Spectral and Magnetic Characterization of Amine Adducts of Copper(II) Valproate

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Abstract

The copper(II) complex of valproic acid and its corresponding pyridine and aniline adducts have been prepared and studied. The complexes were characterized on the basis of elemental analyses, molecular weight determinations, IR, electronic and EPR spectra, as well as variable temperature magnetic susceptibility measurements. All data are consistent with a binuclear structure for the complexes with four valproates as bridges and one donor amine ligand per copper atom in the case of adducts. Singlet–triplet energy separation values were found equal to 320, 344 and 300 cm^{-1} for the copper(II) valproate complex and its pyridine and aniline adducts, respectively.

Introduction

Magnetic exchange interactions between paramagnetic metal ions is a subject of continuous interest. In particular, copper(II) carboxylates capable of forming dimeric structures of $Cu(O_2CR)_2L$ stoichiometry (L = nitrogen donor ligand) have been enthusiastically investigated [1–3] with main emphasis focused on the correlation of their magnetic behaviour and the structural, steric and electronic characteristics of both the substituents R and addents L [1, 3, 4]. In this respect, in order to examine further the influence of the alkyl, R, on the superexchange interaction in copper(II) carboxylates, we synthesized and studied the binuclear complex of copper(II) with valproic acid (2-propylpentanoic acid) which in the form of its sodium salt is a widely used anticonvulsant drug with a wide spectrum of activity [5]. Furthermore, taking under consideration earlier observations concerning the dependence of the magnitude of superexchange interactions on the electron density donor capacity of the axial ligands L [4, 6], we also synthesized and studied the corresponding pyridine and aniline adducts of the parent bis(μ-valproato-*O*,*O'*)copper(II) complex.

Experimental

Physical Measurements

IR spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 1430 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra in chloroform solutions were obtained on a Cary 17DX spectrophotometer. Reflectance spectra of undiluted compounds were measured on a Beckman UV 5240 spectrophotometer. Electron paramagnetic resonance spectra were recorded on a JEOL-JES-ME X-band spectrometer using a MJ-110R-Radiopan nuclear magnetometer, a JES-SH-30X microwave frequency meter and EPR standards. Magnetic susceptibility of polycrystalline samples were measured by the Faraday method over the temperature range 80–290 K, using a sensitive Cahn RG-HV electrobalance. The applied magnetic field was 5.25 KGs. The calibrant employed was $HgCo(NCS)_4$, for which the magnetic susceptibility was taken as 16.44×10^{-6} cm^3 g^{-1} [7]. Diamagnetic corrections were calculated from Pascal's constants [8] and found to be -412×10^{-6}, -510×10^{-6} and -538×10^{-6} cm^3 mol^{-1} for $[Cu(vlp)_2]_2$, $[Cu(vlp)_2py]_2$ and $[Cu(vlp)_2an]_2$, respectively. The value 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of copper(II) ion. Magnetism of samples was found to be field independent. The effective magnetic moments were calculated from the expression

$$\mu_{eff} = 2.83 \sqrt{\chi_M^{corr} T} \text{ BM} \quad (1)$$

Preparation of the Complexes

A light green–blue valproate complex, $[Cu(vlp)_2]_2$, was prepared upon mixing aqueous solutions of sodium valproate (20 mmol) and copper sulphate pentahydrate (10 mmol). The complex was purified by dissolving it in chloroform, filtration and evaporation of the solution to dryness. *Anal.* Calc. for $[Cu(C_7H_{15}COO)_2]_2$: C, 54.91; H, 8.64; Cu, 18.16. Found: C, 55.10; H, 8.80; Cu, 18.10%. Molecular weight: calc. 699.84, found 680.

The preparation of the pyridine and aniline adducts, $[Cu(vlp)_2py]_2$ and $[Cu(vlp)_2an]_2$ respectively, was achieved by addition of an excess of pyridine or aniline in a suspension of the anhydrous complex in diethyl ether until a light green solution was observed. The solution was filtrated and upon evaporation of the filtrate at room temperature green crystals separated in both cases. *Anal.* Calc. for $[Cu(C_7H_{15}COO)_2C_5H_5N]_2$ (mol. wt. = 858.04): C, 58.79; H, 8.22; N, 3.26; Cu, 14.81. Found (mol. wt. = 840) C, 58.62; H, 8.30; N, 3.10; Cu, 14.70%. Calc. for $[Cu(C_7H_{15}COO)_2C_6H_7N]_2$ (mol. wt. = 886.10): C, 59.64; H, 8.42; N, 3.16; Cu, 14.34. Found (mol. wt. = 897): C, 59.76; H, 8.49; N, 3.25; Cu, 14.21%.

