Three Dimensional Structure of the Copper Complex of N,N′-Bis-salicyloyl-hydrazine

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N,N′-Bis-salicyloyl-hydrazine (BSH) is a very efficient copper deactivator. In this study the three dimensional structure of the copper-BSH complex was investigated with a cryotransmission-electron microscope and sterical and energetic calculations.

The neat copper-BSH complex forms a nearly amorphous polymer. By absorption of e.g. gaseous ammonia a hexagonal structure shows up without fundamentally transforming the conformation of the complex. The most dominant lattice periodicities are 0.9 and 1.1 nm as obtained by electron microscopical imaging, electron diffraction and sterical calculations. The model shows that copper is very well shielded in the complex by the surrounding BSH-molecules. Due to this, copper is perfectly deactivated.

Introduction

Copper is a very efficient catalyst for oxidative aging of hydrocarbon compounds [1]. Due to this, the service life of technically used hydrocarbon materials is drastically reduced if they are in contact with copper or copper alloys, and also if they contain impurities of copper.

This problem is of fundamental importance e.g. in the isolation of low voltage wires and cables by organic polymers in the use of mineral oil to cool transformers and in the utilization of lubricants on hydrocarbon basis. The electrical and mechanical properties of these materials will be negatively influenced by copper within a short time if the service temperature is elevated to values above 70 °C.

The main reason for the negative influence of copper is the decomposition of hydroperoxides by copper ions. These are natural products of the oxidation of hydrocarbon compounds and rather stable at normal conditions (see reactions equations (1)–(4)).

$$R^{\cdot} + O_2 \rightarrow R-O-O^{\cdot} \quad (1)$$

$$R-O-O^{\cdot} + RH \rightarrow R-O-O-H + R^{\cdot} \quad (2)$$

$$R-O-O-H + Cu^{+} \rightarrow R-O^{\cdot} + Cu^{++} + OH^{-} \quad (3)$$

$$R-O-O-H + Cu^{++} \rightarrow R-O-O^{\cdot} + Cu^{+} + H^{+} \quad (4)$$

In this way even small amounts of the copper ions, acting as redox catalysts, increase the concentration of radicals in radical-like oxidation processes [2].

In order to prevent this, organic chelating agents deactivating copper ions have been used for some time. For this purpose, complex formation alone is not sufficient. Copper phthalocyanine, e.g., is a very stable complex but it is catalytically active and therefore even used as a catalyst [3]. More decisive for the efficiency of the copper deactivator is the degree of inhibition of contact between the chelated copper ion and the hydroperoxide developed in the polyolefin. Most technically used copper deactivators are hydrazine derivatives. Oxalic acid bis-(benzylidene hydrazine) (OABH), N,N′-bis-(4-hydroxy-3,5-di-tert.-butyl-phenyl-propionyl)-hydrazine

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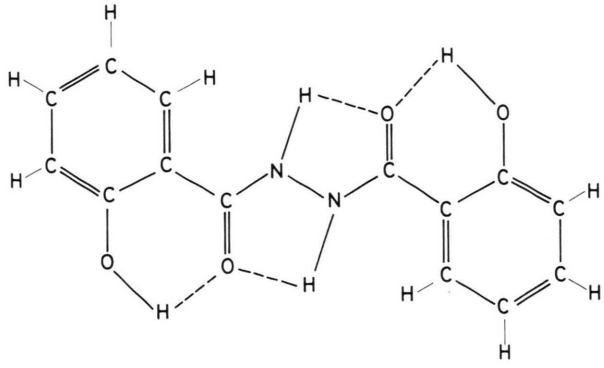


Fig. 1. N,N′-bis-salicyloyl-hydrazine (BSH).

(HBPH) and N-salicylidene-N′-salicyloyl-hydrazine (SSH), for example, are commercially available copper deactivators. Their efficiency was compared with that of N,N′-bis-salicyloyl-hydrazine (BSH) in crosslinked polyethylene in large scale tests. BSH was found to be the product with the highest efficiency [4]. BSH, for instance, imparts crosslinked polyethylene when copper is present with an aging stability which even exceeds the aging stability of the material in the absence of copper.

