

## Structural and Solution Properties of Rhodoximes: the Rh Analogues of Cobaloximes, a Vitamin B<sub>12</sub> Model\*

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Cobaloximes, LCo(DH)<sub>2</sub> where L = neutral ligand, DH = monoanion of dimethylglyoxime and X = monoanionic ligand, have been widely studied in solution and in the solid state. Since then, they have been proposed as a model of the vitamin B<sub>12</sub> system. These studies have furnished a foundation for understanding the mechanism of the Co-C bond cleavage in the vitamin B<sub>12</sub> coenzyme. However, problems relating to the role played by the electronic and steric properties of the ligands around Co require further investigation. Therefore, the study has been extended to the pyRh(DH)<sub>2</sub>R complexes (rhodoximes). In fact, the ionic radius of Rh, larger than that of Co, should diminish the steric interaction between the ligands. The NMR and kinetic results indicate that the transmission of the electronic effects from R to the *trans* neutral ligand in rhodoximes is similar to that observed in cobaloximes: the *trans*-influence and the *trans*-effect have the same trend as already found in the Co analogues. Structural data agree about a less hindered coordination around the metal centre than in the corresponding cobaloximes. Variation of the M-C distances with an increase in the bulk of axial ligand is significantly smoother in the Rh than in the Co complexes. Correspondingly, the *trans*-influence and -effect appear to be more enhanced in rhodoximes. Comparison between the behaviour of cobaloximes and rhodoximes is discussed on the basis of electronic and steric influences.

### INTRODUCTION

Cobaloximes, LCo(DH)<sub>2</sub>R where L = neutral ligand, DH = monoanion of dimethylglyoxime and R = alkyl group, are a well studied model of the vitamin B<sub>12</sub> coenzyme (Figure 1). Previous works<sup>1,2</sup> have furnished a large amount of data which have provided some indications of the relative roles played by steric and electronic effects in the homolytic cleavage of the Co-C bond in the B<sub>12</sub> system.<sup>3</sup> The availability of

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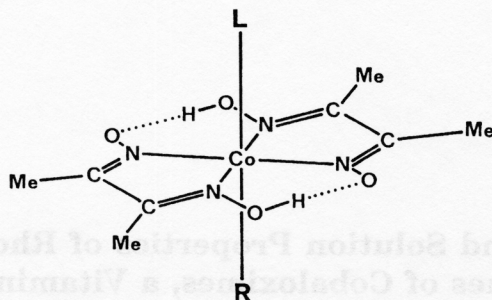


Figure 1. Scheme of a cobaloxime,  $LCo(DH)_2R$ . Rhodoximes have Rh instead of Co.

these data allowed us to rationalize the  $\sigma$ -donating ability of the R groups.<sup>4</sup> On the other hand, it was accepted that the Co–C bond is mainly influenced by the bulk of R, as indicated by the variation with R of the Co–C bond energies<sup>5</sup> and distances.<sup>2</sup> However, the interrelationships between steric and electronic factors were not completely clarified. In fact, recent results on fluoroalkylcobaloximes have suggested that the Co–C bond shortens with the decrease of the donating ability of R.<sup>6</sup>

Therefore, the study has been recently extended to the analogous Rh derivatives of cobaloximes,  $pyRh(DH)_2X$ , hereinafter called rhodoximes, where the steric factor are expected to be less important,<sup>7</sup> since the increased size of Rh, with respect to Co, relieves partially the steric hindrance between the ligands around the metal centre. In fact, the variation of the M–C distances with an increase in the bulk of axial ligand, is significantly smoother in Rh than in the Co complexes.<sup>7</sup> This observation suggests that, since the lengthening of the Rh–C distance is smaller than that of the Co–C one for a given R group, the *trans*-influence and *trans*-effect of the latter should be relatively larger in the Rh derivatives.

## RESULTS AND DISCUSSION

The synthesis, crystallographic characterization, solution NMR and kinetic measurements for the  $pyRh(DH)_2R$  complexes (alkylrhodoximes) with R = Cl, I,  $CH_2CF_3$ ,  $CH_2Cl$ , Me, Et, *n*-pr and *i*-pr are reported in Refs. 7 and 8.

### Solution Properties

The log  $k$  values refer to the pseudo-first order reaction for the displacement of py and 4-CN-py in both Rh and Co complexes and are reported in Table I.  $^{13}C$  chemical shifts,  $\delta$ , are those for the py *para* carbon atom. The differences with respect to the methyl derivate in each series of complexes are given in the Table I.