Results and Discussion

The analytical data observed for the new compounds support both the proposed stoichiometry and their dimeric structure. Moreover, in the case of the parent complex, $[Cu(vlp)_2]_2$, there is no IR evidence for axial coordinated water molecules in contrast with other copper(II) carboxylates [2, 3]. The aniline adduct, $[Cu(vlp)_2an]_2$, is a quite stable compound, whereas the pyridine one, $[Cu(vlp)_2py]_2$, proved to be unstable although well crystallized. For this latter compound the crystal subjected to X-ray structure analysis [9] was sealed in a glass capillary to avoid decomposition during data collection. From the drawing of the crystal structure shown in Fig. 1, it is clear that this complex also exists as a dimer, in agreement with that found in other copper(II) carboxylates [10–14].

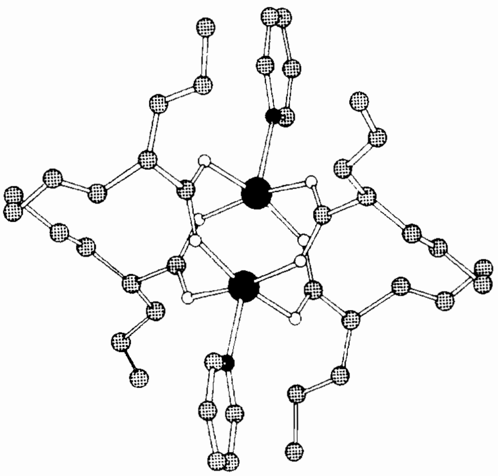

Fig. 1. The structure of pyridine adduct of copper(II) valproate [9].

The frequencies (cm^{-1}) of the most relevant absorption bands in the IR spectra of the studied compounds and their tentative assignments are presented in Table 1. The carboxylate stretching frequencies $\nu_{as}(COO)$ and $\nu_s(COO)$ are observed at *c.* 1600 and 1400 cm^{-1}, respectively. The position of the $\nu_{as}(COO)$ at higher wavenumber than that found for the sodium valproate supports further the bridging nature of the valproate ligand, in accordance with the proposed criterion [15] that a higher value of ν_{as} is indicative of such a coordination mode. The Δ values ($\Delta = \nu_{as} - \nu_s$) of the complexes are greater than that of the sodium salt, quite in line with those found for other copper(II) alkanoates [16]. This observation suggests that the proposed relationship between low Δ values and bridging carboxylate group [15] seems to be inapplicable to copper(II) complexes.

The electronic spectra in chloroform solutions as well as the reflectance spectra of the compounds studied (Table 1) exhibit two bands closely analogous to the spectra of other copper(II) dimers with carboxyl bridges [17]. Band I at about 14 kK may be assigned to the spin allowed $(d_{xz}, d_{yz}) \rightarrow (d_{x^2-y^2})$ [18], whereas band II at about 27 kK is referred as characteristic of the bridging system [19].

The room temperature EPR spectra of powdered samples of the complexes exhibit absorptions typical for the randomly oriented triplet state ($S = 1$) of axial symmetry and were interpreted using the effective spin Hamiltonian [20],

TABLE 1. IR and electronic spectral data for copper(II) valproates

Compound	Infrared spectra (cm^{-1})			Electronic spectra (kK)			
	$\nu_{as}(COO)$	$\nu_s(COO)$	Δ	$CHCl_3$ solution		Reflectance	
				I	II	I	II
Na(vlp)	1570	1423	147				
$[Cu(vlp)_2]_2$	1590	1428	162	14.9	26.2sh	15.1	26.4
$[Cu(vlp)_2py]_2$	1621	1423	198	14.4	25.8sh	14.3	26.7
$[Cu(vlp)_2an]_2$	1613	1425	188	14.7	26.3sh	14.9	26.3

TABLE 2. EPR data of copper(II) valproates

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\lvert D\rvert$ (cm^{-1})	E (cm^{-1})
$[Cu(vlp)_2]_2$	2.01(6)	2.34(1)	2.13(0)	0.344	0.0098
$[Cu(vlp)_2py]_2$[a]	2.06(7)	2.39(2)	2.18(1)	0.361	0.0035
$[Cu(vlp)_2an]_2$	2.02(5)	2.36(9)	2.14(6)	0.349	0.0098

[a] Spectrum indicated signal of monomeric admixture: $g_\perp = 2.02(3), g_\parallel = 2.28(4), g_{av} = 2.11(3)$.

