

1,10-PHENANTHROLINE COMPLEXES OF Fe(II) AND Cu(II) ADSORBED ONTO HECTORITE SURFACES

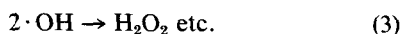
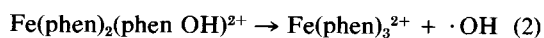
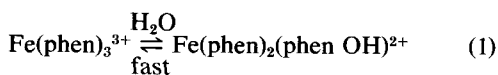
(Received 7 November 1977)

Key Words—Copper, Hectorite, Iron, Phenanthroline.

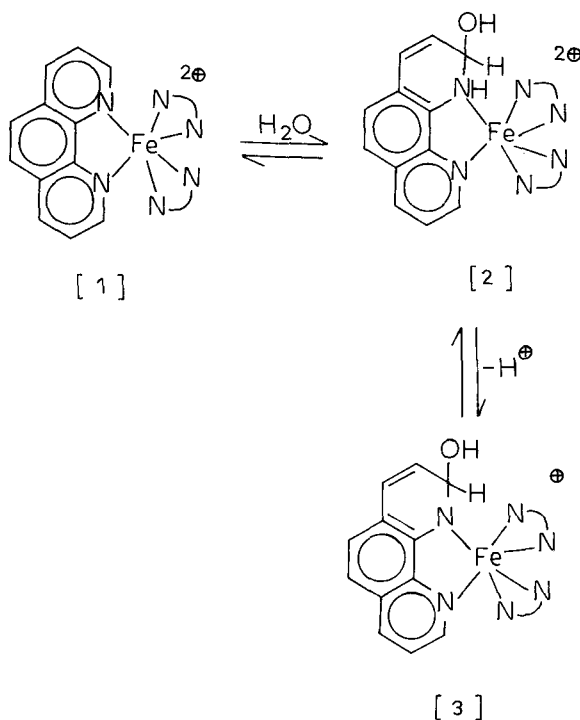
In a paper recently published in this Journal, Berkheiser and Mortland (1977) described some apparently anomalous results for the behavior of the tris-(1,10-phenanthroline)iron(II) $[\text{Fe}(\text{phen})_3^{2+}]$ and tris-(1,10-phenanthroline)copper(II) $[\text{Cu}(\text{phen})_3^{2+}]$ ions. They found that the infrared spectrum of water adsorbed onto $\text{Fe}(\text{phen})_3^{2+}$ hectorite at 50% relative humidity showed bands which were interpreted as arising from the presence of two different kinds of H_2O in the complex. The first of these (3597 cm^{-1}) was attributed to H_2O weakly hydrogen bonded to silicate-oxygen atoms and the second (3400 cm^{-1}) to H_2O coordinated to the complex. Assignment of the latter frequency was based on a study by Burchett and Meloan (1972) of water bound to Fe(II), Ru(II), and Cu(II) tris-complexes of phen and some of its substituted analogues. In addition, Berkheiser and Mortland (1977) also noted that there was a variation in the oxidation potential of the $\text{Fe}(\text{phen})_3^{2+/3+}$ couple on the clay surface which was supposed to have been due to destabilization of the oxidized form compared to the reduced form through interaction with the silicate surface. The behavior of the Cu(II) complex closely paralleled that of the Fe(II) analogue. However, all of these findings can be attributed to the existence of covalently hydrated species (Gillard, 1974, 1975) in equilibrium with the parent complex ions, together with their related pseudo bases as shown in [1]–[3].

We have previously shown that these species exist in aqueous solution (Gillard, Hughes and Williams, 1976; Gillard, Kane-Maguire and Williams, 1976; Al-Obaidi et al., 1977; Gillard and Hughes, 1977) and have shown that they play a dominant role in the reaction of the complexes in aqueous solution. Indeed $\text{Fe}(\text{phen})_3^{3+}$ and the related complexes $\text{Fe}(\text{bipy})_3^{3+}$ and $\text{Fe}(\text{terpy})_2^{3+}$ [bipy = 2,2'-bipyridyl, terpy = 2,2':6',2''-terpyridyl] are entirely unreactive when in their nonhydrated forms (Gillard and Williams, 1977a; Gillard, Kane-Maguire and Williams 1977a,b; Walters et al., 1977).

