

the perchlorate counterion [Cu...O 2.72 (4) Å] to form a pseudo three-coordinate structure.

Despite the similar Cu—N distances among these structurally characterized pyrazole, pyridine and imidazole complexes, only the two-coordinate copper imidazole complexes are inert towards CO in solution, supporting the contention that the Cu—imidazole interaction is a particularly strong one which stabilizes the observed linear structure.

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Structure of a Copper(II) Kinetin Complex

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Abstract. Tris(ethylamine)bis[*N*-(2-furylmethyl)-1*H*-purin-6-aminato]copper(II)-diaquabis(ethylamine)-bis[*N*-(2-furylmethyl)-1*H*-purin-6-aminato]copper(II), [Cu(C₁₀H₉N₅O)₂(C₂H₇N)₃][Cu(C₁₀H₉N₅O)₂(C₂H₇N)₂(H₂O)₂], *M_r* = 1249.40, monoclinic, *P*2₁, *a* = 12.280 (3), *b* = 11.972 (11), *c* = 21.565 (9) Å, β = 106.64 (3)°, *V* = 2961.4 Å³, *Z* = 2, *D_x* = 1.401 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.786 mm⁻¹, *F*(000) = 1312, *T* = 293 (1) K, *R* = 0.064 for 2390 observed reflections with *I* > 3σ(*I*). The crystal structure consists of two types of molecules, Cu(kin)₂(EtNH₂)₂(H₂O)₂ (*A*) and Cu(kin)₂(EtNH₂)₃ (*B*) which are separated by normal van der Waals distances. The coordination of the Cu atom in *A* is distorted octahedral while in *B* it is trigonal bipyramidal.

Introduction. Kinetin (kin) is a representative of a class of compounds known as cytokinins which promote cell division in plants. Cytokinins are N(6)-substituted adenines in their free base as well as their nucleoside and nucleotide forms. Few studies have

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been undertaken on kinetin–metal ion complexes; Cabras & Zoroddu (1987) have recently reported two copper adducts, Cu(kin)₂(ClO₄)₂·H₂O and Cu(kin)₂·4H₂O. Although several structures have been reported for other purine derivatives containing metal ions, no crystal structures have been reported for metal complexes of kinetin to date. Various bonding modes are possible in these complexes, with the site and stereochemistry of metal coordination influenced by, for example, substituent and pH effects.

Cu^{II}–adenine and Cu^{II}–6-hydroxypurine adducts have been shown to be dimeric with the bidentate purine ligand bridging copper centers *via* N(3) and N(9) coordination (Sletten, 1969; De Meester & Skapski, 1971; Sletten, 1970). A Cu^{II}–purine structure has been determined which involves N(7), N(9) bridging between metal centers resulting in polymer formation (Vestues & Sletten, 1981), while a Cu^{II} chloride derivative of guanine consists of a dimer with Cu—N(9) bonding and copper bridging by Cl atoms (Carrabine & Sundaralingam, 1970). In addition, structures of monomeric complexes are known; for example, a theophylline–copper chloride

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Table 1. Final fractional coordinates and isotropic equivalent thermal parameters of selected atoms with *e.s.d.*'s in parentheses
$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

