

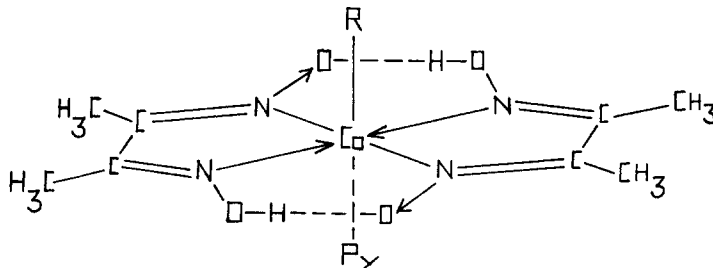
NMR SPECTRA OF COBALOXIMES : UNEXPECTED NONEQUIVALENCE OF METHYL GROUPS

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Summary. ^1H NMR spectra of organocobaloximes indicates the nonequivalence of methyl groups which is attributed to the hydrogen bond formation between the oxime hydrogen and the hetero atom of an axial organic ligand.

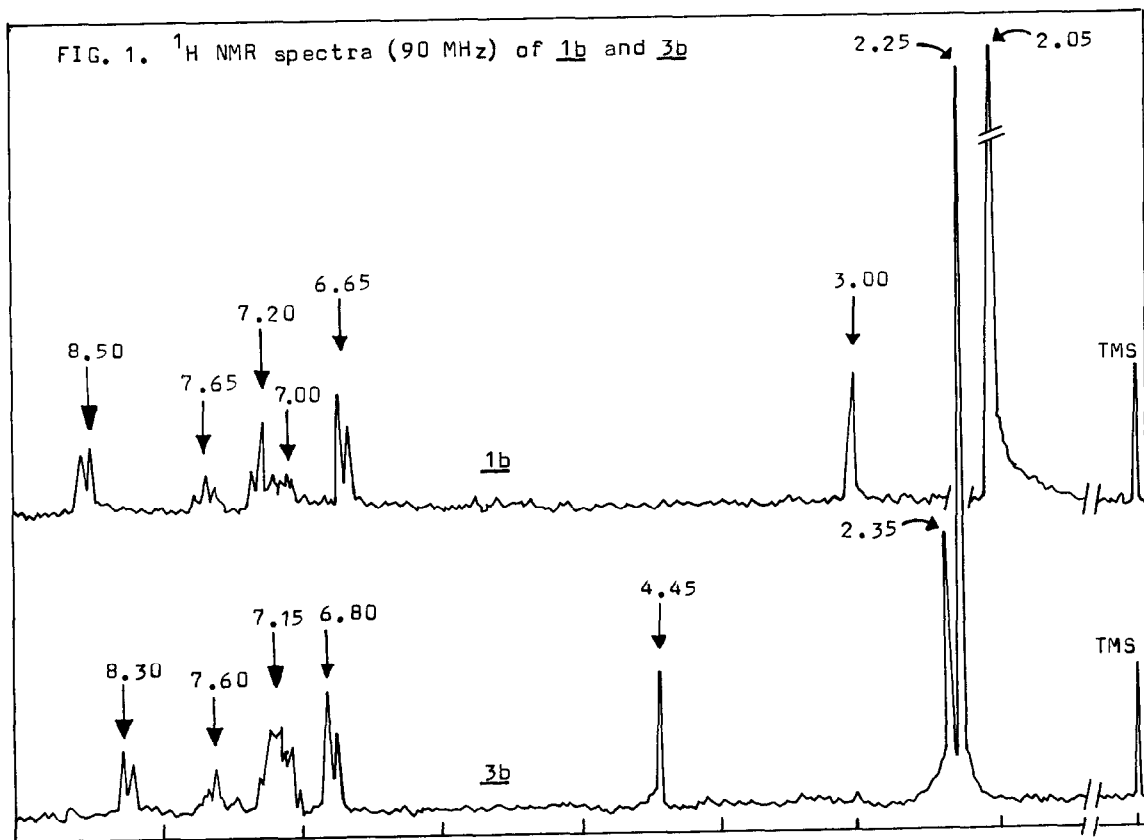
The study of organocobaloximes is very important in view of many similarities in properties with vitamin B₁₂. The compounds are very well characterised by ^1H NMR since the presence of one sharp 12 H singlet around 2.0 δ due to four equivalent methyl groups on equatorial ligands is an excellent indication of the presence of the compound even in the crude product.