The existence of these species elegantly explains the infrared results of the previously mentioned authors. In addition, we have already discussed in some detail (Gillard and Williams, 1977b) how the existence of such equilibria as shown above can affect the values of E° for the Fe(II)-Fe(III) couples of complexes of phen, and hence the variation in the value of the couple reported by Berkheiser and Mortland (1977) is not surprising. They also mention as unusual the fact that water causes very rapid reduction of the $\text{Fe}(\text{phen})_3^{3+}$ species to $\text{Fe}(\text{phen})_3^{2+}$. This is not unusual at all. In fact other workers have commented upon this phenomena for the $\text{Fe}(\text{bipy})_3^{3+}$ (Dwyer and Gyarfás, 1952), $\text{Fe}(\text{terpy})_2^{3+}$, $\text{Ru}(\text{terpy})_2^{3+}$, $\text{Os}(\text{terpy})_2^{3+}$ (Dwyer and Gyarfás, 1954) and $\text{Ru}(\text{phen})_3^{3+}$ ions (Dwyer, et al., 1947). Indeed, it is mentioned by Dwyer and Gyarfás (1952) for the $\text{Fe}(\text{phen})_3^{3+}$ species. The reduction in aqueous solution of this species yields H_2O_2 and O_3 , neither of which oxidizes the Fe(II) complex and is ascribed by us to a mechanism also involving covalent hydrates and/or pseudo bases according to the equations (1) and (3).



Many puzzling anomalies in the chemistry of metal phen complexes similar to those found by Berkheiser and Mortland have been noted in the past. However it seems that the existence of the species described in equilibrium with the parent complex explains the vast majority if not all of them.



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REFERENCES

- Al-Obaidi, K. H., Gillard, R. D., Kane-Maguire, L. A. P. and Williams, P. A. (1977) The reaction of hydroxide and alkoxide ions with platinum(II) complexes of 5-nitro-1,10-phenanthroline and 2,2'-bipyridyl: *Transition Met. Chem.* **2**, 64-66.
- Berkheiser, V. E. and Mortland, M. M. (1977) Hectorite complexes with Cu(II) and Fe(II)-1,10-phenanthroline chelates: *Clays & Clay Minerals* **25**, 105-112.

- Burchett, S. and Meloan, C. E. (1972) Infrared studies of water bound to some extracted phenanthroline and phenanthroline chelates: *J. Inorg. Nucl. Chem.* **34**, 1207–1213.
- Dwyer, F. P. and Gyarfás, E. C. (1952) The preparation of the optical forms of tris-2,2'-dipyridyl iron(III) and tris-1,10-phenanthroline osmium(III) perchlorates: *J. Am. Chem. Soc.*, **74**, 4699–4700.
- Dwyer, F. P. and Gyarfás, E. C. (1954) The oxidation-reduction potentials of systems involving the bivalent and trivalent complexes of iron, ruthenium and osmium with 2,2',2''-terpyridyl: *J. Am. Chem. Soc.* **76**, 6320–6321.
- Dwyer, F. P., Humphreys, J. E. and Nyholm, R. S. (1947) The redox potential of the tris-orthophenanthroline ruthenium ion: *J. Proc. Roy. Soc. N. S. W.* **80**, 212–216.
- Gillard, R. D. (1974) An explanation for anomalies among complexes of *N*-heterocyclic ligands: *Inorg. Chim. Acta* **11**, L21–L22.
- Gillard, R. D. (1975) An explanation for classical anomalies among complexes of 1,10-phenanthrolines and 2,2'-bipyridyls: *Coord. Chem. Rev.* **16**, 67–94.
- Gillard, R. D. and Hughes, C. T. (1977) Novel species in ruthenium-bipyridyl systems: *J. Chem. Soc. Chem. Commun.* In press.
- Gillard, R. D. and Williams, P. A. (1977a) The pH dependent racemization of tris-(1,10-phenanthroline)nickel(II): *Transition Met. Chem.* **2**, 14–18.
- Gillard, R. D. and Williams, P. A. (1977b) On the redox potentials of complexes related to tris-(1,10-phenanthroline)iron(II): *Transition Met. Chem.* **2**, 109–110.
- Gillard, R. D., Hughes, C. T. and Williams, P. A. (1976) Pseudo-base formation in *N*-heterocycles coordinated to metal atoms: *Transition Met. Chem.* **1**, 51.
- Gillard, R. D., Kane-Maguire, L. A. P. and Williams, P. A. (1976) Direct evidence for the existence of a covalently hydrated coordination compound: *Transition Met. Chem.* **1**, 247.
- Gillard, R. D., Kane-Maguire, L. A. P. and Williams, P. A. (1977a) The dependence of the rate of dissociation of transition metal 2,2'-bipyridyl complexes upon covalent hydrate formation: *Transition Met. Chem.* **2**, 47–48.
- Gillard, R. D., Kane-Maguire, L. A. P. and Williams, P. A. (1977b) The racemization and dissociation of some tris-(1,10-phenanthroline) and tris-(2,2'-bipyridyl) complexes of iron(II) and (III): *J. Chem. Soc. Dalton Trans.* In press.
- Walters, W. S., Gillard, R. D. and Williams, P. A. (1977) Covalent hydration and the rate of dissociation of the bis-(2,2';6'2''-terpyridyl)iron(III) iron in acid solution: *J. Chem. Soc. Dalton Trans.* In press.