Kinetic results indicate that there is a significant *trans*-effect in both series of complexes, the stabilizing ability of the R ligand increasing with the increase of its electron-donating ability. However, the *trans*-effect appears to be more enhanced in rhodoximes. This is supported by the variation in log  $k$  in the two series, which is

TABLE I

Values of  $\log k$  for  $(4\text{-CN-py})\text{Co}(\text{DH})_2\text{R}$  and  $\text{pyCo}(\text{DH})_2\text{R}$ , differences in chemical shifts,  $\delta_{\text{Me}} - \delta_{\text{R}}$ , for *py* para carbons in  $\text{pyM}(\text{DH})_2\text{R}$ , for  $M = \text{Rh}$  and  $\text{Co}$ . Data are from Ref. 2 and 7.

R	$\log k$ (Co)	$\log k$ (Rh)	$\delta_{\text{Me}} - \delta_{\text{R}}$ (Rh)	$\delta_{\text{Me}} - \delta_{\text{R}}$ (Co)
$\text{CH}_2\text{CF}_3$	-3.57	-4.87	-0.63	-0.53
$\text{CH}_2\text{Cl}$	-2.51	-3.11	-0.49	-0.38
Me	-1.39	-1.48	0	0
Et	-0.02	-0.24	0.13	0.16
<i>n</i> -Pr	0.08	-0.27	0.13	0.18
<i>i</i> -Pr	1.43	0.80	0.23	0.31

5.7 in rhodoximes and 5.0 units in cobaloximes, going from  $\text{R} = \text{CH}_2\text{CF}_3$  to  $\text{R} = i\text{-pr}$  (Table I). Analogous variations are observed in the M-py distances (see below).

Both in rhodoximes and cobaloximes, the progressive deshielding of the *para* py carbons is associated with the decrease of the electron-donating ability of R. Since this behaviour indicates a diminution of the electron density at the *para* position, for cobaloximes, the difference in chemical shifts  $\delta_{\text{Me}} - \delta_{\text{R}}$ , has been assumed as a measure of the electron-donating ability of R.<sup>9</sup> When these differences in rhodoximes are plotted against those in cobaloximes (Table I), a good linear relationship, with the slope close to unity and correlation coefficient  $r = 0.994$ , is obtained. This indicates that the transmission of the electronic charge between the axial ligands through the metal centre in rhodoximes is modulated by the electron-donating ability of R, in a way similar to that of cobaloximes.

### Structural Properties

The rhodium atom has a distorted octahedral geometry (Figure 1). The two chemically equivalent halves of the equatorial ligand are approximately planar and the values of  $\alpha$ , the dihedral angle between their mean planes, is reported in Table II together with those of  $d$ , the displacement of the Rh atom out of the mean plane passing through the four equatorial N-donor atoms. It is assumed<sup>1,2</sup> that bending towards the alkyl group and displacements towards the neutral ligand are denoted by positive values of  $\alpha$  and  $d$ , respectively. The mean values of bond lengths and of the equatorial moiety for rhodoximes are reported in Figure 2 and compared with those of the cobaloximes. Besides the expected variations due to the different size of the metal centres, *i.e.* in the M-N (equatorial) and the O · · O oxime bridge distances, and in the bond angles,<sup>7</sup> a comparison of the equatorial moieties reveals an interesting dissimilarity between alkylrhodoximes and alkylcobaloximes. The averages over some hundred measurements of each bond length and angle of the cobaloximes equatorial moiety showed an approximate  $D_{2h}$  symmetry.<sup>1</sup> The average values over all the available Rh complexes indicate that the approximate symmetry is lowered to  $C_{2h}$  (Figure 2). The increase of the O · · O distance, 2.49 Å in cobaloximes and 2.67 Å in rhodoximes, is accompanied by a significant difference in the N-O distances. The longer N-O distance is that involving the O bearing the H atom (Figure 2). An analo-