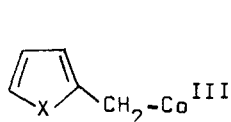
The nonequivalence of methyl groups has been observed only in a few cases. Gaudemer and coworkers noted this phenomenon and speculated that it was due to the presence of an asymmetric centre on the axial sigma bonded ligand.¹ They found that the spectra of a number of related complexes with $\text{Co}-\text{CR}^1\text{R}^2\text{R}^3$ moieties show this feature which is also found in cobaloximes with symmetrical axial alkyl groups, e.g. CH_3 , associated with axial bases containing an asymmetric carbon atom as in $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{COOCH}_3$ or a donor atom which, once bound becomes asymmetric e.g. $\text{C}_6\text{H}_5\text{NHCH}_3$. Recently, the same workers in their stereochemical study of vinyl substitution by transition metal complexes have observed two signals in the ^1H NMR spectra, corresponding to six protons each for the diastereotropic methyl groups of the dioximato moiety in atropisomeric alkenyl cobaloximes.^{1b} A similar nonequivalence has recently been observed by Clifford and Cullen in $\text{CH}_3(\text{CN})\text{CH}-\text{Co}^{\text{III}}(\text{dmgH})_2\text{Py}$.² They have considered free rotation about the axial Co-C bond to explain their observation. In this paper we report the ^1H NMR spectra of a number of compounds.³ In all cases except 1a, 1b and 7a the spectra show the nonequivalence of methyl groups on dimethylglyoxime (equatorial ligands); two signals appearing in 3:1 ratio at about 0.1 ppm apart (refer Table 1, Fig. 1).

Table 1. ^1H NMR spectra (CDCl_3) δ values⁶

Compd. No.	Aromatic	CH_2	dmgH	Py		
				α	β	γ
<u>1a</u>	6.00, 7.40	2.40	2.00	7.30	7.75	8.60
<u>1b</u>	6.65, 7.00	3.00	2.05	7.20	7.65	8.50
<u>2a</u>	6.00, 7.12	2.55	2.00, 2.10	7.15	7.75	8.42
<u>2b</u>	6.75, 7.20	2.85	2.00, 2.10	7.30	7.70	8.50
<u>3a</u>	6.15, 7.15	4.25	2.30, 2.40	7.15	7.60	8.30
<u>3b</u>	6.80, 7.15	4.45	2.25, 2.35	7.15	7.60	8.30
<u>4a</u>	6.30, 7.20	4.15	2.25, 2.35	7.20	7.60	8.25
<u>4b</u>	7.15, 7.25	4.30	2.25, 2.35	7.10	7.60	8.30
<u>5a</u>	6.20, 7.30	4.30	2.30, 2.40	7.15	7.50	8.50
<u>5b</u>	7.15, 7.30	4.15	2.25, 2.38	7.10	7.70	8.40
<u>6a</u>	6.45, 7.35	4.40	2.28, 2.38	7.36	7.70	8.40
<u>6b</u>	7.30, 7.40	4.00	2.25, 2.40	7.10	7.70	8.40
<u>7a</u>	7.00, 8.25	2.85	2.05	7.30	7.60	8.55
<u>7b</u>	7.10, 7.45, 8.20	4.40	2.25, 2.35	7.15	7.55	8.25
<u>7c</u>	7.50, 7.95, 8.50	4.00	2.32, 2.42	7.50	7.95	8.50

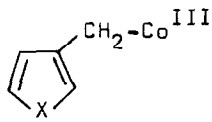


60 MHz and 90 MHz spectra for 2a and 2b are not well resolved and the methyl signals appear as broad singlet at 2.0 δ . However, the nonequivalence (3:1) is clearly visible for the same in 200 MHz spectra run on Bruker machine.



