Direct Observation of the Two Forms of Aquocyanocobyric Acid in Water by Carbon-13 Fourier Transform Nuclear Magnetic Resonance

By DAVID DODDRELL and ADAM ALLERHAND*

(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary Proton-decoupled natural-abundance carbon-13 Fourier transform n.m.r. spectra of aqueous solutions of aquocyanocobyric acid and dicyanocobyric acid were recorded at 15·08 MHz: the spectrum of the first compound showed the presence of two isomers, and many of the carbon atoms showed large chemical shift variations between the two isomers.

We have shown[1] that the sensitivity of the Fourier transform technique[2] extends the use of proton-decoupled natural abundance ^{13}C n.m.r. spectra to dilute (as low as 0·01M) solutions. ^{13}C spectra of corrinoids were appreciably more resolved and simpler to interpret than the corresponding ^{1}H spectra.[1]

Corrinoids with one cyano and one aquo axial ligand[3] can exist in two isomeric forms in the solid state[3] and in solution.[3,4] The only reported effect of this isomerism on ^{1}H n.m.r. spectra is a small splitting (*ca.* 0·05 p.p.m.) of the 10-H of the corrin ring.[4] We now report that there are many resolvable differences in the ^{13}C chemical shifts of the two isomers of aquocyanocobyric acid [$C_{46}H_{67}CoN_{11}O_9$, Figure 1, (A) and (B)]. The proton-decoupled natural-abundance ^{13}C spectrum of aquocyanocobyric acid (0·06M in water) is shown in Figure 2, (B). For comparison, the spectrum of dicyanocobyric acid, which only exists in one form [Figure 1, (C)] is shown in Figure 2, (A). A large number of carbons in aquocyanocobyric acid have appreciably different chemical shifts in the two isomers. There are 60 resolved resonances in the spectrum of aquocyanocobyric acid, but only 38 lines in the spectrum of dicyanocobyric acid. Some resonances were easily assigned (Table) by comparisons with known ^{13}C chemical shifts of other corrinoids.[1] The sample of dicyanocobyric acid was prepared by adding KCN to the solution of aquocyanocobyric acid. The spectrum of dicyanocobyric acid does not contain any peaks attributable to corrinoid impurities. Thus, the additional resonances in the spectrum of aquocyanocobyric acid cannot be due to corrinoid impurities.

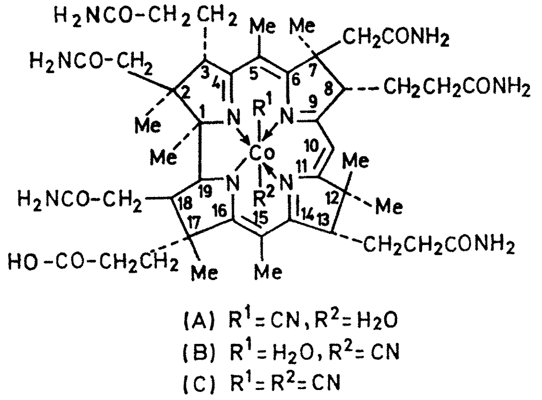

FIGURE 1. *Structure of aquocyanocobyric acid* (A *and* B) *and dicyanocobyric acid* (C).

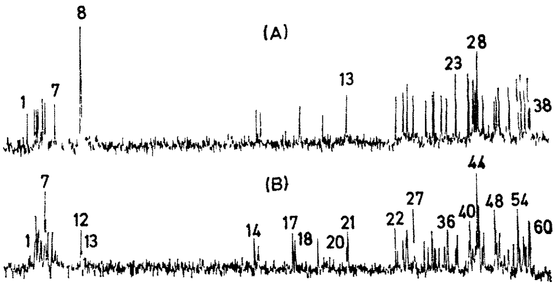

FIGURE 2. *Proton-decoupled natural abundance carbon-*13 *n.m.r. spectra at* 56 °C, *obtained at* 15·08 *MHz by the Fourier transform method, with* 4096 *points in the time-domain and* 250 *p.p.m. sweep widths. Only the range* 4·3—184·3 *p.p.m. upfield from* CS_2 *is shown Peaks are numbered consecutively from right to left.* (A) 0·064M-*aqueous dicyanocobyric acid* (*containing excess of cyanide*), *after* 9591 *scans with a recycle time of* 2·72 s (*total time* 7·2 *h*). *Peak* 8 *includes the resonance of free cyanide.* (B) 0·064M-*aqueous aquocyanocobyric acid, after* 8192 *scans with a recycle time of* 2·72 s (*total time* 6·2 *h*).

Some corrin ring chemical shifts in the ^{13}C *spectrum of cobyric acid*[a]

Assignment[b]	Chemical shift[c] Dicyano[d]	 Aquocyano[e]
5, 15	87·9 (9)	86·7(14)
	89·3(10)	87·7(15), 88·0(16)
10	102·1(11)	99·3(17), 100·1(18)
1	109·8(12)	107·6(19)
19	117·5(13)	117·1(20), 117·4(21)
2	133·8(14)	133·3(22), 134·0(23)
3, 8, 13	136·3(15)	135·9(24)
	137·6(16)	136·8(25), 137·1(26)
	139·5(17)	139·5(27)
7, 12, 17	143·8(18)	142·8(28), 144·1(29)
	145·9(19)	145·4(30), 145·6(31)
	146·4(20)	146·3(32), 146·6(33)

[a] Measured at 15·08 MHz and 56 °C; [b] Carbons written on the same line could not be assigned on a one-to-one basis; [c] In parts per million upfield from CS_2. Estimated accuracy ±0·3 p.p.m. Numbers in parentheses are designations in Figure 2, where peaks are numbered consecutively from right to left; [d] 0·064M-aqueous dicyanocobyric acid; [e] 0·064M-aqueous aquocyanocobyric acid.

The large ^{13}C chemical shift differences between the two isomers of aquocyanocobyric acid are surprising: even some side-chain carbons showed appreciable non-equivalence. It is likely that these chemical shift variations are caused not only by electronic differences, but reflect also some conformational changes of the corrin ring. The signal-to-noise ratio in Figure 2, (B) was not adequate to determine the relative amounts of the two isomers with any precision.

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