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Study of Copper(II) Propionate Adducts with Diphenylphosphinoacetylene and Bis(diphenylphosphino)acetylene

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Light green compounds of the type $Cu(CH_3CH_2COO)_2 \cdot L$ (L=diphenylphosphinoacetylene or bis(diphenylphosphino)acetylene) have been prepared and for the first time copper has been found to remain in oxidation state +2 with such ligands. The magnetic and spectral behaviour has been investigated. Magnetic susceptibilities of the compounds are interpreted in terms of antiferromagnetically exchange-coupled pairs of copper atoms. The spectral data (IR, UV/VIS and ESR) suggest binuclear structures of the copper(II) acetate monohydrate type, where the phosphine molecules L are in the apical positions interacting with the copper(II) atoms, possibly through acetylenic π-bonding.

The behaviour of bis (diphenylphosphino) acetylene * (dppa) as a ligand has been the subject of a number of studies. Carty and Efraty[1,2] have described the preparation and characterization for compounds of composition $M_2X_4L_2$ (M=Pd(II), Pt(II); X=Cl, Br, I or SCN and L=dppa). On the basis of Raman and IR spectra and molecular weight data they have proposed that the structures are binuclear with bridging dppa. While dppa molecules are bidentate and coordinated only through the two phosphorus atoms, the anion ligands are monodentate. Similar conclusions about the coordination of dppa and also of diphenylphosphinomethylacetylene in compounds of zerovalent and divalent palladium and platinum have been reached by Wheelock *et al.*[3] Likewise Carty and co-workers[4,5] have shown for a series of cyclopentadienyliron carbonyl compounds with dppa that dppa is coordinated through its phosphorus atoms. Also for binuclear carbonyl and cyclopentadienyl nickel compounds[6] and for cobalt carbonyl[7] the same conclusion has been reached. In 1968 Carty and Efraty[8,9] prepared and characterized compounds of the type $(CuX)_2(dppa)_3$ (X=Cl, Br, I, NO_3, NCS, BF_4) and $(AuX)_2(dppa)_n$ (n=1: X=Cl, Br, I, NCS; n=3: X=I, NCS; n=4: X=BF_4, PF_6). Although the preparation was started from the salts of Cu(II) and Au(III), they observed only monovalent copper and monovalent gold compounds. dppa as a ligand rapidly reduces solutions of Cu(II) and Au(III) salts and behaves as a bidentate ligand in which the acetylenic bond is uncoordinated.[9] The ligating properties of diphenylphosphinoacetylene (dpa) have not been studied before.

The present study was undertaken to determine the influence of dppa and dpa on the spectral and magnetic properties of copper(II) propionate and to show how reduction of the central atom can be prevented. For this purpose compounds of the general formula $Cu(CH_3CH_2COO)_2 \cdot L$ (L=dpa or dppa) were prepared and their electronic, infrared and ESR spectra, as well as magnetic behaviour (over the temperature range 93–293 K) were studied.

* Or bis(diphenylphosphino)ethyne; recommended by IUPAC.

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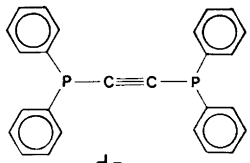

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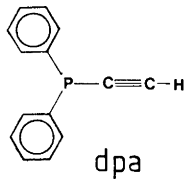

dpa

EXPERIMENTAL

Preparations. The light green $Cu(CH_3CH_2COO)_2$·dpa was prepared by reaction of copper(II) propionate and dpa[10] in equimolar ratios in hot methanol solution. The copper salt (1.5 g) was dissolved in 60 cm^3 of methanol and 1.7 g of dpa was added with stirring. The solution was heated until boiling. After dissolution of dpa the solution was left standing at room temperature. The fine light green microcrystals that formed were filtered off, washed with a small amount of cold methanol and dried at room temperature. Found: C 56.74; H 4.97; Cu 15.55; P 8.34. Calc. for $Cu(CH_3CH_2COO)_2$·dpa C 57.2; H 5.04; Cu 15.56; P 7.83. Crystals of $Cu(CH_3CH_2COO)_2$·dppa were prepared by reaction of copper(II) propionate and dppa[11] in equimolar ratio in hot methanol solution in a similar way as the dpa adduct. Found: C 61.41; H 4.80; Cu 10.44; P 10.18. Calc. for $Cu(CH_3CH_2COO)_2$·dppa: C 63.63; H 5.01; Cu 10.52; P 10.25.

