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## A Search for Perchlorate Complexes. Raman Spectra of Perchlorate Solutions

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The Raman spectra of aqueous solutions of seventeen different metal perchlorates have been obtained in an effort to collect evidence of possible complex formation. Seven of these, the perchlorates of cadmium(II), mercury(I), mercury(II), lanthanum(III), thallium(I), magnesium(II) and manganese(II) exhibited Raman lines in addition to those expected from the perchlorate ion. Of these, only the last three showed Raman lines which could tentatively be attributed to complexes rather than ion-pairs. In all cases these lines were extremely weak and an alternative explanation cannot be excluded with certainty. Even in those cases where extra Raman lines are observed, the association must be very slight.

A fundamental assumption in practically all equilibrium studies on complexes in aqueous solution is that the perchlorate ion forms no complexes. Thus, perchlorates are used to obtain solutions of metal ions free from the effects of complexation, at least insofar as this anion is concerned. A typical example of this is the use of perchlorates to test the Nernst equation and to furnish solutions with precisely known metal ion concentrations for use with Leden's method.<sup>2</sup> At the present time there are reports that cast some doubt upon the validity of this assumption in certain cases. Claims for perchlorate complexes for ferric ion<sup>3</sup> and mercurous ion<sup>4</sup> have been made. In the case of the ferric ion subsequent work has not been in complete accord with this claim.<sup>5,6</sup> The problem can be resolved, in part, by an examination of the Raman spectra of aqueous solutions of perchlorates. The Raman spectra of such solutions should indicate the presence of any covalent or coordinate covalent bond which is present. Since the lines in the Raman spectra originate in vibrations in which there is a change in the polarizability of the bond, they are ideal for detecting the presence of coordinate bonds. It should be recalled that aqueous solutions of a simple salt consisting only of monatomic species give rise to a Raman spectrum in which all of the lines are due to water, while a solution of say lithium nitrate will exhibit frequencies characteristic of the nitrate ion and water only. In many cases Raman spectra have been used to study complex formation and to determine the symmetries of the complexes produced.<sup>7-10</sup> A recent example is the demonstration of Raman lines other than those of  $\text{Ga}_2\text{Cl}_6$  in a mixture of NaCl and  $\text{GaCl}_3$ .<sup>11</sup> These were assigned to the  $\text{GaCl}_4^-$  ion. The detection of ion pairs by this method seems possible only with an

extremely sensitive apparatus and in a situation where the formation of ion-pairs leads to a very considerable polarization of the constituent ions. In most aqueous solutions which contain an appreciable concentration of ion pairs, there seems to be no evidence of such interactions giving rise to detectable Raman lines. For this reason, the data gathered below refer primarily to the question of whether the perchlorate ion shows a detectable tendency to form coordinate-covalent bonds.

Evidence of this type of interaction in aqueous solutions is obtained easily in spite of the complications which may arise in the interpretation of the spectra.<sup>12</sup> An example of the type of complication which may arise can be seen in the case of the nitrate ion. The Raman spectrum of the nitrate ion has been examined by many investigators.<sup>8b</sup> In addition to the possibility of lines due to complex formation, the nitrate ion itself may be capable of existing in two forms in concentrated aqueous solutions of nitrates.<sup>12</sup> In any study of concentrated aqueous solutions of perchlorates the possibility of an analogous phenomenon must be considered.

## Experimental

The Raman spectra were obtained using a Hilger Model ES612 glass prism spectrograph and a Hilger Raman source for the excitation of the mercury lines. The line at 4358Å. was used in this work. The spectra were recorded on anti-halation plates which subsequently were used to obtain photographic enlargements. The pictures were taken with a camera with an  $f/5.7$  shutter. The solutions were prepared from reagent grade perchlorates where these were available with the exception of the mercurous perchlorate which was prepared using the method of Pugh<sup>13</sup> and the perchlorates of lanthanum, cadmium, neodymium and thallium. These latter solutions were obtained by the reaction of the c.p. oxides ( $\text{La}_2\text{O}_3$ ,  $\text{CdO}$ ,  $\text{Nd}_2\text{O}_3$ ) or the metal (Tl) with c.p. perchloric acid. All of the solutions were filtered through a fine sintered glass disk prior to use.

