Fixation of ammoniacal copper preservatives: Reaction of Vanillin, a lignin model compound with ammoniacal copper sulphate solution[1]

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Summary

A model for the fixation of ammoniacal copper preservatives in wood was examined through reaction of vanillin, a lignin model compound, with ammoniacal copper sulphate solution. The compound produced on evaporation of the aqueous ammoniacal solution has been characterized spectroscopically as di(ammine)bis(vanillinato)copper(II); $[Cu(vanillin)_2(NH_3)_2]$. Single crystal X-ray crystallographic studies showed that the crystals of $[Cu(vanillin)_2(NH_3)_2]$ are monoclinic with space group $P2_1$ with a = 5.4172(9), b = 15.452(2), c = 10.4595(9) Å, Z = 2. The ligand arrangement around the Cu(II) is a distorted octahedron. Two Cu-N [2.014(5) and 2.034(5) Å] and two Cu-O (hydroxyl) [1.969(4) and 1.972(4) Å] bonds form a plane with Cu-O (methoxyl) [2.371(3) and 2.388(3) Å] bonds in an axial direction at an angle 75° to the plane. The copper-nitrogen bonding is trans oriented in the plane. Electron spin resonance (ESR) was used to determine the g-tensor and hyperfine tensor elements from both a polycrystalline sample and a DMSO solution. The result suggests that ammoniacal copper wood preservatives can form stable copper-nitrogen-lignin complexes through reaction with guaiacyl units in lignin.

1. Introduction

The vacuum-pressure impregnation of wooden commodities with preservatives, to extend their service life, has been very successful in expanding the use of nondurable wood species in North America. Although chromated-copper-arsenate (CCA) is the most widely used waterborne preservative, it is rarely used to treat Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) heartwood because of poor penetration of the timber. Improved treatment of such refractory wood species can be achieved by using ammoniacal copper-based preservatives such as ammoniacal copper arsenate (ACA), ammoniacal copper zinc arsenate, ammoniacal copper quat and ammoniacal copper citrate.

Despite having been developed half century ago, the fixation mechanism of ammoniacal copper preservatives remains unknown. It has been proposed that upon evaporation of ammonia, water insoluble copper salts, such as copper arsenate in the case of ACA, are precipitated (Hartford, 1972). This hypothesis was challenged when it was observed that ACA-treated spruce poles retained enhanced nitrogen levels more than two years after treatment (Ruddick, 1979), indicating that some nitrogen remained strongly bound in the treated wood. The relationship of the retained nitrogen to copper in the ammoniacal copper treated wood suggested that it may be complexed with the copper or arsenic in the wood. Electron spin resonance (ESR) spectroscopic studies of ammoniacal copper-treated wood (Hughes *et al.* 1994, Ruddick 1992) showed that the copper appeared to be bonded by

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either two or four nitrogen atoms. The ESR spectra of the ammoniacal copper treated wood gave parameters in which the $A_{//}$ was slightly smaller and the $g_{//}$ value larger, than those in the original ammoniacal copper solution. This was interpreted to show that in the treated wood two of the ammonia ligands of the tetramminecopper complex present in the solution have been replaced by copper-oxygen bonding either from water or from the wood substrate (Ruddick, 1992). However, the results still did not define the nature of the interactions between wood and the copper preservatives. For example, the chemical form of nitrogen present in the treated wood and the question of how the copper-nitrogen complex is fixed in the wood remain unanswered.

In order to better understand the nature of the copper complex formed in wood, reactions of ammoniacal copper solution with model compounds were investigated. Since lignin is known to provide an excellent binding potential for preservative components, such as copper (Butcher and Nilsson, 1982), the initial studies focused on lignin model compounds. In this study vanillin was used to imitate the abundant guaiacyl units of lignin in wood, to investigate the possible reaction between lignin and ammoniacal copper solutions. Guaiacyl units constitute 80-90 % of the aromatics in lignin