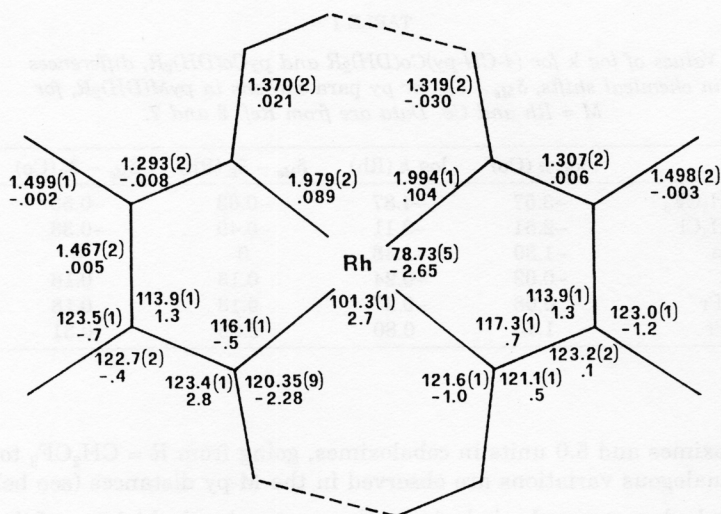


Figure 2. Mean values of the chemically equivalent bond lengths/Å and angles/° for the Rh(DH)<sub>2</sub> moiety. E.s.d.'s are given in parentheses. Differences from the mean values found in cobaloximes are given below each figure.

gous effect, observed in the enol form of the  $\beta$ -diketones, was attributed to the different hydrogen bond force.<sup>10</sup>

The axial bond lengths are listed in Table II. As expected, the Rh–C distances increase with the increasing bulk of R. However, a comparison with the analogous alkylcobaloximes shows that the increase is less enhanced than that observed for the Co–R distances. The slope 0.56 in the linear regression plot (correlation coefficient  $r = 0.98$ ) of the Rh–C distances *versus* the Co–C distances (Table II) confirms that the variation in metal-carbon bond length is smoother for Rh than for Co.

As already observed for cobaloximes,<sup>1,2</sup> the Rh–py distances are influenced mainly by the  $\sigma$ -donating power of the *trans* R group, ranging from 2.144(3) Å when R = CH<sub>2</sub>CF<sub>3</sub> to 2.230(4) Å when R = *i*-pr. Thus, the trend of *trans*-influence follows the trend of *trans*-effect. This distance is even shorter for non-alkyl derivatives being 2.045(1) for R = Cl and 2.079(3) Å for R = I. This result suggests that I is *trans*-influencing the ligand better than Cl. Furthermore, the M–N (axial) bond distance longer in rhodoximes than in cobaloximes is in agreement with the trend suggested for the torsional barrier around the M–py bond, Rh < Co.<sup>11</sup>

Another interesting observation concerning the metal–py distances appears to be due to the change in the mutual influence between the axial ligands, when the metal is varied. As expected, the increase in the *trans*-influence follows the order Cl < CH<sub>2</sub>CF<sub>3</sub> < Me < Et < *i*-pr both in the Rh and the Co series. However, this increase is significantly more enhanced in rhodoximes, as shown by the difference of 0.18 Å between the Rh–py distances when R = Cl and R = *i*-pr, whereas it is 0.14 between the corresponding Co–py distances (Table II). Owing to the less steric interaction be-

TABLE II

Bond lengths / Å of the axial fragment, *py-M-R*, in rhodoximes (*M* = Rh) and the corresponding values for the analogous cobaloximes (*M* = Co). Displacement of the four *N* equatorial donors, *d* / Å, and the bending angles,  $\alpha$  / ° are also reported.

R	M-N	M-C	<i>d</i>	$\alpha$
M = Rh <sup>a</sup>				
Cl	2.046(1)	—	+0.02	+3.2
I	2.079(3)	—	0.00	+1.0
CH <sub>2</sub> CF <sub>3</sub> <sup>b</sup>	2.145(3)	2.059(5)	0.00	-3.2
CH <sub>2</sub> Cl	2.178(3)	2.069(5)	+0.02	+1.1
Me	2.220(3)	2.063(5)	+0.08	+10.8
Et <sup>b</sup>	2.219(2)	2.079(2)	+0.07	+13.0
<i>i</i> -Pr	2.230(4)	2.107(5)	+0.02	+4.3
M = Co <sup>c</sup>				
Cl	1.959(2)	—	0.00	+0.9
CH <sub>2</sub> CF <sub>3</sub>	2.041(2)	2.010(3)	+0.01	+1.0
Me	2.068(3)	1.998(5)	+0.04	+3.2
Et <sup>d</sup>	2.081(3)	2.035(5)	+0.05	+9.1
<i>i</i> -Pr	2.099(2)	2.085(5)	+0.02	+4.0

<sup>a</sup> Refs 7 and 8. <sup>b</sup> Mean values. <sup>c</sup> Ref. 2.

