Metal Complexes of Phytohormones.
Part I. Copper(II) Complexes of 6-Furfurylaminopurine (Kinetin)

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Abstract

Copper(II) complexes with 6-furfurylaminopurine (kinetin = KH) of the types $Cu(KH)_2(ClO_4)_2 \cdot nH_2O$ (1) and the inner complex $Cu(K)_2 \cdot 4H_2O$ (2), were obtained and characterized by magnetic susceptibilities, ESR, electronic and IR spectroscopy. Both compounds are dimeric, probably involving quadruple bridges of kinetin bidentate ligand.

Introduction

In a study of interactions between the growth and inhibition factors of plants and metal ions [1–6], we have examined the compounds obtained by reaction of Cu(II) ion and kinetin, a purine-derived cytokinin (Fig. 1). Cytokinin is said to be a substance that promotes cell division in cultured plant callus tissue. Cytokinins have been found in a wide range of plant tissues; they are particularly abundant in root tips, xylem sap, developing fruits, tumour tissues and germinating seeds. In particular, kinetin, which has similar biological activity and induces cell division in tobacco pith when present in the culture medium at a concentration of 1 $\mu g\ ml^{-1}$, does not occur in plant tissues and is not a naturally occurring substance [7]. It is important to mention that cytokinins are present in tRNA species that respond to mRNA codons with initial letter U [8].

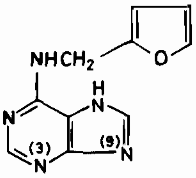

Fig. 1. 6-Furfurylaminopurine (kinetin).

We are interested in studying the interaction of these phytohormones, related compounds and metal ions, in the hope that they will lead to an understanding of the role of trace elements in biochemical processes involving nucleic acids in plants and the effect of the coordination on the biological activity of these ligands.

Experimental

Elemental analyses (C, H, N) were obtained with a Perkin-Elmer 240B instrument. Thermal analyses were carried out on a Perkin-Elmer TGS-2 apparatus under nitrogen or air flow.

Diffuse reflectance electronic spectra were recorded on a Beckman Acta MIV spectrophotometer.

Magnetic susceptibilities were measured at room temperature by using a Bruker B-MB4 electrobalance, with $[HgCo(SCN)_4]$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants.

X-band ESR spectra of polycrystalline samples at 298 and 123 K were obtained using a Bruker ER 2200-SRC spectrometer. The magnetic parameters were derived by standardization with diphenylpicrylhydrazil.

Infrared spectra of solid samples were recorded with a Perkin-Elmer 983 spectrophotometer in KBr, Nujol-phase and spread on NaCl and KBr plates.

Preparation

$Cu(KH)_2(ClO_4)_2 \cdot nH_2O$ (1)

The following procedures were employed for the preparation of the complex of the neutral ligand $Cu(KH)_2(ClO_4)_2 \cdot nH_2O$, ($n$ = 1, 2).

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1 mmol of copper(II) perchlorate hexahydrate was dissolved in 4 ml of water and added to a solution of kinetin (1 mmol) in acetone (35 ml). The resultant mixture, on standing for two days, gave a violet polycrystalline complex. Better yield was obtained by adding diethylether to induce precipitation.

1 mmol of copper(II) perchlorate hexahydrate was dissolved in a mixture of 20 ml ethanol and 10 ml triethylorthoformate and warmed to 50 °C, for 1 h, with stirring. Then 1 mmol of kinetin was added to the metal salt solution. This solution immediately gave a violet polycrystalline compound. Better yield was obtained by adding diethylether.

Complex **1** was also prepared according to the method of Mikulski *et al.* [9], for formation of neutral ligand adducts of purines.

1 mmol of copper(II) perchlorate hexahydrate was dissolved in a mixture of ethanol and triethylorthoformate. Then 2 mmol (or 4 mmol) of kinetin were added to the metal salt solution. After refluxing for four days, the complex precipitated as a violet powder.

$Cu(K)_2 \cdot 4H_2O$ (2)

The following procedure was employed for the preparation of the complex of the monodeprotonated anionic ligand, $Cu(K)_2 \cdot 4H_2O$. 1 mmol of kinetin was dissolved in 50 ml of methanol. Then 0.5 mmol of $CuCl_2$ dihydrate (or $CuSO_4$ pentahydrate), dissolved in 20 ml of water, was added. On adding some drops of dilute NaOH solution, the resulting solution became violet. Then small crystals of the compound slowly separated.

