was kept constant at 0·1 M. and that of bromine varied in the range 0·005 M. to 0·01 M. From these results it could be concluded that the order with respect to bromine is one. The order with respect to p-bromophenol was found to be two, by keeping the concentration of bromine constant at 0·01 M. and varying that of p-bromophenol, the concentration of p-bromophenol being always in large excess. These results differ from what has been reported in the case of phenol where the order with respect to bromine is two and that with respect to phenol is one.[1] The bromination of aromatic substrates in carbon tetrachloride, reported so far, have all involved a first order in aromatic substrate and second order or first order in bromine. Our results indicating second order in substrate and first order in bromine appear to be the first of its kind. The temperature coefficient of the reaction is small of the order of 1 k. cal. indicating that in the bromination of p-bromophenol too a rapid equilibrium involving the formation of a 1 : 1 complex between the halogen and the phenol may be present even though the rate determining step might be different.

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TWO NEW COMPLEXES OF COPPER (II) FERROCYANIDE WITH ETHYLENEDIAMINE AND PROPYLENEDIAMINE

CO-ORDINATION complexes between copper (II) ferrocyanide ethylenediamine and propylenediamine have been prepared. The general molecular formula turns out to be $[Cu(amine)_2]_2[Fe(CN)_6]$. The visible absorption spectra show a single maximum in the vicinity of 650 mμ.

The complexes were prepared by the following method.

One gm. of powdered copper (II) ferrocyanide was suspended in 10 ml. of acetone. A little more than the calculated quantity of amine was added. The reaction mixture was shaken for 12 hours. The resulting complex was filtered, washed with acetone and dried over phosphoric oxide.

1. $[Cu(H_2NCH_2CH_2NH_2)_2]_2[Fe(CN)_6]$.—The complex is blue violet in colour and soluble in water, alcohol and formamide. Found : Cu = 22·04%, N = 33·93%, $H_2NCH_2CH_2NH_2$ = 41·08%, $Fe(CN)_6$ = 36·33%, Cond = 238 mhos, visible absorption band = 648 mμ ; $C_{14}H_{32}N_{14}Fe.Cu_2$ requires Cu = 21·94%, N = 33·86%, $H_2NCH_2CH_2NH_2$ = 41·46%, $Fe(CN)_6$ = 36·58%.

2. $[Cu(H_2NCH_2CH_2CH_2NH_2)_2]_2[Fe(CN)_6]$.—The complex is similar to that of the previous complex in general characteristics and solubility. Found Cu = 19·88%, N = 30·68%, $H_2NCH_2CH_2CH_2NH_2$ = 46·4%, $Fe(CN)_6$ = 33·5%, Cond = 250 mhos, visible absorption band = 650 mμ ; $C_{18}H_{40}N_{14}Fe.Cu_2$ requires Cu = 20·0%, N = 30·87%, $H_2NCH_2CH_2CH_2NH_2$ = 46·62%, $Fe(CN)_6$ = 33·36%.

Copper was estimated as salicylaldoxime complex, nitrogen by Kjeldahl method and ferrocyanide was estimated with chloromine-T.[1] The total amine content was estimated as given by the author.[2] The visible absorption measurements were done in water, on a unicam SP 500 spectrophotometer.

On the basis of percentages of copper, nitrogen, base and ferrocyanide, the molecular formula turns out to be Cu_2.4 amine $Fe(CN)_6$. The molar conductance values indicate the complexes dissociating into three ions.[3] Thus the general formula for the complexes must be written as $[Cu\ (amine)_2]_2[Fe(CN)_6]$.

These complexes exhibit a single band in the vicinity of 650 mμ. The crystal field splitting of five 3 *d* levels also requires the occurrence of only one band for planar complexes. In the ground state the positron thus occupies a t_2 level from where it is excited by providing energy to a *eg* level, giving a single band. This band can be associated with $3\ t_{2g} \rightarrow 3_{eg}$ transition.

