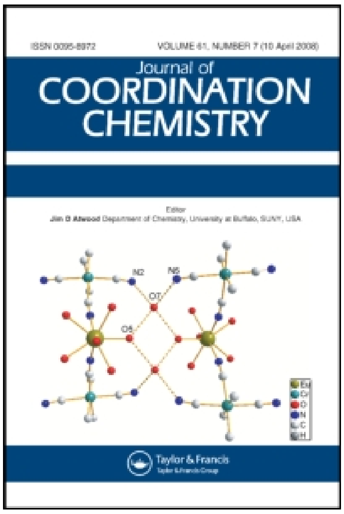

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METAL COMPLEXES OF PHYTOHORMONES. PART III.† A DIMERIC COPPER(II) COMPLEX OF 2,4a,7-TRIHYDROXY-1 METHYL-8-METHYLENGIBB-3-ENE-1,10DICARBOXYLIC ACID 1→4a-LACTONE

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A compound of the type $Cu(GA_3COO)_2.4H_2O(GA_3COOH)$ = 2,4F1a,7-trihydroxy-1 methyl-8-methylengibb-3-ene-1,10 carboxylic acid 1→4 lactone (gibberellic acid) was obtained and characterized by means of magnetic and thermogravimetric measurements, i.r., electronic and e.s.r. spectra at room and low temperature. The spectroscopic measurements are consistent with the fact the ligand appears to behave as a simple carboxylic acid, being able to coordinate to the copper(II) ion in a *syn-syn* configuration giving a "cupric-acetate"-like dimeric species.

Keywords: Gibberellin A3, copper(II), complex, synthesis

INTRODUCTION

Gibberellins are members of a large family of closely related tetracyclic triterpenoid compounds. They were first discovered as metabolites of the ascomycete *Gibberella fujikuroi*. Gibberellins are also found to be present in higher plants. They are all carboxylic acids and are termed gibberellic acids (GA_s). The most dramatic effect of GA_s is their stimulation of stem elongation in dwarf varieties of plants.[1] As with all the natural phytohormones, which are very active within the plant, the exogenous application of these chemical messengers does not always evoke growth responses because of biodegradation or because the rate of endogenous supply is a limiting factor.[2]

In pursuing our aim in studying the interaction of phytohormones, related compounds and metal ions,[3,4] we have prepared and characterized the compound obtained by reaction of copper(II) chloride pentahydrate or copper(II) acetate dihydrate with 2,4a,7-trihydroxy-1-methyl-8-methylengibb-3-ene-1,10 dicarboxylic acid 1→4a lactone (Gibberellic acid: GA_3COOH, Figure 1) as $Cu(GA_3COO)_2.4H_2O$. We present results here.

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† Part 2 is M. A. Zoroddu, R. Dallocchio and M. A. Cabras, *Transition Metal Chem.*, **12**, 356 (1987).
* Author for correspondence.

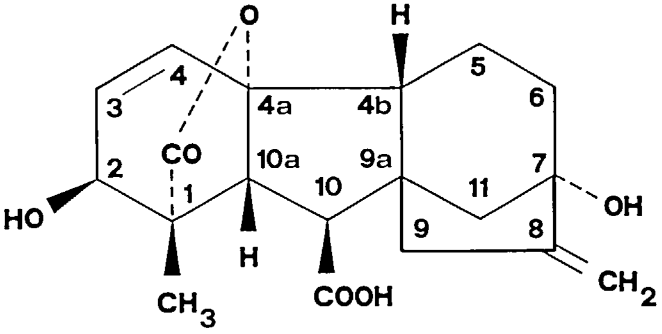

FIGURE 1 Gibberellic acid, GA_3COOH.