## Results and Discussion

The Raman frequencies observed for these solutions are listed in Table I. In general, a slight excess of perchloric acid was added to suppress hydrolysis. The fundamental frequencies reported<sup>14</sup> for the perchlorate ion are 92.1, 163.0, 364.4, 463.0, 629.5, 931.7 and 1107.0  $\text{cm}^{-1}$ . Of these, only the last four are found in the Raman spectra of alkali perchlorates. In pure perchloric acid the strongest line is at 1032  $\text{cm}^{-1}$  while others are at 425, 572, 585, 738 and 1182-1312  $\text{cm}^{-1}$ , this last being a broad band. For sodium

(12) J. P. Mathieu and M. Lounsbury, *Disc. Faraday Soc.*, No. 9, 196 (1950).

(13) W. Pugh, *J. Chem. Soc.*, 1824 (1937).

(14) R. M. Ansidei, *Atti Reale Accad. Ital. Rend. Classe Fis. Mat. Nat. Ser. (7)*, 1, 459 (1940).

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(2) I. Leden, *Z. Physik. Chem.*, **188**, 160 (1940).

(3) J. Sutton, *Nature*, **169**, 71 (1952).

(4) S. Hietanen and L. G. Sillen, (a) *Suomen Kemistilehti*, **B29**, 31 (1956); (b) *Arkiv Kemi*, **10**, No. 2, 103 (1956).

(5) H. Coll, R. V. Nauman and P. W. West, *J. Am. Chem. Soc.*, **81**, 1284 (1959).

(6) K. W. Sykes, *J. Chem. Soc.*, 2473 (1959).

(7) J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Pub. Corp., New York, N. Y., 1939.

(8) (a) K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlags, Leipzig, 1943; (b) *ibid.*, p. 401, 402, 412.

(9) L. A. Woodward, (a) *Annual Repts. Chem. Soc. (London)*, **XXXI**, 21 (1935), (b) *Quart. Rev. (London)*, **10**, 185 (1956) and (c) O. Redlich, E. K. Holt and J. Bigeleisen, *J. Am. Chem. Soc.*, **66**, 13 (1944).

(10) J. P. Mathieu, *J. Inorg. Nuclear Chem.*, **8**, 33 (1958).

(11) H. Gerding and J. A. Koningstein, *Rec. trav. chim.*, **79**, 46 (1960).

TABLE I  
RAMAN LINES OBSERVED WITH AQUEOUS PERCHLORATE SOLUTIONS

Perchlorate	Concentration, mole/liter	Raman lines, cm. <sup>-1</sup>
Hg <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1	171, 402, 467, 625, 832, 874, 933, 1113
Hg(ClO <sub>4</sub> ) <sub>2</sub>	3	402, 467, 625, 832, 874, 933, 1113
Pb(ClO <sub>4</sub> ) <sub>2</sub>	2.07	172, 459, 628, 830, 868, 922, 971
AgClO <sub>4</sub>	6	461, 633, 918, 1085
Fe(ClO <sub>4</sub> ) <sub>3</sub>	2 (+ HClO <sub>4</sub> )	461, 633, 918, 1085
La(ClO <sub>4</sub> ) <sub>3</sub>	0.6 (+ HClO <sub>4</sub> )	(126, 143, 165), <sup>a</sup> 462, 628, 837, 875, 922, 970
TiClO <sub>4</sub>	Satd. at 25°	(45?, 85, 148, 168, 284?, 299?) <sup>a</sup> , 451, 623, 806, 866, 915, 963
KClO <sub>4</sub>	Satd. at 25°	920, 960
Cd(ClO <sub>4</sub> ) <sub>2</sub>	1	(173, 248), <sup>a</sup> 460, 632, 834, 868, 921, 968
Mg(ClO <sub>4</sub> ) <sub>2</sub>	2	(173?, 248?), <sup>a</sup> 460, 632, 834, 868, 923, 968
Ca(ClO <sub>4</sub> ) <sub>2</sub>	2	459, 626, 829, 870, 921, 968
Sr(ClO <sub>4</sub> ) <sub>2</sub>	2	462, 626, 835, 871, 922, 969
Ba(ClO <sub>4</sub> ) <sub>2</sub>	2	459, 627, 830, 868, 923, 968
Zn(ClO <sub>4</sub> ) <sub>2</sub>	1	475, 634, 973, 1020
Mn(ClO <sub>4</sub> ) <sub>2</sub>	1	(113, 155, 230, 310), <sup>a</sup> 450, 618, 765, 827, 865, 913, 960
Nd(ClO <sub>4</sub> ) <sub>3</sub>	1	459, 623, 823, 865, 918, 967
Ce(ClO <sub>4</sub> ) <sub>3</sub>	1 + 2 M HClO <sub>4</sub>	448, 618, 766, 819, 912, 960

