E.P.R. EVIDENCE FOR THE LINKING OF COPPER(II) IONS BY HYPOXANTHINE AND BY 4-AZABENZIMIDAZOLE

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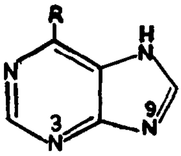
Received November 16, 1970

SUMMARY: E.P.R. studies have shown that hypoxanthine and 4-azabenzimidazole can link discrete pairs of copper(II) ions, which thereby become anti-ferromagnetically spin coupled. Solid compounds containing 1:2 mole ratios of copper(II): purine (or imidazole) derivative were isolated and had S=1 type e.p.r. spectra. However, such spectra were not observed for the polymeric species Cu(4-azabenzimidazole)X_2 (X = Cl or Br). Comparisons are made with analogous adenine compounds of known structure.

INTRODUCTION: The ability of adenine (I,R=NH_2) to bridge pairs of metal ions was first proved by Sletten (1) for its inner complex with copper, $Cu(C_5H_4N_5)_2.4H_2O$. The recent observation (2) that this linking capacity is retained in $[Cu(adenine)_2Cl]_2Cl_2.6H_2O$, even in the presence of chloride ions which very frequently function as bridges has led us to investigate whether this effect is limited to adenine or whether it is shown by purines in general, or even by other molecules containing the same disposition of N(3) and N(9) atoms as in I. Such observations would be of interest in connection with the interactions between nucleic acids and trace metals in biochemical processes. We have used divalent copper as, with this, electronic coupling between pairs of metal ions can be effectively demonstrated, both in the solid state and in solution, by e.p.r. measurements (3-5).



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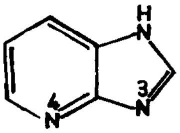

II

RESULTS AND DISCUSSION: The interaction of hypoxanthine (I,R=OH) with cupric chloride or bromide in 2:1 mole ratio in acidified aqueous solution gave blue-green solids of stoichiometry Cu(hypoxanthine)$_2$X$_2$.nH$_2$O(X=Cl or Br). The degree of lattice hydration varied slightly depending on the method of drying the samples, but for air-dried specimens n was usually 2. Corresponding complexes were obtained with 4-azabenzimidazole (II) when this ligand and cupric chloride, bromide, or perchlorate were mixed in 2:1 mole ratio in ethanol. (The halide complexes of II could also be isolated from water, but less satisfactorily than from ethanol. The perchlorate was purple). When 1:1 ratios of II and cupric halides were employed compounds of the type Cu(4-azabenzimidazole)X$_2$ (X=Cl or Br) were obtained.

X-band e.p.r. spectra of polycrystalline samples of all the CuL$_2$X$_2$ compounds (L=hypoxanthine or II) provide very strong evidence that in each