The high efficiency of BSH could also be confirmed with other polymers, cooling oils, and lubricants. Figure 1 shows the chemical structure of BSH.

In order to find the reason for the high efficiency of BSH, it was necessary to synthesize the copper BSH complex and to investigate its chemical and steric structure. This implied the additional synthesis of modified compounds and the application of a recently developed method of structure analysis.

Synthesis and Properties of Copper BSH Complexes

The copper BSH complex can be synthesized by mixing a copper salt solution, e.g. copper acetate in dimethyl formamide (DMF), with a solution of BSH in the same solvent in the molar ratio 2:1. A green solid complex of the composition Cu_2BSH precipitates. It can be filtered off, washed, and dried (yield 91% related to the compound composition $C_{14}H_8N_2O_4Cu_2$: calc. C, 42.53; H, 2.03; N, 7.09; Cu, 32.15; found C, 42.6; H, 2.2; N, 6.5; Cu, 30.2%).

If aqueous ammonia is used as the solvent for BSH and the copper salt, one obtains a blue solid complex of the composition $Cu_2(NH_3)_2BSH$ (yield 93% related to the compound composition $Cu_{14}H_{14}N_4O_4Cu_2$ calc. C, 39.16,; H, 3.29; N, 13.05; Cu, 29.60; found C, 38.91; H, 3.49; N, 12.79; Cu, 28.40).

Both complexes of BSH with copper do not melt. They decompose in air at temperatures of about 270 – 280 °C. Since both complexes are insoluble in all inorganic and organic solvents they must be polymeric:

$$[Cu_2BSH]_n \quad \text{and} \quad [Cu_2(NH_3)_2BSH]_n .$$

A comparison of the Debye-Scherrer patterns of both complexes (Fig. 2) shows that the complex without ammonia is nearly amorphous. In the photometer curve only one broad peak is obtained corresponding to a lattice distance of nearly 1 nm. The diffraction pattern of the complex containing ammonia shows many sharp peaks as normally observed with crystalline compounds.

The blue complex (which contains ammonia) can easily be converted into the green complex (which is free of ammonia) and vice versa. In order to remove the ammonia completely, the blue complex can be heated either in polar solvents, like alcohol or dimethylformamide, or in vacuo or in streaming nitrogen. The green complex obtained in

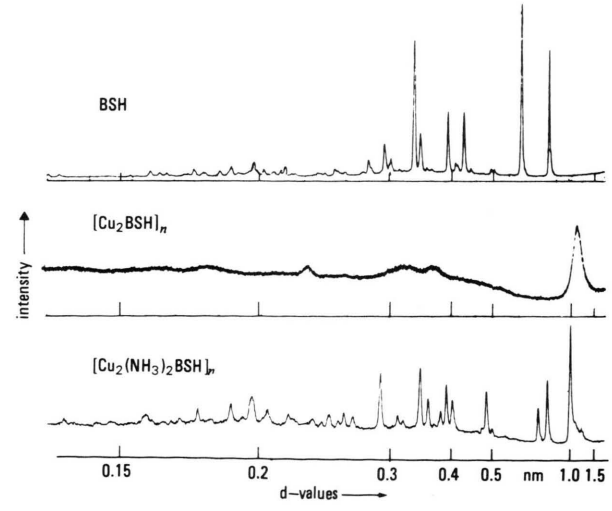


Fig. 2. Photometer curve of X-ray Debye-Scherrer patterns (Cu Kα radiation) of BSH, $[Cu_2BSH]_n$ and $[Cu_2(NH_3)_2BSH]_n$.

this way is identical with the green complex synthesized directly in the absence of ammonia. On the other hand, it is possible to convert the green complex into the blue one by stirring a slurry of the complex in cold aqueous ammonia or by treating the dry solid complex with gaseous ammonia.

