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Extraction of Bis(2,9-Dimethyl-4,7-Diphenyl-1,10-phenanthroline)Cu(1) Perchlorate and Bis(1, 10-phenanthroline)Cu(1) Perchlorates into Nitrobenzene and Chloroform: Role of Water

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NOTE

Extraction of Bis(2,9-Dimethyl-4,7-Diphenyl-1,10-phenanthroline)Cu(I) Perchlorate and Bis(1,10-phenanthroline)Cu(I) Perchlorates into Nitrobenzene and Chloroform: Role of Water

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Summary

The number of molecules of water associated with the bis(1,10-phenanthroline)Cu(I) perchlorate extracted into nitrobenzene was found to be 12 ± 3 and for the bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)Cu(I) perchlorate in chloroform, 0 ± 3.

Previous work (*1–3*) with extracted chelates has shown that there can be several molecules of water associated with metal chelates when they are extracted. One surprising result, however, was that the tris(4,7-diphenyl-1,10-phenanthroline)Fe(II) chelate (*3*) had over 50 molecules of water associated with it. If a model is made of this structure, it can be seen that the six phenyl groups actually provide a "cagelike" framework which might shield or protect the associated water from organic solvent displacements. As a consequence of this, the chelate was prepared without the six phenyl groups present, expecting that the number of associated water molecules would be lower. This was found to be the case since only about one-third of the former amount of water was found (*4*). The work presented in this paper is to carry this one step further.

The previous chelates were octahedral so a tetrahedral chelate was chosen, yet retaining as much of the former system as possible, the idea being to provide a minimum "cage effect." The bis(1,10-phenanthroline)Cu(I) perchlorate was chosen. This system can chelate in a $4s4p^3$ or tetrahedral manner. Using the procedure described in the experimental section, three sets of 16 experiments produced values of 14, 12 and 11 molecules of water associated with the chelate. This is less than the 18 molecules found for the d^2sp^3 configurations previously investigated (*1–4*).

The next step was to make it even more difficult for water to associate with the chelate. If the water was being bonded primarily to the metal ion rather than by the ligands, then a blocking group should allow even less water to be associated. For this the bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)Cu(I) perchlorate was chosen since models show that the methyl groups will fairly effectively shield the *d* orbitals. In this case it has been assumed that the chelate bonding has involved sp^3 orbitals and this left the *d* orbitals essentially available for other reactions. The results based on four sets of 16 experiments indicated that 0 ± 3 molecules of water were present. Two different conditions were employed. In one, the ligand was added as an ethanol solution. Exactly the same amount of ethanol was added at each concentration and to the blank. Although the blank solution water solubility increased, the amount of water present did not increase with increasing chelate concentration. The second condition was that no ethanol was present and the ligand was added to the aqueous phase as a solid. The organic phase was chloroform.

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