<sup>a</sup> Numbers in parentheses refer to lines at the limit of detection.

perchlorate solutions lines are found<sup>5b</sup> at 464, 631, 940 and 1053–1167 cm.<sup>-1</sup> (band) while these same lines in dilute perchloric acid solution occur<sup>6c</sup> at 462, 631, 931 and 974–1172 cm.<sup>-1</sup>. In interpreting the Raman spectra it is first necessary to consider two possible classes of Raman lines which may arise from complex formation involving the perchlorate ion: (1) lines of very low frequency which are fundamental frequencies of an M-ClO<sub>4</sub> linkage and are *prima facie* evidence for the formation of such a bond and (2) lines with frequencies not attributable to any other known species in the system and therefore identified with a complex. Because of experimental difficulties and the halation of the photographic plates, it is very difficult to observe Raman lines of 40 cm.<sup>-1</sup> or less. An additional complicating feature whose presence is always possible is the occurrence of combination lines.

An alternative explanation for some of these lines, suggested by one of the referees, is that the Raman lines arising from water in this region may be observed. The reason for neglecting these in most of the discussion below is that *ultraviolet excitation is necessary*<sup>7</sup> to produce the water frequencies less than 3200 cm.<sup>-1</sup> with measurable intensity. Since such a source was not used and since filters were used to prevent any such excitation from the mercury lamp, such a neglect seems reasonable. When ultraviolet excitation is used weak water bands at 170 and 500 cm.<sup>-1</sup> may be observed. The fact that such lines are even possible would tend to make the interpretation of any faint lines in this region difficult but would lend added support to the conclusion that any perchlorate complexes formed in these systems are indeed very weak ones.

Of the solutions examined, several showed unexpected Raman lines. Many, but not all, of these lines were very, very faint. Before reaching any conclusions concerning the origin of these lines, it is well worth while to examine the behavior of the most nearly analogous compounds, the nitrates. Mathieu and Lounsbury<sup>12</sup> have measured

the Raman spectra of a large number of nitrate solutions and have found, in many cases, additional lines not found with the simple alkali nitrates. These lines could be accommodated into a simple scheme if it was assumed that the nitrate ion exists in two states with a discontinuous path from one state to the next. The ratio of the concentrations of these two forms was found to be directly dependent upon the concentration of nitrate ion in the solutions. It was proposed that as the ionic strength increased, the ionic atmosphere was no longer isotropic and the nitrate ion then assumed a configuration of lower symmetry. It seems that a similar process is much less likely with the perchlorate ion. The spectra observed with the most concentrated solutions of perchlorate (6 M) included the simplest of those observed (*e.g.*, AgClO<sub>4</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub>). For this reason, the discussion below will assume that an analogous process need *not* be considered with solutions of the perchlorate ion.

For solutions of silver perchlorate, the Raman spectrum is quite simple and indicates that no coordinate bond of any detectable strength is formed even in rather concentrated perchlorate solutions. The conclusion is in agreement with previous studies on solutions of silver perchlorate.<sup>15,16a</sup>

The Raman lines observed with lead perchlorate solutions are seven in number. Six of these are also found in barium perchlorate solutions (see below) and can be unambiguously assigned to the perchlorate ion. The seventh, at 172 cm.<sup>-1</sup>, probably arises from the transition which occurs at 163.0 cm.<sup>-1</sup> in the perchlorate ion, where it is one of the fundamental frequencies. A similar line is found in solutions of some divalent and tervalent perchlorates.<sup>15b</sup> It is less probable that such a line arises from the formation of a complex. For such a coordinate bond the force constant, *K*, may be obtained from the relation:  $\nu = (1/2\pi c)(K/\mu)$

(15) M. J. Murray and F. F. Cleveland, *J. Am. Chem. Soc.*, **65**, 2110 (1943).