The chemisorption energy of ammonia has been determined to be 10.5 kJ/mol. This value is too small for a fundamental transformation of the structure of the complex. It suggests a weak chemisorption bond between the ammonia molecule and the chelated copper atom. For this reason we assume that the nearly amorphous complex $[Cu_2BSH]_n$ and the crystalline complex $[Cu_2(NH_3)_2BSH]_n$ have very similar structures. This enables us to determine the structure of the nearly amorphous complex, which is formed during the copper deactivation reaction, by investigating the structure of the corresponding crystalline complex which contains ammonia. However, there is one difficulty. The complex containing ammonia forms crystals with linear dimensions of only a few microns. A complete structure analysis of such small crystals is impossible with classical single crystal X-ray methods. The following four procedures are necessary to determine the structure of the complex: 1) electron diffraction, 2) high resolution electron microscopy, 3) application of model building and computer calculations based on theoretical considerations and experimental results, 4) consideration of all results obtained experimentally and theoretically.

Materials and Methods for Electron Microscopy

In order to obtain the desired thin crystals for electron microscope investigations the following procedure was worked out: 0.1 ml of a 10 mM BSH and 0.1 ml of a 20 mM $CuSO_4$ solution (both in 1.5% aqueous ammonia) were mixed with 10 ml of water and ultrasonicated for about 10 min. The slightly turbid suspension obtained was centrifuged at about 1000 rpm for 20 min. After decantation, 0.5 ml of a suspension of thin crystals was obtained. In order to minimize the disturbance of the electron microscopical patterns by the carrier foil, the $[Cu_2(NH_3)_2BSH]_n$ crystals were deposited on holey carbon foils [5] in such a way that at least a part of the crystals was spread over holes (Figure 3). Experiments were generally carried out with specimens at almost 4 K in the superconducting electron microscope [6] (SCEM) operating at a beam voltage of 220 kV with a beam diameter of 1 to 5 µm, a diffraction length of 60 cm and a current density between $1.5 \cdot 10^{-4}$ and $5.2 \cdot 10^{-2}$ A/cm^2 corresponding to dose rates between 10 and 3200 e/nm^2 s [7]. An Elmiskop 101 was available for the few 300 K investigations where the applied beam voltage was 80 kV. Single crystal patterns were taken from $[Cu_2(NH_3)_2BSH]_n$ at 4 K. The crystals were sufficiently large for the experiments with the available beam parameters (Figure 3).

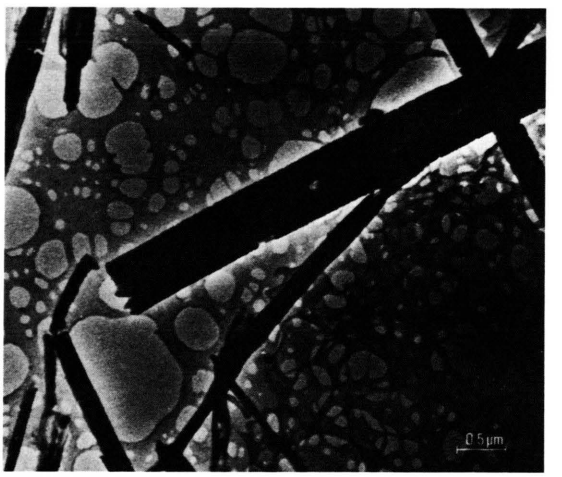


Fig. 3. Survey image of $[Cu_2(NH_3)_2BSH]_n$ crystals on porous carbon foil.

Direct imaging was also carried out at 4 K with the minimum dose for adjustment. The electron optical magnification was 85.000. Specimens which were sufficiently thinned at certain spots with dimethylformamide were suitable for obtaining high resolution images.

