Bonding Mode of the Thiocyanate Ion: the Crystal Structure of Bis(ethylenediamine)copper(II) Thiocyanate Perchlorate

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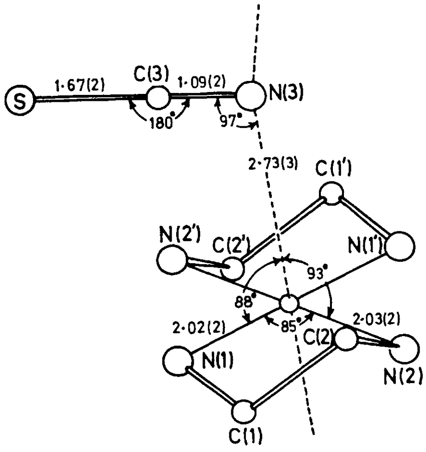
Summary Replacement of SCN^- by ClO_4^- in $Cu(en)_2(SCN)_2$ (en = NH_2–CH_2–CH_2–NH_2) is accompanied by replacement of sulphur by nitrogen of the thiocyanate at the apices of the co-ordination octahedron of the copper ion; it is suggested that SCN^- orientation in the elongated octahedral geometry often found in copper compounds is due to packing and not electronic requirements.

IN our studies on structural changes in compounds of the type $CuL(SCN)_2$ (L = polyamine) which occur when one SCN^- group is substituted by an anion which, like ClO_4^-, has low co-ordinating ability, we have determined the crystal structure of $Cu(en)_2(SCN)(ClO_4)$.

The stereochemistry of the complex is as shown in the Figure. Copper occupies a centre of symmetry and is chelated by the ethylenediamine nitrogen atoms, which are located at the corners of a rectangle with a mean Cu–N distance of 2·02 Å. Unlike the unsymmetrical *gauche* form observed in other copper–ethylenediamine complexes,[1] in



FIGURE

this compound the ethylenediamine ring has an almost symmetrical *gauche* configuration: C(1) is 0·36 Å above the N–Cu–N plane and C(2) is 0·37 Å below. The planes formed by the $Cu(en)_2{}^{2+}$ cations are almost perpendicular to the *c* axis and are stacked along it at $\frac{1}{2}$ *c*. Thiocyanate ions lie on the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ *c*, each nitrogen atom being shared by the apices of the co-ordination octahedrons of two adjacent cations (Cu–N = 2·73 Å). The orientation of thiocyanate is thus opposite to that in $Cu(en)_2(SCN)_2$,[1] where the sulphur atoms of the two SCN^- ions lie on the apices of the octahedron at 3·27 Å from the metal ion.

We believe that the different orientation of thiocyanate in the two structures is not due to electronic effects because of the following considerations. First, the Cu–NCS distance in $Cu(en)_2(SCN)(ClO_4)$ is approximately equal to the sum of the square dsp^2 radius for copper(II) (1·30 Å) and of the van der Waals radius for nitrogen (1·50 Å); secondly, the value of the Cu–N–C_{NCS} angle (97°) is not consistent with a Cu–NCS covalent interaction since the nitrogen atom is equidistant from two copper ions and the thiocyanato C–N distance indicates a triple bond character; since the Cu–SCN distance in the bisthiocyanate compound, taking into consideration the greater van der Waals radius for sulphur (1·85 Å) is even larger than the Cu–NCS distance in $Cu(en)_2(NCS)(ClO_4)$, the copper–thiocyanate interaction in both compounds is essentially ionic, in agreement with an analysis of the three fundamental SCN modes in the i.r. spectra.[2]

If we exclude electronic effects, the occupation of apical octahedral sites by sulphur or nitrogen thiocyanate atoms would be due to reticular or environmental requirements. In $Cu(en)_2(SCN)(ClO_4)$ the nitrogen atom is closer to the metal and, since it has a smaller van der Waals radius than sulphur, the result is a shorter interplanar distance for the cations, and a closer molecular packing; the density (1·76 g cm^{-3}) is quite high. The opposite situation in $Cu(en)_2(SCN)_2$ leads to the formation of hydrogen bonds between the nitrogen at the free end of the thiocyanate and the NH_2 groups of adjacent molecules.

Bis-(*NN'*-dimethylethylenediamine)copper(II) thiocyanate[3] is, in our opinion, a further example of the influence of steric effects on the arrangement of the thiocyanate group. For this compound, a Cu–S_{SCN} interaction was assumed to be most probable;[2] this was also expected, if electronic effects played any role, because of the higher basic strength of the *N*-methyl-substituted amine. The crystal structure shows, however, that the copper co-ordination polyhedron is octahedral with the apical sites occupied by thiocyanato nitrogen atoms at 2·52 Å. This fact, as well as the value of the Cu–NCS angle (129°), is not surprising if we assume the structure to be ionic; the steric hindrance of the methyl groups restricts the free volume at the apical site and Cu–N_{NCS} contact is thus preferred to Cu–S_{CNS}.

Crystal data: $Cu(en)_2(SCN)(ClO_4)$; violet crystals, orthorhombic, space group *Pnam* $a = 15·60(3)$; $b = 7·63(2)$; $c = 10·82(2)$ Å; $U = 1288$ Å^3; $M = 341·31$; D_m (picnometric) 1·74 g cm^{-3}; D_c ($Z = 4$) 1·76 g cm^{-3}. The intensities of *h0l*—*h5l* and *hk0*—*hk2* reflections were collected on an integrating Weissenberg camera, using two crystals mounted along *b* and *c* respectively. The reflections were measured photometrically and reduced to a set of 1275 independent reflections. The structure was solved by Patterson and Fourier methods and refined by isotropic full-matrix least-squares to a conventional *R* value of 0·13.

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