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A STUDY OF COMPLEXES WITH CHELATING LIGANDS CONTAINING STERICALLY HINDERED PHENOLS.

V.* SYNTHESIS, STRUCTURE, AND PROPERTIES OF COMPLEX COMPOUNDS OF COPPER(II) WITH 1-METHOXY-2, 6-DI-tert-BUTYLPHENYL-4-N-SALICYLIDENEIMINATES

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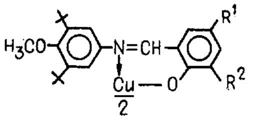
The synthesis, a study of the magnetic and spectral properties, and the determination of the crystal structure have been described for one of a number of complex Cu(II) bis-salicylideneiminates containing a sterically hindered phenol in which the shielded hydroxyl group has been replaced by a methoxy group. It has been established that these complexes are monomeric salicylideneiminate complexes with square-planar coordination of the copper atom.

In a study of complexes with salicylideneimines containing the sterically hindered di-tert-butylphenol substituent on the imine nitrogen atom, it was found [1] that in contrast to the case of the ions Co(II) and Zn(II), in the synthesis of the Cu(II) compounds, oxidative transformation of the ligands takes place. The ease of this transformation is due to the mobility of the hydrogen atom of the sterically hindered hydroxyl group. At the same time, it appeared important to study the influence of the sterically hindered phenol group on the stereochemistry and properties of the corresponding Cu(II) salicylideneiminates (SA). In this connection, the present paper describes the synthesis of inner-complex compounds (ICC) in which the sterically hindered phenolic hydroxyl group was replaced by a methoxy group. The structures and magnetic and spectral properties of the compounds were studied.



R^1=H,Cl,Br
R^2=H,NO_2

EXPERIMENTAL

The Schiff bases L_1H-L_5H (Table 1) were obtained by condensing ortho-hydroxy-aromatic aldehydes [2, 3] with 1-methoxy-2,6-tert-butylaniline [4] in methanol.

a) The Complex $Cu(L_1)_2$. A mixture of 0.002 mole of L_1H with an excess of freshly prepared copper hydroxide in 20 ml of acetone was mixed for 1.5 h with heating to 50°C. A further 100 ml of acetone was then added to the mixture, and the warm reaction mixture was filtered to remove the excess of copper hydroxide, and evaporated to one eighth of its volume. The resulting green crystals were separated, dried, and recrystallized from an acetone–ethanol mixture; mp > 250°, yield 85%.

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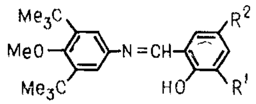
TABLE 1. Frequencies of the Vibrations (cm^{-1}) of the Characteristic Groups in the Infrared Spectra and the Absorption Bands (λ, nm) in the Electronic Spectra of the Schiff Bases



Schiff base	Substituent		m_p, deg	IR spectrum		Electronic spectrum λ_{max} (ε), nm
	R^1	R^2		$\nu_{C=N}$	ν_{OCH_3}	
L_1H	H	H	68	1615	1230	438(4·10^2), 345(2,3·10^4), 325(2·10^4), 268(1,7·10^4), 250(1,7·10^4), 230(4·10^4), 212(6·10^4)
L_2H	Cl	H	101–102	1625	1228	440(1,3·10^2), 350(1,5·10^4), 330(1,3·10^4), 312(1,05·10^4), 265(1,05·10^4), 230(4·10^4), 212(4,5·10^4)
L_3H	Br	H	99–100	1620	1230	355(4,4·10^4), 333(3,6·10^4), 315(2,9·10^4), 270(3,3·10^4), 252(5,9·10^4)
L_4H	H	NO_2	163–164	1625	1245	427(2·10^3), 345(1,6·10^4), 310(1,5·10^4), 242(1,7·10^4), 206(3,3·10^4)
L_5H	Br	NO_2	222–223	1635	1225	425(5,6·10^2), 370(2,6·10^4), 357(3,9·10^4), 340(3,6·10^4), 317(4,2·10^4), 270(3·10^4), 255(4,4·10^4)