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EXTRACTION OF BLUE PEROXYCHROMIC ACID INTO ION-ASSOCIATION SYSTEMS

THE blue peroxychromic acid formed by the addition of hydrogen peroxide to an acidified potassium dichromate solution is very unstable in aqueous solutions but can be stabilized to some extent by the formation of adducts with some donor molecules and the structure then

is suggested as $L \rightarrow Cr\ O_5$, where $L = H_2O$, ether, pyridine, TBP, etc.[1] We have observed that co-ordinating solvents such as tri-*n*-butyl phosphate (TBP), and also ion-association solvents such as tri-*n*-octyl amine, tricaprylyl monomethyl ammonium chloride (ALIQUAT-336), tetraphenyl arsonium chloride ($Ph_4As\ Cl$), tetraphenyl phosphonium chloride ($Ph_4P\ Cl$), and cetyl pyridinium chloride (Cet Py Cl), in suitable diluents have not only proved to be good extractants for the blue peroxychromic acid, but also gave appreciably stable extracts so as to enable the photometric determination of chromium.[2,3]

The ratio of chromium and the extracting anion is found to be 1 : 1 in all the extracts. The spectra of all the extracts have been recorded with a Hilger-Uvispeck Spectrophotometer. It is interesting to note that the absorption at 720 mμ reported in case of TBP-extract is absent in the extracts of the blue peroxychromic acid obtained by extracting with ion-association compounds, although the absorption maximum at 580 mμ remains unchanged in all the above cases. This shows the existence of different extracted species in the above two types of extraction systems. Also, it is reasonable to expect the formation of an anionic species from the essentially neutral blue peroxychromic acid during its extraction with ion association compounds.[2,3] Further, it has been noted that the blue peroxychromic acid in aqueous solutions is adsorbed by solid anion-exchange resins like Dowex-1, but not so with their cationic counterparts.

Dwyer and Gibson[4] have prepared a compound of the blue peroxychromic acid with triphenyl methyl arsonium chloride ($Ph_3MeAs\ Cl$) and assigned the formula of it as $Ph_3MeAs\ CrO_6$. We have prepared the solid compounds of the blue peroxychromic acid with $Ph_4As\ Cl$, $Ph_4P\ Cl$, and Cet Py Cl. The compounds are fairly stable at room tempertures, and by an analogy of Dwyer and Gibson's compound, we expected the formulæ of these compounds to be $Ph_4As\ CrO_6$, $Ph_4P\ CrO_6$, and Cet Py CrO_6 respectively. But surprisingly, these compounds gave test for chlorine and in fact, chromium and chlorine are present in 1 : 1 ratio in all the above compounds. Hence the formulæ of the above compounds are to be denoted as $Ph_4As\ CrO_5\ Cl$, $Ph_4P\ CrO_5\ Cl$, and Cet Py CrO_5 Cl. The analysis and infra-red evidence are in conformity with the existence of the above anionic chloro-peroxy complexes. These facts show the existence of an anionic species of the blue peroxychromic acid such as CrO_5X^- (where X = Cl, HSO_4, etc.) during its extraction by ion-association extraction systems. This incidentally explains the quantitative extraction of the blue peroxychromic acid by tertiary and quaternary amines, which are known to act as extractants by an ion-exchange mechanism.

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EFFECT OF ATROPINE ALONE AND IN *COMBINATION WITH* TRANQUILLISERS ON MORPHINE-INDUCED ANALGESIA

THE utilisation of preanæsthetic medications in pre-operative surgery is well known. Morphine is used to decrease the anxiety, atropine to reduce bronchial secretions and chlorpromazine to diminish pre-operative apprehension. Chlorpromazine is known to be slightly analgesic[1-3] and in combination with morphine, it increases the reaction time to obnoxious stimuli. The observation that atropine combined with chlorpromazine showed further prolongation of analgesic reaction time induced by morphine led us to report this communication.

Mice, weighing 18 to 25 gm. and of either sex, of *C.D.R.I. colony were used in the experiments.* The analgesic reaction time was measured by "Hotplate" technique. A minimum of ten mice were used for each drug, or drug combinations in testing the analgesia. Atropine (1 mg./kg.) and chlorpromazine (8 mg./kg.) were given one hour prior to morphine (15 mg./kg.). A sub-effective dose of morphine (5 mg./kg.) was given to another series of mice alone as well as in combination. All drugs were administered intraperitoneally. Analgesia was measured at every 15 minutes interval after administering morphine. The average analgesic reaction time (*sec.*) was plotted *against time interval (min.)* in the graph.

The results of the present investigation shows that the reaction time in mice to morphine-