Comparison of the Coordination Distances Derived by Extended X-ray Absorption Fine Structure and X-ray Crystallography in a Vitamin B_{12} Model

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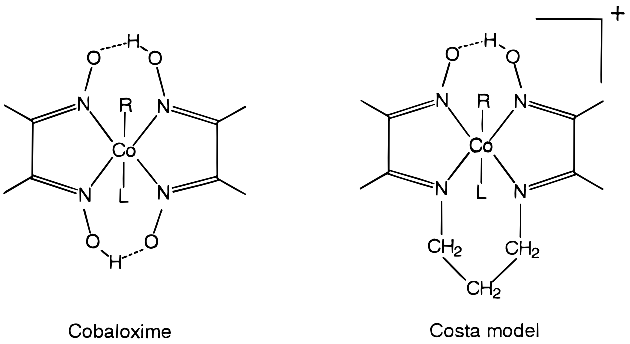
*Summary: The X-ray structures of the vitamin B_{12} models $RCo[(DO)(DOH)pn](H_2O)PF_6$, with $R = CH_2CF_3$ (**1**), CH_2COOMe (**2**), are reported, and the Co−C and Co−O axial distances, determined by XRD and EXAFS, are compared for several R ligands. The XRD distances contradict the previous values determined by EXAFS and lead to a different chemical interpretation of their trends when the alkyl group is varied.*

Crystallographic studies of the vitamin B_{12} models $RCo^{III}(chel)L$,[1] with a large variety of R = alkyl, L = Lewis base, and chel = $(DH)_2$ (cobaloximes) and (DO)(DOH)pn (Costa models)[2] (Chart 1), have provided a large amount of structural data.[1,3] The analysis of these data has allowed a rationalization of the metric features of the R−Co−L fragment, in terms of the electronic and steric properties of the R and L ligands.[4−6] The influence of R is evidenced by a lengthening of the Co−L bond, up to 0.15 Å, with an increase in the σ-donating ability of R, and by a lengthening of the Co−C bond, up to 0.20 Å, with an increase in the bulkiness and σ-donating ability of R.[4b]

Recently, a solid-state EXAFS study of the complexes $RCo[(DO)(DOH)pn](H_2O)(ClO_4)$, with different R groups, has been reported.[7] Surprisingly, the Co−C distances were found to increase in the order i-Pr ≤ i-Bu < CH_2Ph ≈ Me < CH_2COOMe < CH_2CF_3 and the Co−O distances in the order CH_2Ph < Me < i-Pr ≈ i-Bu < CH_2COOMe ≤ CH_2CF_3. These authors pointed out that the Co−C distances lengthen with a decrease in the R σ-donating ability, in contrast with the trends reported for cobaloxime and Costa model complexes containing different L ligands[1,6] and with the crystallographic data available for the aquo Costa models, with R = Me, Et, CH_2Ph, i-Pr.[8]

Chart 1



Cobaloxime Costa model

In order to shed light upon these controversial results, we have determined the X-ray crystal structure of two members of the series $RCo[(DO)(DOH)pn](H_2O)(PF_6)$, with $R = CH_2CF_3$ (**1**), CH_2COOMe (**2**). We aimed also to further contribute to the question whether the coordination geometry in octahedral Co complexes, derived from EXAFS measurements, is accurate enough to analyze trends in strictly related complexes. In fact, structural data of some cobalamins,[9] obtained by EXAFS measurements, have been strongly criticized on the basis of successive accurate XRD studies,[10,11] which have found erratic differences of about 0.2 Å in the Co−N axial distances determined by the two methods.

The ORTEP drawings[12] of the cations of **1** and **2** are shown in Figures 1 and 2, respectively. Axial distances

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[1] Halpern, J. *Science* **1985**, *227*, 869. Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, J. P. *Coord. Chem. Rev.* **1985**, *63*, 1. Randaccio, L.; Bresciani-Pahor, N.; Zangrando; E., Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225.

[2] DH = monoanion of dimethylglyoxime, (DO)(DOH)pn = N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione 2-imine 3-oxime).

