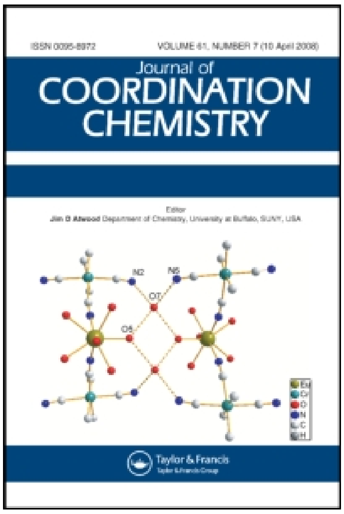

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ELECTRONICALLY INDUCED MOLECULAR DISTORTIONS THE CRYSTAL STRUCTURE OF BIS(TERPYRIDINE)COPPER(II) NITRATE

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ELECTRONICALLY INDUCED MOLECULAR DISTORTIONS THE CRYSTAL STRUCTURE OF BIS(TERPYRIDINE)COPPER(II) NITRATE

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Sir:

Although a large number of mono- and bis-terpy[1] complexes have been prepared,[2] only a few structural studies of the mono-terpy complexes have been reported.[3] Our study of bis(terpy)copper(II) nitrate is the first crystal structure determination of a bis(terpy) complex and reveals an unusual and unexpected angular distortion of the terpy ligand. This distortion results from the d^9 configuration of the Cu(II) ion and from the fact that all six nitrogen atoms of the terpy ligand are coordinated to the copper atom.

Evaporation of an aqueous solution of copper(II) nitrate and terpy in a mole ratio of 1 : 2 gives lime-green crystals of bis(terpy)copper(II) nitrate. The crystals are tetragonal, probable space group $I4_1/a$, with $a = 12.419(3)$ Å and $c = 36.148(11)$ Å. The density calculated for 8 molecules (M.W. of 420.8) per unit cell is 1.563 gm/cm^3 and is in good agreement with the measured value of 1.55 g/cm^3. Three-dimensional intensity data were measured by the stationary crystal-stationary counter method using copper radiation with an automatic diffractometer. All the 2511 independent reflections with $2\theta < 135°$ were measured and the 1667 reflections significantly above the background counts were considered to be observed and used in the analysis.

Since the general positions in $I4_1/a$ are 16-fold, with only eight molecules per unit cell, the bis(terpy)Cu(II) cation is required to be on a 2-fold axis. The positions of the Cu, 2N and 2C atoms on the 2-fold axis were deduced from a three-dimensional Patterson function. The remaining light atoms were located in successive Fourier syntheses. The structure was refined by three least-squares cycles using the full matrix and isotropic thermal parameters to an R of 0.11. Three additional least-squares cycles using the block approximation with anisotropic thermal parameters reduced *R* to 0.078. The hydrogen atoms were located in a different Fourier synthesis and three additional least-squares cycles in which the hydrogen atom contributions were included in the calculations but not refined reduced *R* to 0.059. No unusual thermal parameters were found for any of the atoms in either the cation or anion.

All six nitrogen atoms of the two terpy groups are coordinated to the copper atom forming the distorted octahedral Cu(terpy$_2$)$^{++}$ cation. A view of the cation together with the numbering scheme is shown in Figure 1, with the atoms Cl—Nl—Cu-N3-C9 on the two-fold axis. The Cu—N distances, Cu—Nl of 2.025(5) Å, Cu-N2 of 2.287(4) Å, Cu-N3 of 1.961(5) Å and Cu-N4 of 2.084(4) Å reveal the

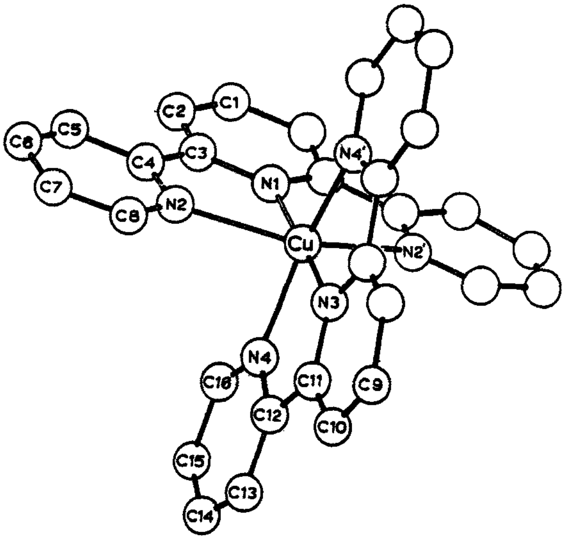

FIGURE 1. The atomic numbering and molecular geometry of the bis(terpyridine)copper(II) cation. The primed atoms are related to the unprimed atoms bt the two-fold axis passing through C9-N3-Cu-N1-C1.

surprising fact that the two terpy ligands are bonded differently to the copper atom. Since in the three mono-terpy complexes studied to date[3] the metal atom-central nitrogen atom bond is shorter than the metal to terminal nitrogen distances, we had anticipated a 2 short–4 long configuration about the central Cu(II) ion. Indeed, the Cu–N3 distance is 0.123 Å shorter than the Cu–N4 distance, in agreement with the differences observed in a Ga-terpy complex of 0.078 Å,[3a] in a Zn-terpy complex of 0.12 Å[3b] and in a Sn–terpy complex of 0.08 Å.[3c] However, the other terpy ligand has Cu–N distances which differ by 0.262 Å, a much larger distance than previously observed. Nevertheless, the C—C distances (which range from 1.363 to 1.393 Å, with an average of 1.375 Å) and the C—N distances (which range from 1.330 to 1.352 Å, with an average of 1.340 Å) are not significantly different from the values in other terpyridine complexes. The difference in the Cu—N distances in the two ligands results from changes in the bond angles in the two five-membered chelate rings formed by each ligand and in the angle of twist between the pyridine rings. The terpy ligand with shorter Cu—N distances has an angle of twist of between the central and terminal pyridine rings of 4.0° which is comparable to the range of values (4 to 6°) found in other terpy complexes.[3] However, the terpy group with the two long Cu—N bonds has a twist angle of only 2.6° between these rings. Therefore, we have a unique example of two initially identical ligands, one of which undergoes an angular distortion as a consequence of the unsymmetrical nature of the d^9 system of the Cu(II) ion to which it is bound.

The present results provide a forceful example of the general rule that in octahedral copper complexes the best donors tend to have the shorter bond distances.[4] A four long-two short configuration for $\mathrm{Cu(terpy)^{++}}$ would violate this principle since the central nitrogen atom is the poorest donor in the terpy ligand. However, because of steric constraints, the ideal situation (with the two central nitrogens furthest away from the copper atom) can not be achieved and the observed configuration must represent a compromise between steric and electronic effects.

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