On the Structure and Water Content of Copper(II) Tricyanomethanide

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Interest has recently been revived in tricyano-methane, $CH(CN)_3$, and related compounds[1-8]. Salts of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} have been prepared and some of their properties investigated.[7] On the basis of their electronic and infrared spectra a polymeric model for their structure has been proposed by Enemark and Holm[7]. Doubt remains, however, as to whether or not water is present in some of these salts. Enemark and Holm state that Fe^{II} and Co^{II} tricyanomethanides retain half a molecule of water per metal atom, that the Ni^{II} compound can be prepared with a variable amount of water, and that the Mn^{II} and Cu^{II} salts retain one fourth of a molecule of water. On the other hand, the model proposed by these same Authors for the structure of these compounds "does not take into account the small amounts of water present"[7]. It should also be noted that in a previous paper[3] the Mn^{II} and Cu^{II} salts were stated to be anhydrous.

In order to substantiate the proposed structure and to find how water, if any, is co-ordinated, the X-ray crystal structure of the copper salt, $Cu[C(CN)_3]_2$, was determined. Additional experiments relating to the suspected presence of water were carried out by thermogravimetric and differential thermal analysis. Samples were prepared both according to the directions of Enemark and Holm[7] and by diffusion[9]. Debye–Scherrer diffraction patterns of powdered crystals prepared by the two different methods are identical.

Crystal data listed below were collected, and the three-dimensional X-ray analysis described was performed, using crystals prepared by diffusion. These are black, yellow when powdered, crystallize in the orthorombic system; $a = 7·176 \pm 0·005$,

$b = 5·471 \pm 0·005$, $c = 10·753 \pm 0·005$ Å; $U = 422$ Å³; $D_m = 1·92 \pm 0·05$ g.cm.$^{-3}$ (by flotation); $Z = 2$; $D_c = 1·918$ g.cm.$^{-3}$;[10] $F(000) = 238$. *Space group* Pmna from systematic absences, morphology, and structure determination. Data from Weissenberg photographs, $CuK\alpha$ ($\lambda = 1·5418$ Å) radiation.

Example of a thermogravimetric determination

	Weight (mg.)	% of Initial sample
Weight of sample	75·3	
260—310 °c loss	1·3	1·75
320—450 °c loss	49·4	65·60
Total loss	50·7	67·35
Residue (CuO)	24·6	32·65
Cu in the residue (electrolytic)	19·5	25·90

Calc. for $Cu[C(CN)_3]_2$: Cu, 26·1; CuO,32·65%
Calc. for $Cu[C(CN)_3]_2,0·25H_2O$: Cu 25·6; CuO, 32·1%.

The X-ray intensities of 414 independent reflections were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the a (6 layers) and the c axis (4 layers). From a three-dimensional Patterson synthesis the positions of all atoms were found, with the copper atom at the special position (centre) chosen as origin and C(3), C(2), and N(2) atoms (Figure) lying on the mirror planes at $x = 0$ and $x = 1/2$. After preliminary Fourier refinement, co-ordinates and anisotropic temperature factors were refined by least-squares. Values at the present stage ($R = 9·9\%$) define, for the ion $C(CN)_3^-$, the bond lengths and angles given in the Figure ($\sigma = 0·01$ Å). The ion

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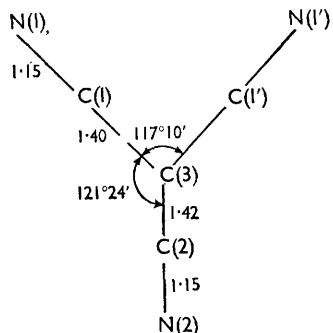[6] P. Andersen and B. Klewe, *Nature*, 1963, **200**, 464.

[7] J. H. Enemark and R. H. Holm, *Inorg. Chem.*, 1964, **3**, 1516.

[8] R. Desiderato and R. L. Sass, *Acta Cryst.*, 1965, **18**, 1.

[9] Details on this method will be given in the forthcoming full crystallographic paper.

[10] Calculated for the anhydrous salt.

C(CN)$_3^-$ is planar within $\pm$ 0·007 Å, with a maximum deviation of 0·015 Å for C(2). Every

Bond lengths and angles in the tricyanomethanide ion. N(1)–C(1)–C(3) and C(3)–C(2)–N(2) groupings are practically linear, the angles at the central atoms C(1) and C(2) being 177°40′ and 178°25′ respectively.

copper atom is surrounded by a distorted octahedron of six CN groups belonging to six different molecules. The four nitrogen atoms of N(1)-type are co-planar and the copper atom lies on this plane, the Cu–N(1) distance being 1·98 $\pm$ 0·01 Å. The two nitrogen atoms of N(2)-type complete the octahedron, at a distance of 2·49 $\pm$ 0·01 Å. The crystal structure is therefore a polymeric structure, consisting of planes of C(CN)$_3^-$ ions intersecting at an angle of about 79°, with Cu^{2+} ions occupying pseudo-octahedral holes[11]. No crystallographic evidence for the presence of water molecules is found.

Thermogravimetric determinations were performed at a rate of heating of 4° c min.$^{-1}$, using a Stanton balance with a sensitivity of 0·1 mg. Both kinds of samples show the same thermogravimetric behaviour, with no variation of weight below 260 °C. A typical result of a thermogravimetric determination is reported.

Differential thermal analyses were performed in the range 25—800°C. Although there are some differences in the results obtained from the two different kinds of samples[12], only exothermal peaks occur.

The results of the X-ray analysis confirm the structure proposed by Enemark and Holm[7] and three different experimental techniques failed to detect the presence of water. For the sample prepared by diffusion there is no crystallographic evidence of water, confirmed also by the remarkable agreement of the calculated with the experimental value of the density. The thermogravimetric determinations show that the first loss of weight takes place at a temperature too high to be related to water and that the percentage of cupric oxide residue is consistent with the calculated amount for the anhydrous compound. Finally, the absence of endothermal peaks in DTA experiments sustains the conclusion that no water is present in any of the samples examined.

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[11] See Fig. 4 in Enemark and Holm's paper.[7]
[12] Samples prepared according to Enemark and Holm show three peaks, at 180 ($\Delta T \sim 3$), 290 ($\Delta T \sim 6$), and 390 °c ($\Delta T \sim 30$). Samples prepared by diffusion do not show peaks below 290 °c.