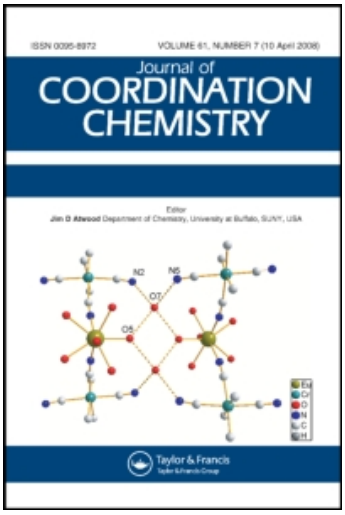


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# Cu(II) Halide and Primary Amine Complexes of Kinetin and 6-Benzylaminopurine

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# CU(II) HALIDE AND PRIMARY AMINE COMPLEXES OF KINETIN AND 6-BENZYLAMINOPURINE

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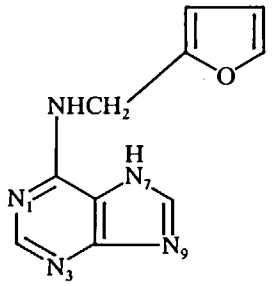
Cu(II) halide and primary amine complexes of kinetin (Kin) and 6-benzylaminopurine (6-BAP) of the type $Cu(Kin)Cl_2$, $Cu(Kin)Br_2$, $Cu(6\text{-}BAP)Cl_2$, and $Cu(Kin)_2(CH_3NH_2)_3$ were synthesized. Low frequency IR absorptions of the halide adducts can be assigned to Cu–X stretches and are suggestive of a *trans* square-planar arrangement about the metal centre. The amine complex exhibits the loss of an aromatic IR N–H stretch, consistent with deprotonation of the purine ring and the formation of a metal complex. Room temperature magnetic susceptibilities are subnormal for mononuclear Cu(II) compounds. N(3)–N(9) bridging between copper centres is postulated by comparison with known metal ion structures of purines; the possibility of N(7)–N(9) bridging cannot however be disregarded.

**Keywords:** Copper(II), purines, kinetin, 6-benzylaminopurine, complexes, synthesis

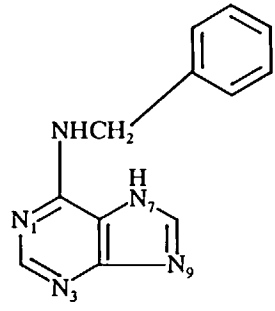


## INTRODUCTION

Cytokinins are substances which stimulate cell division in plants. Compounds with cytokinin activity have been isolated from a variety of plants; they consist of $N_6$ substituted adenine derivatives as well as their nucleoside and nucleotide forms.[1] Two synthetic cytokinins, 6-furfurylaminopurine or kinetin (Kin) and 6-benzylaminopurine (6-BAP), have been found to be effective stimulating agents for plant growth. They have not been isolated from the tissue of higher plants, but are $N_6$ adenines and promote the growth of plant stem pith callus.




kinetin (Kin)




6-benzylaminopurine (6-BAP)

We have investigated the interaction of metal ions with other purines of biological interest, including Cu(II) adducts of theophylline, xanthine, and guanine.[2,3] Complexes of purines and primary amines with Cu(II) have been synthesized having the

general formula $(pur)_nCu(amine)_2 \cdot XH_2O$, where pur = theophylline, xanthine, and guanine, amine = various primary amines, $n = 1$ or 2, and $X = 0$, 1, or 2. In addition, Cu(II)–purine complexes of halides have been prepared with the general formula $(pur)_nCuX_2$, where pur = theophylline, xanthine, and guanine, X = Cl or Br, and $n = 1$ or 2. We now report the synthesis of similar Cu(II) adducts with kinetin and 6-benzylaminopurine. Cabras and Zoroddu have recently prepared two kinetin–Cu(II) complexes, $Cu(Kin)_2(ClO_4)_2 \cdot H_2O$ and $Cu(Kin)_2 \cdot 4H_2O$, and suggest that the compounds are dimeric with quadruple bridges of kinetin bidentate ligands involving N(3) and N(9) ring nitrogen atoms.[4] This type of bonding has been observed in crystal structure determinations of Cu(II)–adenine and Cu(II)–6-hydroxypurine complexes.[5–7] The structure of a polymeric Cu(II)–purine adduct has also been determined, and involves N(7), N(9) bridging between metal centres, a mode of bonding known for imidazole and benzimidazole complexes.[8] In addition, structures of monomeric purine–metal ion complexes have been reported, including those of guanine[9] and theophylline,[10] as well as a dimeric Cu(II)–guanine adduct with copper bridging by chlorine atoms.[11] A wide variety of bonding modes is possible in purine–metal ion complexes; substituent and pH effects influence the site and stereochemistry of metal coordination.[12,13]



