reaction to zero time leads, in effect, to a spectrum of this substance (and any excess reactant and Co^{2+}). The necessity for extrapolation and the corrections for other substances contribute some uncertainty, but we are able to fix the long wave length absorption maximum at 5450–5600 Å., which is quite reasonable for the ion $CrNC^{2+}$.[5,6]

Aquation of CrCN^{2+}. In acid solution $CrCN^{2+}$ slowly loses cyanide ion; $Cr(H_2O)_6^{3+}$ was identified as the product by its absorption spectrum. The rate of this reaction follows the pseudo-first-order rate equation

$$-d[CrCN^{2+}]/dt = k_{aq}[CrCN^{2+}] \qquad (6)$$

Experiments performed at 25.0°, $C_{HClO_4} + C_{NaClO_4} = 1.00$ F, led to the values $10^4 k_{aq}$ (sec.$^{-1}$) = 0.15, 2.7, 3.7 at C_{HClO_4} = 0.05, 0.45, 0.85, respectively, with an rather high uncertainty of *ca.* 20%. The data appear to correlate with a rate equation involving a term in which [H$^+$] appears to a positive power. This situation resembles that found for similar complexes of chromium(III) with strongly basic ligands, *e.g.*, CrF^{2+}[7] and CrN_3^{2+},[8] where the term $k_1[H^+][CrX^{2+}]$ provides an important reaction pathway. It is unlike that for most other complexes CrX^{2+} (*e.g.*, X = I$^-$, Br$^-$, Cl$^-$, NCS$^-$)[7,9-11] where only terms with negative or zero orders with respect to hydrogen ion are found. This behavior has been attributed to the fact that the strongly basic ligand is substantially protonated in the activated complex.[7,8] The magnitude of ΔH^* and ΔS^* for each path should be particularly revealing in this connection.

We plan to study these processes in more detail, especially with regard to measuring the rate constants more accurately and studying the dependence of these rate constants upon hydrogen ion concentration and temperature. We hope to find conditions under which the isocyanide complex, $CrNC^{2+}$, can be isolated and characterized more completely.

(5) Shriver, *et al.*, estimate, from spectra of solids containing different CN$^-$ arrangements, that nitrogen-bonded cyanide ion lies between H$_2$O and NH$_3$ in ligand field strength, and closer to the latter; our result is consistent with this formulation: D. I. Shriver, S. A. Shriver, and S. A. Anderson, *Inorg. Chem.*, 4, 725 (1965).
(6) These observations do not exclude the possibility that the second stage of reaction is a first-order decomposition of a dinuclear cobalt–chromium ion, although this appears a less likely interpretation.
(7) T. W. Swaddle and E. L. King, *ibid.*, 4, 532 (1965).
(8) T. W. Swaddle and E. L. King, *ibid.*, 3, 234 (1964).
(9) J. H. Espenson, *ibid.*, 3, 968 (1964).
(10) F. A. Guthrie and E. L. King, *ibid.*, 3, 916 (1964).
(11) C. Postmus and E. L. King, *J. Phys. Chem.*, 59, 1208 (1955).

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An Infrared Investigation of the Magnesium–Adenosine Triphosphate Complex

Sir:

The question of whether or not the Mg^{2+} ion in the Mg^{2+}–ATP complex is coordinated to the adenine moiety is of the greatest interest to biochemists.[1] The only two infrared investigations of this crucial point are in conflict.[2,3] In the earlier paper, by Epp, *et al.*,[2]

(1) A. Szent Gyorgyi, "Bioenergetics," Academic Press Inc., New York, N. Y., 1957.

a comparison was made between ATP and Mg^{2+}–ATP spectra using KBr disks pressed from powder obtained by freeze-drying solutions *presumably* of one and the same pH, *viz.*, pH 7. The reported spectra differed in that, in addition to a strong 1640 cm.$^{-1}$ band attributed to vibrations characteristic of a nonprotonated adenine moiety, the Mg^{2+}–ATP spectrum also contained a medium intensity band at 1685 cm.$^{-1}$. The presence of this latter band was cited by these authors as evidence that in the Mg^{2+}–ATP complex the Mg^{2+} ion is attached to the adenine moiety and that the positively charged Mg^{2+} ion produces the same effect as a proton on the adenine vibrations.

