Solid Compounds containing the Bis-(1,10-phenanthroline)hydrogen Ion: Infrared Spectra

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1,10-PHENANTHROLINE (phen) crystallizes from water as the monohydrate phen,H_2O. It has been shown[1] that the water molecule is bonded *via* two N · · · H—O bonds. In strongly acidic solution two hydrogen ions are bonded to the phenanthroline,[2] whereas in moderately acidic solutions it is present as the monoprotonated species $H(phen)^+$.[3]

Recently Fahsel and Banks[4] have found two new ionic species, $H(phen)_2^+$ and $H(phen)_3^+$. They suggested that three molecules of phenanthroline are bonded successively, with hydrogen bonds N · · · H–O, to the three molecules of hydration of the hydronium ion, giving rise to the species $n$phen,$H_9O_4^+$ ($n = 1,2,3$).

Alternatively, they suggested that phenanthroline could replace the water in the sphere of hydration of the H_3O^+ ion, to give the species $n$phen,H_3O^+ $(3 - n)H_2O$. The solid compounds H,phen$^+Cl^-$,H_2O[5] and H,phen$^+ClO_4^-$,$2H_2O$[6] have been isolated. In addition, Pfeiffer and Werdelmann[7] have prepared a solid compound, $H(phen)_2^+$-(naphSO_3^-),$2H_2O$ (naphSO_3^- = anion of β-naphthalenesulphonic acid) in which the hydrogen and phenanthroline are in a ratio of 1 : 2. A solid compound with a ratio H : phen of 1 : 3 does not appear to have been isolated.

The fact that solid compounds containing the cations $H(phen)^+$ and $H(phen)_2^+$ crystallized with one or two molecules of water, seemed to confirm Fahsel and Banks' hypothesis, *i.e.* that the hydrogen ion is bonded to phenanthroline *via* one or more molecules of water. However, thermal differential analysis (t.d.a.) has revealed that the naphthalenesulphonate compound begins to lose water at 82°, to give the anhydrous compound which melts at 182°. Also, whilst trying to prepare the compound $H(phen)^+ClO_4^-$,$2H_2O$ by the literature method,[6] we obtained the anhydrous compound directly.

These results indicate that the water is not strongly bound and is not responsible for the stability of the compound.

We found that when boiling aqueous solutions containing phenanthroline and perchloric acid in ratios between 2 : 1 and 0·5 : 1 are cooled the crystalline compound $H(phen)_2^+ClO_4^-$ is precipitated. Satisfactory elemental analyses for this compound have been obtained and t.d.a. reveals no peak up to the m.p. 294°. The compound is soluble in nitroethane in which it has an equivalent conductivity of 84 Ω^{-1}cm.^{2}mole^{-1}, whilst a 1 : 1 electrolyte, Et_4NBr, has a conductivity of 69 Ω^{-1}cm.^{2}mole^{-1} in the same solvent. The molecular weight, by osmometry in the same solvent, was 230, which gives a value of 2·0 for the Van't Hoff coefficient *i*. It can therefore be concluded that this compound contains the ions $H(phen)_2^+$ and ClO_4^-.

The i.r. spectra of the compounds $H(phen)^+$-ClO_4^-, and $H(phen)_2^+X^-$ ($X^- = ClO_4^-$, naphSO_3,-$-2H_2O$, naphSO_3^-) have been recorded. In spite

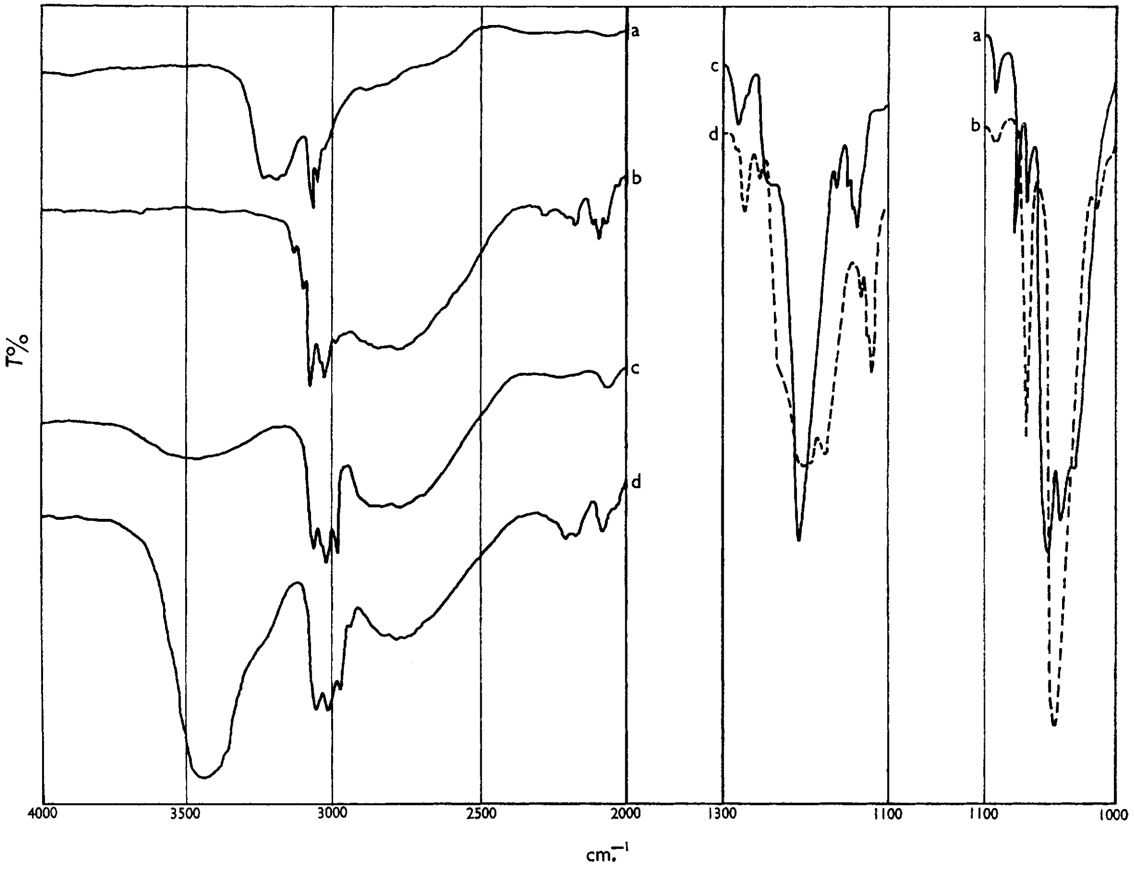
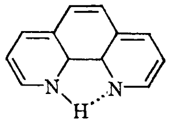