TABLE 2. Physicochemical and Spectral Properties of the Complexes Cu$(L_i)_2$

Complex	mp, deg	μ_{eff}, B.M.	Infrared spectrum		Electronic spectrum λ_{max} (ε), nm
			$\nu_{C=N}$	ν_{OCH_3}	
Cu$(L_1)_2$	>250	1,87	1618	1245	650(1,4·10^2), 500(9,7·10^4), 395(2·10^4), 232(9,4·10^4)
Cu$(L_2)_2$	>250	1,89	1618	1225	245(6,5·10^4), 270(2,4·10^4), 320(2,4·10^4), 335(2,6·10^4), 335(2,9·10^4), 420(2,6·10^3), 500(2,6·10^3), 650(3·10^2)
Cu$(L_3)_2$	>250	1,86	1612	1225	245(6·10^4), 270(2,5·10^4), 318(2,6·10^4), 333(2,5·10^4), 415(4,3·10^3), 490(1,1·10^3), 650(3,6·10^2)
Cu$(L_4)_2$	>250	1,88	1615	1235	255(8,5·10^4), 315(6,1·10^4), 340(7,5·10^4), 355(7,8·10^4), 490(2,1·10^3), 650(3,06·10^2)
Cu$(L_5)_2$	>250	1,85	1610	1225	245(3,1·10^4), 260(4,1·10^4), 325(3,6·10^4), 350(4,3·10^4), 370(5,1·10^4), 375(5·10^4), 490(2·10^3), 650(2,1·10^2)

TABLE 3. Coordinates of the Atoms (× 10^4)

Atom	x	y	z	Atom	x	y	z
Cu	5000	5000	5000	C(10)	0044(23)	2810(24)	8103(17)
O(1)	4946(13)	5635(12)	3490(29)	C(11)	3561(18)	8610(17)	7265(14)
O(2)	1322(13)	9573(12)	8221(11)	C(12)	2261(20)	7250(21)	7374(14)
N	3145(14)	3420(12)	4585(11)	C(13)	4363(14)	8342(19)	6411(13)
C(1)	2610(18)	2410(17)	5526(12)	C(14)	4767(19)	8724(19)	8339(14)
C(2)	3327(16)	1121(17)	5958(12)	C(15)	2213(22)	0009(22)	9290(17)
C(3)	2843(17)	0100(17)	6845(12)	C(16)	2320(19)	3196(18)	3637(12)
C(4)	1723(19)	0467(20)	7302(14)	C(17)	2733(19)	4080(19)	2679(13)
C(5)	0927(20)	1754(19)	6777(13)	C(18)	1777(19)	3738(20)	1696(16)
C(6)	1429(17)	2731(17)	5866(12)	C(19)	2034(24)	4490(23)	0644(14)
C(7)	9508(21)	2062(21)	7070(17)	C(20)	3386(25)	5586(25)	0654(17)
C(8)	8346(25)	0651(27)	7120(17)	C(21)	4362(21)	5966(20)	1628(14)
C(9)	8756(21)	3275(27)	6185(16)	C(22)	4008(21)	5204(20)	2631(13)

b) The Complexes $Cu(L_2)_2$–$Cu(L_5)_2$. A solution of 0.001 mole of $Cu(CH_3COO)_2 \cdot 2H_2O$ in 2 ml of an ethanol–water mixture was added with stirring to a solution of 0.002 mole of the Schiff base L_2L–L_5H in 15-20 ml of acetone, and the mixture was heated to 50° for 1 h. The resulting precipitate was separated, dried, and recrystallized from chloroform. Yield 85-90%.

SPECTRAL DATA

The infrared and ultraviolet spectra were recorded on UR-20 (KBr discs) and Specord UV-VIS spectrometers. The magnetic measurements were made on a Faraday apparatus using $Hg[Co(SCN)_4]$ as standard.

Comparison of the infrared spectra of the Schiff bases and the Cu(II) ICC shows that the bands due to the stretching vibrations of the C=N bond at 1600 cm^{-1} are displaced to lower frequencies by approximately 10-20 cm^{-1} (Tables 1 and 2).