<sup>d</sup> The structural data refer to L = 4N(H)=C(OMe)-py.

tween R and the equatorial moiety in rhodoximes with respect to cobaloximes (see above), a relatively minor lengthening of the M-R distances, due to the bulk of R, occurs in rhodoximes. Therefore, a good  $\sigma$  donor, but bulky R ligand, may in cobaloximes exert a *trans*-influence less than that in rhodoximes, and, consequently, the difference in *trans* metal-py bond, when R = Cl and R = *i*-pr, should be expected larger in rhodoximes than in cobaloximes.

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## REFERENCES

1. N. Bresciani Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers, and P. J. Toscano, *Coord. Chem. Rev.* **6** (1985) 1.
2. L. Randaccio, N. Bresciani Pahor, E. Zangrando, and L. G. Marzilli, *Chem. Soc. Rev.* **18** (1989) 225.
3. S. H. Kim, L. H. Chen, N. Feilchenfeld, and J. Halpern, *J. Am. Chem. Soc.* **110** (1988) 3120; B. P. Hay and R. G. Finke, *J. Am. Chem. Soc.* **109** (1987) 8012; J. M. Pratt, in: H. Sigel and A. Sigel (Eds.) *Metal Ions in Biological Systems*, Vol. 29, Marcel Dekker Inc., New York 1993, p. 229; B. T. Golding, *J. R. Neth. Chem. Soc.* **106** (1987) 342; L. G. Marzilli, in: J. Reedijk (Ed.) *Bioinorganic catalysis*, M. Dekker Inc., 1993, p. 227.
4. N. Bresciani Pahor, S. Geremia, C. Lopez, L. Randaccio, and E. Zangrando, *Inorg. Chem.* **29** (1990) 1043.
5. J. Halpern, *Science* **227** (1985) 869.

6. S. Geremia, L. Randaccio, and E. Zangrando, *Gazz. Chim. Ital.* **122** (1992) 229.
7. L. Randaccio, S. Geremia, R. Dreos Garlatti, G. Tauzher, F. Asaro, and G. Pellizer, *Inorg. Chim. Acta* **194** (1992) 1; L. Randaccio, S. Geremia, R. Dreos Garlatti, G. Tauzher, and E. Zangrando, *Inorg. Chem.* **29** (1990) 3437.
8. S. Geremia, R. Dreos, L. Randaccio, G. Tauzher, and L. Antonini *Inorg. Chim. Acta*, **216** (1994)125.
9. N. Bresciani Pahor, S. Geremia, C. Lopez, L. Randaccio, and E. Zangrando, *Inorg. Chem.* **29** (1990) 1043.
10. G. Gilli, F. Bellucci, V. Ferretti, and V. Bertolasi, *J. Am. Chem. Soc.* **111** (1989) 1023.
11. J. Huet and A. Gaudemer, *Org. Magn. Reson.* **15** (1981) 347.

## SAŽETAK

### Rodoksimi, Rh spojevi analogni kobaloksimima – model za vitamin B<sub>12</sub>

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Od kako su kobaloksimi, LCo(DH)<sub>2</sub>X (L = neutralni ligand, DH = monoanion dimetilglioksima, a X = monoanionski ligand), predloženi kao model za vitamin B<sub>12</sub>, oni se opširno istražuju i u otopini i u čvrstom stanju. Ta su istraživanja stvorila određene temelje za razumijevanje cijepanja veze Co–C u koenzimu vitamina B<sub>12</sub>. No, potrebna su daljnja istraživanja da se objasni uloga elektronskih i steričkih svojstava liganada što okružuju atom Co. Istraživanja su stoga proširena i na komplekse tipa pyRh(DH)<sub>2</sub>R (rodoksime). Ionski je radius Rh veći od radiusa Co, što bi trebalo smanjiti steričku interakciju među ligandima. NMR i kinetički rezultati upućuju na to da je prijenos elektronskih učinaka sa R na neutralni ligand u *trans*-položaju u rodoksimima sličan onom u kobaloksimima: *trans*-utjecaj i *trans*-efekt imaju istu tendenciju kakva je već nađena kod Co analoga, dok je koordinacija oko središnjeg atoma manje ometana nego u odgovarajućim kobaloksimima. Promjena razmaka M–C porastom obujma aksijalnog liganda znatno je ravnomjernija u kompleksima Rh nego kompleksima Co. Suglasno tome, *trans*-utjecaj i *trans*-efekt jače su izraženi kod rodoksima.