Crystal Structure of Bis[acetone-1-naphthoylhydrazinato(−1)]copper(II) and Investigations of Intermolecular Interactions

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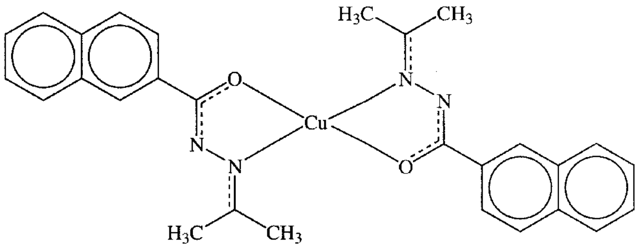
In the crystal structure of the bis(acetone-1-naphthoylhydrazinato)copper(II) complex there are interactions of neighbouring molecules via naphthyl groups; the naphthyl group of one molecule interacts with the copper centre and CH_3 group of another molecule. The geometry of the crystal structure and dispositions of charges in the naphthyl and chelate rings indicate that there are stacking interactions between the aromatic ring and, not only the copper atom, but also the whole chelate ring.

Introduction

In the past decades, investigations of non-covalent forces involving aromatic rings, such as weak hydrogen bonds, π-π interactions, and cation-π interactions, have attracted considerable interest.[1−12] Extended ab initio calculations on the orientation of two benzene molecules have shown that T-shaped and slipped-parallel orientations are more stable than a parallel orientation. It has also been shown that long range interactions such as electrostatic and dispersion interactions are a major source of attraction and that they are responsible for the directionality of the interactions.[13,14]

Noncovalent interactions of aromatic rings in transition metal complexes have been investigated by searching databases of crystal structures,[15−19] by quantum chemical calculations[18−22] and by spectroscopic methods.[23] These interactions play a role in crystal engineering,[11,12,16] and in the stability of metal complexes[10,18,23] and metalloproteins,[17] and it was proposed that these interactions can play a role in the mechanism of enzymatic reactions.[17]

Here we report on a crystal structure of the bis(acetone-1-naphthoylhydrazinato)copper(II) complex (complex I) and the study of a special type of noncovalent interaction between an aromatic ring and a transition metal complex.



Complex I

In transition metal complexes with square planar and square pyramidal geometries, there are possibilities for noncovalent interactions that involve a metal atom. Noncovalent interactions of carbon atoms with the Cu^{II} metal ion have been noticed in our previously published crystal structure of aqua(4-methyl-1-naphth-1-yl-2,3-diaza-1,3,5-heptatriene-1,6-diolato-*N,O,O,'*)copper(II),[24] (complex II) and in other crystal structures of copper(II) complexes.[25−27] Small magnetic interactions transmitted through the interaction between the metal ion and the aromatic ring were recently identified and evaluated by EPR measurements in the crystal structure of the L-(tryptophylglycinato)copper(II) complex.[28]

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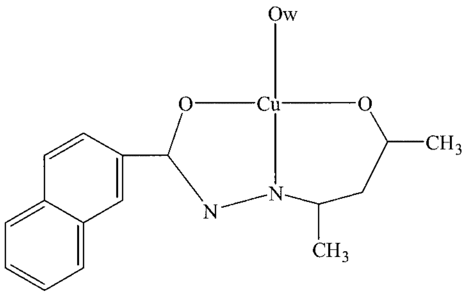


Complex II

For the newly synthesised complex I, a square-planar geometry was anticipated since there is a tendency for bis(chelate) Cu^{II} complexes to adopt such geometries.[29] Due to the absence of hydrogens on the nitrogen and oxygen atoms, the hydrogen bonding potential of this complex is diminished. Thus, it was anticipated that intermolecular contacts of the complex molecules would primarily be determined by the interactions involving aromatic rings. Indeed, in the crystal structure a naphthyl ring is involved in some kind of stacking interaction with a coordination plane of the other molecule.

Results and Discussion

Crystal Structure

The structure is built up of isolated units with a copper ion located at the centre of symmetry. Two molecules of the acetone-1-naphthoylhydrazinato ligand are coordinated through the O and terminal N atoms arranged in a distorted square-planar geometry resulting in a *trans* disposition of these ligands (Figure 1). The Cu−N and Cu−O bond lengths are 2.032(3) and 1.904(2) Å, respectively, while the bite angle of the chelate ring, N5−Cu1−O2 is 80.31°.

