Mononuclear and Binuclear Copper(II) Complexes of 3,5-Diisopropylsalicylic Acid

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Abstract

Several copper(II) complexes of 3,5-diisopropylsalicylic acid and a variety of ligating solvents have been prepared and studied by elemental analysis, and by infrared, electronic, and EPR spectroscopy. In the solid state, all of the compounds are binuclear, carboxylate-bridged $Cu_2(3,5\text{-DIPS})_4(L)_2$, where L may be a vacant site or a coordinating ligand. In non-coordinating solvents such as hexane and dichloromethane, the binuclear structure is retained in solution, but in polar coordinating solvents the dimer dissociates into monomers where the copper is coordinated to two solvent molecules and to two bidentate diisopropylsalicylate ligands through their carboxylic and phenolic oxygen atoms.

Introduction

The copper(II) complex of 3,5-diisopropylsalicylic acid has attracted much interest because of its radioprotectant [1], antiinflammatory, [2] antineoplastic [2, 3] and anticonvulsant [2, 4] activities. The complex is insoluble in water and is normally administered subcutaneously or orally in the form of a suspension in Tween-80, or propylene glycol and 1.4% polyvinylalcohol in saline [1]. The mechanism of action of the drug is not known and the important questions of stability and fate of the complex *in vivo* remain unanswered. Three forms of the complex have been reported [5]: a green binuclear form which has been found to contain two ether molecules bonded apically, one to each copper(II) [6]; a brown form obtained upon heating the etherate at 100 °C at 15 torr overnight; and a tan product obtained upon addition of $CuCl_2$ to an aqueous solution of the sodium salt of 3,5-DIPS, this being the form administered in most pharmacological tests.

We are reporting the results of EPR, infrared, and electronic spectroscopic studies of the green, brown, and tan forms of the copper(II) complexes of 3,5-diisopropylsalicylic acid and of a variety of solvate adducts, both in the solid state and in a variety of solvents.

Experimental

Infrared spectra of KBr disks and nujol mulls of the copper compounds were obtained in the 4000 to 200 cm^{-1} region with a Perkin-Elmer 1330 spectrophotometer. UV–Vis spectra of solutions in a variety of solvents, and of KBr discs and fluorocarbon mulls of solids were recorded in the 200–900 nm region with a Perkin-Elmer λ-3B spectrophotometer. EPR spectra were obtained with a Varian E-9 spectrometer operating at 9.1 GHz with 100 kHz modulation. The microwave frequency was measured using a Hewlett-Packard microwave frequency counter and the magnetic field was calibrated using a Magnion NMR-type gaussmeter. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Synthesis of Tetrakis-μ-(3,5-diisopropylsalicylato)-dicopper(II), $Cu_2(3,5\text{-DIPS})_4$

The complex was prepared in aqueous solution as previously described [5] and recrystallized from ether to give green crystals of $Cu_2(3,5\text{-DIPS})_4$-(diethylether)$_2$ which were dried under vacuum at 100 °C to give a dark tan powder of $Cu_2(3,5\text{-DIPS})_4$. $Cu_2(3,5\text{-DIPS})_4(H_2O)_2$ was prepared from aqueous solution and dried at 50 °C to give a light tan powder. Drying at 100 °C removed one water molecule. Adduct complexes with a variety of coordinating solvents, (including water, acetone, methanol, ethanol, 1,4-dioxane, dimethylsulfoxide (DMSO), ethylene glycol, 1,2-propanediol (propylene glycol), diethylether, dimethylformamide (DMF), acetonitrile, and pyridine) were readily obtained by recrystallization from the appropriate solvent. In most

