Bonding Mode of the Thiocyanate Ion: Crystal Structure of Bis-(1,3-diaminopropane)isothiocyanatecopper(II) Perchlorate

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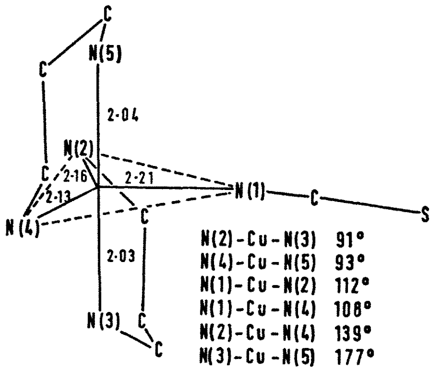
Summary Replacement of SCN^- with ClO_4^- in $Cu(tn)_2(SCN)_2$ (tn = $NH_2{\cdot}CH_2{\cdot}CH_2.CH_2{\cdot}NH_2$) is accompanied by a different bonding mode of the thiocyanate ion; the co-ordination polyhedron of the copper(II) ion in bis-(1,3-diaminopropane)isothiocyanatocopper(II) is a distorted trigonal bipyramid, the co-ordination sites being occupied by amino and thiocyanate nitrogen atoms.

SEVERAL authors have discussed the influence on the metal–thiocyanate linkage of the metal ion, the steric and electronic properties of the other ligands, and the polarity of the solvent.[1,2] Recently Burmeister and Lim[3] and Gutterman and Gray[4] reported two cases where a non-co-ordinated group affects the mode of bonding of thiocyanate, and here we report a structural proof of this effect.

A crystal structure analysis of $Cu(tn)_2(SCN)_2$ (tn = 1,3-diaminopropane)[5] showed that the copper ion is co-ordinated to the four nitrogen atoms of the amine molecules and two sulphur atoms of the two thiocyanate groups (Cu–S = 3·15 Å) in an elongated tetragonal octahedron. This result, as well as spectroscopic investigations on some thiocyanate and perchlorate copper(II) complexes,[6] prompted us to undertake the crystal structure analysis of $Cu(tn)_2(SCN)(ClO_4)$ to investigate the structural effect of the replacement of an SCN^- ion with a ClO_4^- group, which has low co-ordinating ability.

Deep blue prismatic crystals of $Cu(tn)_2(SCN)(ClO_4)$ were obtained by adding a solution of $AgClO_4$ to a stoicheiometric amount of $Cu(tn)_2(SCN)_2$ in hot aqueous solution. The crystals are hexagonal, space group $P6_3$, $a = b = 13{\cdot}75$ ($\pm 0{\cdot}02$) Å; $c = 14{\cdot}52$ ($\pm 0{\cdot}02$) Å; $U = 2379$ Å^3; $M = 369{\cdot}47$; D_m(picnometric) 1·56 g cm^{-3}; $Z = 6$; $D_c = 1{\cdot}55$ g cm^{-3}. The intensities of $hk0$—$hk10$ and $0kl$—$2kl$ reflections were collected on an integrating Weissenberg camera, using crystals mounted along c and a respectively. The reflections were measured photometrically and reduced to a set of 876 independent reflections. The structure was solved by Patterson and Fourier methods and refined by successive three-dimensional Fourier syntheses to an R value of 0·15. The inaccuracy of the refinement is due to the low number of available experimental data (almost all reflections with $2\theta > 100°$ are unobserved) and therefore the estimated standard deviations of bond angles and distances are rather large (1·5° and 0·04 Å for the values in the Figure).

The crystal structure consists of discrete distorted trigonal bipyramidal $Cu(tn)_2(NCS)^+$ cations and ClO_4^- anions. The co-ordination polyhedron of the Cu^{II} ion (Figure) has two amine nitrogen atoms N(5) and N(3) and thiocyanate nitrogen N(1) equatorial, with the other two amino-nitrogen atoms in the apical position. The deviations from 120° of the angles around copper in the equatorial plane result in a distortion of the polyhedron toward a square pyramid, the four amino-nitrogen atoms being in the basal plane. The surprising result of our analysis is that replacement of the SCN^- ion with ClO_4^- is accompanied by bonding of the remaining SCN^- through the nitrogen atom; the Cu^{II} co-ordination number therefore changes from six to five. In the bis(thiocyanate) complex, however, the axial bonds should be classified as semi-co-ordinate, while in the compound reported on here all Cu–N distances fall in the range reported in the literature.



FIGURE

The different bonding of the thiocyanate ion in the two compounds is not easily explained. The molecular structures show that the different steric requirements of the bent Cu–S–C–N over the straight Cu–N–C–S linkage, often used to explain the isomerism of thiocyanate ion, do not play any role in the $Cu(tn)^{2+}$ cation. Moreover, it is clear that the bonding mode of the thiocyanate ion is not, in this case, induced by intramolecular contacts with the terminal atom, as suggested by Gutterman and Gray[4] for the thiocyanatopentacyanocobaltate(III) complex; in fact the molecular packing does not show any close inter- or intra-molecular contact around the sulphur atom.

Further structural results are needed for a study of this problem, and we plan to undertake X-ray crystal structure analyses on a series of thiocyanatecopper(II)–amine complexes.

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