The bond lengths in the chelate ring indicate a delocalisation of electrons in the O2−C3−N4 fragment [C3−O2 1.299(3), C3−N4 1.299(3) Å] and the presence of a localised double bond N5−C16 [1.298(4) Å]. These naphthalene fragments are nearly planar and are twisted with respect to the chelate ring about the C3−C6 bond, the dihedral angle between the mean planes of the naphthalene and chelate rings being 16.20(7)°.

Intermolecular interactions between the outer six-membered ring and the Cu atom link the molecules into an infinite one-dimensional chain along the A axis (Figure 2). The Cu···centroid distance is 3.89 Å, while the distance of the Cu atom to the nearest C atom of the naphthyl ring is 3.185(3) Å. The dihedral angle between the mean planes of the chelate and the aromatic ring involved in the Cu···ring interaction is 16.35°. The second nearest C atom is at a distance of 3.529(4) Å. These arrangements are also associated with C−H···π interactions between the methyl hydrogen atom H(17C) and the inner six-membered ring of the neighbouring molecule (H···centroid 2.80 Å, C−H···centroid angle 132.20°). The corresponding distance from the ring centroid to the projection of the H atom position on the plane of the ring is 0.33 Å. This is in accordance with the preference of the hydrogen bond involved in the X−H··· π interaction to be directed towards the centre of the phenyl ring.[30] Adjacent chains are linked by van der Waals forces and weak C−H···π interactions of the methyl hydrogen atom H18C with the outer six-membered ring (H···centroid 3.01 Å, C−H···centroid angle 160.25°) to form sheets across the *ab* plane. The H···centroid distance

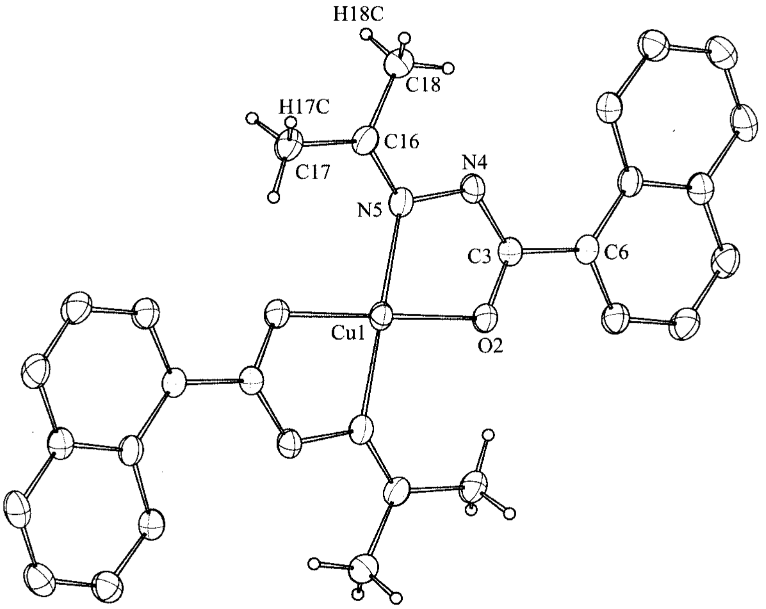


Figure 1. ORTEP[38] view (50% probability ellipsoids) of complex I showing the atom labelling

is slightly larger than the sum of the van der Waals radii of 3.05 Å.[31] However it was shown[32] that, besides the H···acceptor distance, the directional properties of the corresponding fragment must be considered, bearing in mind the tendency of the X−H···acceptor fragment to form a linear angle. The nearest intra- and inter-chain Cu···Cu separation is 6.261(5) and 8.474(7) Å, respectively.