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cases adducts form very readily, even when the crystals are exposed to vapors of the apically ligating molecule. On heating at 120 °C, the apical adducts of ethanol, methanol, acetone, and ether all lost mass corresponding to between 0.90 and 0.96 solvent molecule per copper. The higher temperatures required to remove the other apical ligands resulted in decomposition. *Anal.* Calc. for ($Cu_2C_{52}H_{68}O_{12}$): C, 61.70; H, 6.77; Cu, 12.56. Found: C, 61.38; H, 6.89; Cu, 11.50%. Calc. for ($Cu_2C_{52}H_{68}O_{12}\cdot 2H_2O$): C, 59.58; H, 6.92. Found: C, 59.99; H, 7.01%. Calc. for ($Cu_2C_{52}H_{68}O_{12}\cdot H_2O$): C, 60.53; H, 6.85; Cu, 12.34. Found: C, 60.36; H, 6.84; Cu, 12.27%. Calc. for ($Cu_2C_{52}H_{68}O_{12}\cdot 2C_4H_{10}O$): C, 62.10; H, 7.64. Found: C, 61.99; H, 7.39%.

Results and Discussion

All of these complexes have a common binuclear carboxylate-bridged $Cu_2(3,5\text{-DIPS})_4$ structure in the solid state, similar to that known for a wide variety of copper(II) carboxylates [6–10]. In the presence of a solvent with coordinating capabilities, a solvent molecule additionally coordinates to each copper to give apical adducts, $Cu_2(3,5\text{-DIPS})_4L_2$, where L is the apical solvent ligand. The solid adduct compounds are usually green while removal of the apical ligand results in a brown or dark tan amorphous solid. The solid form of the water adduct is anomalous in that it is an adduct but has a light tan color.

$Cu_2(3,5\text{-DIPS})_4$ is readily soluble in non-polar solvents giving brown solutions where the binuclear structure is retained. In very dilute solutions, the color becomes green, indicating decomposition to mononuclear structures. In solvents with coordinating capabilities, mononuclear species are present and the color of the solution is more variable, ranging from brown, through yellow and green to blue as the coordinating strength of the solvent increases.

Infrared Spectra

In the acid form of the free ligand, $\nu_a(COO^-)$ is observed at 1660 cm^{-1} and $\nu_s(COO^-)$ at 1280 and 1225 cm^{-1}. The sodium salt of 3,5-DIPS has ν_a at 1560 and we assign ν_s to the bands at 1390 and 1360 cm^{-1} although there is also a strong unidentified band at 1250 cm^{-1}.

Infrared spectra for all solid $Cu_2(3,5\text{-DIPS})_4L_2$ adducts are very similar to one another except for peaks attributed to the apical ligands. For the solid binuclear compound with no apical ligands, the asymmetric COO^- stretch occurs as a strong broad peak at 1560 cm^{-1} and the symmetric stretch occurs at 1390 cm^{-1}. On adduct formation, $\nu_a(COO^-)$ increases to 1590 cm^{-1} while $\nu_s(COO^-)$ remains unchanged. The increase in frequency of $\nu_a(COO^-)$ on adduct formation is in agreement with the observations of Bose and Patel [10]. Changing the nature of the apical ligand causes only minor differences in the carboxylate band frequencies and these are obscured by overlap with other bands. The only exception to this is $Cu_2(3,5\text{-DIPS})_4(H_2O)_2$ for which the bands occur at the same frequencies as for the complex with no apical ligands.

Carboxylate peaks for binuclear copper carboxylate complexes commmonly occur near 1620 and 1410 cm^{-1} with a separation, Δ, of 200–220 cm^{-1} which is characteristic of bridging carboxylate groups [7–11]. We observe Δ for $Cu_2(3,5\text{-DIPS})_4$ with no apical ligands to be 170 cm^{-1}, somewhat less than the values of 191 and 218 cm^{-1} Bose and Patel observed for the benzoate and aspirinate complexes of similar structure [10]. They observed that addition of apical solvent ligands typically increases Δ to about 220 cm^{-1} for both benzoate and aspirinate complexes. Our Δ values of 195–210 cm^{-1} for the 3,5-DIPS complexes are slightly smaller, but confirm that the structures of the 3,5-DIPS, aspirinate, and benzoate adduct complexes are very similar.