The ultraviolet spectra of ethanol solutions of the Schiff bases L_1H–L_5H show bands at 210-230, 245-290, and 300-357 nm, assigned respectively to E_1 and E_2 bands and $n \rightarrow \pi^*$ transitions [5]. The band at 425 nm was assigned to the absorption of the quinonoid tautomer with proton transfer [6-8]. In nonpolar solvents (hexane), this band either does not appear or appears with a low intensity. The absorption spectra of all the complexes (solvent $CHCl_3$), in addition to the above bands, show a shoulder at about 500 nm and a band of low intensity at 650 nm, which indicate that the complexes have a planar structure [9-12].

The values found for the magnetic moments are also characteristic of planar complexes [13].

DETERMINATION OF THE CRYSTAL STRUCTURE OF COPPER(II) BIS(1-METHOXY-2,6-DI-tert-BUTYLPHENYL-4-N-SALICYLIDENEIMINATE)

The x-ray structural study was carried out on a "Syntex $P2_1$" automatic diffractometer (Mo radiation, graphite monochromator, $\theta/2\theta$ scanning). The crystals are triclinic, a = 9.338(9), b = 9.184(5), c = 12.814(13) Å, α = 78.77(7), β = 104.76(7), γ = 101.70(6)°, M = 788, Z = 1, V = 1028.6 $Å^3$, space group $P\bar{1}$. The structure was determined by the heavy-atom method and refined by the method of least squares in the anisotropic approximation as far as R = 10.7%. All the calculations were carried out using the XTL programs on a "Nova-1200" minicomputer. The atom coordinates are given in Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION OF RESULTS

The structure of the molecule with the bond lengths and valence angles are shown in Fig. 1.

In the centrosymmetric complex, the copper atom is joined by coordinate bonds to two salicylideneimine oxygen and nitrogen atoms at the corners of a planar square. The bond lengths Cu–O 1.900 and Cu–N 2.029 Å and the valence angle NCuO(1) 88.7°, like all the other bond lengths and angles, coincide within the limits of accuracy with the analogous values in other square-planar SA complexes of copper [14-18].

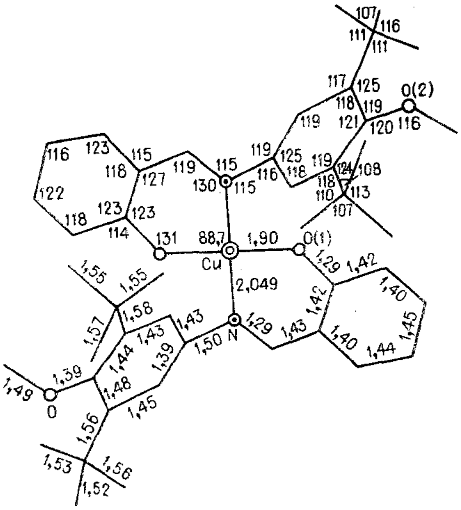


Fig. 1. Structure of the molecule with the bond lengths (Å) and valence angles (deg). Accuracy 0.01-0.03 Å, 0.5-2°.

A characteristic feature of the complex studied is its almost planar structure (with the exception of the substituents on the N atoms). The displacement of the Cu atom from the plane of the metal-containing ring is 0.08 Å (height of the step Δh = 0.16 Å). The planes of the metal-containing ring and the benzene ring conjugated with it are almost coplanar; the dihedral angle between them is 2.7°. Only two cases of a more planar structure are known: bis(N-methyl-SA)Cu [19], whose molecule lies in a mirror plane, and bis(N-p-dimethylaminophenyl-SA)Cu [20]. Thus the conclusion [21] that the introduction of an electron-donor substituent into the phenol group leads to coplanarity of the planes of the metal-containing ring and the phenyl ring in salicylideneiminates is confirmed. It may also be noted that the electron-donor power of the methoxy group is weaker than that of the dimethylamino group, and this explains the greater coplanarity in the case of the dimethylaminophenylsalicylideneiminate complex.