Structure Calculation

The chemical structure of BSH is well known [8]. Its three dimensional structure can be derived from the plane structures of diacetylhydrazine [9] and salicylic acid [10] (Figure 4). In diacetylhydrazine, the H atoms at N and N′ are in trans position. Free rotations around the bonds between the N atoms and C atoms of the carbonyl group are not possible since they have a partial double-bond character like peptide bonds. Free rotation in the BSH molecule might be possible around the bonds between the

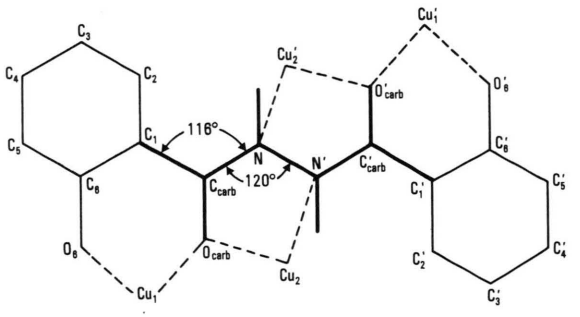


Fig. 4. Chemical structure of BSH (structure of diacetylhydrazine is marked with fat lines, four copper atoms can be linked to one BSH molecule).

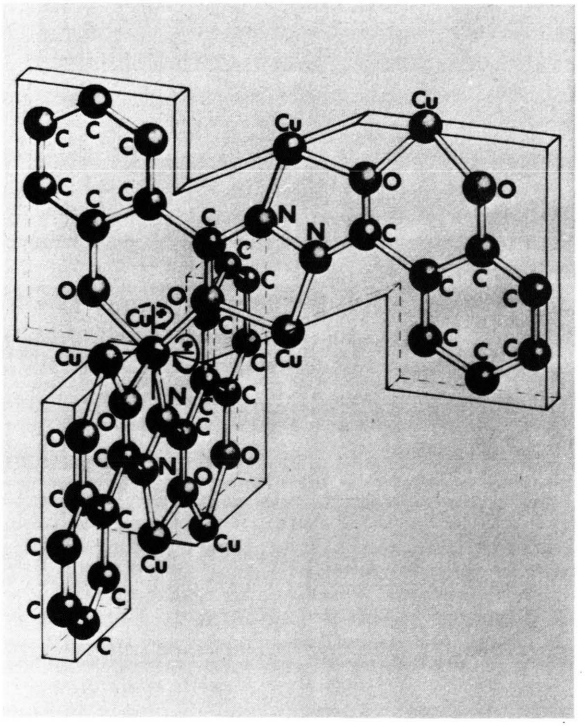


Fig. 5. Two BSH molecules linked with one copper atom (rotation around the space axes described by the angles φ and ψ is indicated). Single BSH-molecules can be described more simply with a Z-shaped board.

C atoms of the carbonyl groups and the benzene rings. But in crystals of salicylic acid, all atoms of the carboxyl group are in the plane of the benzene ring. Since the BSH molecule can be composed by overlapping the two plane molecules of diacetylhydrazine and salicylic acid, we propose a plane structure for BSH.

Considering fundamentally possible arrangements and bond lengths of copper complexes [11], four copper atoms can be linked to one BSH molecule

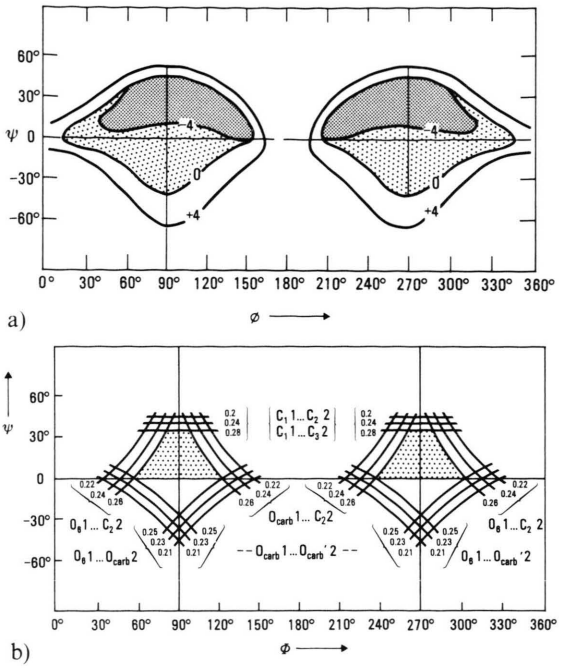


Fig. 6. Interaction between two BSH molecules linked by one copper atom as a function of the rotation angles φ and ψ. a) Energy content (kJ); b) smallest interatomic distance (nm).