EXPERIMENTAL

Elemental analyses were performed using a Perkin-Elmer 240B instrument. Thermal analyses were carried out on a Perkin-Elmer TGS-2 apparatus under air flow at a heating rate of 5°C min^{-1}. Diffuse reflectance electronic spectra were recorded on a Jasco Uvidec 610 spectrophotometer. Magnetic susceptibilities were measured at room temperature by using a Bruker B-MB4 electrobalance with $Hg[Co(SCN)_4]$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. I.r. spectra were recorded in KBr pellets (4000–400 cm^{-1}) or in nujol mulls between polyethylene plates (400–200 cm^{-1}) using a Perkin-Elmer 983 spectrophotometer. X-band e.s.r. spectra of polycrystalline samples at 298 and 110 K were obtained using a Bruker ER 220D-SRC spectrometer. The magnetic parameters were derived by standardization with diphenylpicrylhydrazyl.

Preparation

Dropwise addition of a methanolic solution of copper(II) acetate dihydrate (0.5 mmol, 99.8 mg, 5 cm^3), to a methanolic solution of GA_3COOH (1 mmol, 346 mg, 5 cm^3) resulted in the formation of a blue-green microcrystalline product. Melting point 225–227°C. Anal.: Calc. for $C_{38}H_{50}O_{16}Cu$: C, 55.2; H, 6.05; H_2O, 8.7%. Found: C, 55.0; H, 6.00; H_2O, 8.2%. The same product was obtained by reaction of potassium gibberellate and copper(II) chloride pentahydrate or copper(II) acetate dihydrate in MeOH or H_2O solution. The potassium salt was precipitated by mixing a MeOH solution (10 cm^3) of gibberellic acid (1 mmol, 346 mg) and KOH (1 mmol) MeOH solution (5 cm^3) under magnetic stirring, after the volume was reduced to 5 cm^3 and addition of diethyl ether.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the copper complex was used to monitor the solvent content. The compound loses solvent molecules from 40 to 180°C in a process that seems to involve overlapping steps; the product is then stable up to 200°C. The reflectance electronic spectrum showed a maximum at about 13700 cm^{-1} and a shoulder at about 26300 cm^{-1} (Figure 2). The first band is characteristic of tetragonally distorted copper(II) complexes with oxygen donor atoms. The second is considered diagnostic of carboxylate-bridged dinuclear complexes.[5,6]

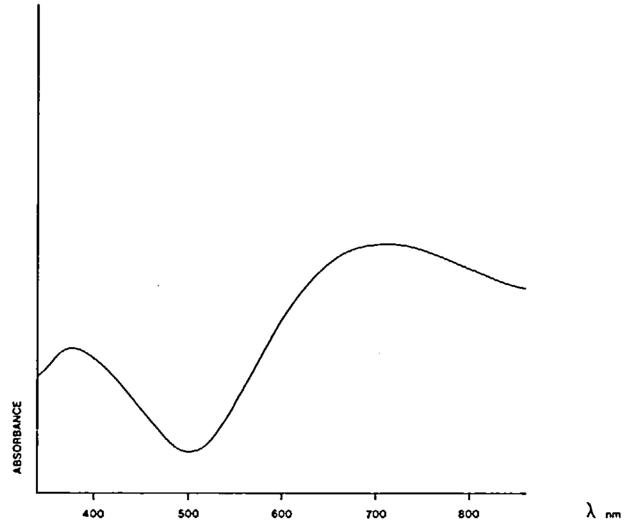

FIGURE 2 Reflectance electronic spectrum of the copper(II) complex.

The compound shows at room temperature a subnormal magnetic moment (μ_{eff} = 1.6 B.M.), indicative of copper–copper antiferromagnetic interactions. The e.s.r. spectrum of the solid compound affords complementary information to the susceptibility results and reveals features typical for a randomly oriented triplet state with $S = 1$. X-band radiation at room temperature, raises a moderately strong absorption at 422.5 G, and a weak absorption at about 6000 G (corresponding to parallel $H_{\parallel 1}$ and $H_{\parallel 2}$ components, respectively), and a strong absorption at 4690 G corresponding to $H_{\perp 2}$ (perpendicular component; Figure 3). A weak absorption at about 3200 G was attributed to the presence of monomeric $S = 1/2$ species. Using the measured positions for the $S = 1$ species and available literature methods,[7-9] we find $D = 0.36$ cm^{-1}, $g_{\parallel}$ 2.40 and $g_{\perp} = 2.09$. These values are in agreement with those found for other binuclear copper(II) carboxylate complexes having a populated spin-triplet state.[10-13] The e.s.r. spectrum is temperature-dependent with the intensity of the triplet signals decreasing with decreasing temperature; the monomer signal increases at the same time.

