To test the ability of the catalyst to hydrogenate selectively, a mixture of 40 mmoles each of 1-pentene and 2-methyl-1-butene was hydrogenated to the absorption of 40 mmoles of hydrogen. The product contained 49% n-pentane, 1% 1-pentene, 1% 2-methylbutane and 49% 2-methyl-1-butene. Similarly, the half hydrogenation of 2-methyl-1,5-hexadiene and 4-vinylcyclohexene produced better than 95% yields of 2-methyl-1-hexene and 4-ethylcyclohexene.

The hydrogenation of 3-hexyne proceeded rapidly to the absorption of 50% of the hydrogen required to saturate the compound, and very slowly beyond. Gas chromatographic examination of the product at the 50% point revealed the formation of cis-3-hexene in a purity of 98–99%.

These results indicate that this catalyst should be very useful for selective hydrogenations in synthetic chemistry.

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TETRAHEDRAL $NiCl_4^{2-}$ IN MOLTEN SALTS. THE COMPLETE SPIN-ALLOWED SPECTRUM OF 3d ORBITAL TRANSITIONS

Sir:

We have measured the complete spin-allowed spectrum of 3d orbital transitions for $NiCl_4^{2-}$ in solution in molten salts at high temperatures. These measurements include the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition near 4000 cm.$^{-1}$, which, though rarely observed, is an important diagnostic test for tetrahedral Ni^{2+} complexes. The $NiCl_4^{2-}$ spectrum was observed for solutions of $NiCl_2$ in CsCl and KCl melts. The results are typified by the spectrum shown in Fig. 1, which is for a solution in CsCl at 680°.
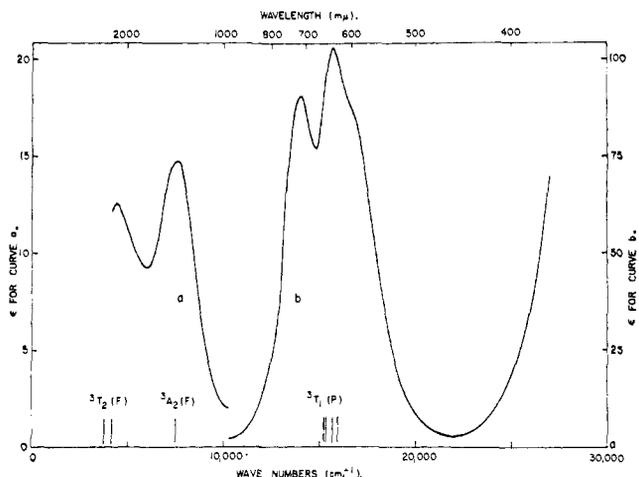

Fig. 1.—Absorption spectrum of $NiCl_2$ dissolved in molten CsCl at 680°. The molar extinction coefficient scale for the visible spectrum, curve b, is on the right while the scale for the infrared spectrum, curve a, is on the left. Computed values of the excited-state energy levels for $Dq = 370$ cm.$^{-1}$ are indicated immediately above the wave-number scale.

Three spin-allowed orbital transitions are predicted for tetrahedral Ni^{2+} complexes, $^3T_1(F) \rightarrow {}^3T_2(F)$, $^3A_2(F)$, $^3T_1(P)$. Measurement of all three transitions is required to check ligand-field theory. Liehr and Ballhausen[1] calculated the energies of these transitions, including spin–orbit fine structure, as functions of Dq.

(1) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

The spectrum in Fig. 1 fits the Liehr and Ballhausen calculations for a Dq of about 370 cm.$^{-1}$ and also agrees with that measured by Weakliem[2] for Ni^{2+} impurity ions at tetrahedral sites in a Cs_2ZnCl_4 crystal. The bands in the melt are decidedly broader than those in the crystal, presumably because of the high temperatures.

The importance of measurements of the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition for the identification of tetrahedral nickel(II) complexes in molten salts is the following. The spectra of tetrahedral and octahedral complexes of $d^{2,8}$-configuration ions are similar since three regions of spin-allowed absorption in the visible and near-infrared are predicted for both structures. Two spectral characteristics have been proposed as tests to distinguish between them. First, the ligand-field splitting of the ^3F term is only about half as great for a tetrahedral complex as for the corresponding octahedral complex, which means that an absorption band should occur in the 4000–5000-cm.$^{-1}$ region for tetrahedral fields but not for octahedral fields. Second, the intensity of the tetrahedral spectrum should be much greater than that of the octahedral spectrum because of the absence of an inversion center in a tetrahedral field. The utility of this latter test for nickel(II) complexes in molten salts is a cloudy issue at present. Until recently it was supposed that the intensity of an electronically allowed transition is at least 10^2 times that of a vibronic transition.[3] However, the electronically allowed transitions of tetrahedral (or approximately tetrahedral) $NiCl_4^{2-}$ in organic solvents[4,5] prove to be no more than 30 times as intense as the vibronic transitions of, for example, the octahedral hexaaquo nickel(II) ion.[6] Furthermore, all of the nickel(II) complexes in molten salts that have been reported to be octahedral[7,8] have anomalously intense spectra so that the bands reported here for tetrahedral $NiCl_4^{2-}$ are only about twice as intense.[9]

Previous measurements of the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition have been confined to nickel-doped inorganic crystals[2,10] and the $NiI_2(P-n-Pr-Ph_2)_2$ complex dissolved in CH_2Cl_2.[11] The $NiCl_4^{2-}$ complex has been studied in non-fused-salt solutions[4,5,12] and in crystals with organic cations[13] but the reported spectra do not include the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition.

