Short Communications

An EPR Study of Some Copper(II) Complexes

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The magnetic susceptibilities of copper(II) iodoacetate, copper(II) β-iodopropionate, copper(II) α,α'-dichloropropionate and their dioxan adducts were recently studied at various temperatures.[1-3] All the complexes have susceptibility maxima at temperatures in the range 270 ± 50 K. This antiferromagnetic behaviour is typical of dimeric copper(II) carboxylates with an effective spin of one (1). The prototype is copper(II) acetate monohydrate in which four acetate groups bridge two copper(II) ions in *syn-syn* conformation.

Results and discussion. The well-resolved EPR spectra obtained for the polycrystalline samples at room temperature in all cases contained the absorption bands of axially symmetric dimeric species. The spectra of copper(II) α,α'-dichloropropionate and its dioxan adduct show besides bands of the triplet state also bands of the doublet state arising from monomeric impurity (the average splitting factor values are $g = 2.14$ and 2.11, respectively). The magnetic parameters of the triplet states of the compounds are listed in Table 1 together with average splitting factor values derived from magnetic susceptibilities.[1-3] The $pK_a{}^\circ$ value[4] of the iodoacetic acid and the magnetic parameters of the corresponding derivative are compared with the values[4-7] for the other halogeno-

substituted acetic acid derivatives in Table 2. The introduction of fluorine, chlorine, bromine or iodine atom into acetic acid results in an increase in the strength of the acid in the given order. This is a result of the σ-electron attracting effects of the halogen atoms. The decrease of the electron densities of the oxygen atoms weakens the covalent metal-oxygen bonds and leads to a decreased overlapping of the orbitals of the two unpaired electrons in the dimeric unit. This is shown by the values of the exchange coupling constant (Table 2). However, the value of the zero field splitting parameter $|D|$ increases. This parameter includes contributions from both exchange and dipole-dipole interaction and these effects are opposite in sign.

In addition to the three typical absorption bands of an axially symmetric dimeric structure, ther eis also a very weak absorption band at 2550 G in the spectrum of copper(II) iodoacetate and at 2680 G in the spectrum of copper(II) β-iodopropionate, and four bands at 2450, 3620, 4140 and 5220 G in the spectrum of the dioxan adduct of the latter compound. Regarding the EPR spectra of the compounds at the temperature of liquid nitrogen, we note an absorption band due to a monomeric impurity in the spectrum of copper(II) α,α'-dichloropropionate and in the spectrum of its dioxan adduct (average splitting factor values 2.13 and 2.05). In the spectra of all other compounds except the dioxan adduct of copper(II) iodoacetate is a weak band due to a monomeric impurity at about 3100 G, which is not seen in the room temperature spectra. The intensities of the absorption bands of the triplet state decrease with decreasing temperature as a consequence of the depopulation of the triplet state. The expected z-direction absorption bands on the high field side were not found in the spectra recorded at liquid nitrogen temperature.

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Table 1. Magnetic parameters of dimeric species at room temperature.

	$g_\perp$	$g_\parallel$	g_{av}	g_{av} [a]	$|D|/cm^{-1}$
$Cu(ICH_2COO)_2$	2.12	2.36	2.20	2.18	0.333
$Cu(ICH_2COO)_2O.5C_4H_8O_2$	2.11	2.36	2.20	2.18	0.329
$Cu(ICH_2CH_2COO)_2$	2.03	2.38	2.15	2.04	0.340
$Cu(ICH_2CH_2COO)_2O.5C_4H_8O_2$	2.08	2.34	2.17	2.21	0.340
$Cu(CH_3CCl_2COO)_2$	2.09	2.38	2.19	2.18	0.354
$Cu(CH_3CCl_2COO)_2O.5C_4H_8O_2$	2.09	2.38	2.19	2.16	0.357

[a] From magnetic susceptibility.

Table 2. Magnetic parameters and $pK_a°$ values of copper(II) halogeno-substituted acetates.

	$|D|/cm^{-1}$	$g_\parallel$	$-2J/cm^{-1}$	$pK_2°$ (25°C)
$Cu(ICH_2COO)_2$	0.333	2.36	280	3.18
$Cu(BrCH_2COO)_2$	0.344	2.36	254	2.90
$Cu(ClCH_2COO)_2.H_2O$	0.350	2.38	230	2.86
$Cu(FCH_2COO)_2.H_2O$	0.374	2.39	—	2.59

The x- and y-direction absorption bands for copper(II) iodoacetate, its dioxan adduct and the dioxan adduct of copper(II) β-iodopropionate are split at liquid nitrogen temperature into two bands, showing that the zero-field splitting parameter E is non-zero. Consequently, the x- and y-directions of the atomic structure are not equivalent. We note for all the compounds except copper(II) β-iodopropionate hyperfine lines on the low field side of the axial resonance. Seven lines can be identified in some of the spectra. This is expected as a result of the interaction between the dimeric unit and the unpaired electrons. The hyperfine coupling constant is approximately 65×10^{-4} cm^{-1}.

Experimental. All the complexes were prepared as described earlier.[1-3] X-band EPR spectra of polycrystalline samples of the complexes were measured at room and liquid nitrogen temperatures on a Varian Model E 4 spectrometer. The external magnetic field was 2000 and 5000 G and scan range ∓ 2000 G in both cases. The microwave frequency was 9520 MHz at room temperature and 9120 at the temperature of liquid nitrogen. The scan time was 8 min.

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