Two Adducts of *NN'*-Ethylenebis(salicylaldiminato)copper(II)

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FIVE-COVALENCY is an established feature of copper(II) co-ordination compounds and it is apparently maintained in some complexes in spite of molecular distortions.[1] We have undertaken an investigation aimed at elucidating factors responsible for this and report here three-dimensional *X*-ray analyses of two adducts of *NN'*-ethylenebis-(salicylaldiminato)copper(II). This complex itself is dimeric in the solid state with Cu–O bonds of 2·41 Å completing the now familiar square-pyramidal stereochemistry about the metal atom.[2] Although these crystals are green, as are their solutions in benzene, a red colour is evident in some solvents or in the presence of some organic solutes. Dark red solids, often unstable in air, were sometimes obtained by subsequent evaporation and two of these, which proved to be chloroform and *p*-nitrophenol adducts of the complex, allowed a full *X*-ray study.

The crystal data for the chloroform adduct are: $a = 13{\cdot}42$, $b = 7{\cdot}54$, $c = 17{\cdot}88$ Å, $\beta = 96{\cdot}0°$, $z = 4$, space group $P2_1/n$.

Data for the nitrophenol adduct are:
$a = 7{\cdot}95$, $b = 11{\cdot}72$, $c = 14{\cdot}67$Å, $\alpha = 130{\cdot}3°$, $\beta = 96{\cdot}4°$, $\gamma = 95{\cdot}0°$, $z = 2$, space group $= P\bar{1}$. Intensity data for both compounds were obtained with Cu-K_α *X*-radiation.

Structural solutions were approached through the usual Patterson and heavy-atom syntheses, subsequent least-squares refinement bringing the current *R*-factors to 0·133 (chloroform adduct) and 0·164 (nitrophenol adduct). Individual isotropic temperature-factors have been assumed for all atoms.

The molecular arrangement for the chloroform adduct is seen in the Figure. Some significant bond lengths are shown, their approximate standard deviations being 0·01 Å for bonds to copper and 0·03 Å for bonds between light atoms. Other bond-lengths and -angles, not shown, have expected values. The molecules maintain the dimeric association found in the parent compound through the formation of two Cu–O bonds of 2·79 Å, each metal atom being five-co-ordinate with a square-pyrimidal configuration. The chloroform

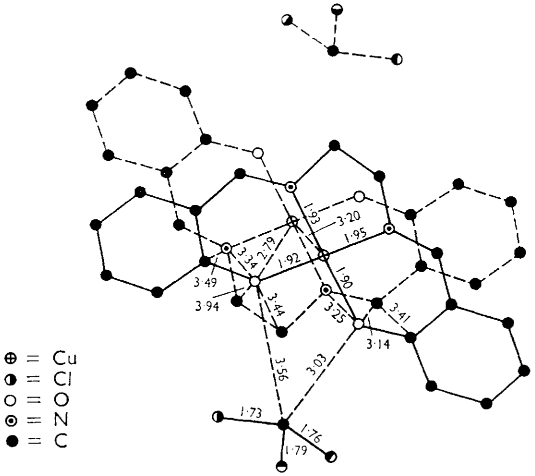

FIGURE. (*Bond lengths in Å*)

molecule is clearly hydrogen-bonded to the oxygen atom not involved in the intramolecular bonding but comparison with the parent compound suggests relatively small changes as a result—the colour is different, the Cu–O "dimeric" bonds are slightly longer and there are minor differences in the distortions in the individual chelating groups.

The compound with *p*-nitrophenol again shows a hydrogen-bonded association between the complex and the organic adduct. Here, however, even though the nitrophenol lies well away from the complex the five-co-ordinate geometry of the copper atom is lost. The complex molecules are still arranged in pairs but the distance between them has increased—to about 3·3 Å—and there are no clearly defined atom-to-atom bonds. The copper atom of one molecule comes over the chelate ring of another, and *vice versa*, to give a large number of intermolecular contacts ranging from 3·36 (O–N) to 3·53 (Cu–N) and 3·57 Å (O–C) in a manner similar to that found in *NN'*-ethylenebis(acetylacetoneiminato)copper(II).[3]

The mode of dimerisation thus varies from the strong directional interactions seen in the green parent complex to the weak molecular association now found in the nitrophenol adduct. Whether this is a direct result of the hydrogen-bonding to a donor atom or arises from an environmental change consequent upon the size of the adducts is not immediately clear, although it may be significant that the shorter, and presumably stronger, hydrogen-bond of 2·66Å occurs in the phenol compound. (That in the chloroform adduct is 3·03Å.) Possibly however both effects are important and help to explain the variation in co-ordination arrangement sometimes found in a complex when polymorphs are obtained by crystallisation from different solvents.[4]

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