2. Materials and methods

Reaction of vanillin with ammoniacal copper solution
Vanillin, copper sulphate and ammonium hydroxide were laboratory grade chemicals. Vanillin (1 g, 0.0066 mol) was dissolved in 20 ml of 5% ammonium hydroxide solution. To this solution was added dropwise, with stirring, 20 ml of an ammonical copper solution (0.0030 mol of $CuSO_4$ in 5% ammonium hydroxide solution). Evaporation of the ammonia from the vanillin-ammoniacal copper solution under reduced pressure at 40°C, produced a green crystalline precipitate. The green solid was filtered, washed with distilled water to remove excess ammonium hydroxide until the eluting solution attained the pH of the distilled water (pH = 6). The green polycrystalline solid was dried under vacuum at 40 °C, washed three times with ether to remove unreacted vanillin and finally vacuum dried at room temperature for eight hours. A single crystal of the copper-vanillin complex was obtained through careful recrystalization in an ammonium hydroxide solution.

Analysis of the green crystalline solid
The FTIR spectra were recorded as KBr discs using a Perkin-Elmer 1600 Spectrophotometer, scanning from 4000-400 cm^{-1}. The fast atom bombardment mass spectrum (FAB) was obtained on a Kratos Concept II HQ mass spectrometer with thioglycerol matrix. The ESR spectra of a polycrystalline sample of $[Cu(vanillin)_2(NH_3)_2]$ and a DMSO solution were collected with a Bruker ECS 106 spectrometer equipped with a variable temperature unit, operating at a frequency of 9.60 GHZ (X-band) and 50 KHZ field modulation. The elemental analysis was performed by the Canadian Microanalysis Co. The elemental analysis of the green vanillin-copper-ammonia complex is: Found: C, 47.87%; H, 4.92%; N, 6.81%; Cu, 16.0%; $C_{16}H_{20}N_2O_6Cu$ requires: C, 48.01%; H, 5.01%; N, 7.01%; Cu, 15.9%.

X-ray structure determination

The X-ray single crystal structure analysis was performed at the Department of Chemistry, UBC, using a Rigaku AFC6S diffractometer with graphite monochromated Mo-Ka radiation.

3. Results and discussion

During reaction with an aqueous ammoniacal copper sulphate solution, vanillin formed a green water-insoluble complex upon evaporation to dryness. This complex was insoluble in both water and common organic solvents although was found to be slightly soluble in DMSO. The nature of the complex was characterized using X-ray crystallography, FTIR and ESR.

X-ray structural examination:

The structure of the complex determined by X-ray crystallography is comprised of a central copper (II) ion bonded to two vanillin and two ammonia molecules. The perspective view of the complex with numbering system is presented in Fig. 1. In the complex, both the methoxy and phenolic oxygen atoms of each guaiacyl unit coordinate to the copper, together with nitrogen from two ammonia molecules to form a six coordinated molecule. The unit cell contains two symmetrically related complexes. The selected inter-atomic bond distance and angles are listed in Table 3 and 4 respectively.

The copper atom displays a distorted octahedral coordination. The Cu-O (phenolic oxygen atoms) at *ca.* 1.97 Å and the N-O (ammonia nitrogen) *ca.* 2.02 Å form a square plane around the central copper. The very distorted octahedral configuration is completed by the Cu-O (methoxy oxygen atoms) at *ca* 2.38 Å which are coordinated at an angle about 75° to the plane, at a greater distance than the in plane phenolic oxygen. The Cu-N bond lengths of 2.014 and 2.034 Å are typical of copper(II) nitrogen bond lengths (Coughlin, *et al.*, 1984). The planar Cu-O bond lengths of 1.972 and 1.969 Å and longer axial Cu-O lengths of 2.371 and 2.388 Å are consistent with those observed for other distorted octahedral structures (Hobson, *et al.*, 1973). The Cu-O (hydroxyl) distances are shorter than these of Cu-O (methoxyl). This is due to the difference between the electron density of hydroxyl oxygen (rather ionic) and that of methoxyl oxygen (neutral). The differences between the two Cu-N bond lengths and the two Cu-O (phenolic) bond lengths were not statistically significant.

In each unit hydrogen bonding occurs between the two adjacent complexes through the carbonyl and hydroxyl oxygen atoms and hydrogen on the ammonia. The hydrogen-oxygen intermolecular bond distances are between 2.09-2.51 Å. This strong hydrogen bonding arises from the delocalization of electron to the carbonyl oxygen from the conjugated benzene ring, resulting in greater electronegativity on the oxygen atoms. A packing diagram has been depicted in Fig. 2.

