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Metal Ion Assisted Proton Transfer from a Coordination Water Molecule to an Amino Acid

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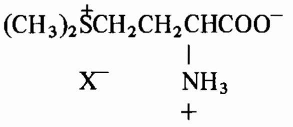
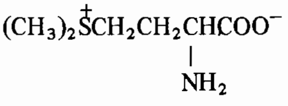
Orgel[1] and Jencks[2] have suggested that the role of a metal ion in protein is to increase the acidity of bound water molecules, and this is of probable importance in the mechanism of such enzymes as carbonic anhydrase action. We wish to report here an observation of metal ion assisted polarisation of a coordinated water molecule, and subsequent proton transfer to an amino acid, in the complex D,L-bis(methylsulphoniummethioninate)aquocopper(II) perchlorate.

D,L-methylsulphonium perchlorate ($LHClO_4$) (I; X = ClO_4) exists, as do all amino acids, as a zwitterion in the solid state. However, this interesting species, after deprotonation upon complexation is still a zwitterionic ligand (II) and coordinates as a formally neutral ligand. Highly unusual properties have been associated with complexes containing cationic ligands[3], but no systematic study has been made on ligands which contain both a formal cationic and anionic centre. Our results with, D,L-methylsulphoniummethioninate (II) indicate that novel, unpredictable results await investigators of zwitterionic ligand complexes:



$$X^- \quad (CH_3)_2\overset{+}{S}CH_2CH_2\underset{\underset{+}{NH_3}}{\underset{|}{C}}HCOO^-$$

LHX (I)



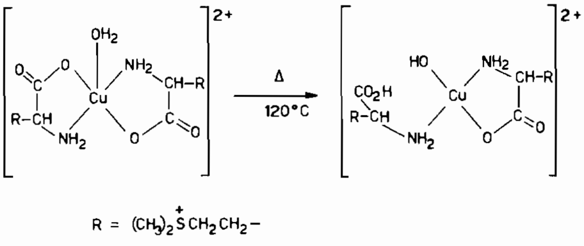
$$(CH_3)_2\overset{+}{S}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOO^-$$

L (II)

A copper(II) complex of the zwitterion, L (II) was prepared by mixing $LHClO_4$ (1.5 g) in water (50 cm^3) with $CuCO_3$ (0.3 g) and heating to 60 °C for 1 hour. The resultant blue solution was filtered while hot and, on cooling, blue needles (1.4 g) were deposited. Analytical data indicate that this complex is $CuL_2(H_2O)(ClO_4)_2$. *Anal.* Calc. for $C_{12}H_{28}N_2S_2O_{13}Cl_2Cu$: C, 13.5; H, 5.2; N, 5.2; S, 12.0; Cu, 11.9%. Found: C, 13.5; H, 5.0; N, 5.2; S, 11.8; Cu, 12.0%.

The solid state infrared spectra (KBr discs and Nujol mulls) exhibit bands at 3540 cm^{-1} and 1660 cm^{-1} assignable (after comparison with the spectrum of a deuteriated sample) to ν(OH) and $\delta(OH_2)$, respectively. The presence of the wagging vibration at 812 cm^{-1} is indicative of coordinated H_2O[5]. Bands at 1620 cm^{-1} and 1390 cm^{-1} are due to $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$, respectively. No splitting of the perchlorate frequencies at ~ 1100 or at 620 cm^{-1} are observed, indicating that the perchlorate ions retain their T_d symmetry and are uncoordinated[4]. The complex is a unibivalent electrolyte in water (Λ_o = 219 ohm^{-1} cm^2 M^{-1} in 10^{-3} M solution), and the electronic absorption spectra in water and the solid state are very similar, an unsymmetrical band occurring at 16.0 kK (ϵ = 586). The magnetic moment of $[Cu(L)_2(H_2O)](ClO_4)_2$ is typical of copper(II) complexes, μ_{eff} = 1.85 B.M.

When this complex is heated on a hot-stage a striking colour change from blue-purple to blue occurs at 120 °C. Infrared and electronic spectra of samples heated to 113 - 118 °C for up to 15 minutes are identical with those of unheated complexes, but the spectra of samples heated to 120 °C, even for only 1 minute, are considerably altered – though analytical data (C,H,N,Cu) are identical for unheated and heated complexes. The ν(OH) and $\delta(OH_2)$ bands have disappeared, and two new bands appear at 1770 cm^{-1} (C=O stretch) and 1429 cm^{-1} (a combination of C–O stretch and OH in-plane deformation vibrations) due to the $-CO_2H$ group[6]. The $\nu(COO^-)$ vibrations are still evident, though of diminished intensity. The only plausible explanation of these observations is*



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*We have indicated the structure of $[Cu(L)_2(H_2O)](ClO_4)_2$ to be a pentacoordinate monomer, but a hexacoordinate dimeric species involving bridging agno groups is also possible.

i.e. a rearrangement involving the protonation of a coordinated $-CO_2^-$ group by the H_2O, resulting in the formation of a $-CO_2H$ and $-OH^-$ groups. The $\nu(OH)$ does not appear as a single frequency, but is presumably shifted to lower frequencies by hydrogen bonding. The bands in the infrared spectrum due to ionic perchlorate groups are unchanged. The solid state visible spectrum of $[Cu(LH)(L)(OH)_2(ClO_4)_2]$, $\mu_{eff} = 1.81$ B.M., exhibits a broad absorption at 15.3 kK. The complex can be recrystallised unchanged from water, and in this solvent it is a uni-bivalent electrolyte ($\Lambda_0 = 229$ ohm^{-1} cm^2 M^{-1}).

As far as we are aware this type of rearrangement is unique in simple inorganic chemistry and serves to confirm the suggestions of Orgel[1] and Jencks[2]. Moreover, the complex $[Cu(LH)(L)(OH)](ClO)_2$, which results from the rearrangement of $[Cu(L)_2(H_2O)](ClO_4)_2$, contains the novel combination of cationic, zwitterionic, and anionic donors to the same metal atom.

References

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