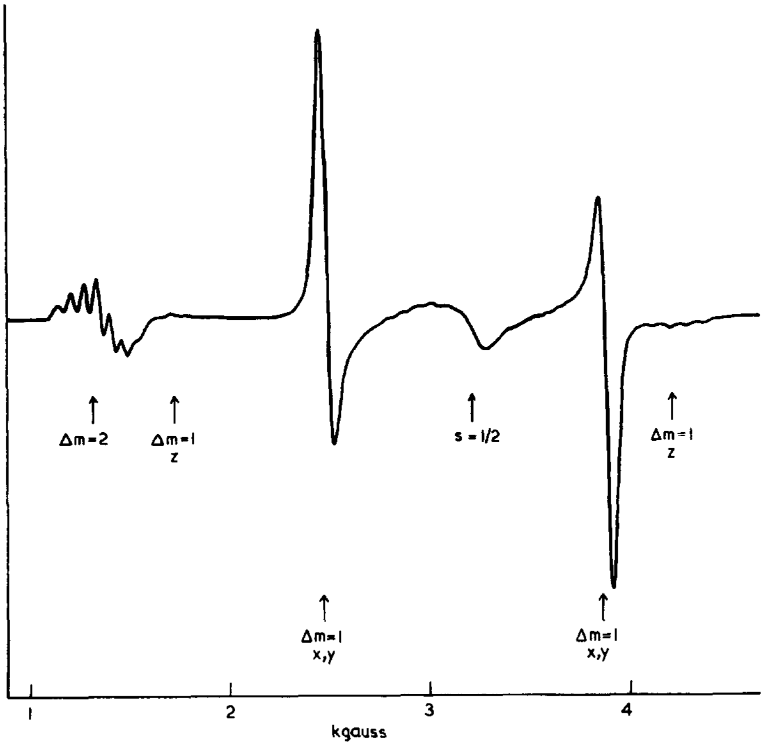

Figure 1. X-Band e.p.r. spectrum of polycrystalline Cu(4-azabenzimidazole)$_2$Br$_2$.2H$_2$O at 96° K.

case the purine or the substituted benzimidazole molecules, respectively, bridge discrete pairs of copper(II) ions, as in the analogous adenine systems described previously. Typical e.p.r. spectra are shown in Figures 1 and 2, together with the band assignments.

These spectra can be satisfactorily analysed to yield quantitative parameters on the basis of antiferromagnetic spin-coupling between pairs of copper(II) ions, yielding a thermally populated S=1 state J cm^{-1} above an S=0 ground state. Copper hyperfine structure is usually resolved on the $\Delta m=2$ transition (Figure 2), and on the z-components of the $\Delta m=1$ transitions, but not on the x,y $\Delta m=1$ bands. The range of parameters calculated from these spectra for the various CuL_2X_2 compounds may be summarised as: L=hypoxanthine, g_{xy}2.05, g_z2.17-2.23, D 0.094-0.096cm^{-1}; L=4-azabenzimidazole, g_{xy}2.05, g_z2.25-2.29, D 0.124-0.134 cm^{-1}, with, in all cases, E too small to be resolved.

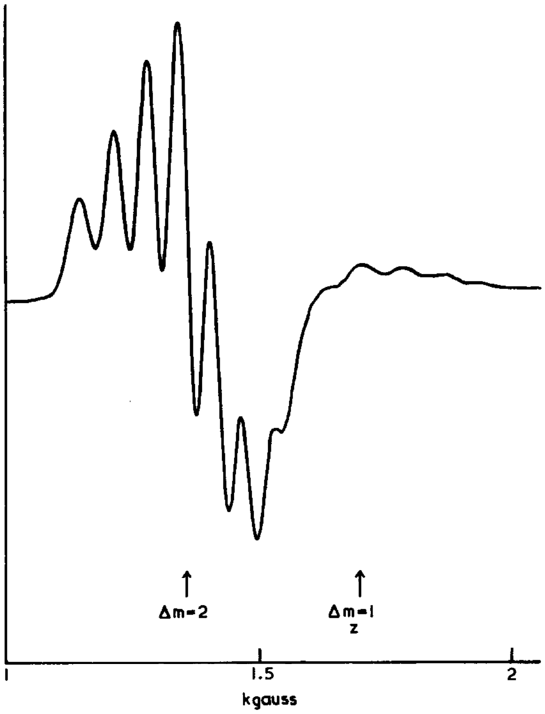

Figure 2. The $\Delta m=2$ region of Figure 1 at higher signal level.

In contrast to the CuL_2X_2 compounds the Cu(4-azabenzimidazole)X_2 complexes showed only a single broad e.p.r. band in the g=2 region. It appears likely, therefore, that these compounds adopt chain polymeric structures with halide bridges, related to that found (6) for the trinuclear adenine complex $Cu_3Cl_8(C_5H_6N_5)_2 \cdot 4H_2O$. However, it must be emphasized that whereas the observation of a clear S=1 type of e.p.r. spectrum provides good evidence for the linking of pairs of copper (II) ions, the presence of a band only in the g=2 region cannot be taken as showing the absence of bridging purine groups. Adenine bridges are indeed present in $Cu_3Cl_8(C_5H_6N_5)_2 \cdot 4H_2O$ in addition to chloride bridges, although here also the e.p.r. spectrum is of the more common S=$\frac{1}{2}$ type.

ACKNOWLEDGEMENT: We thank the University of London for the award of a Post-graduate Studentship to S.V.W.

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