[3] Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E. *Inorg. Chim. Acta* **1990**, *168*, 115. Toscano, P. J.; Brand, H.; Geremia, S.; Randaccio, L.; Zangrando, E. *Organometallics* **1991**, *10*, 713 and references therein. Sekine, A.; Ohashi, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2183. Geremia, S.; Randaccio, L.; Zangrando, E. *Gazz. Chim. Ital.* **1992**, *122*, 229. Hirota, S.; Polson, S. M.; Puckett, J. M., Jr.; Moore, S. J.; Mitchell, M. B.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 5646 and references therein.

[4] (a) Geremia, S.; Randaccio, L.; Zangrando, E.; Antolini, L. *J. Organomet. Chem.* **1992**, *425*, 131. (b) Randaccio, L.; Geremia, S.; Zangrando, E.; Ebert, C. *Inorg. Chem.* **1994**, *33*, 4641 and references therein. (c) De Ridder, D. J. A.; Zangrando, E.; Burgi, H. B. *J. Mol. Struct.* **1996**, *374*, 63.

[5] Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Charland, J. P.; Marzilli, L. G. *Organometallics* **1986**, *5*, 1938. Datta, D.; Sharma, G. T. *J. Chem. Soc., Dalton Trans.* **1989**, 115. Bresciani-Pahor, N.; Geremia, S.; Lopez, C.; Randaccio, L. *Inorg. Chem.* **1990**, *29*, 1043. Brown, K. L.; Satyanarayana, S. *J. Am. Chem. Soc.* **1992**, *114*, 5674.

[6] Polson, S. M.; Cini, R.; Pifferi, C.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 314.

[7] Giorgetti, M.; Berrettoni, M.; Conti, P.; Di Cicco, A.; Marassi, R.; Ascone, I. *Organometallics* **1996**, *15*, 3491.

[8] Zangrando, E.; Parker, W. O., Jr.; Bresciani-Pahor, N.; Thomas, L. B.; Marzilli, L. G.; Randaccio, L. *Gazz. Chim. Ital.* **1987**, *117*, 307. For the Me derivative, the equatorial ligand is closely related to (DO)(DOH)pn with the methyl groups on the oxime side replaced by ethyl groups (Chart 1).

[9] (a) Sagi, I.; Chance, M. R. *J. Am. Chem. Soc.* **1992**, *114*, 8061. (b) Sagi, I.; Wirt, M. D.; Chen, E.; Frisbie, S.; Chance, M. D. *J. Am. Chem. Soc.* **1990**, *110*, 8639.

[10] Kratky, C.; Färber, G.; Gruber, K.; Wilson, K.; Dauter, Z.; Nolting, H.; Konrat, R.; Kräutler, B. *J. Am. Chem. Soc.* **1995**, *117*, 4654.

[11] Kräutler, B. J.; Konrat, R.; Stupperich, E.; Färber, G.; Gruber, K.; Kratky, C. *Inorg. Chem.* **1994**, *33*, 4128.

[12] The synthesis and crystallization of compounds **1** and **2** are given in ref 13. Crystallographic data for **1**: $C_{13}H_{23}CoF_9N_4O_3P$, M_r = 544.25, monoclinic, space group $P2_1/c$, a = 6.9013(7) Å, b = 14.5348(14) Å, c = 21.217(2) Å, β = 99.035(7)°, V = 2101.8(4) Å^3, Z = 4, D_c = 1.720 g/cm^3, μ(Mo Kα) = 0.994 mm^{-1}, final R1, wR2, and GOF 0.0549, 0.1577, and 1.029 for 297 parameters and 6229 unique observed reflections with $I > 2\sigma(I)$. Crystallographic data for **2**: $C_{14}H_{26}CoF_6N_4O_5P$, M_r = 534.29, monoclinic, space group $P2_1/c$, a = 11.652(2) Å, b = 15.374(2) Å, c = 12.707(2) Å, β = 109.469(13)°, V = 2146.0(6) Å^3, Z = 4, D_c = 1.654 g/cm^3, μ(Mo Kα) = 0.959 mm^{-1}, final R1, wR2, and GOF are 0.0511, 0.1401, and 1.034 for 298 parameters and 6234 unique observed reflections with $I > 2\sigma(I)$. Data were collected at 293 K using an Enraf-Nonius CAD4 single-crystal diffractometer with the Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by the heavy-atom method. Refinement was carried out by full-matrix least squares of F^2 for all data using SHELXL-93.

