The Crystal Structure of the γ-Form of Bis-(N-methylsalicylaldiminato)copper(II)

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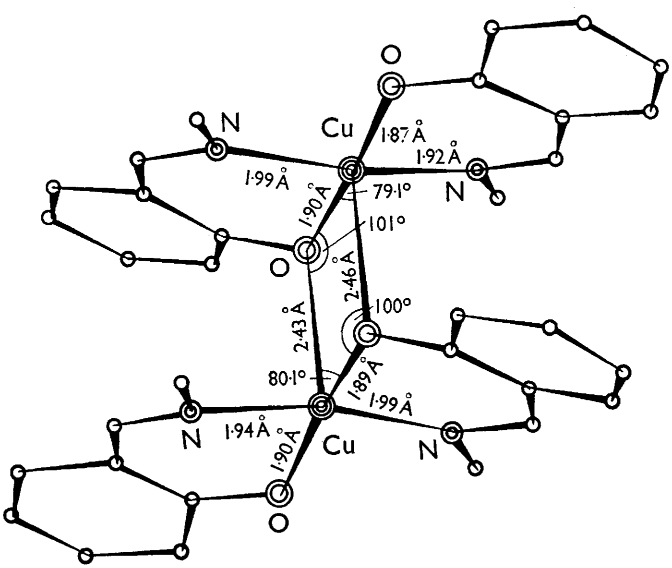
CO-ORDINATION complexes with organic ligands commonly form discrete molecules whose structure is normally thought to be dictated by the bonding requirements of the donor groups and central metal atom. A given metal may display a number of geometries under the influence of different ligand atoms[1] and examples of different symmetries with the same ligands are also known.[2] We report an investigation which establishes three geometries for a complex of copper(II) and verifies the structural versatility of such compounds.

A structural study of the γ-form of bis-(N-methylsalicylaldiminato)copper(II) has been made by means of a three-dimensional X-ray analysis. The α-form has been similarly studied[3] and the structure of the β-form is known through the analysis of its isomorphous nickel(II) analogue.[4] The crystal data for the γ-form are; $a = 18{\cdot}86$, $b = 10{\cdot}25$, $c = 14{\cdot}64$ Å, $Z = 8$, space group = $P2_12_12_1$. Intensity data were collected using Cu-$K\alpha$ X-radiation.

The full structural solution was approached through the usual three-dimensional Patterson and heavy-atom syntheses and least-squares refinement terminated at an R-factor of 0·10 for 1604 observed reflexions. Individual anisotropic temperature factors were refined for the copper and oxygen atoms and individual isotropic factors for the remainder.

Some bond-lengths and -angles are shown in the Figure, their approximate standard deviations being 0·015 Å for bonds to copper, 0·035 Å for bonds between light atoms, 0·5° for angles at copper, 1° for angles at oxygen and nitrogen and 2° for angles at carbon atoms. Other bond-lengths and -angles, not shown, have normal values. The two molecules of the crystallographic asymmetric unit form a dimer with two Cu–O bonds between the halves. Each metal atom is five-co-ordinate in a distorted square-pyramidal configuration and each is displaced out of its co-ordination plane, by 0·11 and 0·13 Å respectively, towards the fifth donor atom. The two halves of the dimer are distorted, not in the umbrella shape seen in bis(dimethylglyoximato)copper(II)[5] but rather in the stepped configuration of bis-(N-phenylsalicylaldiminato)copper(II)[6] or one form of bis(salicylaldehydato)copper(II).[7] This bending is further complicated—for example the two benzene rings of a bis-(N-methylsalicylaldiminato)copper "half" are not coplanar but inclined at an angle of 12° and there appears to be a larger and a shorter Cu–N bond in each such "half" associated with further minor distortions.

It is now disclosed that bis-(N-methylsalicylaldiminato)copper(II) in its three crystalline forms exhibits three different stereochemistries. The α-form contains perfectly planar molecules polymerised into chains by weak Cu–Cu bonds (3·33 Å) in the octahedral positions, the β-form, as exemplified by the isomorphous nickel(II) analogue possesses planar four-co-ordination with some non-planarity of the chelate rings and the α-form contains dimeric molecules with five-fold co-ordination about the copper atom. Postulates that phenomena associated with a number of transition-metal



FIGURE

complexes of *N*-methylsalicylaldimine—*e.g.*, anomalous paramagnetism, polymerisation,[8] solid-solution formation[9]—result from changes in molecular geometry are thus further confirmed. Clearly in some circumstances the bonding requirements of a metal such as copper are not rigid as sometimes supposed but are subject to manipulation by other forces in the environment.

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