Spectroscopic analysis

FTIR spectroscopy

The FTIR spectra of the polycrystalline green solid and pure vanillin were compared. The peak at 3200 cm^{-1} in the spectrum of pure vanillin was assigned as the OH stretching vibration. However, in the spectrum of the complex, new peaks appeared in the region of 3200-3400 cm^{-1}, which were due to N-H vibration. The peak with a broad shoulder at 730 cm^{-1} in the spectrum of vanillin due to the phenolic OH out of plane deformation was absent in the spectrum of the green solid. This observation supported the conclusion, that the phenolic hydroxyl group was involved in the formation of the copper complex. The spectrum of the copper complex also contains a new peak at 448 cm^{-1}. This was assigned to Cu-N bonding (Hathaway and Tomlinson, 1970). The peak at 1150 cm^{-1} due to C-O-C bonding in pure vanillin was shifted to 1120 cm^{-1} in the complex, consistent with the coordination of methoxyl oxygen.

The mass spectrum of the green crystalline solid showed a peak at m/e = 366 which was assigned as an $(M\text{-}2NH_3)^+$ fragment. From the mass spectrum and elemental analysis, the formula of the complex can be expressed as $[Cu(vanillin)_2(NH_3)_2]$.

ESR spectroscopy

At room temperature, the polycrystalline powdered sample of the green solid gives rise to an exchange narrowed anisotropic unresolved ESR spectrum (Fig. 3a), which does not exhibit hyperfine splitting, but provides $g_{//}$ and $g_{\perp}$, values of 2.295 and 2.06 respectively. X-ray crystallographic study showed that the coordination around the Cu(II) ion is a O_2N_2 square plane with two oxygen donors forming a distorted elongated octahedron; the elongation axis is at 75° to the O_2N_2 plane. The g-value of 2.295 corresponds to the elongated O-Cu-O axis and the magnitude of $(g_{//} - 2)/(g_{\perp} - 2)$ suggests a ground state in which the hole resides in the $d_{x^2-y^2}$ orbital (Hathaway and Tomlinson, 1970).

The green complex $[Cu(vanillin)_2(NH_3)_2]$ dissolved sufficiently in DMSO that an ESR spectrum was observable. The ESR spectrum of the solution at 115K is shown in Fig. 3b. Although the $g_{//}$ and $A_{//}$ features are well resolved, the features in the perpendicular region are less resolved. Nonetheless, the lineshape in that region is typical of an orthorhombic system. The spectrum was simulated using the parameters given in Table 3. The g-values agree well with those from the pure green powder. The $A_{//}$ and $g_{//}$ values are typical of a $CuO_2N_2O_2$ chromophore (Peisach and Blumberg, 1974; Pilbrow, 1990). All of the above suggests that the complex retains the structure $[Cu(vanillin)_2(NH_3)_2]$ in DMSO.

The vanillin-copper complex showed a much smaller $A_{//}$ and a larger $g_{//}$ value than those of copper sulphate in ammonium hydroxide solution. This change in the spectral parameters of the vanillin-copper complex is consistent with the replacement of two of the ammonia ligands in tetrammine copper ions by copper-oxygen bonding (Senesi, *et al.*, 1989, Ruddick, 1992), reflecting the somewhat more ionic environment. Wood treated with an aqueous $Cu(en)_2SO_4$ solution has the largest $A_{//}$ and smallest $g_{//}$, indicating that copper complex in the $Cu(en)_2SO_4$ treated wood has four equatorial copper-nitrogen donor bonds (Farkas and Kurzak, 1990). ESR parameters of the vanillin-copper complex is in good agreement with that of ammoniacal copper carbonate treated wood (Ruddick, 1992), suggesting the vanillin-copper complex appears to have the same configuration as copper in the wood treated with ammoniacal copper carbonate, in which two copper-oxygen and two copper-nitrogen equatorial bonds form a plane.

