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THE COPPER(II) PERCHLORATE-L-ARGININE SYSTEM. THE USE OF PRESSURE TO EFFECT A NOVEL IONIC → BIDENTATE PERCHLORATE REARRANGEMENT

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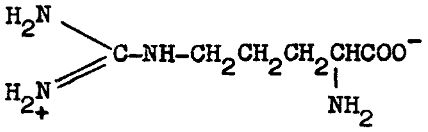
Quite recently there has been some considerable interest in the effect of pressure on chemical systems,(1,2) but these have been spectral studies of stereochemical changes of metal complexes in solution. We should like to report here a unique solid-state molecular rearrangement brought about by pressure.

The amino acid arginine is, like all amino acids, a zwitterion in the solid state, and it may thus be expected to complex to metal ions as a neutral

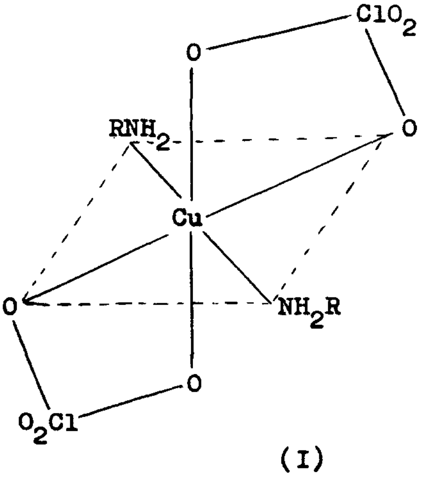


(= ArgH)

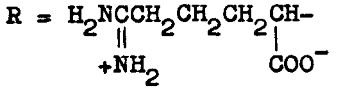
zwitterionic species or, by deprotonation of the guanido group, as an anion.

When l-arginine and $Cu(ClO_4)_2.6H_2O$ (2:1 molar ratio) are mixed in a small amount of water with vigorous stirring, a blue microcrystalline precipitate is obtained, $[Cu(ArgH)_2(ClO_4)_2]$ (I). Analyses: Calc. C, 23.6; H, 4.6; N, 18.3%. Found C, 23.8; H, 4.7; N, 18.1%. The infrared spectrum in Nujol has bands at 1140, 1115, 1085 cm^{-1} and at 635, 630, and 625 cm^{-1}, indicative of bidentate perchlorato-groups.(3) While both the carboxylate and amine stretching vibrations are susceptible to H-bonding effects, it is significant that the $\nu(COO^-)$ bands in the spectrum of the complex and free ligand are very similar, whereas the $\nu(NH_2)$ bands are shifted to much lower energy in the complex than in the ligand, which is indicative of Cu-N bonding.(4) Moreover, the visible spectrum suggests a CuN_2O_4 coordination moiety$^{(5)}$ in the solid state. Although electronic spectra of copper(II) complexes are usually of quite limited assistance in structural assignments, Graddon and Munday have investigated the electronic spectra of a number of Cu(II)-amino acid complexes of known structure, and from their conclusion a band at 620mμ in $[Cu(ArgH)_2(ClO_4)_2]$ is a strong indication of $Cu-N_2O_4$ coordination. In particular, the position of the band is at much too high energy for it to result from a CuO_6 moiety (resulting from the ligand coordinating via the bidentate perchlorato- and carboxylato-groups) which absorbs at 800mμ. Thus, the structure of this complex is undoubtedly (I), which, apart from containing bidentate perchlorato-groups contains a rare example of monodentate amino acid ligands.

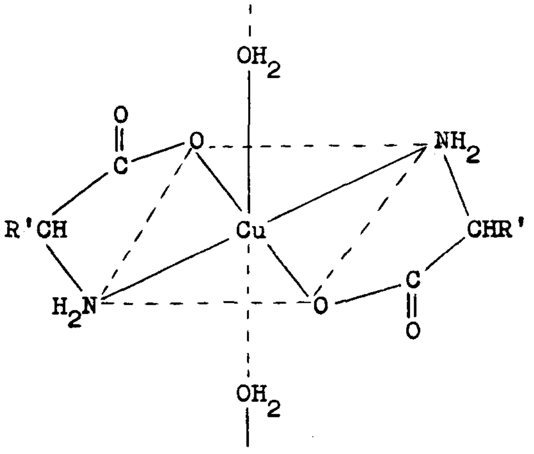
When (I) is recrystallised from water over a 24 hr period, a complex of formula $[Cu(ArgH)_2(H_2O)](ClO_4)_2$, (II), is obtained. Analyses: Calc. C, 23.1; H, 4.8; N, 17.9%. Found C, 23.5; H, 5.1; N, 17.5%. The i.r. spectrum in Nujol contains bands assignable to water, and to coordinated amino- and carboxylato- groups; in particular bands at 1095 cm^{-1} and 620 cm^{-1} indicate that recrystallisation of (I) has caused the perchlorato- groups to become ionic.$^{(3)}$ The solid state reflectance spectrum of complex (II) consists of



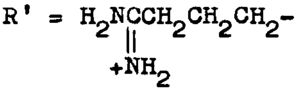
(I)



$$R = H_2N\underset{\substack{\| \\ +NH_2}}{C}CH_2CH_2CH_2\underset{\substack{| \\ COO^-}}{C}H-$$



(II)



$$R' = H_2N\underset{\substack{\| \\ +NH_2}}{C}CH_2CH_2CH_2-$$

an absorption at 635mμ, which is again indicative of a CuN_2O_4 complex. We <u>suggest</u> structure (II) for this complex, one in which the H_2O ligand acts as a bridge.

When (II) is pressed in a KBr die the resulting infrared spectrum indicates that the water molecule and carboxylato- groups have once again been replaced by bidentate perchlorato- groups, and the reflectance spectrum of the KBr disk has an absorption at 620mμ, similar to that of an authentic sample of (I). Thus, the following process may be envisaged:

$$\underset{\text{(II)}}{[Cu(ArgH)_2(H_2O)](ClO_4)_2} \xrightleftharpoons[H_2O]{\text{pressure}} \underset{\text{(I)}}{[Cu(ArgH)_2(ClO_4)_2]} + H_2O$$

This novel effect of pressure may be contrasted with the usual effect of a KBr die on coordinated perchlorate, which is to displace the perchlorate in favour of bromide ion.(6) In (II) pressure forces the ionic perchlorate to coordinate as the rare bidentate perchlorato- group.

We have investigated this pressure rearrangement thoroughly, and have concluded that the rearrangement does not occur until the complex (II)-KBr mixture is put under extreme pressure. Thus merely mixing (II) with KBr or hand-grinding does not bring this rearrangement about, because the electronic spectrum is still identical to that of the unmixed (II).

As far as we can ascertain, the use of pressure in effecting a rearrangement of groups within the <u>same</u> molecule is unique. In view of the interesting results obtained by Quagliano and co-workers with cationic arsine ligands(7) it seems that zwitterionic ligands may also be a fruitful field for further investigation. We have observed a similar pressure-induced rearrangement phenomenon in our studies on nickel(II) perchlorate-l-arginine systems.(8)

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