We find the infrared bands of the apical ligand are often weak, and can not definitely assign bands to coordinated water, methanol, or acetonitrile. Where unambiguous apical ligand bands are observed, the shifts on coordination are generally quite similar to published data [12]. For example, for *p*-dioxane [13, 14] the wagging mode shifts from 1127 to 1112 and the rocking mode from 827 to 872; the S=O stretch of DMSO from 1055 to 1012 [10, 11]; the C=O stretch of DMF from 1680 to 1669 [10]; the C=O stretch of acetone from 1710 to 1650; the asymmetric C–O stretch of ether from 1122 to 1060; and the C–O stretch of ethanol from 1060 to 1042 cm^{-1}. Some of the important apical ligand bands are given in Table I.

Electronic Spectra

The ligand dissolves in 95% ethanol to give a light tan solution which has intense absorption peaks at 240 and 315 nm with a much weaker shoulder at about 540 nm. These peaks decrease in energy by about 5 nm on binding of copper(II) but are not sensitive to compound structure.

Electronic spectra of the brown $Cu_2(3,5\text{-DIPS})_4$ solid in KBr pellets have bands at 320 nm due to a ligand transition, and 445 nm due to a charge transfer transition [15]. A weak d–d transition occurs at about 690 nm. Electronic spectra of the tan $Cu_2(3,5\text{-DIPS})_4(H_2O)_2$ solid in KBr pellets are almost identical.

$Cu_2(3,5\text{-DIPS})_4$ is readily soluble in non-polar solvents giving brown solutions where the binuclear structure is retained. The absorption spectrum of hexane or dichloromethane solutions has the charge

TABLE I. Infrared Data for Solid Adduct Compounds[a]

Apical ligand	$\nu_a(COO^-)$	$\nu_s(COO^-)$	Δ	Axial adduct bands
H 3,5-DIPS	1660	1280	380	
Acetone	1590	1392	198	1650
Ethanol	1595	1386	209	1042
Methanol	broad	1390		1150, 1120
Ethylene glycol	1590	1390	200	1042, 1078
Propylene glycol	1590	1380	210	1140, 993, 928, 841
Diethylether	1590	1390	200	1060
p-Dioxane	1585	1385	200	1112, 872, 895
Acetonitrile	1590	1390	200	
Pyridine	1590	1388	202	1038, 1065
DMSO	1590	1390	200	1012
DMF	1590	1390	200	1669
Water	1560	1390	170	
None	1560	1390	170	
Na 3,5-DIPS	1560	1390	170	

[a]All units are in cm^{-1}.

TABLE II. Spectroscopic Data for Solutions[a]

Solvent	Electronic transitions			EPR parameters (cm^{-1})		
	Color	λ_{max} (nm)		$g_\parallel$	g_m	$A_\parallel$
Hexane	brown	445	725		binuclear	
Dichloromethane	brown	455	710		binuclear	
Pyridine	blue		670	2.273	2.061	0.0185
Pyridine/chloroform	blue–green			2.304	2.062	0.0170
Wet solvents (water)	yellow–green		690	2.366	2.077	0.0146
Chloroform	green		700	2.370	2.072	0.0136[b]
Diethylether	green		710	2.372	2.078	0.0144
Acetonitrile/chloroform	green		700	2.334	2.059	0.0175
Acetonitrile	green		725	2.306	2.074	0.0171
Acetone	green		690	2.360	2.076	0.0146
			730	2.333	2.072	0.0166
				2.310		0.0175
DMF	olive green		740	2.372	2.075	0.0141
Ethanol	yellow	440	745	2.373	2.078	0.0140
Methanol	yellow–brown	440	750	2.376	2.085	0.0142
Propylene glycol	yellow–green	430	760	2.381	2.082	0.0138
DMSO	yellow–green	420	770	2.372	2.081	0.0149