Effect of complex formation on wood properties

Ammoniacal copper solution readily formed a water insoluble complex with vanillin, providing support for the hypothesis that, during fixation, ammoniacal copper preservatives react with the guaiacyl units on lignin to form stable copper-nitrogen complexes. The formation of such complexes supports the finding of enhanced nitrogen content in ammoniacal copper treated wood observed by Ruddick (1979). It may also help explain the changes which occur in the physical properties of the ammoniacal copper treated wood. The water insoluble copper complexes formed in the treated wood will be expected to be highly leach resistant (Hughes, *et al.*, 1994; Ruddick, 1992), and may also induce water repellent properties in the wood (Jin and Preston, 1992). The formation of cross-linked copper-lignin complexes in ammoniacal copper treated wood may also be responsible for the enhanced protection against photodegradation (Hon and Chang, 1985), reported to occur in ammoniacal copper treated wood during above ground weathering exposure tests (Jin, Archer, and Preston; 1991).

4. Conclusions

Ammoniacal copper solution reacted with vanillin, a lignin model compound, to form a stable water-insoluble copper complex. It is proposed that a similar reaction between ammoniacal copper ions and lignin to form a diammine copper lignin complex in wood, is a key reaction during fixation. The structure of the complex was characterized by FTIR, GC-MS, ESR and an X-ray structure analysis. The crystallographic examination confirmed that two of the ammonia ligands of the tetrammine copper complex were replaced by copper-oxygen bonding from hydroxyl and methoxyl groups in vanillin. The Cu-O (phenolic oxygen atoms) and the Cu-N (ammonia nitrogen) form a square plane around the central copper. The very distorted octahedral configuration is completed by the Cu-O (methoxy oxygen) which are coordinated to the plane containing the phenolic oxygen and ammonia nitrogen atoms and at a greater distance than the in plane phenolic oxygen. The ESR parameters determined in this work will provide an important bench mark in the use of $g_{//}$ and $A_{//}$ plots in identifying Cu(II) binding sites in wood preservation (Hughes *et al.*, 1994). The characteristics of the complex can explain the properties of the ammoniacal copper treated wood.

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7. References

Butcher, J.A. and T. Nilsson. 1982. Influence of variable lignin content amongst hardwood on soft-rot susceptibility and performance of CCA preservatives. Int., Res. Group on Wood Pres. Doc. No: IRG/WP/1151.

Coughlin, P.K., A.E. Martin, J.C. Dewan, E.I. Watanabe, J.E. Bulkowski, J.M. Jehn and S.J. Lippard. 1984. Synthesis and structure of the imidazolate-bridged dicopper(II) ion in two binucleating macrocycles. Inorg. Chem. 23:1004-1009.

Hartford, W.H. 1972. Chemical and physical properties of wood preservatives and wood preservative systems. In Wood deterioration and its prevention by preservative treatments. Vol. 2. Preservatives and preservative system. Syracuse University Press. p1-120.

Hathaway, B.J. and D.E. Belling. 1970. The electronic properties and stereochemistry of mono-nuclear complexes of the copper(II) ion. Coordin. Chem. Rev. 5:143-207.

Hathaway, B.J. and A.A.G. Tomlinson. 1970. Copper (II) ammonia complexes; Coordin. Chem. Rev., 5:1-43.

Hobson, R.J., M.F.C. Ladd and D.C. Povey. 1973. Substituted phenol as ligands (III): Crystal and molecular structure of bis(4-formyl-2-methoxyl phenolato)bis(pyridine)copper(II). J. Cryst. Mol. Struct. 3:377-388.

Hon, David N-S and Shang-T. Chang. 1985. Photoprotection of wood surfaces by wood-ion complexes. Wood and Fiber Science 2:92-100.

Hughes, A.S., R.J. Murphy, J.F. Gibson and J.A. Cornified. 1994. Electron paramagnetic resonance (ESR) spectroscopic analysis of copper based preservatives in *Pinus sylvestris*. Holzforschung 48:91-98.

Jin, L., K.J. Archer and Alan F. Preston. 1991. Surface characteristics of wood treated with various AAC, ACQ and CCA formulations after weathering. Int. Res. Group on Wood Pres. Doc. No. IRG/WP/2369.