## EXPERIMENTAL

### *Preparation of Cu(Kin)$Cl_2$, Cu(Kin)$Br_2$, and Cu(6-BAP)$Cl_2$*

The synthetic procedure was similar to that used for previously reported copper halide–purine complexes.[2,3] Some 5.0 mmol of either $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ were refluxed with 5.0 mmol of the respective purine in methanol for 1 h and filtered by vacuum. Elemental analyses are listed in Table I.

TABLE I
Elemental analyses of Cu(II) halide and Cu(II) primary amine complexes of kinetin and 6-benzylaminopurine.

| Compound | Colour | | %C | %H | %N | %Cu |
|---|---|---|---|---|---|---|
| $Cu(Kin)Cl_2$ | green | Calc: | 34.24 | 2.57 | 19.97 | 18.12 |
| | | Found: | 34.26 | 2.56 | 19.85 | 18.21 |
| $Cu(Kin)Br_2$ | orange-brown | Calc: | 27.30 | 2.05 | 15.93 | 14.45 |
| | | Found: | 28.30 | 2.19 | 16.02 | 14.21 |
| $Cu(6\text{-}BAP)Cl_2$ | green | Calc: | 40.05 | 3.06 | 19.47 | 17.66 |
| | | Found: | 39.83 | 3.08 | 19.28 | 17.48 |
| $Cu(Kin)_2(CH_3NH_2)_3$ | blue | Calc: | 47.21 | 5.30 | 31.13 | 10.86 |
| | | Found: | 47.11 | 5.32 | 30.96 | 11.06 |

### *Preparation of Cu(Kin)$_2$($CH_3NH_2$)$_3$*

The synthetic procedure was similar to that used for previously reported copper–purine adducts with primary amines.[14,15] Some 5.0 mmol of $CuSO_4 \cdot 5H_2O$ and 5.0 mmol of kinetin were dissolved separately in 40% methylamine in $H_2O$ and then mixed with stirring. Blue crystals formed after several days; they were filtered by

vacuum, washed sequentially with 40% methylamine and $H_2O$, and dried using ethyl ether. Elemental analyses are listed in Table I.

IR spectra were measured in Nujol mulls between high-density polyethylene windows (600–200 $cm^{-1}$) and in KBr pellets (4000–500 $cm^{-1}$) using a Perkin-Elmer 1430 spectrophotometer. Room-temperature magnetic susceptibility measurements were conducted on a Gouy balance of standard design. Elemental analyses were performed by Galbraith Laboratories.

## RESULTS AND DISCUSSION

Kinetin and 6-benzylaminopurine exhibit two secondary amine N–H vibrations in the 3200–3300 $cm^{-1}$ region; the higher energy peak is assigned to ring N–H stretching and the lower energy peak to side chain aliphatic N–H stretching (Table II). These vibrations shift to higher frequencies in $Cu(Kin)Cl_2$, $Cu(Kin)Br_2$, and $Cu(6\text{-}BAP)Cl_2$, while aromatic C–H vibrations lessen in intensity. Prominent C=C and C=N skeletal bands in the 1600 $cm^{-1}$ region are altered upon complex formation; the higher energy band shifts slightly to higher frequencies, while that of lower energy markedly loses intensity and shifts slightly to lower frequencies. Low frequency absorptions can be assigned to Cu–Cl or Cu–Br modes in the halide adducts; the Cu–Br/Cu–Cl frequency ratio in $Cu(Kin)Br_2$ and $Cu(Kin)Cl_2$ is 0.74, in agreement with ratios of other reported complexes of this type, and confirms their assignments. This was the only region of the 4000–200 $cm^{-1}$ IR spectra where significant differences were noticed in these two compounds. The single M–X stretching vibration in the halide complexes suggests a *trans* square planar arrangement of halides about the copper atom. Prominent low frequency ligand bands in kinetin are changed upon copper halide adduct formation; a strong peak at 518 $cm^{-1}$ shifts to 593 $cm^{-1}$ in $Cu(Kin)Cl_2$ and 590 $cm^{-1}$ in $Cu(Kin)Br_2$, while a peak of medium intensity at 450 $cm^{-1}$ shifts to higher frequencies and forms two new peaks in the 510 to 540 $cm^{-1}$ region. Low frequency ligand bands shift only slightly to higher frequencies in $Cu(6\text{-}BAP)Cl_2$ from those of 6-benzylaminopurine.