(16) (a) A. E. Hill, *ibid.*, **43**, 254 (1921); **44**, 1163 (1922); (b) R. M. Ansidei, *Boll. sci. facolta chim. ind. Bologna*, **18**, 116 (1940).

$\mu)^{1/2}$ , where  $\mu$  is the reduced mass of the system and  $c$  is the velocity of light. Here  $\mu = (M_{\text{Pb}} + 2 \times M_{\text{ClO}_4^-} / M_{\text{Pb}} + 2 + M_{\text{ClO}_4^-})$  and  $K = 0.01 \times 10^5$  dynes/cm. While this is certainly a reasonable value for the force constant of such a bond as would be formed between the ions  $\text{Pb}^{+2}$  and  $\text{ClO}_4^-$ , it is rather difficult to explain why this same line would occur in the Raman spectra of aqueous solutions of cadmium and magnesium perchlorates. For this reason it seems more suitable to identify it with one of the fundamental frequencies of the perchlorate ion.

The Raman spectrum of 2 *M*  $\text{Fe}(\text{ClO}_4)_3$  which contained a sufficient quantity of perchloric acid to give a colorless solution (by suppression of hydrolysis) also was very simple with each line due to the perchlorate ion. In view of the considerable controversy over this system, it must be stated that these results hold for perchlorate ion concentrations up to about 3 *M*. Earlier work includes a report<sup>17</sup> of a complex of the type  $[(\text{ClO}_4)\text{Fe}-\text{O}-\text{Fe}(\text{ClO}_4)(\text{H}_2\text{O})]^{++}$ , and solid salts of perchloro-ferric acid<sup>18</sup> which were formulated as containing  $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$  even though written somewhat differently, e.g.,  $\text{Na}[\text{Fe}(\text{ClO}_4)_4] \cdot 6\text{H}_2\text{O}$ . In 1922, Hardtmann<sup>19</sup> used measurements in the region 2400-4000 Å. to support his claim that perchlorate containing ferric ion complexes could form. Subsequently, Sutton<sup>3</sup> interpreted measurements in roughly the same region as indicating the presence of an ion-pair  $\text{Fe}^{+3}-\text{ClO}_4^-$  with a formation constant of  $0.475 \pm 0.075$ . A reexamination of older data<sup>20</sup> has led Sykes<sup>6,21</sup> to estimate the same formation constant at  $6.7 \pm 0.7$  for an ionic strength of 0.0236 and  $3.7 \pm 0.7$  at an ionic strength of 0.0437. Coll, Nauman and West,<sup>5</sup> from a study of the  $\text{Fe}^{+3}-\text{Cl}^-$  system in concentrated perchloric acid and sodium and magnesium perchlorates, proposed that a more reasonable explanation of some of the observations on concentrated perchloric acid solutions was one based on a variation of the degree of hydration of the ferric ion in such solutions. These would be expected to have an effect on the absorption spectra which would be difficult to assess accurately. A further fact adduced by these authors to support this view is the fact that ferric perchlorate is less soluble in 70% perchloric acid than in more dilute solutions, a behavior just the reverse of what would be expected if a species such as  $\text{FeClO}_4^{+2}$  were present to any appreciable extent. Here also the alternative explanation of a rather general medium effect on the absorbance seems a possible and a preferred description of the processes occurring.<sup>22</sup> The great simplicity of the Raman spectrum observed here lends support to these arguments.