FIGURE. *I.r. spectra of the* ν(N–H), ν(CClOH), ν(ClO_4), *and* ν(SO_3) *stretching regions of* (a) $H(phen)^+ClO_4^-$; (b) $H(phen)_2^+Cl_4O^-$; (c) $H(phen)_2^+naphSO_3^-$; (d) $H(phen)_2^+$ $naphSO_3^-,2H_2O$.

of the complexity of these spectra it is possible to identify with certainty the bands due to the stretching vibrations ν(N–H), ν(C–H), ν(ClO_4), and ν(SO_3), which are shown in the Figure. The position of the broad band at *ca.* 2800 cm.$^{-1}$ due to the ν(N–H) stretching mode does not vary with the nature of the anion, as shown by a comparison of spectra (b), (c), and (d) in the Figure. In addition, absorption due to the ClO_4^- group in $H(phen)_2^+$ ClO_4^- at 1050 cm.$^{-1}$, (b), and that due to the SO_3^- group at 1200 cm.$^{-1}$, (c), in $H(phen)_2^+naphSO_3^-$, are single peaks which indicates that there is no specific interaction between cation and anion.

In the spectrum of $H(phen)_2^+naphSO_3^-,2H_2O$ the band at 3500 cm.$^{-1}$ is due to the water and is absent in the anhydrous compound. The single peak for the SO_3^- group in the anhydrous compound, is split in the hydrate indicating that the water is bound directly to the anion.

In the compounds with the ion $H(phen)_2^+$ the band at 2800 cm.$^{-1}$ due to the N–H group is very broad and is displaced towards lower wave numbers with respect to the free N–H stretching frequency expected at *ca.* 3300 cm.$^{-1}$. This indicates the presence of a strong hydrogen bond of the type N–H · · · N. This bond could be either intramolecular of the type



or intermolecular.

If the interaction were of the first type the band at 2800 cm.$^{-1}$ ought to be present also in the spectrum of $H(phen)^+ClO_4^-$. Instead ν(N–H) appears, (a), at a much higher frequency (3200 cm.$^{-1}$), as normally found in the perchlorates of monoammines.[8] Whereas the ClO_4^- band is split into more components indicating an interaction N–H ··· O, the band at 3200 cm.$^{-1}$ is broad enough to suggest a further weak intramolecular interaction of the type N–H ··· N.

It can be concluded that a strong intermolecular N–H ··· N hydrogen bond exists in the ion $H(phen)_2^+$, although, given the particular structure of phenanthroline, an interaction with the other two nitrogen atoms cannot be excluded. In other words, it can be considered as an interaction between a hydrogen atom and four nitrogen atoms.

A preliminary *X*-ray analysis of $H(phen)_2^+ ClO_4^-$ has shown that the compound crystallizes in a triclinic cell with four molecules per unit and that the shortest axis is *ca* 7·4 Å. This precludes a regular tetrahedral arrangement of nitrogen atoms about the hydrogen ion, as $H(phen)_2^+$ would then have dimensions greater than 7·4 Å. Furthermore, the proposed tetrahedral arrangement of oxygen atoms around the hydrogen ion in $H(NO_3)_2^-$,[9] is not confirmed by other studies.[10,11]

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[1] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. F. Smith Chemical Co., Columbus, Ohio, 1944.

[2] D. W. Margerum, R. Bystroff, and C. V. Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211; R. Riccardi and P. Franzosini, *Boll. sci. Fac. Chim. ind. Bologna*, 1957, **15**, 25; R. H. Linnel and A. Kaczmarczyk, *J. Phys. Chem.*, 1961, **65**, 1156.

[3] L. G. Sillen and A. E. Martell, *Chem. Soc. Special Publ.*, no. 17, 1964.

[4] M. J. Fahsel and C. V. Banks, *J. Amer. Chem. Soc.*, 1966, **88**, 878.

[5] Beilstein II, XXIII, 235.

[6] P. Pfeiffer and W. Christeleit, *Z. anorg. Chem.*, 1938, **239**, 137.

[7] P. Pfeiffer and B. Werdelmann, *Z. anorg. Chem.*, 1949, **261**, 201.

[8] G. Werner and K. Keller, *Chem. Ber.*, 1960, **93**, 1982.

[9] G. C. Dobinson, R. Mason, and D. R. Russel, *Chem. Comm.*, 1967, 62.

[10] R. D. Gillard and R. Ugo, *J. Chem. Soc. (A)*, 1966, 549.

[11] B. D. Faithful and S. C. Wallwork, *Chem. Comm.*, 1967, 1211.