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The Supercomplex Nature of Buff's 'Ferrocyanäthyl.' First Example of a Homoleptic Hydrogen Isocyanide (CNH) Metal Complex

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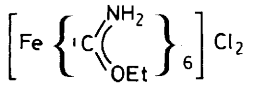
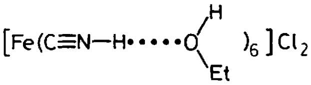
Buff's 'ferrocyanäthyl' consists of hexakis(hydrogen isocyanide)iron^{2+} chloride, the cation of which is stabilized through strong hydrogen bonding $\{d[(FeC)N \cdots O(H)Et]$ 2.509(3) Å$\}$ to a second co-ordination sphere of six molecules of ethanol.

In 1854, Buff reported that on passing a rapid stream of gaseous HCl through a concentrated solution of $H_4Fe(CN)_6$ in ethanol, he obtained a nicely crystalline yet highly air-sensitive material, which analysed as $[H_4Fe(CN)_6 + 2\ HCl + 6\ EtOH]$ (**1**).[1] In the years to follow, several formulations[2] were offered in addition to Buff's own, which was that of a tetra(ethyl isocyanide)iron complex, $[Fe(CN)_2(CNEt)_4 + 2\ EtCl + 6\ H_2O]$. In 1888, Freund very unconventionally considered the compound to be a hexacarbene (!) moiety (**2**), which in the light of our isolation and structural characterization of a similar cobalt(III) species appeared quite plausible.[3,4] Still, our recent findings on very stable discrete H-bridged adducts of $Cr(CO)_5CNH$ with a variety of O- and N-donors[5] made us favour a third structural possibility for (**1**), *viz.* that of a supercomplex† (**3**) consisting of a central $[Fe(CNH)_6]^{2+}$ octahedron‡ which is linked *via* six hydrogen bonds to a second ligand sphere of six molecules of ethanol.



$$[Fe\{C(NH_2)(OEt)\}_6]Cl_2$$

(2)



$$[Fe(C{\equiv}N{-}H\cdots O(H)Et)_6]Cl_2$$

(3)

This assumption has now been proven correct by an *X*-ray study of Buff's compound,§ which was carried out using a technique by which the unstable crystals were rapidly cooled to a temperature near that of liquid N_2 in order to prevent loss of the attached solvent molecules.[6]

The complex cation with S_3 crystallographic symmetry is shown in Figure 1.¶ The most intriguing feature of the structure is undoubtedly the highly unsymmetrical yet extremely short intermolecular H-bond, the N $\cdots$ O separation measuring only 2.509(3) Å. Obviously, there is a general pronounced tendency of CNH complexes for H-bridge formation, not only in their well known co-ordination polymers $\{$*e.g.* $[H_3Co(CN)_6]\}$[7] but also in discrete molecules and ions (see earlier). A second, though much weaker H-bond seems to be operative between the supercomplex cation and the chloride

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† Concerning the use of the term 'supercomplex,' see *e.g.* M. F. Manfrin, L. Moggi, V. Castelvetro, V. Balzani, M. W. Hosseini, and J. M. Lehn, *J. Am. Chem. Soc.*, 1985, **107**, 6888.

‡ This cation has been claimed to exist in solutions of $H_4Fe(CN)_6$ in anhydrous HF: R. J. Gillespie and R. Hulme, *J. Chem. Soc., Dalton Trans.*, 1973, 1261.

§ *Crystal data* for (**3**) $C_{13}H_{48}Cl_2FeN_6O_6$: colourless needles, M = 565.3, trigonal, space group $P\bar{3}$ (No. 147), a = 12.533(3), c = 5.7475(15) Å, U = 781.8(9) Å^3, D_c = 1.20 g cm^{-3}, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 6.88 cm^{-1}. 3043 Reflections were collected at −100(5) °C on a four-circle diffractometer in the range $2 \leqslant 2\theta \leqslant 52°$. Redundant data were averaged ($R_{av,I}$ = 2.1%) leaving 1019 unique reflections. The structure was solved by heavy atom methods and refined [non-H atoms anisotropic; the positional parameters of H(1) and H(2) were taken from a difference Fourier map which showed all hydrogen positions; those of H(1) were refined isotropically, the remaining H's were entered in idealized positions and not refined] to R = 0.0543, R_w = 0.0773 for 835 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. The strongest residual peak in the final difference Fourier map was 0.59 e Å^{-3} located 0.187 Å from O. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ It should be emphasized that the N–H(1) distance of 0.81(4) Å, though somewhat short, is not significantly different (at the 3σ level) from the average N–H value (0.87 Å) in amines: M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