The more recent investigation of Khalil and Brown[3] was carried out in D_2O solution. These authors concluded that when the ratio of the absorbances of the 1630 and 1670 cm.$^{-1}$ bands equalled 1.2 a 50% protonation of the adenine moiety was indicated. The Mg^{2+} ion decreased the pD corresponding to this half-protonation to 4.4 from a value of 4.55 in absence of Mg^{2+}. However, they did *not* feel that this small pD lowering was due necessarily to coordination of Mg^{2+} by the adenine moiety, but pointed out that the ionizable adenine proton might simply experience an electrostatic field effect from the Mg^{2+} attached to the triphosphate group.

We have obtained solid-state spectra in the manner described by Epp, *et al.*, but have done so over a pH range of 3–9 by lyophilizing solutions containing equimolar concentrations (0.038 *M*) of Na_2ATP and $MgCl_2$ after adjustment to the various pH values with either HCl or NaOH. Two series of experiments, in duplicate, were run. In one series the original solutions contained no KBr, but the lyophilized powders were mixed with KBr powder in preparing the disks. In the second series the solutions contained 3.5% KBr initially. Spectra of ATP in the absence of Mg^{2+} were also obtained over the same pH range, both in the absence and in the presence of KBr initially.

Whether Mg^{2+} was present or absent the spectra show (i) a gradual decrease in the intensity of a 1695 cm.$^{-1}$ band simultaneously with a gradual increase of a 1650 cm.$^{-1}$ band as the pH of the original solution was raised from 3 to 9; (ii) no 1695 cm.$^{-1}$ band above pH 6; and (iii) about equal intensities for the 1695 cm.$^{-1}$ band of the pH 3 spectrum and the 1650 cm.$^{-1}$ band of the pH 6 spectrum (within about a 10% reproducibility).

These two bands show about equal intensity in the ATP spectra corresponding to pH 4.45 ± 0.15, whether KBr was absent or present initially. The presence of Mg^{2+} ion caused only a small increase in the pH of equal band intensities, a pH value of 4.65 ± 0.15 being obtained in the absence of KBr and 4.9 ± 0.15 being obtained in the presence of KBr.

These results may appear to be at variance with those of both Epp, *et al.*, and Khalil and Brown. The cause of the discrepancy between our results and those of Epp, *et al.*, seems quite clear. The latter prepared their Mg^{2+}–ATP solution by adding Mg^{2+} ions to an ATP solution which had been adjusted to pH 7. A simple titration shows that such a solution actually has a pH

(2) A. Epp, T. Ramasarma, and L. R. Wetter, *J. Am. Chem. Soc.*, 80, 724 (1958).
(3) F. L. Khalil and T. L. Brown, *ibid.*, 86, 5113 (1964).

of about 5.5, rather than 7, because of reaction of Mg^{2+} with ATP releasing protons from the terminal phosphate group. The spectra compared by Epp, *et al.*, therefore, represented lyophilization products from a pH 7 ATP solution and a pH 5.5 Mg^{2+}–ATP solution. In fact, their Mg^{2+}–ATP spectrum is very similar to our pH 5.3 Mg^{2+}–ATP spectrum.

Since titration curves show that the adenine moiety in an Na_2ATP solution is completely deprotonated at just about pH 5.5, one might suppose that comparison of their two spectra is still valid with respect to the point under discussion. This would be true for aqueous solution spectra but not for spectra of their lyophilization products. The effective pH near the adenine moiety and its pK undoubtedly change significantly during the freeze-drying process because of temperature and ionic strength changes, as shown by the fact that there is a weak 1695 cm.$^{-1}$ band even in our pH 5.9 ATP spectrum.

Our results are not at all in disagreement with those of Khalil and Brown. Solid-state spectra, such as ours, can suggest reaction of Mg^{2+} with the ATP adenine moiety even if such reaction does not occur in solution. The act of freeze-drying itself probably forces the Mg^{2+} ion in the dry powder to lie so close to an adenine moiety (not necessarily in the same molecule as the phosphate to which the Mg^{2+} binds) that the Mg^{2+} has an even greater electrostatic effect on the adenine moiety than in solution. Thus, in the crystal the Mg^{2+} charge produces an increase in the intensity of the 1695 cm.$^{-1}$ vibration (as suggested by Epp, *et al.*) which, though small, is larger than the intensity decrease (obtained in D_2O by Khalil and Brown) resulting from increased ionization of the adenine proton. The over-all effect, however, is considerably less than that reported by Epp, *et al.*, and seems much too small to be considered as indication of actual coordination of Mg^{2+} by the adenine moiety.