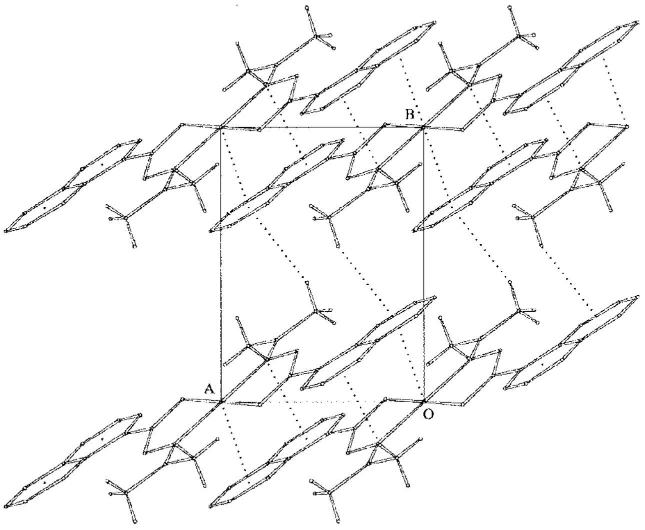
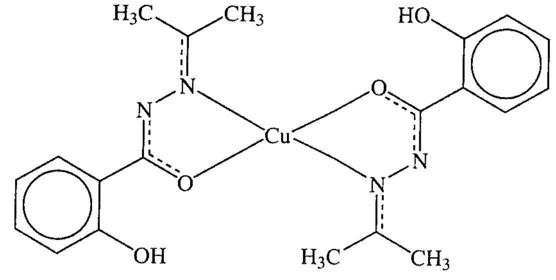


Figure 2. Arrangement of molecules into chains along the a axis and interchain contacts (dotted lines: C−H···π, and Cu···centroid)

We noticed that intermolecular forces in this crystal structure are similar to the forces reported in the previously published crystal structure of compound II.[24] In that structure, the molecules in the unit cell form chains with alternating O−H···π and Cu-naphthalene interactions. This arrangement is associated with a distance of 3.52/3.68 Å for the Cu···centroid of the six-membered ring, and a Cu···C distance of 3.116/3.061 Å.

A comparison of the two crystal structures shows that in both crystals a chain formation is achieved via X−H···π and Cu···phenyl contacts, associated with the distance of the Cu-centroid of the six-membered ring, in the range of 3.5−3.9 Å. The six-membered ring in both crystal structures is in a slipped-parallel position with respect to the chelate ring.

It is also interesting to compare the structure of complex I with the crystal structure of bis(*N*-isopropylidene-*N*′-salicyloylhydrazinato)copper(II) (complex III).[33] Although the ligands are very similar, the OH group on the aromatic ring in complex III has a large influence on the intermolecular interactions. Oxygen atoms have a large affinity to interact with Cu^{II} ions, hence in this crystal structure there is a Cu−O interaction (Cu···O distance of 2.764 Å), and no interaction of the Cu^{II} atom with the aromatic ring.



Complex III

Chelate Ring−Aromatic Ring Contacts

Chelate rings with delocalised bonds are considered to be similar to aromatic rings.[19,34] We assume that the slipped-parallel orientation in the structures of complexes I and II is a result of the balance of interacting forces, similar to that for two benzene molecules, for which the slipped-parallel orientation is very stable.[13] The slipped-parallel orientation can also been found in crystal structures of metal complexes, as can the usual π-interaction for aromatic nitrogen-containing ligands.[15] Since it is known that electrostatic interactions are important for interactions between aromatic rings,[13] we calculated the charges for complex I. Some atoms of the chelate ring are partially positively charged [Cu (0.6), C3 (0.3)], while some atoms are partially negatively charged [O2 (−0.6), N4 (−0.3), N5 (−0.3)]. The geometry of the crystal structure shows that the partially positively charged atoms of the chelate ring (Cu and C) have the shortest distance to the partially negatively (−0.07) charged carbons of the aromatic ring (C1···C14 3.185 Å, C12···C3 3.393 Å), whereas the nitrogen atoms from the chelate ring have the shortest distance to the partially positively (0.07) charged hydrogen atom (N4···H13 2.942, N5···H13 2.975 Å) (Figure 3).