Jin, L and Alan F. Preston 1992. Commercial development of ACQ in the United States. Canadian Wood Preservation Association, Proceeding, 13:43-54.

Peisach, J. and W.E. Blumberg 1974. Structural implications derived from the analysis of electron paramagnetic resonance spectra of natural and artificial copper proteins. Arch. Biochem. Biophys., 165:691-708.

Pilbrow, J.R. 1990. Transition ion electron paramagnetic resonance. Oxford express. P20.

Ruddick, J.N.R. 1979. The nitrogen content of ACA-treated wood. Material und Organismen. 14(4)301-312.

Ruddick, J.N.R. 1992. The fixation chemistry of copper based wood preservatives. Proc. Can. Wood Preserv. Assoc., 13:116-137.

Senesi, N., G. Sposito and G.R. Bradford. 1989. Iron, copper, and manganese complexation by forest leaf litter. For. Sci., 35(4):1040-1057.

Table 1. Selected bond lengths (Å) for vanillin-copper-ammonia complex

Atom	Atom	Distance	Atom	Atom	Distance
Cu(1)	O(1)	1.969(4)	Cu(1)	O(2)	2.371(3)
Cu(1)	O(4)	1.972(4)	Cu(1)	O(5)	2.388(3)
Cu(1)	N(1)	2.014(5)	Cu(1)	N(2)	2.034(5)
O(1)	C(1)	1.310(6)	O(2)	C(2)	1.368(6)
O(2)	C(8)	1.410(6)	O(3)	C(7)	1.216(7)
O(4)	C(9)	1.322(6)	O(5)	C(10)	1.359(6)
O(5)	C(16)	1.343(6)	O(6)	C(15)	1.211(9)
C(1)	C(2)	1.433(7)	C(1)	C(6)	1.398(7)
C(2)	C(3)	1.369(6)	C(3)	C(4)	1.380(7)
C(4)	C(5)	1.394(9)	C(4)	C(7)	1.474(7)
C(5)	C(6)	1.391(7)	C(9)	C(10)	1.458(7)
C(9)	C(14)	1.383(7)	C(10)	C(11)	1.363(7)
C(11)	C(12)	1.394(7)	C(12)	C(13)	1.407(8)
C(12)	C(15)	1.439(9)	C(13)	C(14)	1.384(7)

Table 2. Selected bond angles (°) for vanillin-copper-ammonia complex

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O(1)	Cu(1)	O(2)	75.2(2)	O(1)	Cu(1)	O(4)	179.7(2)
O(1)	Cu(1)	O(5)	105.1(1)	O(1)	Cu(1)	N(1)	90.0(2)
O(1)	Cu(1)	N(2)	89.2(2)	O(2)	Cu(1)	O(4)	104.9(2)
O(2)	Cu(1)	O(5)	177.2(2)	O(2)	Cu(1)	N(1)	90.3(2)
O(2)	Cu(1)	N(2)	88.5(2)	O(4)	Cu(1)	O(5)	74.8(1)
O(4)	Cu(1)	N(1)	89.8(2)	O(4)	Cu(1)	N(2)	91.0(2)
O(5)	Cu(1)	N(1)	92.5(2)	O(5)	Cu(1)	N(2)	88.8(2)
N(1)	Cu(1)	N(2)	178.7(2)	Cu(1)	O(1)	C(1)	120.3(3)
Cu(1)	O(2)	C(2)	108.8(3)	Cu(1)	O(2)	C(8)	131.5(3)
C(2)	O(2)	C(8)	119.6(4)	Cu(1)	O(4)	C(9)	121.6(3)
Cu(1)	O(5)	C(10)	109.5(3)	Cu(1)	O(5)	C(16)	129.9(3)
C(10)	O(5)	C(16)	120.6(4)	O(1)	C(1)	C(2)	121.6(4)
O(1)	C(1)	C(16)	121.7(5)	C(2)	C(1)	C(6)	116.8(4)
O(2)	C(2)	C(1)	113.5(4)	O(2)	C(2)	C(3)	124.7(4)
C(1)	C(2)	C(3)	121.8(5)	C(2)	C(3)	C(4)	119.9(5)
C(3)	C(4)	C(5)	120.3(5)	C(3)	C(4)	C(7)	120.7(6)
C(5)	C(4)	C(7)	119.0(5)	C(4)	C(5)	C(6)	120.0(5)
C(1)	C(6)	C(5)	121.2(5)	O(3)	C(7)	C(4)	124.2(6)
O(4)	C(9)	C(10)	120.1(4)	O(4)	C(9)	C(14)	122.1(4)
C(10)	C(9)	C(14)	117.7(4)	O(5)	C(10)	C(9)	113.6(4)
O(5)	C(10)	C(11)	126.3(4)	C(9)	C(10)	C(11)	120.1(5)
C(10)	C(11)	C(12)	121.3(5)	C(11)	C(12)	C(13)	118.8(5)
C(11)	C(12)	C(15)	121.7(6)	C(13)	C(12)	C(15)	119.4(5)
C(12)	C(13)	CC(14)	120.7(5)	C(9)	C(14)	C(13)	121.2(5)
O(6)	C(15)	C(12)	126.7(7)				