[a]The complex is insoluble in *p*-dioxane, ethylene glycol, and water. [b]Binuclear species are also present.

transfer band at 445 nm ($\epsilon_M = 900$) and the d–d band at 725 nm ($\epsilon_M = 90$). In solvents with coordinating capabilities, mononuclear species are present. The color of the solution is largely determined by the position of the minimum between the d–d band and the charge transfer band and is very sensitive to small changes in the position of either band, ranging from brown, through yellow and green to blue as the coordinating strength of the solvent increases (Table II). The color of the solution is therefore not a reliable guide to structure. The energy of the d–d transition increases as the coordinating strength of the solvent increases. The charge transfer band also increases in energy and is hidden under the more intense ligand bands for the stronger ligands, so that only in methanol and ethanol solutions is the band clearly resolved. Most known binuclear copper carboxylates have a charge transfer transition near 375 nm [7–9, 15] which is thought to be characteristic of binuclear copper carboxylates. However charge transfer bands have also been observed between 400 and 450 nm for mononuclear copper salicylate compounds [13, 16], and are observed for our mononuclear compounds

TABLE III. Spectroscopic Data for Solid Adduct Compounds

Apical ligand	Electronic transitions (nm (μm^{-1}))		Color
None	445(2.25)	690(1.45)	brown
Dioxane		660(1.52)	green
Ether	420(2.38)sh	665(1.50)	green
Acetone		675(1.48)	green
Ethylene glycol	410(2.44)sh	690(1.45)	green
Propylene glycol		690(1.52)	green
Ethanol	410(2.44)sh	700(1.43)	green
DMF		700(1.43)	green
Acetonitrile		705(1.42)	green
Pyridine		710(1.41)	green
Water	445(2.25)	720(1.39)	brown
DMSO		725(1.38)	green
Methanol	430(2.33)	740(1.35)	green

[a]Prepared by evaporation of chloroform, dichloromethane, or hexane solutons; or by heating the ether adduct.

in solution so that the presence of the band does not seem to be restricted to binuclear compounds.

Evaporation of these solvents leaves green residues of the adduct complexes. Although $Cu_2(3,5\text{-DIPS})_4$ is not appreciably soluble in ethylene glycol and *p*-dioxane, the solid also becomes green or blue–green respectively due to apical coordination of these solvents. Spectra of the green apical adducts in the solid state (Table III) show ligand bands at 245 and 320 nm and a weak d–d band between 640 and 740 nm, but the 445 nm charge transfer band is shifted to higher energy and usually appears only as a shoulder near 410 nm. We observe the energy of the charge transfer band to increase as the apical ligand changes, in the order: none ≈ water < methanol < ether ≈ ethanol < pyridine in agreement with the common observation that the energy of this band increases as the strength of the apical ligand increases [7]. The energy of the d–d band increases in a completely different order: methanol < water < pyridine < acetonitrile < ethanol < ethylene glycol ≈ propylene glycol ≈ none < acetone < diethylether < dioxane. This order is similar to that found by Kato *et al.* [9] for the order of formation and strength of interaction in binuclear compounds (water, pyridine < methanol < ethanol, acetone < none < dioxane < diethylether), and to that found by Melnick *et al.* [11] for the order of increasing $-2J$ for copper benzoates (nicotine < antipyrine < benzoic acid ≈ aryl-*N*-oxides < DMSO ≈ butanol < pyridine < anhydrous < ethanol). Copper(II) alkylcarboxylates do not follow this trend [7].