(Fig. 4) if each copper atom can be linked with only two of its coordination positions. Two of these copper atoms are part of six-membered rings, the other ones are part of five-membered rings (Figure 4). Since four coordination positions of each copper atom have to be occupied with ligands, a further BSH molecule can be linked to each of these copper atoms. Linkage of two BSH molecules over a common copper atom can be achieved in two ways:

1. Linking five-membered with five-membered rings and six-membered with six-membered rings provides a planar or a fiber structure whose formation should not be hindered by bulky substitution of H atoms at the benezene rings. As a matter of fact, the formation of the complex is, however, hindered by these substitutions [8].

2. Linking five-membered to six-membered rings (Fig. 5) generates a three-dimensional complex composed of (Cu_2BSH) subunits whose formation should be hindered by bulky substitutions of H atoms at the benzene ring.

This model is in agreement with the chemical results of complex formation and is discussed further.

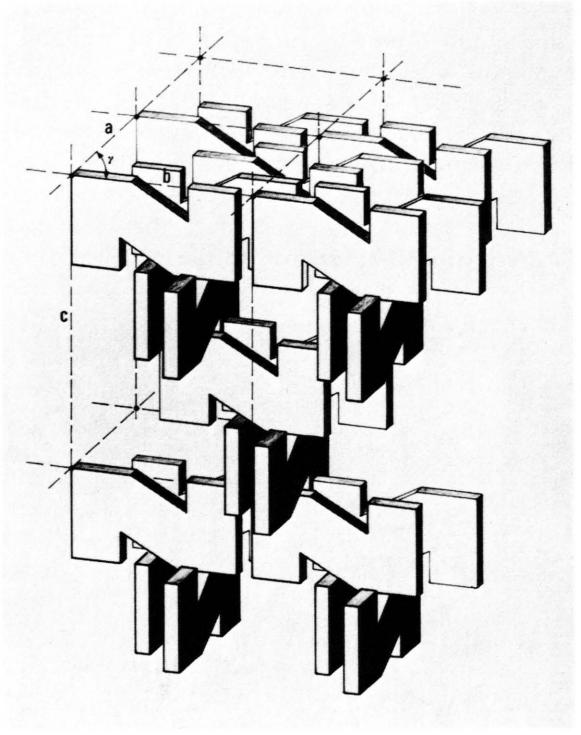


Fig. 7. *Z*-shaped board model of a face centered rectangular ($\gamma = 90°$) lattice of $[Cu_2BSH]_n$, $\varphi = 90°$ or 270°, $\psi = 0°$.

Table 1. Constants of the rectangular elementary cells of $[Cu_2BSH]_n$ dependent on the angles ψ.

ψ	$a = b$ (nm)	c (nm)	V(nm^3)	ϱ (g/cm^3)
0°	1.20	1.98	2.85	3.68
10°	1.37	1.86	3.48	3.01
20°	1.53	1.72	4.00	2.63
30°	1.67	1.55	4.32	2.43
40°	1.80	1.36	4.43	2.37
50°	1.92	1.17	4.32	2.43

The BSH molecules can be rotated around the space axes varying the angles φ and ψ. In zero postion both residues are coplanar. Figure 5 shows the positions $\varphi = 90°$, $\psi = 0°$. For each pair of conformation angles φ and ψ the interatomic distances as well as the energy content have been calculated by the Kitaigorodskii function [12] using the van der Waals distances between the atoms determined by Ramachandran et al. [13]. These calculations manifest two energetically and sterically allowed regions (Fig. 6) around $\varphi = 90°$, $\psi = 0°$ and $\varphi = 270°$, $\psi = 0°$. Both regions are energetically equivalent since they are mirror images of each other. The sterically allowed regions (Fig. 6) are enclosed by lines of forbidden contacts.

