Crystal Structure of $K_2[ReN(NC)_4],H_2O$

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NITRIDO-COMPLEXES of rhenium are now well established.[1] The salt $K_2[ReN(NC)_4],H_2O$ has been prepared[2] from $ReNBr_2(PPh_3)_2$ and KCN, and the Re≡N stretching frequency in the i.r. spectrum of this salt is broadened and split into a doublet in the solid, and is about 100 cm.$^{-1}$ lower than in solution.[2] A similar lowering and splitting of the $\nu_{W=O}$ band has been observed in $WOCl_4$ on comparison of the gas-phase spectrum[3] and the solid-state spectrum, attributed[4] to interaction of the oxygen of one $WOCl_4$ group with a neighbouring tungsten in the solid. The crystal structure[5] of $WOCl_4$ consists of infinite chains of alternating oxygen and tungsten atoms, with four chlorines around each tungsten atom. The crystal structure of $K_2[ReN(NC)_4],H_2O$ has been determined in order to provide an explanation of its unusual i.r. spectrum.

X-Ray diffraction data were collected using Cu-K_α radiation by the multiple-film, equi-inclination Weissenberg method and the intensities of 300 reflections, from layers 0, 1, 2, and 3 up the *c* axis, were estimated visually. The crystals are orthorhombic with $a = 15{\cdot}27$, $b = 8{\cdot}16$, $c = 3{\cdot}97$ Å, $Z = 2$, $D_c = 2{\cdot}689$, $D_m = 2{\cdot}661$ g.cm.$^{-3}$, space group *Imm*2.

The crystallographically required symmetry of the $K_2[ReN(NC)_4],H_2O$ molecule is *mm*2 (C_{2v}) with the diad axis along the Re≡N bond. Since there are only two molecules per unit cell, the atomic positions are given by[6] rhenium and nitrogen at 2a; oxygen at 2b; two potassiums at 4e; 8 carbons and 8 nitrogens at 8e for the space group *Imm*2 (C_{2v}^{20}) No. 44. This places the rhenium and the nitride nitrogen atoms in infinite chains, alternating rhenium and nitrogen, similar to the tungsten and oxygen chains[5] in $WOCl_4$. The nitrogen is assymetrically placed between the rhenium atoms, the alternating Re–N bond lengths are 1·53 and 2·44 Å.

The structure has been refined with the cyanide groups bonded both through the carbon atoms and through the nitrogen atoms using neutral atom scattering factors.[7] Each structure gave the same interatomic distances and

angles within one standard deviation. The isotropic temperature factors for the atoms in both the nitrogen-bonded and the carbon-bonded structures are shown in the Table. Comparison of the plausibility of the two sets of

Isotropic temperature factors, B, for nitrogen- and carbon-bonded structures (Å²)

Nitrogen-bonded structure		*Carbon-bonded structure*	
Atom	*B*	Atom	*B*
Re	0·24	Re	0·21
N	0·81	C	−0·03
C	1·28	N	2·13
N[a]	3·04	N[a]	2·89
O	5·60	O	5·35
K	2·14	K	2·12

[a] Nitrido-nitrogens.

rhenium, nitrogen, and carbon relative values leads us to prefer the nitrogen-bonded structure, in which the isotropic temperature factors increase in the order Re<N<C. However, the thermal vibrations may be seriously affected by the high absorption for which no corrections have been made The final *R* factor for the isocyanide structure is 5·06%; for the cyanide structure it is 5·27%. The N≡C bond distance is 1·31 Å which is significantly longer than the usual 1·16 Å for cyanide complexes.[8]

The Re–N–C configuration is bent, as shown in the Figure, with the Re atom about half way between the plane defined by the four carbon atoms and that defined by the four nitrogen atoms. The ReNC angle of 136·2° is very similar to the CuNC angle of 139·1 ± 1·6° in the spiral chains[9] of $K[Cu(CN)_2]$. No bent carbon-bonded cyanide groups have been reported,[8] except for $CuCN,NH_3$,[10] but the isoelectronic nitrosyl (NO^+) group is known to form bent bonds.[11]

No explanation is offered at present as to why the cyanide group appears to be bonding through the nitrogen.

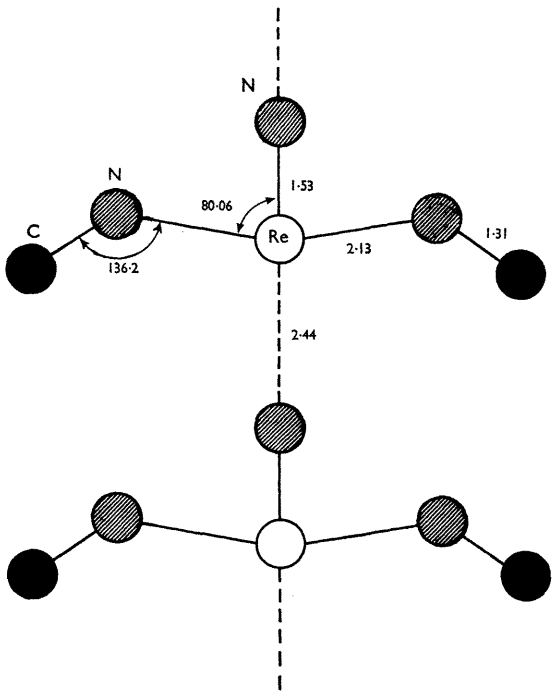

FIGURE. *Diagram of the structure showing the chains of alternating rhenium and nitrogen atoms, and the eclipsed and bent* Re–N–C *groups. The isocyanide groups above and below the plane of the paper are omitted for clarity. The bond lengths are in* Å *and the angles in degrees.*

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