For solutions of cerous perchlorate a rather

similar situation is found. The Raman spectrum shows no lines which can be attributed to any species other than the perchlorate ion or perchloric acid. In view of earlier claims<sup>23,24</sup> for the existence of a  $\text{CeClO}_4^{+2}$  complex, this lends support to the view that effects due to changes in the ionic medium were interpreted erroneously in these cases. Newton and his co-workers<sup>25,26a</sup> have examined this medium effect in greater detail and found some rather considerable changes of this type. Attempts to obtain Raman spectra of cerium(IV) perchlorate solutions failed because of their color and the extensive photodecomposition which occurred on illumination. For solutions up to 0.01 *M* in Ce(IV), Moore and Anderson<sup>26b</sup> found no evidence for a Ce(IV)- $\text{ClO}_4^-$  complex.

With solutions of both mercurous and mercuric perchlorates, the Raman spectra show a line at 402  $\text{cm}^{-1}$  not found in the other Raman spectra and not easily attributed to the perchlorate ion. The relative intensities of this line in the two cases is in the order expected on the basis of the potentiometric studies of Hietanen and Sillen.<sup>4</sup> These investigators found that the variation of the equilibrium constant for the reaction  $\text{Hg}^{+2} + \text{Hg} \rightleftharpoons \text{Hg}_2^{+2}$  in a perchlorate medium could be explained on the basis that the mercurous ion formed a stronger complex with the perchlorate ion than the mercuric ion. While the nature of such complexes cannot be specified exactly, it is reasonable to assume that the perchlorate ion is more distorted than it could be in an ion-pair. The most disturbing element in this analysis is the fact that this Raman frequency is the same for both mercuric and mercurous perchlorates. Previous spectrophotometric data on mercuric perchlorate solutions<sup>27</sup> have been cited as possibly supporting the presence of such a complex, but this was before the difficulties caused by the varying medium were fully appreciated. A careful study<sup>28</sup> of the ultraviolet absorption spectrum of mercurous perchlorate solutions was used to examine the dissociation equilibrium of the mercurous ion. Here, too, a medium effect was observed in which the molecular extinction coefficient varied in a linear manner with the concentration of added perchloric acid or sodium perchlorate. Unfortunately, the effect of these two reagents was not the same, the perchloric acid being more than one and a half times as effective as sodium perchlorate in reducing the molecular extinction coefficients.

Solutions of cadmium perchlorate show only two very, very faint Raman lines other than those arising from the perchlorate ion. Such behavior is consistent with the observation<sup>2</sup> that an electrode reversible to the cadmium ion shows a potential which follows the Nernst equation as the concentra-

(17) G. Jander and K. F. Jahr, *Kolloid Beihefte*, **43**, 303, 305, 323 (1936).

(18) R. F. Weinland and F. Engraber, *Z. anorg. allgem. Chem.*, **84**, 340, 368 (1913).

(19) Hardtmann, diss. Leipzig, 1922, cited in Abegg's "Handbuch" IV Band, 3 Abt., 2 Teil B, p. B305, B140 (Fig. B43).

(20) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

(21) K. W. Sykes, *Spec. Pub. Chem. Soc. (London)*, No. 1, 64 (1954).

(22) E. L. King, Sr. M. J. M. Woods, O.P., and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5016 (1958).

(23) L. J. Heidt and J. Berestecki, *ibid.*, **77**, 2049 (1954).

(24) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

(25) T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, **75**, 2449 (1953).

(26) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957), and private communication cited in ref. 22; (b) R. L. Moore and R. C. Anderson, *J. Am. Chem. Soc.*, **67**, 167 (1945).

(27) H. Fromherz and K. H. Lih, *Z. physik. Chem.*, **A167**, 103 (1933).

(28) W. C. Higginson, *J. Chem. Soc.*, 1438 (1951).

tion of cadmium is varied in a medium containing large amounts of sodium perchlorate. The possibility that the cadmium ion forms a very weak complex is consistent with the Raman spectrum. An alternative possibility which must be considered is the formation of an ion-pair. An ion pair might give rise to faint Raman frequencies by distortion of either the aquo-cadmium ion or the perchlorate ion. The possibility of a very slight amount of hydrolysis here is very unlikely but cannot be excluded completely. In summary it appears that any perchlorate complex formed by the cadmium ion must be an extremely weak one.