This result is typical for dimeric systems with a singlet ground state and a thermally accessible triplet excited state. At 110K, the absorption at about 3200 G was used to calculate $g_{\parallel}$ and $g_{\perp}$ for the monomeric $S = 1/2$ species ($g_{\parallel} = 2.32$; $g_{\perp} = 2.06$).

Proof that this line is not a part of the triplet state is demonstrated by the fact that it shows, in the $g_{\parallel}$ region, four hyperfine coupling lines with one copper nucleus, $I = 3/2$, giving $A_{\parallel} = 126.6$ G (double the value with respect to the splitting of the $H_{\parallel 1}$

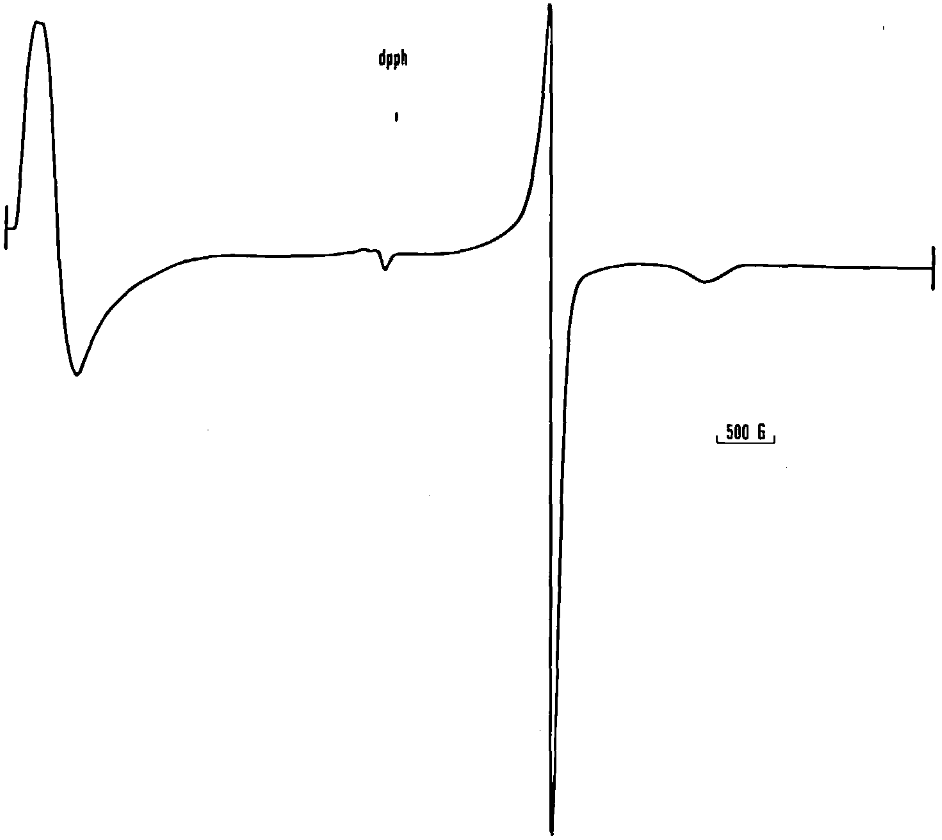

FIGURE 3 E.s.r. spectrum of the complex at room temperature.

component of the dimeric signal). The line-widths of the high- and low-field absorptions were about two times that of the absorption at about 4690 G. At 110 K, hyperfine structure was only clearly observed on the $H_{\parallel 1}$ component of the triplet absorptions. The expected 1:2:3:4:3:2:1 septet from the two equivalent copper(II) nuclei gave a splitting constant of 63.3 G and this agrees with the value observed in some other dimeric copper(II) carboxylates.[14] The absence of splitting of the $H_{\perp 2}$ line shows that distortion from axial symmetry can be neglected and no hyperfine splitting was observed (probably as a consequence of a much smaller value of $A_{\perp}$), as is found for similar complexes. The e.s.r. spectrum of the dehydrated compound shows absorptions of the S = 1 species, but there is significantly more monomer present, indicating that dehydration has led to some breakdown of the binuclear structure.

