The Crystal Structure of $K_3Mn(CN)_5NO \cdot 2H_2O$

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The mode of coordination of the nitrosyl group in transition metal complexes has been the object of considerable discussion in recent years. An extensive programme of research into the crystal structures of the transition metal nitrosyls has therefore been started at this Department. A series of pentacyanonitrosyl metal ions are among those compounds which have been studied, the structure of the first member, $K_2Cr(CN)_5NO$ having been determined by Vannerberg.[1] The structure of $K_3Mn(CN)_5NO \cdot 2H_2O$ has now also been determined and is in the process of refinement.

$K_3Mn(CN)_5NO \cdot 2H_2O$ was prepared according to Cotton, Monchamp, Henry and Young's modification [2] of the method due to Hieber, Nast and Proeschel,[3] whereby $K_3Mn(CN)_6$ is treated with an alkaline solution of hydroxylamine.

The crystal structure of $K_3Mn(CN)_5NO \cdot 2H_2O$ has been investigated by single crystal methods. The unit cell has the dimensions $a = 17.60$ Å, $b = 7.01$ Å, $c = 11.49$ Å, $\beta = 118°$. The space group proved to be *Cc*. The density was determined to be 1.9 gm/cm³. Consequently there are four formula units per unit cell. The atomic parameters listed in Table 1 have been found by means of three-dimensional Patterson and Fourier syntheses.

The manganese atoms are octahedrally coordinated by five cyanide groups and one nitrosyl group. The Mn—CN bond distances vary within the range 1.95 and 1.99 Å, whereas the Mn—NO bond distance is 1.65 Å, in accordance with the postulate of Ballhausen and Gray.[4] The distances between the oxygen atoms of the water molecules and the cyanide and nitrosyl groups indicate the presence of hydrogen bonding. An *R*-factor of 0.109 has been obtained and further refinement of the structure is in progress. A complete report of the investigation will be published shortly.

Table 1. Space group *Cc*, all atoms occupying 4 *a*.

Atom		*x*	*y*	*z*
Mn		0.000	0.000	0.000
K		0.251	0.143	0.364
K		0.747	0.862	0.668
K		0.493	0.041	0.236
C	CN group	0.414	0.382	0.339
N		0.364	0.295	0.250
C	CN group	0.578	0.625	0.674
N		0.626	0.694	0.773
C	CN group	0.937	0.879	0.582
N		0.896	0.798	0.621
C	CN group	0.070	0.232	0.054
N		0.114	0.372	0.090
C	CN group	0.918	0.787	0.958
N		0.871	0.664	0.935
N	NO group	0.052	0.119	0.433
O		0.087	0.219	0.391
H_2O		0.242	0.021	0.085
H_2O		0.739	0.991	0.932

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