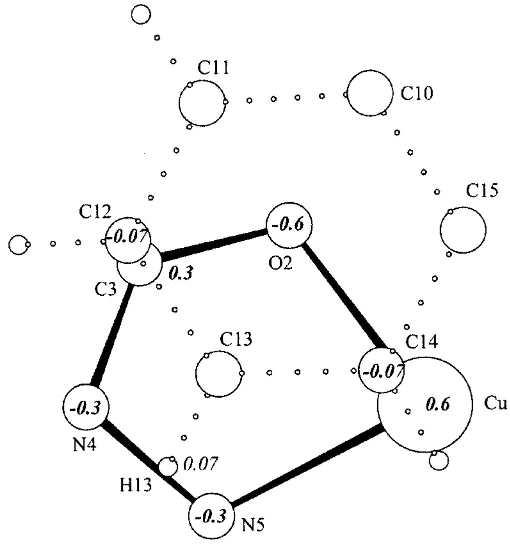


Figure 3. Interaction of the chelate ring and aromatic ring in complex I showing partial atomic charges; orientation is in the direction normal to the chelate mean plane; the aromatic ring is represented by dots

It should be mentioned that in the crystal structure of complex III[33] there is no slipped-parallel orientation of the chelate and phenyl ring; however, inspection of the crystal packing showed that the shortest distances between atoms from two molecules are the distances between partially positively charged atoms and partially negatively charged atoms (Cu···O 2.764 Å, N1···C7 3.354 Å).

Conclusion

In the crystal structure of bis(acetone-1-naphthoylhydrazinato)copper(II) the intermolecular distances between the copper and aromatic carbons indicates that interactions may occur. A mutual slipped-parallel orientation of the chelate and the aromatic ring, similar to the stable orientation of two benzene molecules, suggests that these interactions involve not only the copper atom but also the whole chelate ring. This assumption is supported by analysis of the distances in the crystal structure connected with the partial atomic charges on the aromatic ring and the chelate ring. This indicates that a modification of the chelate ring could modify the interaction of the aromatic ring with the Cu^{II} atom, in square-planar copper(II) complexes.

Experimental Section

Preparation

A synthesis of the title compound has been reported[35] although crystals of the product were not suitable for X-ray diffraction analysis. In the modified procedure the compound was unexpectedly obtained from a reaction of an acetone/ethyl alcohol (1:1) solution of acetone-1-naphthoylhydrazone and a methyl alcohol solution of $Cu(NO_3)_2{\cdot}3H_2O$ and NH_4NCS (molar ratio 1:1:2, respectively). After precipitation of CuNCS, the solution was filtered, allowed to stand and after a few days, crystals of the title complex suitable for X-ray diffraction were obtained.

X-ray Crystallography

Crystal data for $C_{28}H_{26}CuN_4O_2$: M = 514.07, monoclinic space group $P2_1/c$, $a = 6.261(5)$ Å, $b = 8.474(5)$ Å, $c = 21.830(5)$ Å, $\beta = 90.110(5)°$, $V = 1158.2(12)$ Å^3, $D_c = 1.474$ mg/m^3, λ (Mo-K_α radiation) = 0.71073 Å, $F_{000} = 534$. Diffraction data were measured on a Stoe 4-circle diffractometer with graphite monochromator, using $\omega/2\theta$ scans. Lattice parameters were determined from 43 reflections in the range $15 < 2\theta < 30$. 5866 reflections were measured ($\theta < 28$), of which 2786 were independent. The data were corrected for Lorentz and polarisation factors, but not for absorption. The structure was solved by direct methods using SIR92 [36] and refined by applying a full-matrix least-squares method based on F^2, including all reflections. All non-hydrogen atoms were refined anisotropically using SHELXL-97.[37] Hydrogen atoms were included at calculated positions and allowed to ride on their parent atoms. The refinement converged at $R = 0.051$, and w$R = 0.1453$ for 2068 reflections satisfying the condition $I > 2\sigma(I)$, (w$R = 0.1565$ for all reflections). The maximum and minimum residual electron densities in the final ΔF map were 0.797 and −0.521 e/Å^3, respectively. The structure diagram was generated using ORTEP 3[38] and geometrical analysis was performed using PLATON-99.[39] All calculations were done using WinGX as an integrated system for all the crystallographic programs.[40]

CCDC-183111contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details

Quantum chemical calculations of partial charges were performed on a model system built from the crystal structure, using the B3LYP[41,42] method and LACVP** basis set. Calculations were done with the Jaguar 4.1 program.[43]

Acknowledgments

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