Spectral studies. Infrared spectra (KBr pellets) in the region 300–4000 cm^{-1} were recorded on a Perkin Elmer Grating Infrared Spectrophotometer Model 577. Electronic spectra (Nujol mulls) in the range 10–28 kK were recorded with a Beckman DK-2A Ratio Recording Spectrophotometer and in the region 12.5–50 kK (methanol solutions) on a Perkin Elmer 402 Spectrophotometer. ESR spectra of polycrystalline samples were recorded at room temperature on a Varian Model E4 Spectrometer.

Magnetic measurements. The measurements were carried out over the temperature range 93–293 K using the Gouy method and copper(II) sulfate pentahydrate as calibrant.[12] Diamagnetic corrections were calculated from Pascal's constants.[13] The effective magnetic moments were calculated using the expression $\mu_{eff}=2.83(\chi_M^{corr} T)^{1/2}$. In the calculations the cgs/emu system was used throughout.

RESULTS AND DISCUSSION

Copper(II) compounds with dpa and dppa seem not to have been reported before. Carty and Efraty[9] observed only monovalent compounds despite their use of Cu(II) salts in the preparation. The critical factor seems to be the molar ratio of Cu(II) and dppa. When an equimolar ratio of reaction products is used, or Cu(II) in excess, dppa does not reduce metal atom.[1,2] If dppa is used in excess, however, rapid reduction of metal atoms results.[3,9] It has also been found that the dimeric structure of copper(II) acetate is effective for stabilization of oxidation state of Cu(II).[14] Equimolar amounts of Cu(II) propionate and dppa or dpa were used for the preparation of the title compounds. Copper(II) propionate has a binuclear structure in which the two copper(II) atoms are held together by four triatomic bridges of carboxylic groups.[15] The binuclear structure has been shown to exist also in methanolic solution.[16]

Infrared spectra of the compounds were recorded with a view to examining the bonding between the ligands and the central copper(II)

Table 1. The absorption bands due to stretching vibrations of P–C_6H_5 and C≡C bonds, respectively.

	ν(P–C_6H_5)/cm^{-1}	ν(C≡C)/cm^{-1}
dpa	1090	2032
dppa	1090	–
$Cu(CH_3CH_2COO)_2$·dpa	1092	2024
$Cu(CH_3CH_2COO)_2$·dppa	1093	2025, 2120

atom (Table 1). The absorption band at ≈1090 cm^{-1} has been attributed to the P–C_6H_5 bond of the free ligand,[9] and in both of the present compounds there is an absorption at ≈1090 cm^{-1}. We conclude that the phosphorus atoms are not coordinated to copper atom in the case of either dpa or dppa, since the band is found at a higher wavenumber when the phosphorus atoms are attached to the metal.[9,17] There are no strong absorptions in the region 1160–1250 cm^{-1} due to ν(P=0). Thus the phosphines cannot exist in the corresponding oxidized forms.[18] The absorption due to ν(C≡C) is IR inactive in dppa because of the symmetry, whereas in dpa the same vibration is active. The absorption band at 2032 cm^{-1} has been attributed to this vibration.[19] A weak band is observed in the infrared spectrum of $Cu(CH_3CH_2COO)_2$·dpa at ≈2025 cm^{-1} and thus the ν(C≡C) is shifted to a lower wavenumber relative to the corresponding band of the free dpa. In this same region the infrared spectrum of $Cu(CH_3CH_2COO)_2$·dppa exhibits two weak absorption bands, at 2025 cm^{-1} and 2120 cm^{-1}. These findings seem to us to indicate interaction between copper(II) and the acetylenic bond. The absorption bands at ≈1615 cm^{-1} in $Cu(CH_3CH_2COO)_2$·dpa and ≈1620 cm^{-1} in $Cu(CH_3CH_2COO)_2$·dppa can be assigned to the asymmetric stretching vibration of the carboxyl group. The corresponding symmetric vibration occurs at ≈1390 cm^{-1} in both samples. These stretching frequencies, ν_{as}COO and ν_sCOO, appear at very similar energies to those reported for copper(II) alkanoates,[20] which suggest that both oxygen atoms of the propionate anion are bonded to Cu(II) atoms in a syn-syn configuration.