Four (Cu_2BSH) subunits can be assembled to a compact tetramer if every fourfold coordinated copper atom becomes a part of a six-membered as well as a five-membered ring, and all rotation angles at the copper atoms have a value of $\psi = 0$ and alternating φ values of 90° and 270° (Figure 6). In this case, there are always two non-directly linked BSH residues which are parallel to one another. With ψ values smaller than 0°, a tetrameric combination of four (Cu_2BSH) subunits is sterically impossible, since the non-directly linked BSH residues can not approach distances less than 0.3 nm (Figure 7). Therefore, only angle combinations in the shaded areas of Fig. 6b are allowed.

Using tetramers of (Cu_2BSH) for single lattice points, a face centered lattice can be constructed with four tetramers in the elementary cell (Figure 7). The volume of the elementary cell can be calculated from its dimensions ($a = b = c$, Fig. 7). Density values of the $(Cu_2BSH)_n$ lattice can be calculated from the volume and the weight of the elementary cell (Table 1).

If the planes of the BSH molecules are parallel to one another ($\psi = 0°$), a density of $\varrho = 3.68$ g/cm^3 is calculated. This value is much higher than the experimentally measured density of $\varrho = 2.2$ g/cm^3. A sterical hindrance does not yet occur in the (Cu_2BSH) tetramers of such a model, but it occurs if these tetramers are assembled into the face centered lattice (Figure 7). For ψ angles larger than zero, however, the calculated densities approach the measured value (Table 1).

A distorted tetrahedral coordination at the copper atoms is obtained, for $\psi = 27.7°$ and $\varphi = 90°$ or 270°. These values are energetically and sterically allowed (Fig. 6) and effect distorted tetrahedral coordinations at the copper atoms which are generally known from the literature [14].

Comparison of Experimental Results and Structure Calculations

Electron diffraction patterns and direct images of lattice lines [7] have been obtained from single crystals of the complex $[Cu_2(NH_3)_2BSH]_n$. These results have been compared with Fourier transforms

calculated from the atomic coordinates and lattice constants of the face centered $[Cu_2BSH]_n$ lattice whose (Cu_2BSH) units are associated with the rotation angles $\varphi = 90°$ or 270° and $\psi = 27.7°$ at the connecting copper atoms. Calculated and measured values cannot, however, agree since electron diffraction shows a nearly hexagonal lattice while the Fourier transform has been calculated for a model with a rectangular elementary cell.

The only remaining freedom to change this model is the variation of φ in the region of 90° or 270° (Figure 6). A tetramer of (Cu_2BSH) with φ-angles of 60° and 300° and ψ-angles of 27.7° (Fig. 8) can, however, be assembled into a hexagonal lattice (Fig. 9) whose calculated Fourier transform is in relatively good agreement with the nearly hexagonal reciprocal lattice observed for the complex $[Cu_2(NH_3)_2BSH]_n$ by electron diffraction (Fig. 10).

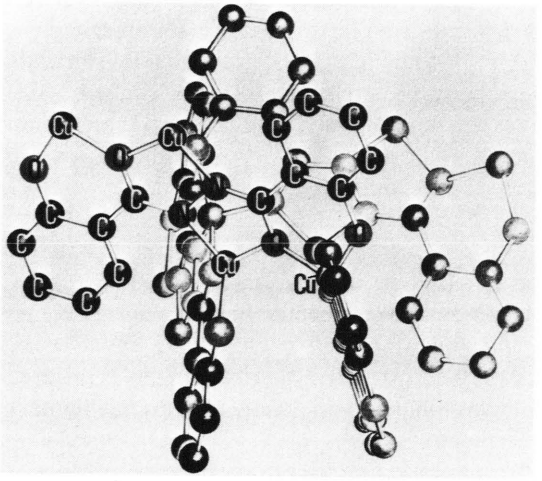


Fig. 8. Tetramer of (Cu_2BSH) units, $\varphi = 60°$ or 300°, $\psi = 27.7°$.