EPR Spectra

Solids

EPR spectra of the solid adduct compounds are very temperature dependent, with the signal increasing as the temperature is raised, the reverse of that predicted by simple Curie Law behaviour. The spectra are characteristic of strongly coupled Cu(II) ions with axial symmetry [17] for which

$$\mathcal{H} = g\beta HS + D(S_z^2 - 2/3)$$

where $S = 1$ and the other symbols have their usual meaning. The value of D is calculated to be 0.390 ± 0.005 cm^{-1}, with $g_\parallel = 2.37$ and $g_\perp = 2.06$. These are very similar to the parameters reported for many exchange-coupled copper(II) binuclear compounds although the D value is amongst the highest reported [7, 11, 18]. A slight rhombicity is observed in the $H_\perp$ peak for the complex with no apical ligands and for the water adduct, but this is not enough to be resolved at X-band. Although temperature dependent magnetic susceptibility measurements would be required for an accurate determination of $-2J$, the temperature dependence shows that the coupling is antiferromagnetic with $-2J$ at least 300 cm^{-1}. All the adduct compounds displayed very similar EPR parameters, which shows that the apical ligand has little influence on the copper–copper interaction. In all spectra, small signals due to monomeric impurity were observed, as is usual for binuclear copper carboxylates [19].

The brown complex formed by heating the diethylether adduct also had a second binuclear species, characterized by a $\Delta m_s = 2$ resonance at $g = 4.19$ and a broad doublet $\Delta m_s = 1$ resonance. This signal displays normal temperature dependence indicating that any exchange coupling is small. Although the presence of a monomer signal prevents complete analysis of this spectrum, the signals are typical of pairs of dipolar-coupled copper(II) ions such as those observed with 5-sulfosalicylate [20]. Small amounts of similar species are observed in solids obtained by heating various other solvent adducts to drive off the apical solvent molecules. This suggests that the drying process causes collapse of the crystal structure producing additional copper–copper interactions. X-ray diffraction of crystals prepared by heating the dietherate adduct showed a large proportion of amorphous matter.

Solutions

Apart from a weak monomer impurity signal, no EPR signals were observed at any temperature for frozen hexane solutions of $Cu_2(3,5\text{-DIPS})_4$. We conclude that the copper–copper interaction has increased over that for the solid and that the triplet state is not appreciably populated at temperatures below −94 °C, when hexane melts. The EPR spectra of frozen dichloromethane solutions show signals that are essentially identical to those of the solid and display a similar temperature dependence. At room temperature no signal is observed. These results show that the binuclear structure of the solid

is preserved in this non-coordinating solvent. In addition, however, there are weak monomer signals and also weak spectra with many 'parallel' lines due to dipolar-coupled Cu(II) ions although these are not stable. In chloroform solution, there are also strong binuclear signals, but there is significantly more monomer present indicating that this more polar solvent has led to a greater breakdown of the binuclear structure. All of the adduct compounds are soluble in chloroform solution, and EPR spectra show that there is a mixture of binuclear and often more than one mononuclear species present in these solutions. Addition of small additional amounts of the apical ligand to the chloroform causes changes consistent with an equilibrium between $Cu(3,5\text{-}DIPS)_2$ <==> $Cu(3,5\text{-}DIPS)_2L$ <==> $Cu(3,5\text{-}DIPS)_2L_2$ for acetone, acetonitrile, and pyridine, and possibly for other adducts too, although these species have too similar EPR parameters to allow definite conclusions.

In polar oxygen-donor solvents, the EPR spectra are typical of monomeric Cu(II) ions coordinated with oxygen atoms in a tetragonally-elongated octahedral arrangement [21]. The EPR parameters of the mononuclear compounds present in these solutions are similar to those reported for copper(II) salicylate in DMSO [22] where the salicylate ligand is thought to be bidentate [23, 24]. These parameters indicate that 3,5-DIPS is coordinating through a protonated phenolic group; the EPR parameters for $Cu(sal)_2^{2-}$ which has a deprotonated phenolic group [22] are very different from those we observe. Several workers have suggested that salicylates bond to copper(II) in aqueous solution through a deprotonated phenolic group [25–27]. However, in very weakly basic solvents it is more likely that this group is protonated. Except for the strongly coordinating nitrogen-donor solvents, pyridine and acetonitrile, these EPR data are characterized by similar $g_\parallel$ values and only slightly different $A_\parallel(Cu)$ values, which indicates that the solvent in general does not affect the structure greatly. We take this as evidence that the mononuclear complexes in solution all have a planar coordination of two bidentate 3,5-DIPS ligands with solvent molecules coordinating along the remaining axis. Such coordination has little effect on the $g_\parallel$ and $A_\parallel(Cu)$ values except when this bond is stronger than the bond with the phenolic oxygen, as with nitrogen-donor ligands.

