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THE DIMERIC STRUCTURE OF $\left[C_4H_4AgClO_4\right]_{\underline{n}}$: A REINVESTIGATION OF THE NUCLEAR MAGNETIC RESONANCE SPECTRUM

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In a previous paper[1] we reported that the hydrogen nuclear magnetic resonance spectrum of the complex $\left[C_4H_4AgNO_3\right]_{\underline{n}}$ dissolved in a saturated solution of $AgClO_4$ in D_2O consisted of a single resonance with chemical shift $\tau \sim 2.9$. This led us to conclude that the complex is monomeric (n=1) with a C_4H_4 ligand group. The infrared spectrum was sufficiently complex that such a monomeric formulation was only consistent with a low symmetry for the 'cyclobutadiene' ligand. As we had

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[1] M. Avram, H.P. Fritz, H. Keller, Gh. Mateescu, J.F.W. McOmie, N. Sheppard and C.D. Nenitzescu, Tetrahedron, 19, 187 (1963).

stated in a preliminary communication[2], on the basis of the infra-red spectroscopic evidence alone ' a dimeric structure containing an ethylene-type hydrocarbon ligand cannot entirely be ruled out '.

A C_8H_8 hydrocarbon, syn-tricyclooctadiene (previously termed cis-tricyclooctadiene),[3,1] is obtained by decomposition of the silver nitrate complex with aqueous sodium chloride. The fact that the complex can readily be reformed from the C_8H_8 hydrocarbon has always provided the strongest chemical argument in favour of a dimeric formula for the complex. The recent preparation of the anti-tricyclooctadiene, and the formation from this of an analogous complex with silver nitrate[4], led us to investigate under comparable conditions the NMR spectra of the complexes formed from these isomeric hydrocarbons. We now find that a freshly prepared solution of the original silver nitrate complex from the syn hydrocarbon (dissolved, as before, in a saturated solution of $AgClO_4$

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[2] H.P. Fritz, J.F.W. McOmie and N. Sheppard, Tetrahedron Letters, No. 26, 25 (1960).

[3] M. Avram, Gh. Mateescu, J.G. Dinulescu, E. Marica and C.D. Nenitzescu, Tetrahedron Letters, No. 1, 21 (1961).

[4] M. Avram, J.G. Dinulescu, E. Marica, Gh. Mateescu and C.D. Nenitzescu, Chem.Ber. (in press).

in D_2O) gives two resonances at τ = 2.74 and 5.83 which are of equal intensity; in a period of some hours these are completely replaced by the single resonance at $\tau \sim 2.9$ that we have previously reported.[1] In our earlier investigation there had been some delay between preparing the solution and studying its spectrum caused by filtration or evaporation procedures.

Syn-tricyclooctadiene itself gives two resonances at τ = 3.8 and 6.5 in benzene solution.[1] The new spectral data for the silver complex therefore leave little doubt that this retains C_8H_8 as the ligand, with the resonance of the ethylenic CH's shifted slightly to lower fields (relative to that from the cyclobutane CH's) as in the NMR spectra of other olefine-silver complex ions.[5,6] The decomposition product, whose resonance at $\tau \sim 2.9$ had previously led us to infer the presence of a 'cyclobutadiene' ligand, appears to be some form of complex between cyclooctatetraene and the silver ion. A saturated filtered D_2O solution of cyclooctatetraene in silver perchlorate gives a resonance within 0.1 parts per million

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[5] D.B. Powell and N. Sheppard, J.Chem.Soc., 2519 (1960).

[6] L.W. Reeves, Canad.J.Chem., **38**, 736 (1960).

(0.1 τ units) of this value, and addition of small amounts of cyclooctatetraene to the original solution of the decomposition product gave a single combined resonance. Cyclooctatetraene is also produced in small quantity, together with cis-tricyclooctadiene, when the silver nitrate complex is decomposed by aqueous sodium chloride.

The group characteristic infra-red frequencies of the CH and C=C bonds in the complex ion agree with the tricyclooctadiene formulation for the hydrocarbon ligand providing that the band at 2997 cm^{-1}, which we previously assigned to an ethylenic CH vibration,[2] may be attributed to a CH vibration of the cyclobutane ring. This is the strongest band in the CH region and the analogous strong band of the parent hydrocarbon consists of a close doublet at 2975-2967 cm^{-1}; the implied shift to higher frequencies on complex formation is not unreasonable.

The spectra of trans-tricyclooctadiene and its complex, and a more detailed discussion of the present spectra, will be presented later.

Experimental

The hydrogen NMR spectra were obtained at 60 Mc/s. with a Varian A60 spectrometer. Calibration was made by the side-band method to ± 0.2 c/s relative to the residual proton signal (τ value assumed to be 5.24) in the $AgClO_4$/99.5% D_2O solution of the silver nitrate complex.