The alkaline earth perchlorates, with the possible exception of magnesium, show a common set of Raman lines. Since there are lines here which are not found in the Raman spectrum of sodium perchlorate solutions, it is necessary to consider whether these can be due to complex formation. For the lines at 830, 870 and 970  $\text{cm}^{-1}$  the answer must be no. These lines are of such a constant frequency with the different alkaline earth perchlorates that they cannot be reasonably assigned to any coordinate linkage between these cations and the perchlorate anion. With magnesium perchlorate there are two additional very, very faint lines at 173 and 248  $\text{cm}^{-1}$ . The 173  $\text{cm}^{-1}$  line probably is associated with the 163  $\text{cm}^{-1}$  line of the perchlorate ion while the 248  $\text{cm}^{-1}$  line may be a combination line arising from the 92.1 and 163.0  $\text{cm}^{-1}$  lines or may be due to the formation of a very weak complex.

Neodymium and lanthanum perchlorates again showed the six lines found with the alkaline earth perchlorates. Lanthanum perchlorate also showed three exceedingly faint lines at 123, 143 and 165  $\text{cm}^{-1}$ . Since the properties of these ions are otherwise very similar this difference is quite unexpected. A previous spectrophotometric study of the  $\text{Nd}^{+3}\text{-ClO}_4^-$  system<sup>29</sup> showed that evidence of complexation could be obtained only in very concentrated (11.8 *M*) perchloric acid. The Raman spectrum is in full accord with this insofar as more dilute solutions are concerned. Studies of the apparent molar refraction of lanthanum perchlorate solutions<sup>30</sup> indicate that this decreases significantly in solutions more concentrated than 2 *M*. Because of the high charge on the lanthanum ion it is conceivable that these effects are concerned primarily with the rearrangement of water molecules in its environment, though a very weak complex is quite possible.

Potassium perchlorate is relatively insoluble in water, but a saturated solution does exhibit lines at 920 and 960  $\text{cm}^{-1}$ . These result solely from the perchlorate ion and also are among the strongest of the lines observed in the solutions of the heavier alkaline earth perchlorates. It recently has been found<sup>31a</sup> that there is no chemical shift in the

nuclear spin resonance spectrum of  $\text{Na}^{23}\text{ClO}_4$ . W. Geffcken<sup>31b</sup> suggested that the formation of ion pairs might be responsible for the observed concentration dependence of the equivalent refraction of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{Al}(\text{ClO}_4)_3$  but suggested other, equally possible, explanations also.

Zinc perchlorate also shows only lines attributable to the perchlorate anion. The Raman spectrum reported here is slightly different from that reported earlier by da Silveira.<sup>31c</sup> The most obvious line lacking in our results is one at 183  $\text{cm}^{-1}$  which was found for solutions of several zinc salts. It is quite likely that this line arises from hydrolytic products as our solutions, which contained a slight excess of perchloric acid, showed no such lines. Dye and his co-workers<sup>31d</sup> have calculated association constants for zinc perchlorate from conductance data and obtained values from 3 to 19. In view of our results this particular manner of using the conductance data (originally due to Davies) to obtain complexity constants seems not completely justified, though the presence of ion pairs in any such system seems extremely probable.

The Raman spectrum of manganous perchlorate solutions shows unexpected complications in the form of very weak lines in the region 113–310  $\text{cm}^{-1}$ . Because of the known tendency of  $\text{Mn}(\text{II})$  to form complexes with ligands containing oxygen donors, it seems reasonable to suggest that a  $\text{Mn}^{+2}\text{-ClO}_4^-$  complex species may be present here.

For solutions of thallos perchlorate the Raman spectra contains such a large number of additional lines of very low frequency that the presence of some sort of a complex is extremely likely. Robinson and Davies<sup>31e</sup> estimated the dissociation constant of thallos perchlorate to be about unity. Thallos perchlorate also exhibits very low activity and osmotic coefficients in aqueous solution at 25°.<sup>31f</sup>