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## Structure of Some Platinum– and Palladium–Carbon σ-Bonded Complexes

Sir:

Some unusual complexes of dicyclopentadiene with platinum(II) or palladium(II) have been formulated by Chatt[1] as chloro-bridged dimers (2a) containing both a platinum(II)– or palladium(II)–carbon σ-bond and a π-coordinate bond from the remaining olefin ligand to the metal. The usually labile σ-bonded platinum(II) or palladium(II) complexes gain their stability from the olefin ligand, which affords large crystal field splitting.[2]

The reaction of dicyclopentadienedichloroplatinum or -palladium (1, M = Pt or Pd) with methanol,[1] or the direct reaction of dicyclopentadiene with sodium chloroplatinate or palladate in methanol,[3] produces the σ-bonded complex 2a. Although the type of metal-ligand linkage was described by Chatt,[2] and some of the many structural problems surrounding the isomerism in the organic ligand have been recognized,[4] the stereoisomerism associated with the organic moiety has not been established.
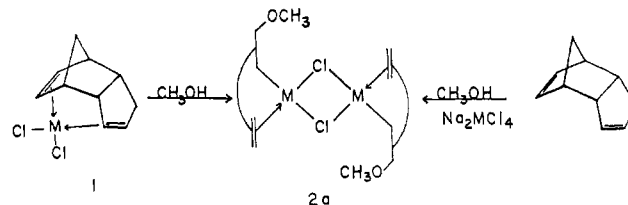
The two unequivalent double bonds in dicyclopentadiene present two different sites for the methoxy metalation. Moreover, the addition may occur *cis*, with the addends either *endo* or *exo*, or the reaction may proceed by a *trans* addition, with the metal either *exo* or *endo*. The relationship of the remaining double bond to the addends (*i.e.*, whether the remaining double bond is positioned closer to the metal or methoxy addend) doubles the number of possible isomers. Finally, rearrangement often occurs in ionic additions to *endo*-dicyclopentadiene to provide products containing the *exo*-dicyclopentadiene skeleton.[5] The 5,6-double bond (norbornene bond) is known to be much more reactive than the 2,3-double bond with respect to ionic additions. Thus, if only oxymetalation of the 5,6-double bond is considered, there are sixteen *dl*-pairs possible for an individual organic portion only.

This addition is somewhat analogous to the oxymercuration reaction of dicyclopentadiene in which *cis–exo* addition takes place at the 5,6-double bond without rearrangement.[6,7] Complexation with an *exo*-platinum or -palladium, however, would not be expected since intramolecular coordination with the remaining double bond would be impossible.

We have now established the structure of the organic ligand and the configuration associated with its bonding to the metal accordingly. Reduction of the complex 2 (M = Pt or Pd) by hydrogen or with sodium borohydride afforded only octahydro-*exo*-5-methoxy-4,7-*endo*-methanoindene (3), as established by comparison with an authentic sample.[7] Thus, the position on the ring and the *exo* arrangement of the methoxy group in the complex (2b) was established, but this provides no information as to the configuration of the metal, *exo* or *endo*.

The complexes 2b were too insoluble in solvents which would not react with them, so that suitable n.m.r. spectra could not be obtained. The *endo* position of the metal was confirmed by the n.m.r. spectrum of its

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(3) K. A. Hoffman and J. V. Narbutt, *Ber.*, 41, 1625 (1908).
(4) R. B. King, *Inorg. Chem.*, 2, 528 (1963).
(5) See, for example, S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Juvale, *J. Am. Chem. Soc.*, 84, 3918 (1962); S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963), and references therein.
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(2) (a) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959); (b) G. Calvin and G. E. Coats, *ibid.*, 2008 (1960); (c) J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *J. Am. Chem. Soc.*, 83, 2768