The CuCl: 1,1-Diphenyl-2-picrylhydrazyl Free Radical Complex

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Although copper ion and hydrazine form a complex readily,[1] none of the disubstituted hydrazines has shown any evidence of complex formation.[2] The reactions of DPPH with copper acetylacetonates[3] and with ferrous ions[4] have been reported. These brief communications are concerned only with the rate of the *apparent* disappearance of free DPPH as monitored by its characteristic visible absorption at 527 mμ, and it was not certain what the nature of the reaction was. The present preliminary report describes the reaction of 2,2-diphenyl-1-picrylhydrazine ($DPPH_2$) and the 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) with Cu(I)Cl and the characterization of the new copper free radical complex formed. Both the $DPPH_2$ and the DPPH reactions lead to the identical solid CuCl: DPPH paramagnetic complex which is remarkably stable. The presence of an unpaired electron in the DPPH ligand may contribute to the donor ability of the molecule to form a metal complex.

The brown solid complex CuCl:DPPH has been prepared *via* different methods involving the reactions of either DPPH with CuCl or $DPPH_2$ with $CuCl_2$ in suitable solvents. The complex can be recrystallized from chloroform and ether and melts with decomposition at 176—178°C. Results of the elementary analysis and molecular weight determinations are consistent with the 1:1 ratio CuCl:DPPH complex. When the complex was dissolved in dilute nitric acid in the presence of Ag^+ ion, gentle heating of the solution regenerated the free DPPH radicals which could be seen readily by the appearance of the characteristic purple color (527 mμ). Prolonged heating resulted in further protonation of DPPH to give the hydrazine. The complex was also found to be unstable in strong acids.

The IR spectrum of the complex in the region 600—4000 cm^{-1} is similar to that of DPPH. The UV-visible absorption spectrum of the complex is, however, distinctly different from that of free DPPH. The characteristic visible absorption band at 527 mμ in the uncomplexed DPPH free radical is probably due to the picryl ring having appreciable delocalized unpaired spin and the second band at ~330 mμ is ascribed to the diphenylamino moiety. The new complexed DPPH absorption spectrum retains the band at ~319 mμ but the visible band at 527 mμ disappears. This suggests that the coordination of Cu^+ ion is probably *via* the picryl ring:

In acid solutions, the complex is not stable; the Cu^+ is oxidized to the Cu^{2+} state and thelig and DPPH is liberated thus regenerating the visible absorption band at 527 mμ.

The oxidation state of copper in the paramagnetic free radical complex was studied by electron spin resonance. The ESR spectrum of the polycrystalline complex shows a single symmetrical line with $g=2.002$. For comparison the Cu(II) complex $Cu^{2+}(N_2H_4)_2(HSO_4^-)_2$ was prepared[1] and its powder ESR spectrum gives the characteristic anisotropic Cu(II)lines. When the CuCl:DPPH complex was dissolved in a degassed benzene solution, a five-line ESR spectrum with additional poorly resolved hyperfine structures resembling a DPPH spectrum, was observed. Since the ESR spectrum of DPPH in a degassed benzene solution is very complicated and has not yet been analysed in detail, it is not practical to speculate on assignments of the CuCl:DPPH spectrum based on some poorly resolved structure. However, ESR spectra of free radical complexes with metal chlorides have been observed with hyperfine couplings assigned to the metal and the chlorine nuclei.[5] γ-Irradiation of the complex CuCl:DPPH in solid state leads to a weak ESR spectrum having the appearance of the paramagnetic Cu^{2+} ion. Detailed investigation of the radiation damage of copper complex is in progress. Based on the ESR results, the copper ion in the solid complex CuCl: DPPH is thought to be in the +1 state. Complementary chemical evidence also showed that the chloride ligand is tightly bound to the copper, characteristic of Cu(I) compounds.

The high resolution PMR spectra of the complex CuCl: DPPH in deuterated acetone or chloroform solvents taken at various temperatures, showed resonance absorptions due to two different groups of protons with intensities in the ratio of 5:1. The large absorption centered at ~538 cps is assigned to the protons on the unsubstituted phenyl rings while the other small absorption at ~435 cps is due to the protons on the picryl ring. In the spectrum of uncomplexed DPPH, the spin delocalization on the picryl ring renders the NMR absorption of the protons on the picryl ring too broad for detection. When the DPPH is complexed to the copper ion *via* the picryl ring, the coordination probably twists the picryl ring more out of the plane of the unpaired electron orbital thus reducing the probability of delocalization and sharpening the picry proton peaks for observation. An X-ray study has shown[6] that in the solid DPPH the picryl ring and the other two phenyl rings are not coplanar with the hydrazine backbone. Thus the observed resonance due to the picryl protons in the complex agrees with the optical absorption evidence suggesting the coordination *via* the picryl ring.

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