The Structure of the Five-co-ordinate Complex, Bromoazido-1,1,7,7-tetraethyldiethylenetriaminecopper(II)

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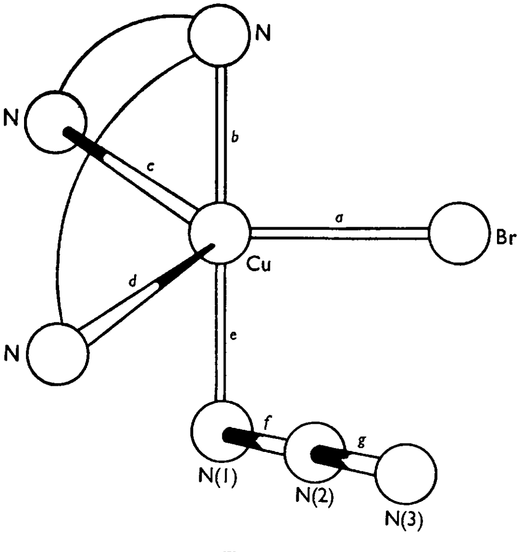
INFORMATION concerning the nature of the bonding of the azide group in co-ordination compounds is limited.

I report the crystal structure of the five-co-ordinate complex $\mathrm{Cu(Et_4dien)N_3Br}$, where ($\mathrm{Et_4dien}$ = 1,1,7,7-tetraethyldiethylenetriamine, $\mathrm{Et_2N{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NEt_2}$).

Dark green, triclinic crystals of bromoazido-1,1,7,7-tetraethyldiethylenetriaminecopper suitable for *X*-ray work were crystallized from acetonitrile. The unit cell had the dimensions $a = 12{\cdot}95$, $b = 7{\cdot}65$, $c = 9{\cdot}87$ Å, $\alpha = 80{\cdot}7$, $\beta = 113{\cdot}2$, $\gamma = 100{\cdot}0°$, $Z = 2$, space group $P\bar{1}$. Intensities of 1002 non-zero reflections were estimated visually from equi-inclination Weissenberg photographs using Zr-filtered Mo-K_α radiation. The Cu and Br positions were obtained from a three-dimensional Patterson syntheses and the light atoms were placed by successive difference Fourier syntheses. Least-squares refinement of positional, scale, and thermal parameters was terminated when the shifts in the positional parameters were less than their estimated standard deviation. The final *R*-factor was 10·1%.

A perspective drawing of the co-ordination sphere of the complex is given in the Figure. The geometry around the Cu-atom can be viewed as a distorted trigonal bipyramid with the azide group occupying one of the axial positions of the complex, and with the bromide ion equatorial. The unusual Cu–Br distance and the distortion from the trigonal bipyramidal geometry is attributed to non-bonded repulsions and steric hindrance around the Cu-atom. Similar steric factors have been observed in $\mathrm{Co(Et_4dien)Cl_2}$.[1]



FIGURE

Of particular interest are the structural results obtained for the azide group and its mode of co-ordination to the Cu-atom. The structural results for the Cu–$\mathrm{N_3}$ bond angle and the N(1)–N(2) and N(2)–N(3) bond lengths are different from those obtained for the complex $\mathrm{[Co(NH_3)_5N_3]^{2+}}$ (124·8°, 1·208 and 1·45 Å)[2] and for the complex $\mathrm{[Cu(N_3)_2(NH_3)_2]}$[9] (121·4°, 1·19 and 1·14 Å for the mono co-ordinated azide)[3] but similar to the values obtained for the structure of cyanuric triazide[4] (114°, 1·26 and 1·11 Å) and methyl azide[5] (120°, 1·24 and 1·10 Å), which are taken as the values of a covalently-bonded azide.[6] Thus I conclude that the Cu–$\mathrm{N_3}$ bond is more covalent than the Co–$\mathrm{N_3}$ bond and that in valence-bond structures the dominant resonance forms are

$$\mathrm{Cu{-}\ddot{N}{=}\overset{+}{N}{=}\overset{-}{N}{:}} \text{ and } \mathrm{Cu{-}\underset{\cdot\cdot}{\overset{-\cdot\cdot}{N}}{-}\overset{+}{N}{\equiv}N{:}}$$

It is reasonable to suggest that the differences between the Co–$\mathrm{N_3}$ and Cu–$\mathrm{N_3}$ bond angles and the N–N bond lengths could be associated with the nature of the axial position of the trigonal bipyramidal geometry.

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