Anal. Calc. for $Cu(KH)_2(ClO_4)_2 \cdot H_2O$ (1), $C_{20}H_{20}CuN_{10}O_{11}Cl_2$: C, 33.8; H, 2.81; N, 19.70; Cl, 9.96; H_2O, 2.53. Found: C, 33.7; H, 3.00; N, 19.71; Cl, 10.0; H_2O, 3.0%. Calc. for $Cu(K)_2 \cdot 4H_2O$ (2), $C_{20}H_{24}CuN_{10}O_6$: C, 42.6; H, 4.25; N, 24.84; H_2O, 12.7. Found: C, 42.59; H, 4.30; N, 24.65; H_2O, 11.0%.

The complexes are soluble in acetone and ethanol, and sparingly soluble in tetrahydrofuran; in methanol the colour of the solution changes from violet to green.

Results and Discussion

Measurement of magnetic susceptibility at room temperature gave values of $\mu_{eff} = 1.5$ and 1.65 B.M. for compounds **1** and **2**, respectively. They are lower than the values of 1.8 to 2.22 B.M. usually found for mononuclear copper(II) compounds and appear to be in the same range of values found in copper(II) acetate diaquo as well as in a number of square pyramidal binuclear Cu^{2+} complexes with adenine neutral ligand and adenine monodeprotonated anionic ligand. These compounds were first reported by Weiss and Venner [10] and were later shown by means of crystal structure determinations to involve quadruple bridges of bidentate adenine binding through the N(3) and N(9) ring nitrogen [11–14].

X-band electron spin resonance spectra of polycrystalline samples are shown in Fig. 2. They afford complementary information to the susceptibility results in that they confirm the binuclear structure; in fact they are similar to that found for the dimeric adenine complexes [15, 16].

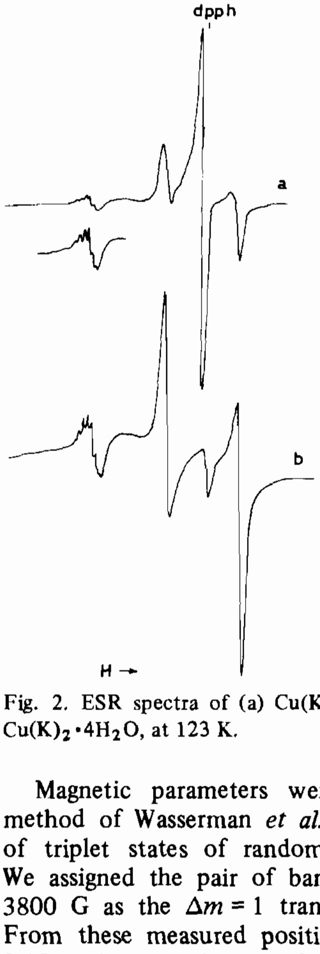

Fig. 2. ESR spectra of (a) $Cu(KH)_2(ClO_4)_2 \cdot H_2O$, and (b) $Cu(K)_2 \cdot 4H_2O$, at 123 K.

Magnetic parameters were obtained using the method of Wasserman *et al.* [17], for the spectra of triplet states of randomly oriented molecules. We assigned the pair of bands at about 2600 and 3800 G as the $\Delta m = 1$ transitions H_{xy1} and H_{xy2}. From these measured positions we obtained $g_{xy} = 2.03$ and 2.04, the zero-field splitting parameters $D = 0.12$ and 0.11 cm^{-1} for compounds **1** and **2**, respectively.

At 123 K on the band at about 1400 G, hyperfine structure is visible from the two equivalent copper nuclei with $A = 71$ G, confirming that this band arises from the dimeric unit, although for compound **1** only six of the expected seven lines were resolved.

The band at about 3200 G is due to non-dimeric (doublet species) copper(II). The proof that this line is not part of the triplet spectrum is based on the fact that the intensity of the line increases with decreasing temperature. The diffuse reflectance spectra exhibited a single broad band with maximum at 550 and 560 nm for compounds **1** and **2**, respectively, and they are compatible with a pentacoordinated configuration and a CuN_4O absorbing species. The IR spectrum of compound **2** showed split triplet ν_3 (1120, 1090, 1040), and ν_4 (640, 630, 615 cm^{-1}) (ClO_4) bands, indicative of the presence of both ionic and coordinated perchlorate.

Such systems containing closely held and electronically interacting pairs of metal ions may be very important in nature, since this arrangement has been found in several other molecules of biological significance [18–24], and it also persists with these phytohormones.

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