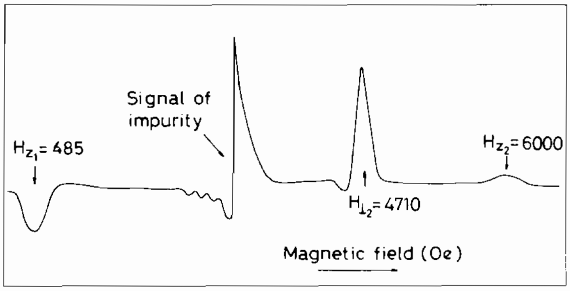

Fig. 2. X-Band (9.2 GHz) EPR spectrum of powdered sample of $[Cu(vlp)_2py]_2$ at room temperature.

$$\mathcal{H} = g\beta HS + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) - \tfrac{2}{3}D \qquad (2)$$

where D and E are the zero-field splittings (axial and rhombic, respectively) and x, y, z the main axes of the coordinate system with respect to the Cu–Cu vector. Observed EPR spectra of all the complexes studied display three lines namely H_{z1}, H_{z2} and $H_{\perp 2}$. The D, E, $g_\perp$, $g_\parallel$ and g_{av} parameters calculated by the method of Wasson *et al.* [21] and summarized in Table 2, are closely comparable to those found in other binuclear copper(II) carboxylates [2]. In the EPR spectrum of the unstable $[Cu(vlp)_2py]_2$ complex, shown in Fig. 2, besides the aforesaid lines typical for the dimer, a signal at magnetic field *c.* 3000 Oe corresponding to a monomeric admixture [22, 23] was observed. However, no such a signal has been observed in the EPR spectra of the other compounds, excluding thus the presence of any monomeric species.

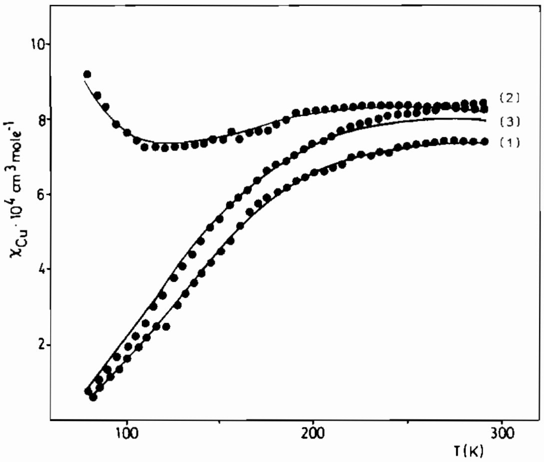

Fig. 3. Temperature dependence of magnetic susceptibility of $[Cu(vlp)_2]_2$ (1), $[Cu(vlp)_2py]_2$ (2) and $[Cu(vlp)_2an]_2$ (3). The solid lines represent calculated susceptibilities and the circles show experimental values.

Variable temperature (290–80 K) magnetic susceptibility measurements were performed on powdered samples of the complexes investigated and the results are summarized in Table 3 and Fig. 3. In the case of $[Cu(vlp)_2]_2$ and $[Cu(vlp)_2an]_2$ complexes the magnetic susceptibility course in the temperature

TABLE 3. Magnetic data for copper(II) valproates[a]

T (K)	$[Cu(vlp)_2]_2$		$[Cu(vlp)_2py]_2$		$[Cu(vlp)_2an]_2$	
	$\chi_{Cu}^{corr} \times 10^6$	μ_{eff} (BM)	$\chi_{Cu}^{corr} \times 10^6$	μ_{eff} (BM)	$\chi_{Cu}^{corr} \times 10^6$	μ_{eff} (BM)
80	66	0.21	924	0.77	80	0.21
100	167	0.37	765	0.78	195	0.40
125	301	0.55	726	0.85	380	0.62
150	450	0.73	744	0.94	527	0.80
175	598	0.91	765	1.03	674	0.97
200	664	1.03	825	1.15	736	1.09
225	712	1.13	842	1.23	798	1.20
250	730	1.21	840	1.31	823	1.28
275	748	1.28	834	1.37	840	1.36
290	748	1.31	830	1.39	848	1.40

