

Mixed Copper(II)–Palladium(II) Acetates

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(Received May 5, 1986)

Abstract

The reaction of $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{MeCO}_2)_4]$ with $[\text{Pd}_3(\text{MeCO}_2)_6]$ gives the new polynuclear mixed metal acetates $[\text{Cu}_2\text{Pd}(\text{MeCO}_2)_6]$ and $[\text{Cu}_2\text{Pd}_4(\text{MeCO}_2)_{12}]$. Electronic, ESR and IR spectra and antiferromagnetism suggest the former has a triangular and the latter an octahedral arrangement of metal atoms. The relative magnitudes of the antiferromagnetic interactions are discussed.

Introduction

Most metal carboxylates adopt cluster structures [1]. These are almost invariably compounds of one metal in one oxidation state or of one metal in mixed oxidation states, as for example in $[\text{Mn}_3\text{L}_3\text{O}(\text{RCO}_2)_6]$, $[\text{L} = \text{py}$ [2] or 3-Clpy [3]] and corresponding iron compounds [4]. Carboxylates containing a mixture of different metals are much rarer. The examples so far confirmed crystallographically are $[\text{M}_2\text{M}'\text{L}_3\text{O}(\text{RCO}_2)_6]$ [5], $[\text{CrFeML}_3\text{O}(\text{RCO}_2)_6]$ [6], $[\text{Cr}_3\text{W}_3\text{O}_3(\text{Me}_3\text{CCH}_2\text{O})(\text{Me}_3\text{CCO}_2)_{12}]$ [7] and $\text{Zn}_2\text{ML}_2(\text{MeCH:CHCO}_2)_6$ [8].

In addition to these there is a brief report [9] that palladium(II) acetate reacts with some other metal acetates. With copper(II) the products were suggested to be $[\text{CuPd}(\text{MeCO}_2)_4]$ and $[\text{CuPd}_2(\text{MeCO}_2)_6]$. This paper describes our reinvestigation of this reaction and our evidence for a new type of carboxylate structure involving an octahedron of metal atoms.

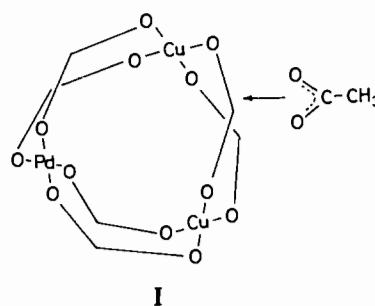
Results and Discussion

We find that the reaction of $[\text{Pd}_3(\text{MeCO}_2)_6]$, with $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{MeCO}_2)_4]$ in 1:3 molar ratio gives a 54% yield of the previously reported $[\text{CuPd}_2(\text{MeCO}_2)_6]$, and a 26% yield of $[\text{Cu}_2\text{Pd}(\text{MeCO}_2)_6]$, but not $[\text{CuPd}(\text{MeCO}_2)_4]$ as previously reported. These two compounds were separated by the former's greater solubility in ethyl acetate and are now considered separately.

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$[\text{Cu}_2\text{Pd}(\text{MeCO}_2)_6]$

We believe this compound adopts the molecular structure I, which is the structure of $[\text{Pd}_3(\text{MeCO}_2)_6]$ [10] with two palladium atoms replaced by coppers; there are two acetate bridges between each pair of metal atoms.



The observation of just one antisymmetric and one symmetric carboxylate stretching frequency ($1590, 1450 \text{ cm}^{-1}$) in the IR spectrum suggests all six acetate ligands are in a similar environment. Both bands are broad and may contain overlapping contributions from those acetates which bridge two copper atoms and those which bridge one copper and one palladium atom.

The diffuse reflectance electronic spectrum resembles those of binuclear copper(II) carboxylates [11] in showing a maximum at 14700 cm^{-1} which is retained in ethyl acetone solution ($\epsilon = 32.6 \text{ cm}^{-1} \text{ mol}^{-1}$), but the broad band obviously has some unresolved weaker components at lower energy. A strong charge-transfer band obscures the 27000 cm^{-1} transition usually also found in $[\text{Cu}_2\text{L}_2(\text{RCO}_2)_4]$ compounds.

The magnetic susceptibility remains in the range $(1.47\text{--}1.28) \times 10^{-3}$ per Cu atom over the temperature range $292\text{--}80 \text{ K}$ (Table I). This corresponds to a fall in magnetic moment of 1.73 to $0.91 \mu_{\text{B}}$. The best fit to the usual Bleaney–Bowers [12] equation gives $g = 2.00 \pm 0.04$ and $J = -100 \text{ cm}^{-1}$. Thus the compound is slightly less antiferromagnetic than the well-known $[\text{Cu}_2\text{L}_2(\text{RCO}_2)_4]$ complexes, where J is of the order of -110 cm^{-1} [1c]. This also is consistent with our proposed structure, which has