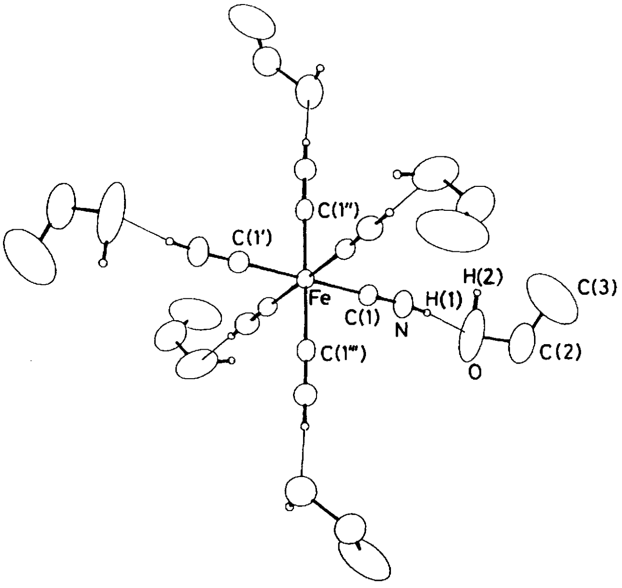

Figure 1. ORTEP drawing of the [Fe{CNH · · · O(H)Et}$_6$] cation in [Fe{CNH · · · O(H)Et}$_6$]Cl$_2$ showing the numbering scheme adopted. Fe resides on a special position (site symmetry 3-bar). The asymmetric unit contains 1/6th of the cation. Selected bond lengths (Å): Fe–C(1) 1.893(2), C(1)–N 1.138(3), N–H(1) 0.81(4), H(1) · · · O 1.70(4). Selected bond angles (°): C(1)–Fe–C(1') 180.0, C(1)–Fe–C(1'') 90.82(8), C(1)–Fe–C(1'') 89.18(8), Fe–C(1)–N 178.4(2), C(1)–N–H(1) 176(3), N–H(1)–O 174(4). Primed atoms represent transformed co-ordinates of the type (') $-x, -y, -z$; ('') $-y, x - y, z$; (''') $y, y - x, -z$.

anions throughout the crystal lattice; this is indicated by the nonbonding O · · · Cl distance [2.996(2) Å] which is well below the sum of the van der Waals radii (3.25 Å).[8]

In contrast to (**3**) (in which the second sphere co-ordination occurs entirely by H-bonding), quite large MCN · · · $(H)\underset{+}{N}$ separations have been found in the closely related systems of hexacyanometallates with polyammonium macrocyclic receptors, and it was assumed that Coulombic forces played the most important role in the formation of these supercomplexes.[9] Note, however, that here we are dealing with hydrogen bonds to co-ordinated cyanide (as distinguished from H-bonding from co-ordinated CNH) which in general seems to be markedly weaker [*cf.* Pr^{i}O(H) · · · NCCo^{III} (corrinoid) 2.74 Å].[10]

As Buff's original intention was to prepare ethyl isocyanide [or (ethyl isocyanide) iron complexes], it is noteworthy that (**3**) can be regarded as a trapped intermediate in this preparation. To arrive at the final product, only a small shift of the bridging H(1) towards the oxygen atom is required, followed by some rotary movement of the ethyloxonium|| part which brings the alkyl group near the isocyano nitrogen. (Actually, as has been shown later, this conversion is readily achieved by warming the reaction mixture to >80 °C.[11,12])

Furthermore, similar intermediates and introductory mechanistic steps may well be assumed in the novel hydroisocyanation reactions with CNH complexes particularly of epoxides, but also of aziridines, enones, heteroallenes, and even higher alkylated alkenes.[13]

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|| Baeyer's early description of Buff's complex as an oxonium salt of the type {(EtOH$_2$)$_4$[Fe(CN)$_6$] + 2 EtOH$_2^+$Cl$^-$} was thus remarkably close to reality (*cf.* ref. 2).