The electronic spectra of the compounds were measured in Nujol mulls and in methanol solution. The solution as well as solid samples show, for both compounds, a wide asymmetric absorption band with maximum at about 14.5 kK (690 nm) and a shoulder at about 25.6 kK (390 nm). The band at about 14.5 kK is due to *d-d* transitions of the copper(II) atom and the band at about 25.6 kK is considered to be characteristic

Table 2. ESR data for $Cu(CH_3CH_2COO)_2$·dpa and $Cu(CH_3CH_2COO)_2$·dppa.

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\lvert D\rvert$/cm^{-1}
$Cu(CH_3CH_2COO)_2$·dpa	2.08_6	2.34_0	2.17_4	0.330
$Cu(CH_3CH_2COO)_2$·dppa	2.09_1	2.34_2	2.17_8	0.334

Table 3 Magnetic data for $Cu(CH_3CH_2COO)_2$·dpa and $Cu(CH_3CH_2COO)_2$·dppa.

	$Cu(CH_3CH_2COO)_2$·dpa ($-\Delta\cdot10^{-6}$=302.4)		$Cu(CH_3CH_2COO)_2$·dppa ($-\Delta\cdot10^{-6}$=429.5)	
T/K	$\chi_M^{corr}\cdot10^{-6}$	μ_{eff}/B.M.	$\chi_M^{corr}\cdot10^{-6}$	μ_{eff}/B.M.
93	292	0.47	205	0.39
113	327	0.54	245	0.47
133	372	0.63	295	0.56
153	460	0.75	342	0.65
173	530	0.86	371	0.72
193	580	0.95	366	0.75
213	590	1.00	401	0.83
233	585	1.05	414	0.88
253	630	1.13	433	0.93
273	635	1.18	475	1.02
293	637	1.22	489	1.07

of the spin-spin interaction of the bridging system.[21] The band locations are very similar to those of the binuclear copper(II) carboxylates.[22]

The well-resolved ESR spectra obtained for the polycrystalline samples at room temperature are typical of a triplet state in which $|D| \geq h\nu$; that is, resonances were observed at $H_I \approx 300$ G, $H_{II} \approx 4650$ G and $H_{III} \approx 5960$ G. From the shape of the spectra we can assume that the compounds are axially symmetric dimeric or polymeric species. The values obtained for the spin Hamiltonian are given in Table 2. ESR studies of binuclear copper(II) carboxylates have often shown a small but significant fraction of the copper(II) ions to be present in a magnetically dilute form.[23] The spectra of both of the present compounds show a very weak absorption band at about 3220 G, which indicates the presence of this impurity ($g_{iso}=2.11$). The obtained ESR data (Table 2) are comparable with those found for copper(II) compounds with a binuclear structure of copper(II) acetate monohydrate type.[24]

Magnetic susceptibility data of powdered samples are given in Table 3. The magnetic susceptibilities are seen to decrease with decreasing temperature indicating antiferromagnetic interaction between the copper(II) atoms. The fit between the data and the Bleaney-Bowers equation[25] is reasonably good and the $-2J$ values are 287(14) cm^{-1} for $Cu(CH_3CH_2COO)_2 \cdot dppa$ and 282(10) cm^{-1} for $Cu(CH_3CH_2COO)_2 \cdot dpa$.

The experimental data lead us to propose binuclear units whith a square pyramidal stereochemistry around each copper(II) atom. dpa and dppa are semicoordinated to Cu(II) atoms in the apical position, seemingly through acetylenic π-bonding. If we are right, these would be the first copper(II) compounds to display such a bonding. Other studies of the compounds are in progress to verify our conclusion.

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