Table 3. The ESR parameters for vanillin-copper complex, copper solution and the copper treated wood at room temperature.

	$A_{//}$ $\times 10^{-4}$ cm^{-1}	$g_{//}$	$g_{\perp}$
$CuSO_4$ in NH_4OH[1]	193	2.24	-
$CuSO_4$ in H_2O[1]	138	2.40	2.07
Vanillin-Copper-Ammonia complex			
-in solid[2]	-	2.295	2.06
-in DMSO[3]	175	2.295	2.054 ($g_{xx} = 2.045$, $g_{yy} = 2.063$)
Wood treated with			
$CuCO_3/NH_4OH$[4]	166	2.27	2.07
$[Cu(en)_2]SO_4$ in water[4]	190	2.20	2.06

[1] data from Ajiboys and Brown (1990); [2] at room temperature, [3] at 115 K, DMSO = dimethyl sulfoxide, the parameters were obtained by a simulation of the spectrum using the program CLPOW provided by the Illinois ESR Research Center. [4] data from Ruddick (1992).

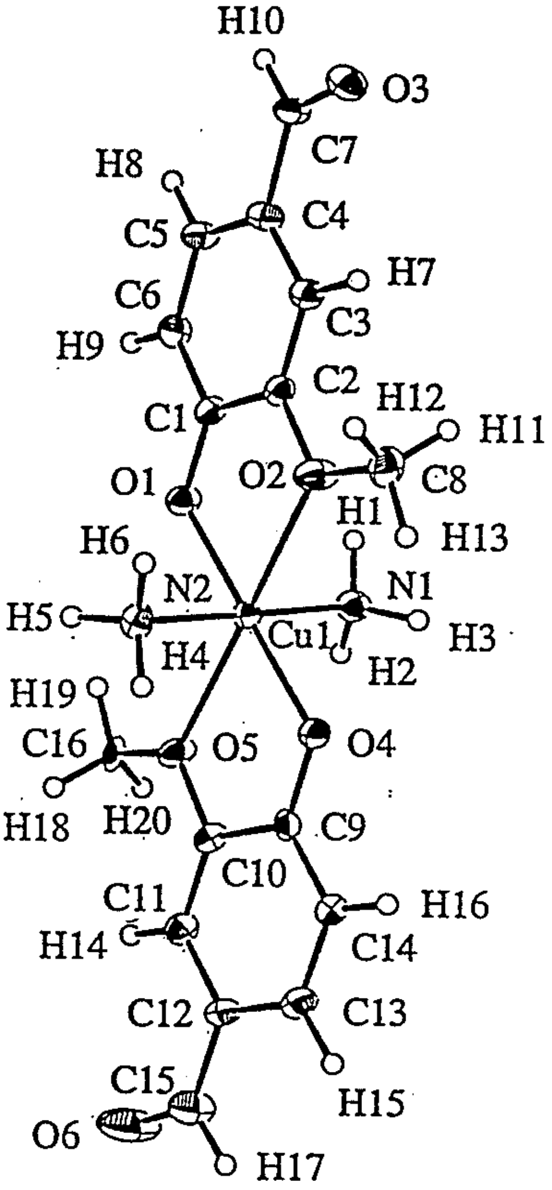

Fig. 1. Perspective view of Cu(II)-bis(vanillinato)bis(ammonia) with the atomic numbering; 33% probability thermal ellipsods are shown for the non-hydrogen atoms.