Some other perchlorates which have been reported or tentatively postulated include those of beryllium<sup>17</sup> and titanium.<sup>32</sup> There is no conclusive evidence for such complexes in either case. Also an earlier report of a perchlorate containing an activated complex of chromic ion<sup>33</sup> has been followed by alternative interpretations<sup>34,35</sup> which do not involve such a species. The perchlorate ion also differs from other anions in not exhibiting any effect on the  $\text{Fe}(\text{II})\text{-Fe}(\text{III})$  exchange<sup>36</sup> or on the  $\text{Cr}(\text{II})\text{-Cr}(\text{III})$  exchange.<sup>37</sup> It has also been stated that no claim of catalysis involving the perchlorate ion in such reactions ever has been confirmed.<sup>36</sup>

A somewhat different situation is encountered in non-aqueous solvents of low dielectric constant. Studies on these systems indicate extensive ion-pair formation and possible complexation<sup>38</sup> but

(29) P. Krumholz, *J. Phys. Chem.*, **63**, 1313 (1959).

(30) J. E. Roberts and N. W. Silcox, *J. Am. Chem. Soc.*, **79**, 1789 (1957).

(31) (a) O. Jardetzky and J. E. Wertz, *ibid.*, **82**, 318 (1960); (b) W. Geffcken, *Z. phys. Chem.*, **B5**, 118 (1929); (c) A. da Silveira, *J. Chem. Phys.*, **7**, 380 (1939); (d) J. L. Dye, M. P. Faber and D. J. Karl, *J. Am. Chem. Soc.*, **82**, 316 (1960); (e) R. A. Robinson and C. W. Davies, *J. Chem. Soc.*, 574 (1937); (f) R. A. Robinson, *J. Am. Chem. Soc.*, **59**, 84 (1937).

(32) J. Beukenkamp and K. D. Herrington, *ibid.*, **82**, 3025 (1960).

(33) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(34) H. A. E. Mackenzie and E. A. M. Milner, *Trans. Faraday Soc.*, **49**, 1437 (1953).

(35) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

(36) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(37) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(38) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 2739 (1953).

since the dielectric constant of the mixture in which these studies were carried out (75/25 dioxane/water) is about 13, an interpretation involving ion pair formation is preferable. Earlier Raman studies on perchlorates in various alcohols<sup>39</sup> revealed that the actual positions of the Raman lines varied with the salt under study. Here also no report of any perchlorate complexes was made.

There are three factors which make it very difficult to *prove* that the extra lines found in some of these Raman spectra have their origin in a coordinate linkage between the perchlorate ion and a cation. The first of these is the extreme faintness of the extra lines in conjunction with the proximity of many of them to the exciting line. The second factor is the difficulty of completely eliminating the hydrolytic products as possible sources of the observed very weak Raman lines. This becomes an increasingly troublesome factor as the charge on the cation increases. The third factor is the possibility that these extra lines may be due to the water itself.

(39) J. Goubeau, *Z. Physik. Chem.*, **36B**, 45 (1937).

In summary, of the perchlorates examined, only those of  $\text{Hg}^{+2}$ ,  $\text{La}^{+3}$ ,  $\text{Tl}^{+}$ ,  $\text{Cd}^{+2}$ ,  $\text{Mg}^{+2}$  and  $\text{Mn}^{+2}$  show any irregularities in their Raman spectra. These irregularities were for the most part very faint and lead only to the inference that complexes *may* be present. This inference is most strongly supported in the case of the perchlorates of  $\text{Tl}^{+}$ ,  $\text{La}^{+3}$  and  $\text{Mn}^{+2}$  using the intensities of the lines as a basis. Since one of the purposes of this study was to determine the validity of the procedure, generally used in studying complexes in aqueous solution, of starting with the non-complex perchlorates, it is necessary to ask how the results of this study bears on this question. From the intensities of the extra lines observed and the rarity of their occurrence, it may safely be said that the perchlorates will, in general, be far more satisfactory as examples of simple salts than salts of any other common anion.