The EPR parameters for $Cu(sal)_2(py)_2$ in chloroform solution are $A_\parallel(Cu) = 0.0170$ cm^{-1} and $g_\parallel = 2.299$ while the analogous aspirinate complex has $g_\parallel = 2.284$ and $A_\parallel(Cu) = 0.0174$ cm^{-1} [28]. When the $Cu_2(3,5\text{-}DIPS)_4(py)_2$ adduct complex is dissolved in 99/1 chloroform/pyridine, a signal with $g_\parallel = 2.304$, $A_\parallel(Cu) = 0.0170$ cm^{-1}, $g_m = 2.062$ is observed. This species probably has one coordinated pyridine. Higher ratios of pyridine give the species observed in pure pyridine which has two coordinated pyridine molecules per copper. Similarly, in 99/1 chloroform/acetonitrile a second species with $g_\parallel = 2.334$, $A_\parallel(Cu) = 0.0175$ cm^{-1}, $g_m = 2.069$ is observed.

In both acetone and diethylether, more than one species is observed unless special precautions are taken to dry both solid and solvent (Table II). The EPR parameters of the second species observed in acetone solution are very similar to those reported [22] for CuSal dissolved in DMSO. No structure has been assigned to this species but the ligand is though to have a deprotonated phenolic group. Thus water appears to assist deprotonation of the phenolic group, as expected from its basicity.

The $g_\parallel$ values are in the order: pyridine < acetonitrile < acetone < wet solvents (water) < DMSO ≈ ether ≈ DMF ≈ methanol ≈ ethanol ≈ chloroform < propylene glycol, which appears to be opposite to the order of strength of the apical ligand. The $A_\parallel(Cu)$ values follow the opposite order to $g_\parallel$ as expected for mononuclear copper(II) complexes [21]. The energy of the d–d transition decreases in the order: pyridine < wet solvents (water) < chloroform < ether < acetonitrile < acetone < DMF < ethanol < methanol < propylene glycol < DMSO, which is somewhat different. This can be attributed to differences in bond covalency, which affect the EPR parameters more strongly than the d–d band maxima.

Based upon these results it is suggested that all of the solids, whether brown or green, are binuclear compounds as are the brown solutions. Solutions in coordinating solvents contain only monomers.

There is a correlation between pharmacologic activities and lipophilicity [1–4]. Solid forms of copper(II) 3,5-diisopropylsalicylate are all binuclear carboxylate bridged species, and this structure persists in non-polar solvents, such as the normal application vehicles. These binuclear complexes are quite insoluble in water because of the hydrophobic isopropyl groups which protrude from the copper salicylate core, and this lack of solubility makes them resistant to solvation. However, once the binuclear complex is solubilized in polar solvents, it rapidly dissociates into mononuclear species, which readily undergo ligand exchange. It is therefore probable that the efficacy of the complex is in large part due to its hydrophobic and lipophilic character and to its resistance to hydrolysis which enables transport of the complex across biomembranes and between biocompartments. The nature of the active therapeutic component remains in doubt but it is likely that the observed pharmacologic effects are due, in part, to physico-chemical properties of the complex since neither inorganic forms of copper nor the ligand alone are as active as the complex. The zinc complex of 3,5-DIPS, which is

probably monomeric, has also been found to be ineffective in pharmacological test systems.

A suitable test of the importance of the binuclear structure may be clinical studies with other metal complexes that can be expected to form similar structures with 3,5-DIPS such as Ni(II) or Co(II), although both of these have a more reactive axial site than the analogous Cu(II) complex.

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