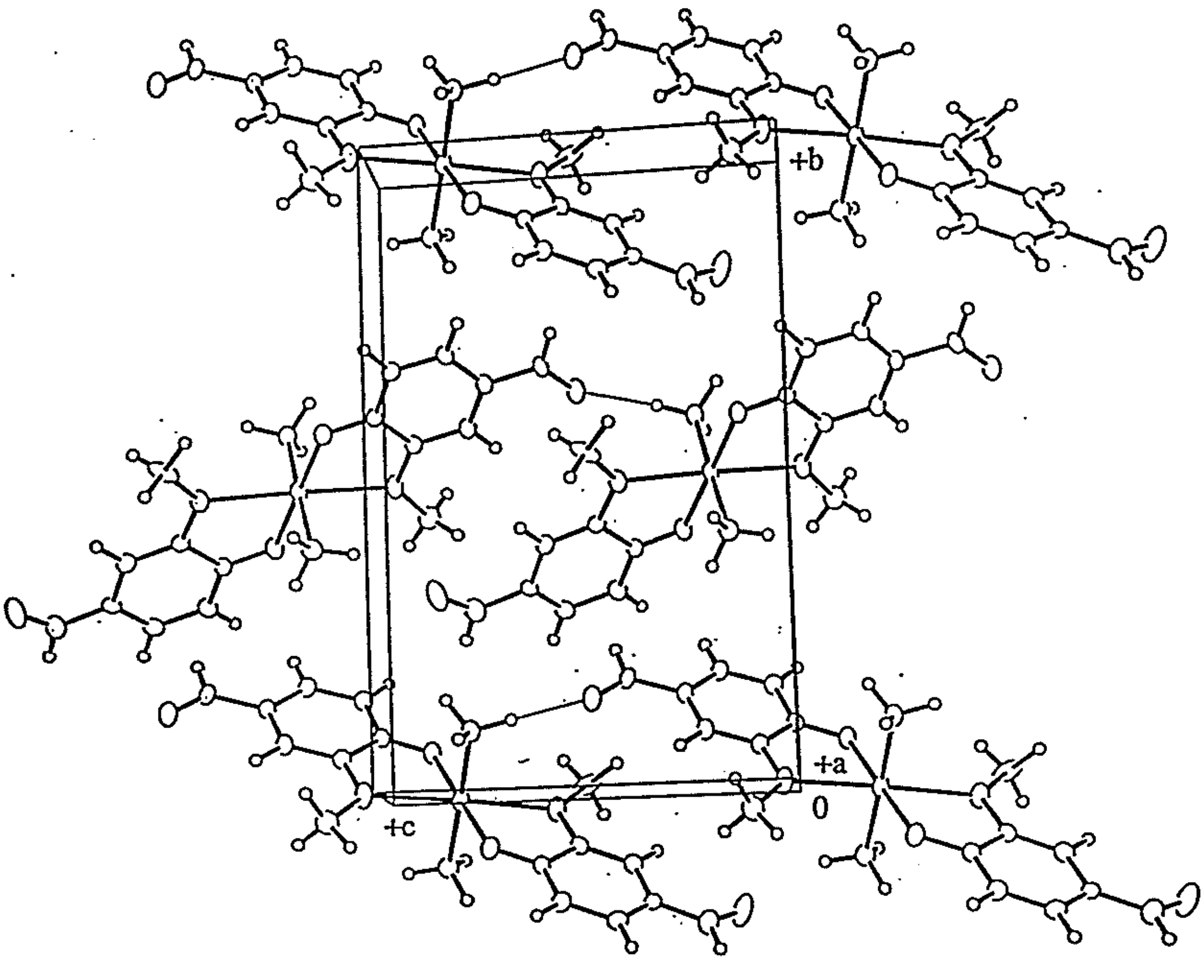

Fig. 2. The packing of Cu(II)-bis(vanillinato)bis(ammonia) in a monoclinic unit cell. The hydrogen bonds are indicated by thin lines.