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Table 1. Comparison of Co−C and Co−O Axial Distances (Å) Determined by XRD and EXAFS and Relative Differences, Δ (Å), in $RCo[(DO)(DOH)pn](H_2O)^+$ Cations[a]

	Co−C			Co−O		
R	XRD[b]	EXAFS[c]	Δ	XRD[b]	EXAFS[c]	Δ
Me	1.977(4)	2.041(7)	−0.064	2.103(3)	2.127	−0.024
CH_2CF_3	**1.989(3)**	2.067(10)	**−0.078**	**2.062(2)**	2.219	**−0.157**
CH_2CO_2Me	**2.015(3)**	2.056(9)	**−0.041**	**2.024(2)**	2.206	**−0.182**
Et	2.020(3)			2.109(2)		
CH_2Ph	2.052(2)	2.040(8)	0.012	2.099(1)	2.102	−0.003
i-Pr[d]	2.055(5)	2.021(10)	0.034	2.138(3)	2.160	−0.022
	2.090(3)		0.069	2.128(2)		−0.032
i-Bu		2.029(12)			2.159	

[a] Data obtained in the present work are given in boldface type. [b] Reference 8. [c] Reference 7. [d] Two crystalline modifications. The difference between the two values for the XRD Co−C distance could be partially due to the different accuracies of data and partially attributed to the different steric interactions of the *i*-Pr group with the equatorial moiety in the two crystalline modifications.[8]

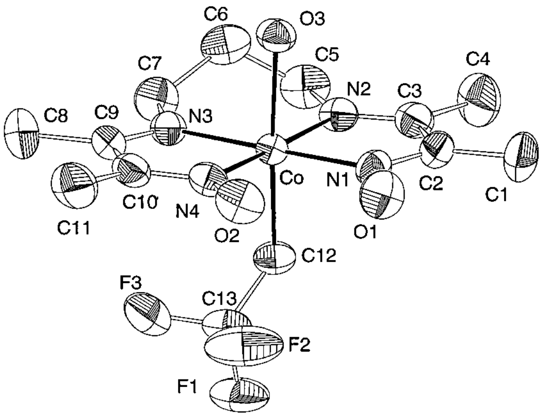

Figure 1. ORTEP diagram with the atom-labeling scheme for **1**. Thermal ellipsoids are drawn at 50% probability. For the sake of clarity, the PF_6^- anion and H atoms are not depicted. Selected bond distances (Å) and angles (deg): Co−N1= 1.887(3), Co−N2 = 1.889(3), Co−N3 = 1.912(3), Co−N4 = 1.918(3); Co−C12−C13 = 121.5(3).

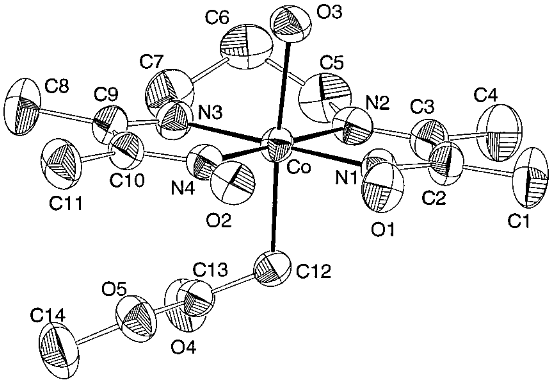

Figure 2. ORTEP diagram with the atom-labeling scheme for **2**. Thermal ellipsoids are drawn at 50% probability. For the sake of clarity, the PF_6^- anion and H atoms are not depicted. Selected bond distances (Å) and angles (deg): Co−N1 = 1.883(2), Co−N2 = 1.893(2), Co−N3 = 1.910(2), Co−N4 = 1.918(2); Co−C12−C13 = 115.4(2).