In frozen DMSO solution it was possible to observe triplet signals showing that the binuclear structure is preserved in this solvent, but there is more monomer present.

I.r. carboxylate bands have been assigned based on data available in the literature.[15,16] The mode of coordination of carboxylate groups has often been deduced from the magnitude of the observed separation Δ between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$.

The observed $\nu_s(CO_2)$ at 1420 cm-1 with respect to that of the potassium salt of GA_3COOH (1400 cm^{-1}) should be indicative of the presence of bidentate carboxylic ligands. The symmetric (CO_2) stretching vibration is shifted only by some few cm^{-1} (in the range 1610–1620 cm^{-1}). The Δ separation between $\nu_s(CO_2)$ and $\nu_{as}(CO_2)$ is in the range 200 cm^{-1}, as expected for similar compounds. The broad band at about 3450 cm^{-1} can be attributed to ν(OH) of water.

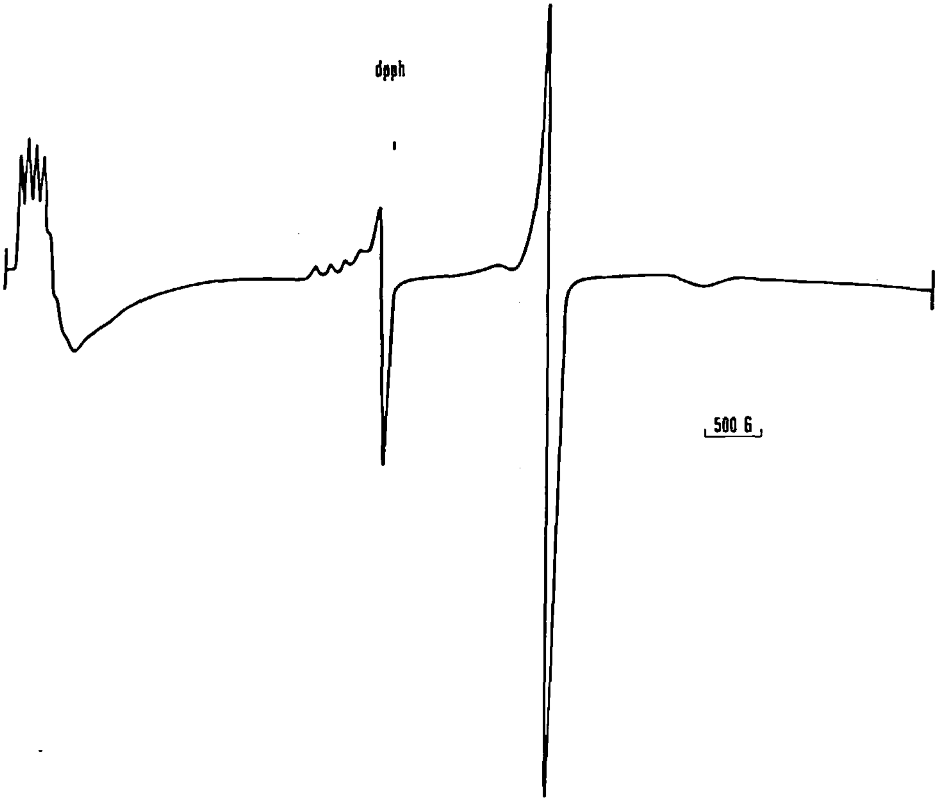

FIGURE 4 E.s.r. spectrum of the complex at 110 K.

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