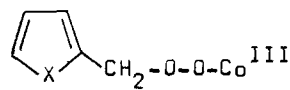
X = O, 1a

X = S, 1b



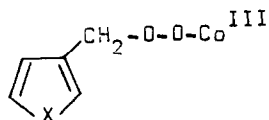
X = O, 2a

X = S, 2b



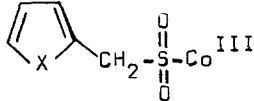
X = O, 3a

X = S, 3b



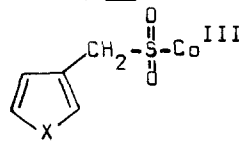
X = O, 4a

X = S, 4b



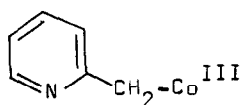
X = O, 5a

X = S, 5b

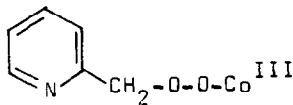


X = O, 6a

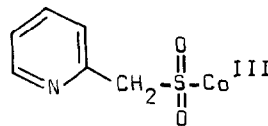
X = S, 6b



7a



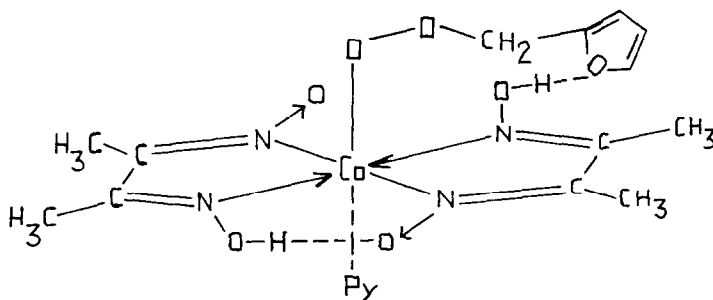
7b



7c

$\text{Co}^{\text{III}} = \text{Co}(\text{dmgH})_2\text{Py}$

In view of the fact that alkyl, benzyl, allyl, allenyl cobaloximes and their dioxy adducts do not show such an effect,⁴ the nonequivalence must be due to the presence of hetero atom present in the axial organic ligand. The models of 3a and 3b indicate that the hetero atom lies directly above the oxime hydrogen. The main reason for the nonequivalence might, therefore, be due to the formation of a hydrogen bond between the oxime hydrogen and the hetero atom of the axial organic ligand.



The suggestion is supported by the fact that the salt formation of uncoordinated pyridine (axial organic ligand) in 7b with hydrochloric acid leads to the disappearance of the nonequivalence of methyl groups. Interestingly, ^1H NMR spectra of $\overline{\text{O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-Co}^{\text{III}}}$ and its dioxy adduct do not show such a phenomenon indicating the necessity of an aromatic hetero atom for such a process.⁵

References

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 (b) D. Cabaret, M. Maigrot, Z. Welvart, K.N.V. Duong and A. Gaudemer, J. Am. Chem. Soc., 106, 2870 (1984).
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3. The compounds were available from another study. B.D. Gupta and Sujit Roy (unpublished results).
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 (c) P. Bougeard, M.D. Johnson and G.M. Lampman, J. Chem. Soc. Perkin (I), 849 (1982).
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6. 1a, 1b, 2a, 2b and 7a were recorded on 60 MHz (JEOL PMX-60), 90 MHz (Varian EM-390) and 200 MHz (Bruker) machines. The rest of the spectra were run on 60 MHz and 90 MHz. The separation of the oxime methyl groups was distinctive in both 60 MHz as well as 90 MHz.

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