in the $RCo[(DO)(DOH)pn](H_2O)^+$ series, determined by XRD, are given in Table 1. In agreement with previous analyses,[1,4,6] the XRD trends indicate a lengthening of the Co−O bond on going from the less to the more electron donating R group, whereas the Co−C bond lengthens with an increase in the bulkiness and electron donating ability of R.[14] The aquo derivative series in cobaloximes is not available; however, the XRD Co−C distances of Table 1 can be compared with those reported for the corresponding $RCo(DH)_2(py)$ series.[1] A good linear correlation ($r = 0.995$)[15] between the two sets of data is found and confirms that, in B_{12} models, the trend of the Co−C distances, when R is varied, is scarcely affected by the types of equatorial and L ligands.[1,4b,6]

Axial distances, determined by XRD and EXAFS, are compared in Table 1. A fair agreement is found only for the CH_2Ph derivative. In the other complexes, the Co−C distances, determined by EXAFS with an estimated error of about 0.01 Å,[7] are longer (up to 0.08 Å) when R = Me, CH_2CF_3, CH_2COOMe and shorter (up to 0.07 Å) for R = *i*-Pr, with respect to the corresponding distances determined by XRD. The Co−O distances obtained by XRD are all shorter, and the greatest differences (up to 0.18 Å) are found for the two derivatives reported in the present work. This suggests a dramatic underestimate of the error in the EXAFS distances.[7] In addition to the above large discrepancies in distances, the comparison shows that the trends derived by EXAFS and by XRD are essentially opposite. Therefore, the trend suggested for Co−C bond lengths by the EXAFS analysis, in contrast with many previous works on vitamin B_{12} models, is again not confirmed by the present XRD results. Consequently, the chemical conclusions derived by EXAFS[7] should be refuted. The same applies to the Co−O distances, for which even larger differences between XRD and EXAFS results are observed.

In our opinion, this and previous studies[10,11] open the problem of the degree of reliability of the coordination distance values derived by EXAFS, when the coordination shells overlap strongly, with implications not only in inorganic chemistry but also in metalloenzyme structural studies.[16] To our knowledge, proper critical analyses have not been reported yet. However, a recent review[16] compares Rh−X distances determined by EXAFS in the solid state with those determined by XRD in several Rh complexes. The comparison indicates

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(13) Parker, W. O.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1986**, *25*, 1303.

(14) The combined effect of the steric and electronic properties of R on the Co−C distance has been extensively discussed.[4b] For example, in the $RCo(DH)_2py$ series, this distance is 1.949(5) Å, when R is the moderately bulky and relatively poorly σ-donating CF_3 group. It increases to 1.998(5) Å for the less bulky but strongly σ-donating Me group and to 2.160(4) Å when R = adamantyl, which has a large bulk and a strong σ-donating ability.[4b]

(15) The regression was carried out for six points, using the mean value of the two Co−C distances for the *i*-Pr derivative of the Costa model. Data for the alkylcobaloximes are taken from ref 1. Final equation: $d_{\mathrm{Co-C(Costa\ model)}} = [1.09(6)]d_{\mathrm{Co-C(cobaloxime)}} - 0.206(4)$, where figures in parentheses are the estimated errors in the coefficients.

(16) Bertagnolli, H.; Ertel, T. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 45.

that, when X = P, the difference is not larger than 0.03 Å, whereas when X = O and C, differences up to 0.10 Å are found. There is no doubt that EXAFS spectroscopy is an important technique in many respects. However, the present work suggests that when the coordination distances are close to each other and involve only light atoms, the reliability of the EXAFS analysis is notably reduced, even taking into account the multiple-scattering contribution.[7] Therefore, it is highly desirable to understand better how to avoid overinterpretation of the data.[16] A combined EXAFS and XRD study on other Co octahedral complexes will be completed in due course.

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Supporting Information Available: Tables of crystal data and collection and refinement parameters, positional parameters, bond distances and angles, hydrogen atom coordinates, and anisotropic thermal factors (9 pages). Ordering information is given on any current masthead page.

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