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Preliminary communication

ELECTRON ADDITION AND PHOTOCHEMICAL PROCESSES FOR ALKYLCOBALOXIMES AT LOW TEMPERATURES; AN ELECTRON SPIN RESONANCE STUDY

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Summary

Electron capture by methyl(pyridine)cobaloxime in 2-methyltetrahydrofuran at 77 K gave a $\sigma^\star$ anion, the electron being largely confined to the metal $3d_{z^2}$ orbital with a relatively low spin density on carbon as estimated from the ^{13}C hyperfine splitting. The pyridine ligand was probably lost since no ^{14}N hyperfine coupling was detected. Ultraviolet photolysis resulted in homolysis of the metal—carbon bond, both fragments being detected by ESR spectroscopy when methanol (CD_3OD) was the solvent.

We recently reported results of our ESR study of electron addition to alkylcobalamins and related compounds [1,2] together with our results for the photolysis of these derivatives in rigid matrices at 77 K [3]. One of our aims in this work was to add an electron into the metal—carbon $\sigma^\star$ orbital, and to study the spin distribution by ESR spectroscopy, since no such study has yet been reported. In view of the strength, and covalent character of this bond, we are not surprised that our endeavour failed. For methylcobalamin we deduced that electron addition initially occurred into the corrin $\pi^\star$ orbital, and this was followed on annealing by transfer into the metal $d_{x^2-y^2}$ ($\sigma^\star$) orbital. We were therefore most interested in a recent paper by Hashino et al. describing very similar studies of various cobaloximes [4]. They conclude that, for the pyridine derivatives $XCo(py)L_4$, where L_4 represents the oxime ligands, when X is Cl or benzyl, this group is effectively lost as the anion on electron capture [4], but when X is methyl, the electron is captured into the Co—Me $\sigma^\star$-orbital. The resulting ESR spectrum for the methyl derivative (Fig. 1a) is certainly quite different from those usually associated with Co^{II} with 5 or 6 ligands particularly with respect to the small shift in g (Table 1). It seemed to us that this assignment of the SOMO might well be correct, so we decided to use methyl labelled with ^{13}C, in order to verify the assignment and probe the structure.

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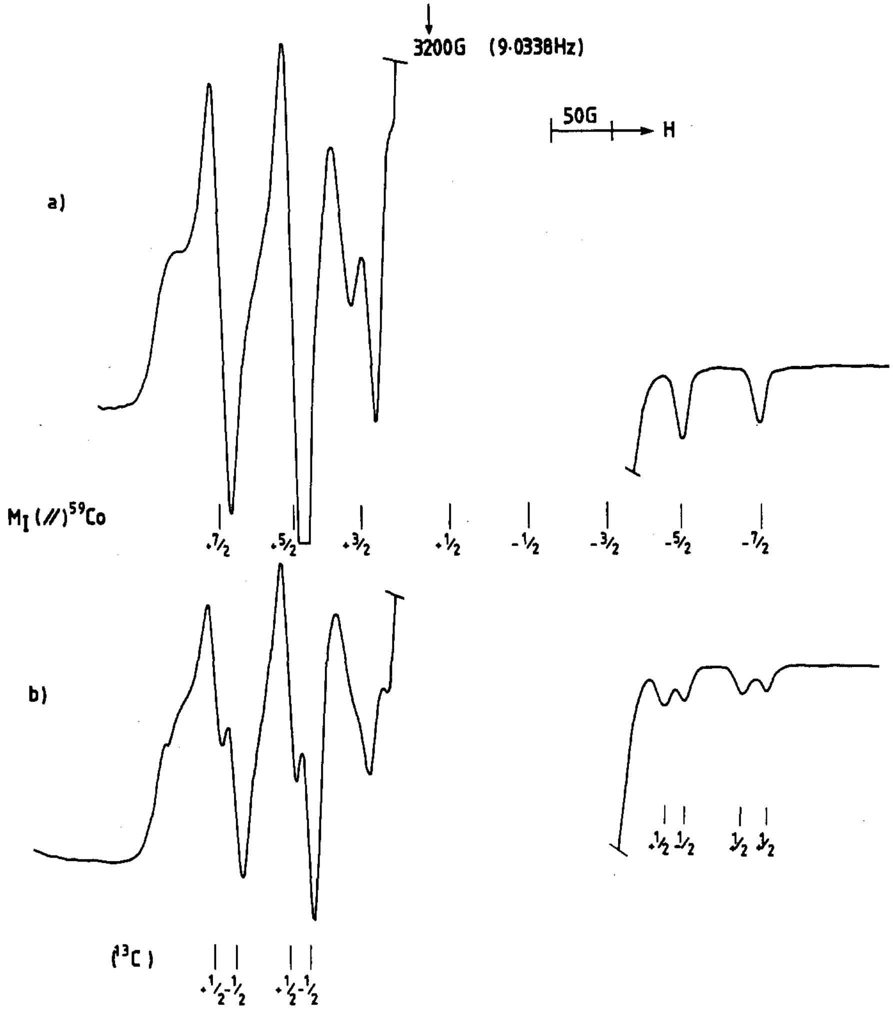