Gruen and McBeth[7] proposed that the tetrahedral $NiCl_4^{2-}$ complex is formed when $NiCl_2$ is dissolved in fused CsCl, Cs_2ZnCl_4 and pyridine hydrochloride. This proposal was based on measurements of the $^3T_1(F) \rightarrow {}^3T_1(P)$ band in the visible region. The present measurements leave little room for doubt that this proposal is essentially correct, although Furlani and Morpurgo[5] point out that the complex structure of the visible band may indicate that the $NiCl_4^{2-}$ ion is mildly distorted from the configuration of a regular tetrahedron.

(2) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(3) See, for example, T. M. Dunn, "The Visible and Ultra-Violet Spectra of Complex Compounds," in "Modern Coordination Chemistry," edited by J. Lewis and R. G. Wilkins, Interscience Publishers, New York, N. Y., 1960, p. 379.

(4) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(5) C. Furlani and G. Morpurgo, *Z. Physik. Chem.* (Frankfurt), **28**, 93 (1961).

(6) C. Furlani, *ibid.*, **10**, 291 (1957).

(7) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

(8) K. E. Johnson and T. S. Piper, *Discussions Faraday Soc.*, **32**, 32 (1961).

(9) For a discussion of the anomalous intensity of octahedral complexes in melts, see D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

(10) R. Pappalardo, D. L. Wood and R. C. Linares, Jr., *J. Chem. Phys.*, **35**, 1460 (1961).

(11) R. G. Hayter, Mellon Institute, private communication.

(12) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960).

(13) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

The spectra of $NiCl_2$ dissolved in melts of NaCl and LiCl do not fit the pattern for tetrahedral complexes. These results and the experimental method will be described in a later paper.

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THE TAUTOMERIC STRUCTURE OF DEOXYCYTIDINE

Sir:

The existence of cytidine as the amino tautomer in both monomeric and helical polynucleotide structures has been demonstrated in previous infrared studies on D_2O solutions.[1,2] This conclusion constituted evidence against a recently proposed DNA model[3] involving bonding to the N_7 rather than the N_1 positions of the purines.[4,5]

A recent paper[6] extended earlier n.m.r. investigations.[7,8] of the nucleosides to some deoxynucleosides in dimethyl sulfoxide solution and reported that deoxycytidine, in contrast to cytidine, exists in the imino form in this solvent as well as in D_2O. The subsequent discussions[6] of N_7 G–C bonding in the alternative DNA structure and of mechanisms of DNA–RNA interaction were based upon the existence of the imino tautomer.

We have observed the n.m.r. spectrum of purified deoxycytidine in dimethyl sulfoxide (Fig. 1A) and found that it is quite different from the one assigned to this compound by Gatlin and Davis and that, in fact, it strongly supports the amino structure. There are no NH peaks on the low field side of the H_6 doublet but instead a peak at -44 c.p.s. (relative to the aromatic peak of toluene) on the high field side of the doublet. This peak has an area indicating two protons and is assigned to the NH_2 group. The assignment of nucleoside n.m.r. peaks has been discussed in several papers.[6-8]

The spectrum of deoxycytidine hydrochloride (Fig. 1B), on the other hand, is similar in all significant features to that reported recently for deoxycytidine.[6] The difference between the spectra in Fig. 1A and 1B (and presumably between 1A and the spectrum reported by Gatlin and Davis as that of deoxycytidine) must be attributed to protonation rather than tautomerism.[9,9a]

(1) H. T. Miles, *Biochim. Biophys. Acta,* **35,** 274 (1959).

(2) H. T. Miles, *Proc. Natl. Acad. Sci.,* **47,** 791 (1961).

(3) R. Langridge and A. Rich, *Acta Cryst.,* **13,** 1052 (1960).

(4) K. Hoogsteen, *ibid.,* **12,** 822 (1959).

(5) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 504.

(6) L. Gatlin and J. C. Davis, Jr., *J. Am. Chem. Soc.,* **84,** 4464 (1962).

(7) C. D. Jardetzky and O. Jardetzky, *ibid.,* **82,** 222 (1960).

(8) J. P. Kokko, J. H. Goldstein and L. Mandell, *ibid.,* **83,** 2909 (1961).