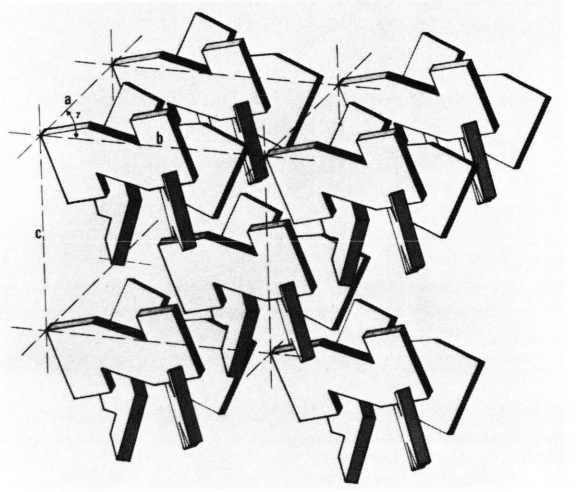
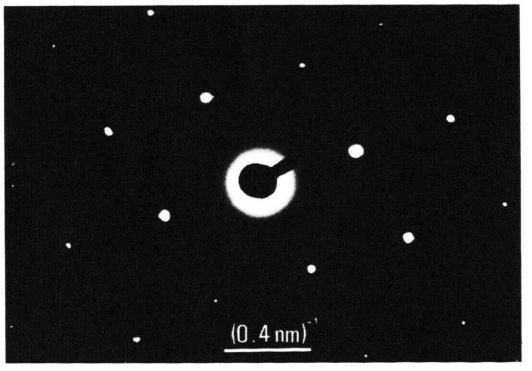
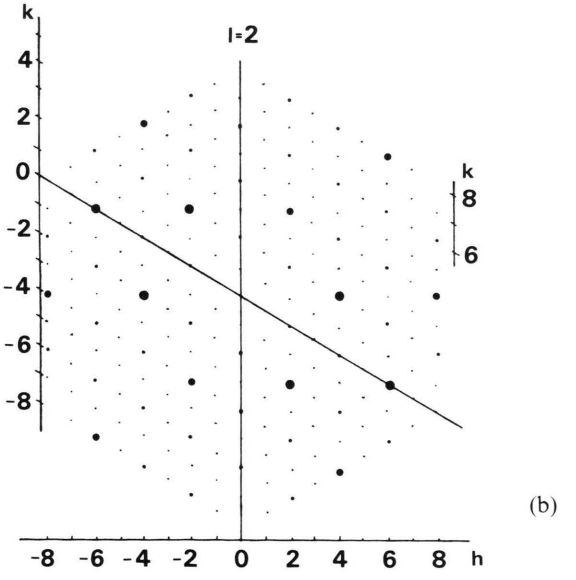


Fig. 9. *Z*-shaped board model of a face centered hexagonal ($\gamma = 60°$) lattice of $[Cu_2BSH]_n$, $\varphi = 60°$ or 300°, $\psi = 27.7°$, $a = b = 1.81$ nm, $c = 1.52$ nm.



(a)



(b)

Fig. 10. Comparison of the reciprocal lattice of $[Cu_2(NH_3)_2BSH]_n$ obtained by electron diffraction (a) and computer calculation (b).