TABLE I. Magnetic Data for Copper–Palladium Acetates

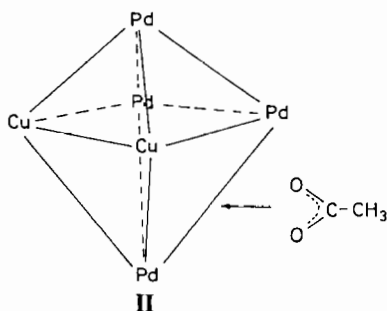
| PdCu ₂ (OCOCH ₃) ₆ | | | | Pd ₄ Cu ₂ (OCOCH ₃) ₁₂ | | | |
|--|------------------------|------------|------------|---|------------------------|------------|------------|
| T (K) | $\chi_m (\times 10^3)$ | $1/\chi_m$ | μ (BM) | T (K) | $\chi_m (\times 10^3)$ | $1/\chi_m$ | μ (BM) |
| 79.8 | 1.303 | 769.3 | 0.91 | 86.9 | 3.655 | 273.8 | 1.59 |
| 93.7 | 1.303 | 769.3 | 0.99 | 102.7 | 3.272 | 303.0 | 1.64 |
| 107.5 | 1.347 | 746.0 | 1.08 | 118.0 | 3.099 | 324.0 | 1.71 |
| 122.5 | 1.379 | 730.6 | 1.16 | 136.7 | 2.929 | 341.7 | 1.79 |
| 137.6 | 1.360 | 739.9 | 1.22 | 157.1 | 2.674 | 374.2 | 1.83 |
| 156.2 | 1.471 | 682.2 | 1.36 | 176.8 | 2.421 | 413.7 | 1.85 |
| 176.7 | 1.385 | 727.6 | 1.40 | 197.4 | 2.206 | 453.4 | 1.87 |
| 196.9 | 1.360 | 739.9 | 1.46 | 214.5 | 2.119 | 472.2 | 1.91 |
| 215.4 | 1.439 | 696.3 | 1.57 | 235.3 | 2.051 | 488.2 | 1.96 |
| 235.8 | 1.347 | 746.0 | 1.59 | 253.9 | 1.968 | 509.1 | 2.00 |
| 255.9 | 1.285 | 780.3 | 1.62 | 269.2 | 1.863 | 538.3 | 2.00 |
| 252.6 | 1.326 | 755.4 | 1.70 | 282.2 | 1.662 | 603.1 | 1.94 |
| 284.4 | 1.319 | 759.1 | 1.73 | 290.5 | 1.764 | 568.0 | 2.02 |
| 291.6 | 1.278 | 783.9 | 1.73 | | | | |

two bridging acetates between the copper atoms as against four in the binuclear carboxylates, thus weakening the superexchange pathway.

The X-band ESR spectrum of polycrystalline [Cu₂Pd(MeCO₂)₆] shows a resonance centred round $g = 2.2$, but about 1 kG broad and showing no hyperfine structure. In frozen ethyl acetate solution the ESR spectrum of a monomeric copper(II) complex is seen with $g_{\parallel} = 2.381$, $g_{\perp} = 2.080$, $A_{\parallel} = 95$ G and $A_{\perp} \sim 20$ G. We conclude the cluster dissociates in solution. We do not observe the half-field line associated [13] with binuclear copper(II) compounds, but which is sometimes missing even when exhibited by closely related compounds [14].

[Cu₂Pd₄(MeCO₂)₁₂]

We at first supposed this compound to have the constitution [CuPd₂(MeCO₂)₆], with a structure also like that of [Pd₃(MeCO₂)₆] but with only one palladium atom replaced by copper. However, the discovery that the compound was antiferromagnetic (see below) forced the conclusion that there must be at least two copper atoms per molecule, and the most likely formulation is as the octahedral cluster II in which one acetate ligand could bridge each adjacent pair of metal atoms over the twelve edges of the octahedron.



Slow decomposition in solution or on the heated probe of our mass spectrometer has prevented molecular weight determinations and we have not succeeded in crystallising the compound.

The IR spectrum supports this formulation in again showing just one band each for the carboxylate stretching modes, at 1610 and 1450 cm⁻¹ and the solid state electronic spectrum resembles that of [Cu₂PdMeCO₂)₆] in showing a broad maximum at 14 700 cm⁻¹.

This complex is also antiferromagnetic (Table I), with values of $g = 2.04$ and $J = -50$ cm⁻¹. Thus this is less antiferromagnetic than [Cu₂Pd(MeCO₂)₆], which also agrees with our proposed structure, which has just one carboxylate bridge to act as a superexchange pathway between the two copper atoms. The existence of significant antiferromagnetism probably shows the two copper atoms to be *cis* to one another.

The ESR spectrum gives strong support for a structure with two copper atoms per molecule. As for the companion molecule, the spectrum shows a broad absorption round $g = 2.2$ but a weak half-field line was in fact observed, as expected for a copper(II) dimer.

Experimental

[Cu₂(H₂O)₂(MeCO₂)₄] (0.97 g, 2.5 mmol) and [Pd₃(MeCO₂)₆] (0.60 g, 0.89 mmol) were warmed in glacial acetic acid (80 cm³) at 50 °C for 30 min. After evaporation to dryness the products were removed from undissolved starting material by extraction with chloroform (150 cm³). This solution was evaporated and the residue stirred with ethyl acetate (50 cm³), leaving blue–green [Cu₂Pd(MeCO₂)₆] (0.40 g, 26%). Evaporation of the ethyl acetate solution gave dark

green $[\text{Cu}_2\text{Pd}_4(\text{MeCO}_2)_{12}]$ (0.91 g, 54%). *Anal.* (calculated values in parentheses): $[\text{Cu}_2\text{Pd}(\text{MeCO}_2)_6]$: C, 25.0 (24.92); H, 3.0 (3.14); Cu, 21.1 (21.09). $[\text{Cu}_2\text{Pd}_4(\text{MeCO}_2)_{12}]$: C, 23.7 (23.62); H, 3.1 (2.98); Cu, 7.2 (6.94)%.

Infrared and electronic spectra were obtained on Perkin–Elmer 577 and 330 spectrophotometers respectively, ESR spectra on a Decca X-3 spectrometer and magnetic data on a Faraday balance already described [15].

Acknowledgement

We thank Dr. K. D. Sales for helpful discussions about ESR spectra, the University of London Central Research Fund and the Royal Society for providing magnetochemical equipment and SERC for a CASE studentship with the valued collaboration of ICI Petrochemicals and Plastics Division.

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