(9) The distinction between tautomerism and protonation in cytidine is made clear in ref. 2, which includes infrared evidence that cytidine is protonated at the N_3 position (the ring nitrogen not occupied by the sugar). Protonation at N_3 was supported previously by C. A. Dekker, using evidence from ultraviolet spectroscopy (*Ann. Rev. Biochem.,* **29,** 453 (1960)). Evidence that deoxycytidine and its hydrochloride have completely different structures in dimethyl sulfoxide as well as in D_2O is provided also by the infrared spectrum in this solvent. The hydrochloride has strong bands at 1720 and 1678 cm.$^{-1}$, while the free nucleoside has a strong band at 1651 cm.$^{-1}$ with a shoulder at ~1625 cm.$^{-1}$. The spectra and the deductions from them are closely analogous to those presented for the solvent D_2O (ref. 2).

(9a) The two peaks on the low field side of the H_6 doublet in Fig. 1B are presumably the external NH protons, but judgment on this and other points in the spectrum of the hydrochloride is reserved, pending further study. This reservation in no way affects the main point of the paper, which is concerned with the free nucleoside.
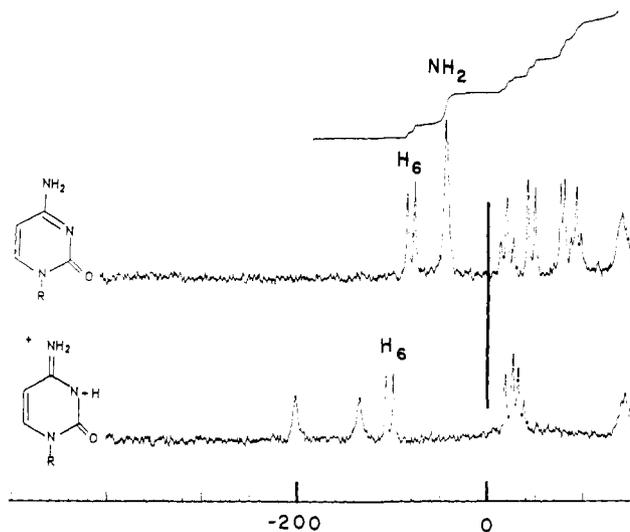

Fig. 1A (top).—60-Mc. n.m.r. spectrum of deoxycytidine in dimethyl sulfoxide (integration curve is above spectrum). Field increases from left to right. Aromatic toluene reference peak is indicated by vertical bar. Darker index marks are 200 c.p.s. apart.

Fig. 1B (lower).—60-Mc. n.m.r. spectrum of deoxycytidine hydrochloride in dimethyl sulfoxide; indexing as in Fig. 1A.
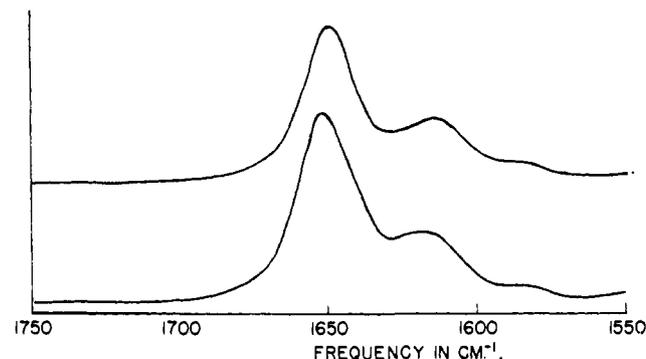

Fig. 2.—Infrared spectra of cytidine (upper curve) and deoxycytidine (lower curve) in D_2O solution, pH 7, 25-μ path length. Ordinate is absorbance on arbitrary scale.

The infrared spectrum of deoxycytidine in D_2O solution (Fig. 2) has a strong carbonyl band at 1651 cm.$^{-1}$ and a weaker ring vibration at 1618 cm.$^{-1}$ We have shown[2] that a well defined amino model compound has a strong band at 1649 cm.$^{-1}$ and a weaker one at 1625 cm.$^{-1}$, while an imino model has bands at 1671, 1657 and 1579 cm.$^{-1}$, with none near 1620 cm.$^{-1}$, thus supporting the amino and ruling out the imino form of cytidine and of deoxycytidine.

We conclude that the evidence reported here, together with that presented in ref. 2, clearly establishes the amino structure of deoxycytidine in D_2O and in dimethyl sulfoxide. The report of the imino form[6] is incorrect and can therefore provide no support for an N_7 bonding structure for DNA or for information transfer processes based upon such a structure.

The deoxycytidine hydrochloride was obtained from the California Corporation. The free nucleoside was prepared by neutralizing the hydrochloride with an equivalent of sodium hydroxide, evaporating the water, and extracting repeatedly with methanol in order to separate the nucleoside from the sodium chloride. The deoxycytidine was recrystallized five times from methanol–ether to a m.p. of 213–216° (Kofler, uncor.).[10]

(10) O. Schindler, *Helv. Chim. Acta,* **32,** 979 (1949), reported m.p. 212–214° for deoxycytidine.