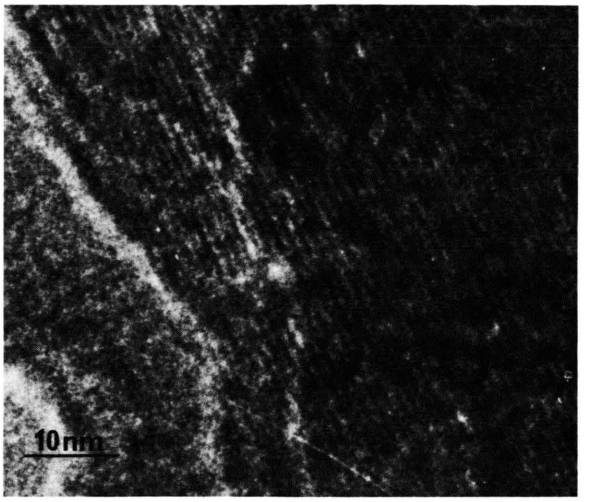


Fig. 11. Micrograph with 1.1 nm lattice lines of BSH. Beam voltage 220 kV, accumulated fluence $3.5 \cdot 10^4$ e/nm^2, electron optical magnification 80 000:1.

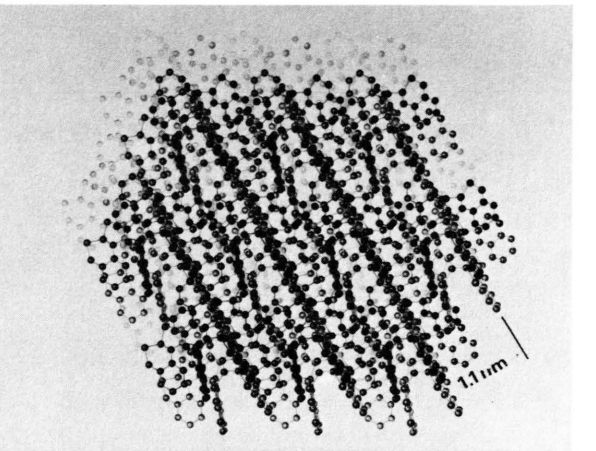


Fig. 12. "Three dimensional" model of the copper BSH complex. Three layers of tetramers each containing 10 units give an impression of the three-dimensional construction, where the 1.1 nm periodicity is especially prominent.

In the nearly hexagonal complex $[Cu_2(NH_3)_2BSH]_n$, the copper atoms are five-fold coordinated. The fifth position is occupied by ammonia. These positions can form an approximate quadratic pyramid. Copper complexes with quadratic pyramidal coordination have been described in the literature [14].

According to the Fourier transform, the lattice lines of 1.1 and 0.9 nm give the most intensive reflections, and we can detect just these lines on the direct image [15]. In Fig. 11 the 1.1 nm lattice periodicity can be recognized. Figure 12 shows the three dimensional model of $[Cu_2(NH_3)_2BSH]_n$ in a position where this lattice periodicity can be clearly seen. In fact, experimental results and theoretical calculations are in good agreement.

Conclusion

The model of $[Cu_2BSH]_n$ derived from experimental data and theoretical calculations is able to explain all experimental results:

1. The measured density $\varrho = 2.2$ g/cm^3 and the calculated value $\varrho = 2.4$ g/cm^3 agree reasonably.

3. The angles at the chelated copper atoms in $[Cu_2BSH]_n$ have a certain range of variation in the energy minimum. Corresponding to this variation the lattice distances fluctuate. This explains why the complex appears nearly amorphous. Ammonia diffuses into to complex forming a fifth coordination bond to each copper atom. In doing so, the angles of the four BSH ligands at the copper are fixed by the space requirement of the NH_3 molecule and the complex containing ammonia appears to be crystalline.

2. A relatively good agreement has been obtained between the calculated Fourier transform of $[Cu_2BSH]_n$ and the results of electron diffraction and direct imaging with high resolution electron microscopy of the complex $[Cu_2(NH_3)_2BSH]_n$.

4. Our model shows that copper is shielded very well in all directions in the complex by the surrounding BSH molecules. Certainly small molecules like ammonia are able to diffuse into the complex in order to interact with copper. Bulky reactants, however, developed in the oxidation of hydrocarbon material can not reach the copper. Consequently, the complex performs its task of copper deactivation perfectly.

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