Fig. 1. First derivative X-band ESR spectra obtained from methyl(pyridine)cobaloxime in 2-methyltetrahydrofuran after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent anions; (a) CH_3(py)cobaloxime; (b) $^{13}CH_3$(py)cobaloxime.

TABLE 1

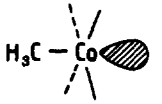
SOME EXPERIMENTAL ESR PARAMETERS FOR DERIVATIVES OF METHYL(PYRIDINE)-COBALOXIME

Compound	Nucleus	Hyperfine coupling constants (G)^a			g-values		
		A_z	A_x	A_y	g_z	g_x	g_y
[CH_3(py)cobal-oxime]$^-$	^{59}Co	62.5	ca. 42	ca. 42	2.002	2.099	2.099
	^{14}N	<4	—	—			
	^{13}C	19	ca. 17	ca. 17			
[CH_3(py)cobal-oxime]$^{-b}$	^{59}Co	58.4	—	—	2.002	2.11	2.11

[a] $G = 10^{-4}$ T. Corrected when necessary: the $^{59}Co_{\perp}$ data are rough approximations. [b] Ref. 4.

Our results give an unambiguous extra doublet splitting associated with the $M_I = \pm \frac{1}{2}$ levels of the ^{13}C nucleus (Fig. 1b). This probably confirms the $\sigma^\star$ structure proposed [4] although we had expected a larger ^{13}C hyperfine interaction. The data given in Table 1 can be processed in the usual way [6] to give approximate orbital populations on carbon. This gives ca. 1.7% $2s$ character. The estimated $2p_z$ character (ca. 2%) has a relatively large error. If we assume that the methyl group retains ca. sp^3 character, the total spin-density on carbon cannot be greater than ca. 6%. A similar calculation based on the ^{59}Co hyperfine coupling parameters requires a knowledge of signs, which we have been unable to derive. However, if like signs are assumed, impossibly low-spin densities result. If we require that the orbital be primarily $3d_{z^2}$ then the signs used in Table 1 are the only suitable ones. This gives 46.5% spin density on cobalt. The small value for A_{iso} (−7 G) requires considerable admixture of positive $4s$ character to reduce the coupling from the normal spin-polarisation value in the region of −100 G.

We thus have a complex having a unique optical spectrum [4] with apparently ca. 6% spin density on a carbon atom. There is no ^{14}N coupling for the axial pyridine ligand. Since this is normally in the 15—20 G range this almost certainly means that this ligand has relaxed away from the cobalt atom. Again, the relatively narrow features preclude major spin density on the four in-plane nitrogen atoms. It seems to us that the simplest explanation of these results is that the unpaired electron in an orbital with its major density on the distal side of the methyl group, taking the place of the pyridine ligand, as in I. This cannot be achieved by $4s$ admixture alone, but addition of $4p_z$ gives the required effect. Since the $4p$ orbitals are more extended than $3d$ their contribution to the anisotropy is greatly reduced. An approximate calculation suggests that if there were ca. 42% $4p_z$ character and 42% $3d_{z^2}$ character the whole of the anisotropy and spin density would be accounted for.



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The low ^{13}C hyperfine coupling for a $\sigma^\star$ electron is nevertheless a surprise. We have recently shown that the complexes $[HNi(CN)_4]^{2-}$ and $[HPt(CN)_4]^{2-}$ have ca. 30% spin density on hydrogen [7]. The form of the g-tensor components and ^{195}Pt hyperfine coupling are similar to those for cobalt, but there has been a dramatic fall in the ligand spin density for the cobalt complex. Unfortunately our attempts to prepare $[R^{\bullet}{-}Pt(CN)_4]^{2-}$ derivatives have been unsuccessful. We conclude that, in contrast with methylcobalamin, the present complex loses the fifth ligand (py) to give a $3d'_{z^2}$ complex which is stable at 77 K. Hashino et al. have suggested that on annealing, the methyl group is lost and a Co^I derivative is formed. This conclusion seems reasonable to us, and our results were similar to theirs [4].