[a] Selected from 43 experimental points.

function is characteristic for the pure dimeric forms of copper(II) carboxylates [1–3, 23–25]. Actually, magnetic moments for these two dimers at 290 K have the maximum values 1.32 and 1.42 BM, respectively and display the decreasing with temperature lowering to identical minimal value 0.21 BM at 80 K, resulting from the decreasing population of the triplet state (S = 1) relative to the population of the singlet state (S = 0) [18]. On the other hand, magnetic susceptibility course in the temperature function for the $[Cu(vlp)_2py]_2$ complex is anomalous. Magnetic susceptibility shows the maximum for 250–260 K; the temperature lowering is followed by a decrease of the magnetic susceptibility value to 105 K and next by its considerable increase. The magnetic moment instead, decreases systematically with the temperature lowering from 1.39 BM at 290 K to 0.77 BM at 80 K. Such a behaviour is characteristic for dimers containing a noticeable admixture of the monomeric form of the complex. The best fit lines, in each case, were calculated from the modified Bleaney–Bowers equation [20] for exchange-coupled pairs of Cu(II) ions

$$\chi_{Cu}^{corr} = \left[\frac{N g_{dim}^{2}\beta^{2}}{3kT}\left(1 + \frac{1}{3}\exp^{-2J/kT}\right)^{-1}\right](1 - X) + \left(\frac{N g_{imp}^{2}\beta^{2}}{4kT}\right)X \qquad (3)$$

where X represents the mole fraction of the monomeric admixture and the other symbols have their usual meaning. The spectroscopic splitting factors g_{dim} and g_{imp} were obtained from the EPR spectra and used as constants in the least-squares fitting process. The criterion for the determination of the best fit was the minimization of the sum of the squares of the deviations, A, where

$$A = \sum_{i}(\chi_i^{calc} - \chi_i^{exp})^2/(\chi_i^{exp})^2 \qquad (4)$$

The best fit parameters are given in Table 4, along with the values of enthalpy ($\Delta H°$) calculated from the observed magnetic susceptibilities by the method of Hatfield *et al.* [26] and found to be in agreement with the values of electron spin coupling constant, $-2J$.

TABLE 4. Exchange parameters of the copper(II) valproate dimers

Compound	$-2J$ (cm^{-1})	X	A	$\Delta H°$ (cm^{-1})
$[Cu(vlp)_2]_2$	320	0.00	7.06×10^{-9}	298
$[Cu(vlp)_2py]_2$	344	0.16	8.61×10^{-9}	315
$[Cu(vlp)_2an]_2$	300	0.00	2.71×10^{-8}	296

The structure of the unstable $[Cu(vlp)_2py]_2$ complex has already been resolved [9] and proved to be dimeric similar to that of most of copper(II) carboxylates. Its magnetic and spectroscopic properties are consistent with such a structure although in subsequent experiments some monomeric admixtures were present. The data of the $[Cu(vlp)_2]_2$ complex studied indicate that it has analogous structure. Magnetic investigations on copper(II) carboxylate adducts of aniline type bases with extended Cu–Cu coupling have classified them in two major classes. Adducts of various alkanoates [18, 27, 28] have $-2J$ values near 100 cm^{-1} for which a polymeric structure has been proposed [1], and adducts of copper arylcarboxylates which display $-2J$ values from 252 to 334 cm^{-1} and have been proposed to posses dimeric structure [29]. The $-2J$ value for the $[Cu(vlp)_2an]_2$ complex is 300 cm^{-1} and thus is likely to have a dimeric structure in contrast to the other copper(II) alkanoates. Finally, the $-2J$ value derived for the pyridine adduct is higher than this for the aniline adduct, supporting thus the well known relation between the basicity of the axial ligands and the magnitude of magnetic interaction in dimeric copper(II) carboxylates [6].

It is obvious that the magnetic exchange interactions in the dimers under investigation are propagated through the central Cu_2O_8 moiety. However, as the local symmetry of this moiety remains unchanged at the presence of the axial ligands, the same magnetic orbitals must be responsible for the superexchange processes observed in these molecular magnetic systems. Therefore, one should expect analogous $-2J$ values, which is the case for the studied compounds. On the other hand, the small differences observed in $-2J$ values could be possibly attributed to differences in their magnetic orbital energies induced by the electronic effects of the axial ligands.

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