The configuration of the bonds at the tertiary nitrogen atom indicates that it has sp^2 hybridization (the height of the pyramid at the N atom is 0.02 Å). The dihedral angle formed by the plane of the phenyl ring C(1)-C(6) with the coordination plane CuON is 95.2°, that with the plane of the SA fragment is 81°, and that with the planar fragment $\begin{matrix}C(1)\\C(16)\end{matrix}\!\!>\!N-Cu$ is 82.7°, indicating that there is little π-conjugation of the phenyl ring with these parts of the complex (hindered phenol fragment). This deviation from the energetically favorable planar structure is apparently due to the tendency to decrease the steric hindrance created by the bulky 1-methoxy-2,6-di-tert-butylphenyl substituent.

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A STUDY OF THE STRUCTURE OF THE MOLECULES OF 3,7,10-CARBONYL-CONTAINING GERMATRANES BY X-RAY STRUCTURAL ANALYSIS AND NMR SPECTROSCOPY

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An x-ray structural study of the molecule of 1-phenylgermatrane-3-one (the phenyl derivative of 2,8,9-trioxa-5-aza-1-germa-bicyclo[3,3,3]undecane) has been carried out. Its ^{13}C NMR spectra and the PMR spectra of the 3,7,10-carbonyl-containing analogs of 1-methylgermatrane have been studied. It has been shown that the flattening of the half-rings with the carbonyl group is accompanied by an increase in the torsional angles of the remaining chains of the atrane bicyclic system, which in solutions undergoes rapid (on the NMR scale) synchronous conversion.

The present paper describes a continuation of earlier studies of the structures of the molecules of derivatives of germatrane [1, 2]. X-ray structural analysis and NMR spectroscopy were used to study the structure of 1-phenyl- and 1-methylgermatrane-3-one, 1-methylgermatrane-3,7-dione, and 1-methylgermatrane-3,7,10-trione. All the substances were synthesized and purified by the published methods [1]. The experimental data for the complete determination of the structure of 1-phenylgermatrane-3-one were obtained on a CAD-4-SDP automatic x-ray diffractometer (the crystals are orthorhombic, a=10.379(7), b=13.597(7), c=18.118(9) Å, space group Pbca, Z=8, d_{calc}=1.54, 1626 independent reflections). The structure was determined by the direct method and refined by the method of least squares in the anisotropic approximation as far as R=6.8%. All the calculations were carried out on a BESM-4 computer using the programs of the sets "RENTGEN-70" and "KRISTALL." The general form of the molecule and the numbering of the atoms are shown in Fig. 1. The coordinates of the atoms and the isotropic temperature factors are given in Table 1, and the bond lengths and valence angles in Table 2. The NMR spectra were recorded on BS-467C "TESLA" (^1H) and WP-80 "Bruker" (^{13}C) spectrometers. TMS was used as internal standard.

As in all atrane compounds of the elements of group IVB of the periodic system, the coordination of the germanium atom in the molecule of 1-phenylgermatrane-3-one is close to that of a trigonal bipyramid, with three oxygen atoms in the equatorial plane. The germanium atom is displaced by 0.25 Å below this plane towards the substituent. The interatomic distance Ge...N (2.203 Å) differs only slightly from the analogous distances in all the molecules previously studied $C_2H_5\overset{\downarrow}{Ge}(OCH_2CH_2)_3\overset{|}{N}$ 2.24 Å [3] $\alpha\text{-}C_{10}H_7\overset{\downarrow}{Ge}(OCH_2CH_2)_3\overset{|}{N}$ 2.24 Å [4] and $ICH_2\overset{\downarrow}{Ge}(OCH_2CH_2)_3\overset{|}{N}$ 2.19 Å [5]. The distance from the nitrogen atom to the equatorial plane is 1.96 Å. The introduction of the carbonyl group into one of the three half-rings of 1-phenylgermatrane is accompanied by a characteristic change in various structural parameters of this molecule. The length of the Ge−O(2) bond increases to 1.861 Å, and that of the bond O(2)−C(3) decreases to 1.318 Å. Thus a definite redistribution of electron density takes place along the chain of bonds. The half-ring Ge−O(2)−C(3)−C(4)−N,

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