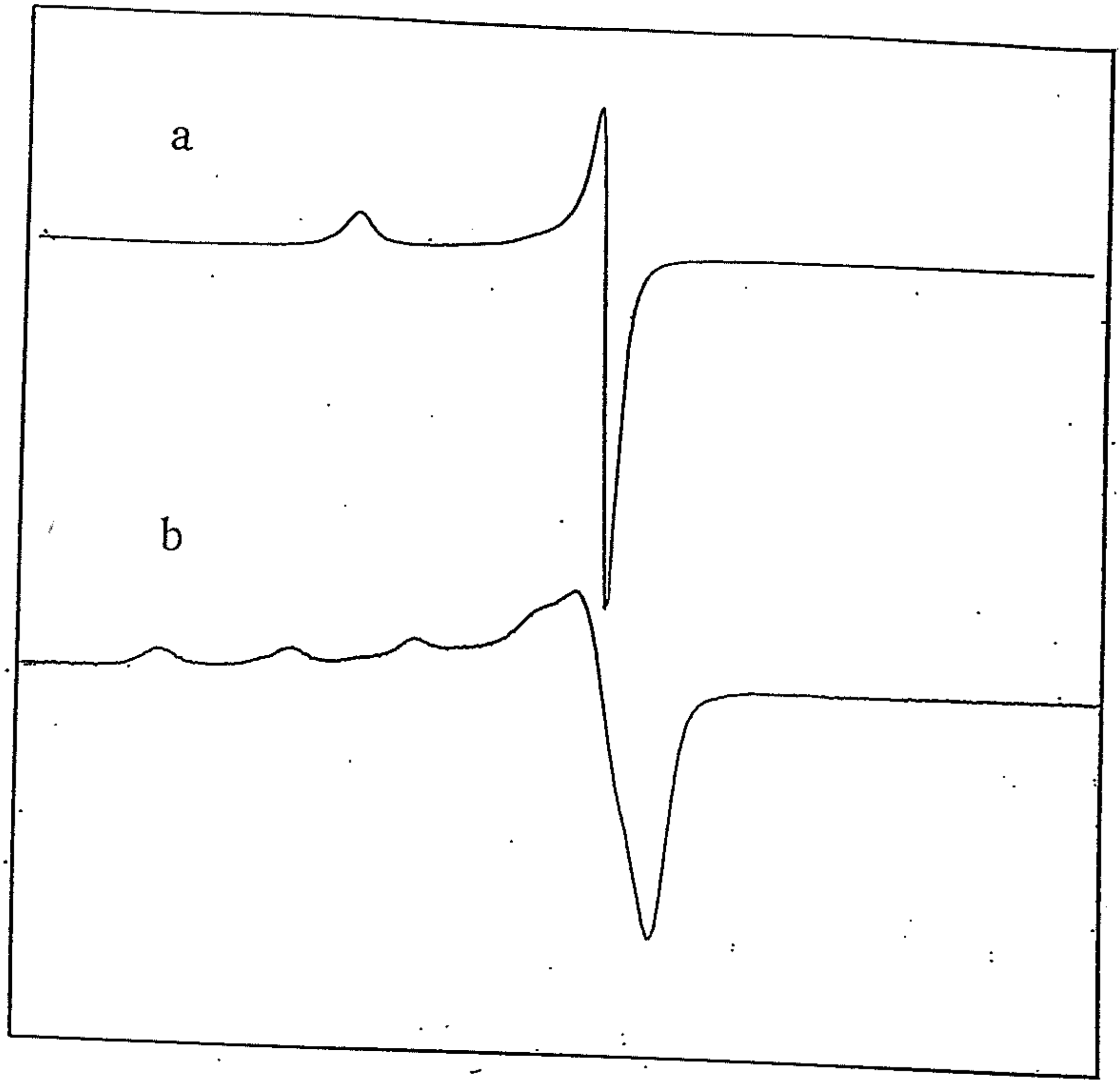

Fig. 3. ESR spectra of vanillin-copper complex a) solid at room temperature. b) in DMSO solution at 115 K.