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[CONTRIBUTION FROM THE WHITMORE CHEMICAL LABORATORY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

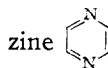
## Protonation Effects on $n \rightarrow \pi^*$ Transitions in Pyrimidine<sup>1</sup>

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The T  $\rightarrow$  S luminescence spectra at 77° in several rigid glasses are reported for pyrimidine and pyrimidine hydrochloride. The emission is assigned  ${}^3B_1(n, \pi^*) \rightarrow {}^1A_1$  from the mirror image relationship with the  ${}^1A \rightarrow {}^1B_1(n, \pi^*)$  absorption spectrum in pyrimidine. The o,o band is observed at  $28290 \pm 30 \text{ cm.}^{-1}$  yielding an experimental singlet-triplet interval of  $2630 \text{ cm.}^{-1}$  between o,o bands. Both the observed singlet-triplet interval and the observed principal vibrational progression ( $1080 \text{ cm.}^{-1}$ ) in the spectrum (corresponding to the  $1066 \text{ cm.}^{-1}$  angular ring distortion) suggest the  $\sigma$  orbitals of the nitrogen atoms are not in  $sp^2$  hybridization in the excited state. The observed pyrimidine hydrochloride emission proves that the N...H hydrogen bond is broken or is very weak in the excited state. A similar conclusion is drawn from the pyrazine hydrochloride emission (also reported), thus placing the well known  $n \rightarrow \pi^*$  absorption blue shift on a sound basis. A relationship between H-bond energy and the absorption blue shift is proposed and tested on the three diazines.

In a previous communication (I)<sup>2</sup> the effect of a hydrogen bonding solvent mixture (EPA) on the  $n \rightarrow \pi^*$  absorption and emission spectra of pyra-



zine was reported. The present investigation

on the solvent effects on pyrimidine



throws light on another aspect of the problem—the hydrogen bonding in the excited state.

### Experimental

Pyrimidine (Nutritional Biochemicals Corporation) was purified by vacuum distillation. Absorption measurements of  $n \rightarrow \pi^*$  bands of pyrimidine in isopentane, isopentane-ethanol mixtures and of pyrimidine hydrochloride in ethanol were carried out on a Beckman model DU quartz spectrophotometer with a recording accessory of Warren Electronics Inc.

EPA (5, 5, 2 parts by volume of ether, isopentane and ethanol), methylcyclohexane-isopentane (1:4), 1-butanol-isopentane (3:7) and isopropyl alcohol-ethanol (1:1) glasses at 77°K. were used as solvents for emission. The T  $\rightarrow$  S

emission spectra were recorded on a Perkin-Elmer model 13 spectrophotometer using an f/1 quartz lens to focus the emission on the slits. The instrument is equipped with a fused silica prism and RCA IP28 photomultiplier tube. Samples of pyrimidine were excited at 77°K. using an unfiltered G.E. AH-6 lamp. A blade phosphoroscope, with chopping frequency in excess of 1,000 c.p.s., was used to eliminate the exciting beam. The high quantum yield of emission allowed the spectra to be recorded at slits of 0.02–0.05 mm.

As an extension of the work on pyrazine (I) the emission spectra of both pyrazine hydrochloride and pyrimidine hydrochloride in EPA and in isopropyl alcohol-ethanol glasses were recorded. The hydrochlorides were prepared by condensing the vapor of the base with HCl gas. Pyrimidine hydrochloride (white solid) showed a quite different absorption spectrum from that of free base (*cf. H* in Fig. 3).

The results are reproduced in Figs. 1, 2, 3 and 4.

**Assignment of the Transition.**—The band shape of the observed T  $\rightarrow$  S emission (Fig. 1) is similar to the  $n \rightarrow \pi^*$  absorption spectrum in the vicinity of  $34,000 \text{ cm.}^{-1}$  (Fig. 2). The  $34,000 \text{ cm.}^{-1}$  S  $\rightarrow$  S<sup>1</sup> transition has been assigned on the basis of rather crude theoretical reasons<sup>3</sup> as  ${}^1B_1(n, \pi^*) \leftarrow {}^1A_1$  involving an excited  $\pi^*$  MO derived from the benzene MO with  $(n, \pi^*)$  electron population (A).

(3) (a) S. F. Mason, *J. Chem. Soc.*, 1240 (1959). (b) L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

(1) Presented at the Symposium on Molecular Structure and Spectroscopy, June 13–17, 1960, Columbus, Ohio. This work is supported by the Office of Naval Research.

(2) V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **33**, 381 (1960).