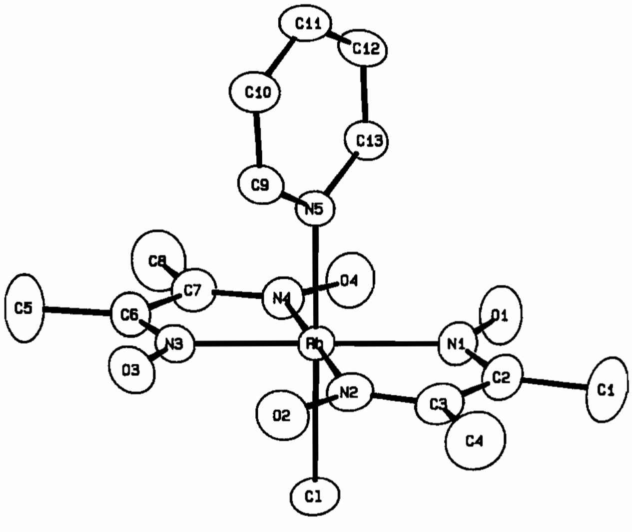

Fig. 1 ORTEP drawing (50% probability) with labelling scheme for non-hydrogen atom of **I**.

On the other hand, when the bulk of L increases, as in PPh$_3$Co(DH)$_2$X derivatives (Table 5) the steric *trans*-influence of L, which bends the DH units towards X, provokes a further lengthening of the Co–X bond [10]. As consequence, the *trans*-influencing ability of X decreases and the Co–L bond lengthening should be less enhanced. In fact, the difference between the Co–L distances in the Cl and i-pr derivatives is 0.08 Å when L = PPh$_3$ and 0.14 Å when L = py. Thus the

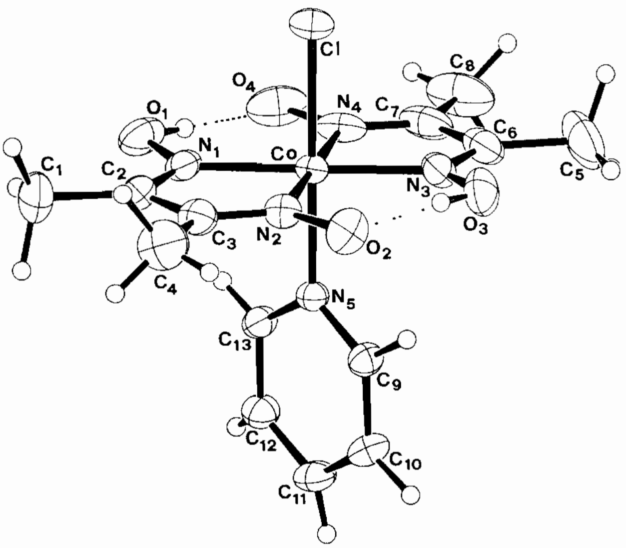

Fig. 2. ORTEP drawing (50% probability) with labelling scheme for non-hydrogen atom of **II**

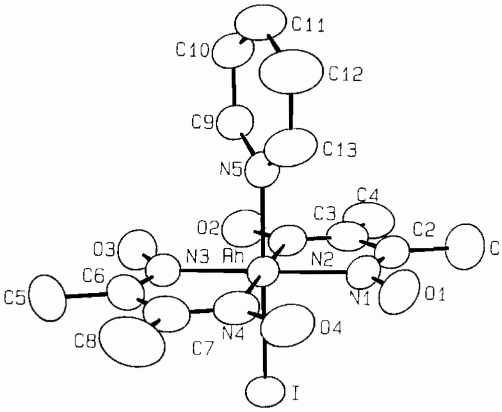

Fig. 3. ORTEP drawing (50% probability) with labelling scheme for non-hydrogen atom of **III**. Only the I atom in the highest occupancy is depicted.

TABLE 5. Axial bond lengths (Å) in **I**, **II** and **III** and in some related rhodoximes and cobaloximes

LM(DH)$_2$X	M–L	M–X
pyRh(DH)$_2$Cl (**I**)	2.046(1)	2.3290(4)
pyCo(DH)$_2$Cl (**II**)	1.959(2)	2.229(1)
pyRh(DH)$_2$I (**III**)	2.079(3)	2.6423(4)
PPh$_3$Rh(DH)$_2$Cl	2.327(1)	2.381(1)
PPh$_3$Co(DH)$_2$Cl	2.327(4)	2.277(4)
pyRh(DH)$_2$i-pr	2.230(4)	2.107(5)
pyCo(DH)$_2$i-pr	2.099(2)	2.085(3)

steric influence interacts significantly with the electronic *trans*-influence of X even more when L and X are bulky ligands.

It is worthwhile noting that in the chloro derivatives the Rh–P and Co–P distances have the same value (Table 5), in contrast to the corresponding Rh–py and Co–py ones which are 2.046(1) and 1.959(2) Å, respectively.

Supplementary material

Hydrogen atom coordinates, anisotropic thermal parameters, tables of the bond lengths and angles, and tables of observed and calculated structure factors are available from the authors on request.

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