On UV photolysis, dilute solutions of a range of alkyl(pyridine)cobaloximes in 2-methyltetrahydrofuran (MTHF) gave the well known MTHF radical signals together with broad perpendicular cobalt features at ca. $g_\perp = 2.29$ with no well defined parallel lines. However, using CD_3OD solvent gave $\dot{C}D_2OD$ radicals together with narrow features for $R^{\bullet}$ radicals ($^{\bullet}CH_3$ gave a 1/3/3/1 quartet, A 22.5 G,

CH_2CH_3 gave a triplet, *A* 22 G and a quartet, *A* 26 G). A similar broad $g_\perp$ feature was also observed. In the particular case of the isobutyl derivative, in addition to $D_2\dot{C}OD$ and $Me_2CH\dot{C}H_2$ radicals, well-defined features for $Me_3C^\bullet$ radicals were observed (Fig. 2).

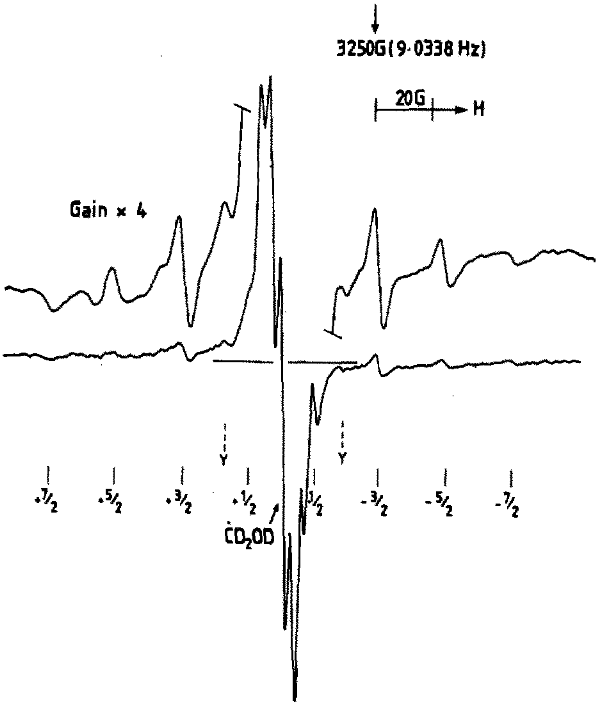

Fig. 2. First derivative X-band ESR spectra obtained from isobutyl(pyridine)cobaloxime after exposure to ultraviolet light, at low microwave power, showing features assigned to $Me_3\dot{C}$ radicals. It is suggested that these are formed from hot $Me_2CH\dot{C}H_2$ radicals by a 1-2 proton shift.

We conclude that photolysis ruptures the cobalt—carbon bonds and the radicals move away with sufficient energy to prevent radical return or even extensive pair-trapping, though the presence of broad features does suggest that pair-trapping occurs to some extent. This again contrasts with our results for alkylcobalamins for which pair-trapping was extensive [1,3].

On annealing, the broad features assigned to Co^{II} was lost because of facile dimerisation. However the monomer could be trapped using oxygen to give $pyCo(L_4)O\dot{O}$ peroxy radicals, or using excess pyridine, to give the dipyridine complex $(py)_2CoL_4$, both of which were detected by ESR spectroscopy.

References

1 D.N. Ramakrishna Rao and M.C.R. Symons, J. Chem. Soc. Chem. Comm., (1982) 954.
2 D.N. Ramakrishna Rao and M.C.R. Symons, J. Chem. Soc. Faraday I, in press.
3 D.N. Ramakrishna Rao and M.C.R. Symons, J. Chem. Soc. Perkin II, in press.
4 M. Hashino, S. Konishi, Y. Terai, and M. Imamura, Inorg. Chem., 21 (1982) 89.
5 Our interpretation of the ESR spectra differ from that of Hashino et al. but we agree with their conclusions; this will be discussed in our full paper.
6 M.C.R. Symons, Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy, Van Nostrand—Reinhold Co. Ltd., Wokingham, 1978, p. 26.
7 M.C.R. Symons, M.M. Aly, and J.L. Wyatt, J. Chem. Soc. Chem. Comm., (1981) 176.