TABLE II

Selected ir frequencies ($cm^{-1}$) of Cu(II) halide and primary amine complexes of kinetin and 6-benzylaminopurine.

| Compound | ν(N–H) | Skeletal bands | ν(Cu–X) | Ligand bands |
|---|---|---|---|---|
| Kin | 3255s, 3205s | 1620vs, 1590vs | | 518s, 450m |
| $Cu(Kin)Cl_2$ | 3305s, 3255s | 1630vs, 1580m | 310s | 593s, 540w, 510w |
| $Cu(Kin)Br_2$ | 3300s, 3245s | 1630vs, 1580m | 230s | 590s, 540w, 515w |
| $Cu(Kin)_2(CH_3NH_2)_3$ | 3255s | 1615vs, 1555m | | 572w, 523w, 455w |
| 6-BAP | 3260m, 3210m | 1620vs, 1595vs | | 520w, 478vw |
| $Cu(6\text{-}BAP)Cl_2$ | 3320s, 3280s | 1630vs, 1580m | 315m | 532w, 481vw |

Room temperature magnetic susceptibility measurements gave values of 1.53 BM and 1.38 BM for $Cu(Kin)Cl_2$ and $Cu(Kin)Br_2$, respectively, and 1.16 BM for $Cu(6\text{-}BAP)Cl_2$. These values are lower than those usually found for mononuclear Cu(II) compounds, and are most likely due to magnetic exchange interactions.[16] They are consistent with measured magnetic susceptibilities of adenine and hypoxanthine

Cu(II) compounds whose structures consist of quadruple bridges of bidentate purine ligands connecting two Cu(II) centres through the N(3) and N(9) ring nitrogen atoms. N(7) would thus be protonated and N(1) lost as a possible coordination site due to the bulky 6-amino substituent; the crystal structures of kinetin[17] and 6-benzylaminopurine[18] clearly demonstrate that N(1) is sterically blocked to coordination. Each copper atom could adopt *trans* square-planar geometry with two halide atoms and a N(9) or N(3) atom from the two purine rings.

$Cu(Kin)_2(CH_3NH_2)_3$ exhibits the loss of an aromatic N–H stretch from that of kinetin alone, while the aliphatic N–H stretch shifts to higher wavenumbers as in the halide complexes; this is consistent with the deprotonation of the purine ring, either at N(7) or N(9), and the formation of a metal complex. Two broad skeletal bands in the 1600 $cm^{-1}$ region shift to lower frequencies while low frequency kinetin ligand absorptions shift to higher wavenumbers upon complexation. A 1.58 BM magnetic susceptibility value for this compound is consistent with the above values for kinetin and 6-benzylaminopurine halide complexes, and suggests that dimeric or polymeric products have formed. Cu–N stretching vibrations in the low frequency IR spectrum are difficult to assign because of ligand bands; consequently, no proposals concerning the geometry of the copper atom can be made.

Kinetin and 6-benzylaminopurine N(3)–N(9) bridging between copper centres for complex formation is consistent with known metal ion structures of adenine and hypoxanthine, and would not be destabilized by nonbonding interactions from bulky side groups on C(6). N(7)–N(9) bridging between copper centres for dimer or polymer formation cannot be disregarded, however, N(1) is the only purine nitrogen atom effectively blocked from coordination to metal atoms due to bulky C(6) substituents. The low magnetic moments of the four complexes suggests that magnetic exchange interactions occur in a similar fashion to other purine–metal ion complexes, and that dimeric or polymeric complexes are therefore likely to be present.



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