Molecule	x	y	z	B _{eq}
Molecule A				
Cu	0.5666 (1)	0.2520†	0.76494 (9)	2.73 (4)
O(W1)	0.664 (1)	0.129 (1)	0.3575 (5)	5.0 (3)*
O(W2)	0.481 (2)	0.349 (2)	0.650 (1)	14.7 (8)*
N(2)	0.671 (1)	0.242 (2)	0.6288 (5)	4.1 (4)
N(4)	0.717 (1)	0.264 (1)	0.7470 (5)	2.5 (3)
N(7)	0.450 (1)	0.120 (1)	0.8767 (5)	3.1 (3)
N(9)	0.416 (1)	0.251 (1)	0.7828 (5)	2.9 (3)
N(11)	0.598 (1)	0.407 (1)	0.8104 (5)	2.6 (3)
N(12)	0.533 (1)	0.109 (1)	0.7075 (6)	3.4 (3)
C(2)	0.745 (1)	0.258 (2)	0.6891 (6)	2.3 (3)
C(5)	0.820 (1)	0.273 (1)	0.7920 (6)	2.4 (4)
C(12)	0.384 (1)	0.190 (1)	0.8320 (7)	2.3 (4)
C(15)	0.315 (1)	0.302 (1)	0.7498 (6)	2.1 (4)
C(21)	0.626 (1)	0.400 (2)	0.8831 (8)	4.3 (4)*
C(22)	0.647 (2)	0.517 (3)	0.913 (1)	8.5 (7)*
C(23)	0.414 (2)	0.070 (2)	0.6800 (9)	4.7 (5)*
C(24)	0.403 (2)	-0.033 (2)	0.638 (1)	7.0 (6)*
Molecule B				
Cu	0.0540 (1)	-0.3706 (2)	0.73912 (9)	3.14 (4)
N(2)	0.180 (1)	-0.312 (1)	0.6198 (6)	3.3 (3)
N(4)	0.213 (1)	-0.381 (1)	0.7315 (5)	3.0 (3)
N(7)	-0.115 (1)	-0.141 (1)	0.7758 (6)	3.7 (4)
N(9)	-0.095 (1)	-0.346 (1)	0.7579 (6)	3.1 (3)
N(11)	-0.021 (1)	-0.458 (1)	0.6396 (7)	4.2 (4)
N(12)	0.082 (1)	-0.512 (1)	0.8013 (6)	3.6 (4)
N(13)	0.048 (1)	-0.208 (1)	0.7033 (6)	4.2 (4)
C(1)	0.233 (1)	-0.301 (2)	0.5750 (8)	5.5 (5)
C(2)	0.246 (1)	-0.349 (1)	0.6767 (7)	2.3 (4)
C(12)	-0.151 (1)	-0.252 (2)	0.7705 (7)	2.9 (4)
C(15)	-0.173 (1)	-0.429 (2)	0.7525 (8)	3.6 (4)
C(21)	-0.129 (2)	-0.408 (3)	0.597 (1)	8.2 (7)*
C(22)	-0.175 (2)	-0.456 (2)	0.530 (1)	7.5 (6)*
C(23)	0.088 (3)	-0.493 (3)	0.871 (1)	12 (1)*
C(24)	0.166 (3)	-0.450 (4)	0.901 (2)	15 (1)*
C(25)	0.137 (2)	-0.129 (2)	0.749 (1)	7.2 (6)*
C(26)	0.128 (2)	-0.018 (3)	0.712 (1)	11.3 (9)*

* Refined isotropically.

† Fixed y coordinate to define the origin.

adduct consists of pentacoordinate copper in a square-pyramidal arrangement involving two *cis* Cl atoms, theophylline N(7), and two H₂O molecules (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1979), while another theophylline-copper chloride structure shows copper in a flattened tetrahedral environment with bonds to two N(7) atoms from separate theophylline molecules and two Cl atoms (Biagini Cingi, Manotti Lanfredi & Tiripicchio, 1983). In this paper we report the synthesis and structure of a novel Cu^{II}-kinetin complex containing ethylamine.

Experimental. The synthetic procedure was similar to that used in previously reported copper-purine adducts with primary amines (Zitzman, Krebs & Birdsall, 1978; Birdsall & Zitzman, 1979). 5.0 mmol of CuSO₄·5H₂O and 5.0 mmol of kinetin were dissolved separately in 35% ethylamine/H₂O and then mixed with stirring. Blue crystals formed after several days; they were filtered, washed sequentially with 35% ethylamine and H₂O, and dried using diethyl ether. A crystal of approximate dimensions

Table 2. Geometry for the first coordination sphere of Cu atoms

	A	B
Cu—O(W1)	2.47 (1)	—
Cu—O(W2)	2.65 (2)	—
Cu—N(4)	1.99 (1)	2.01 (1)
Cu—N(9)	1.99 (1)	2.01 (1)
Cu—N(11)	2.04 (1)	2.32 (1)
Cu—N(12)	2.05 (1)	2.09 (2)
Cu—N(13)	—	2.04 (2)
N(4)—Cu—N(9)		
	176.0 (6)	171.7 (5)
N(4)—Cu—N(11)		
	88.4 (5)	92.0 (5)
N(4)—Cu—N(12)		
	88.7 (5)	91.3 (6)
N(4)—Cu—N(13)		
	—	87.3 (6)
N(4)—Cu—O(W1)		
	86.6 (4)	—
N(4)—Cu—O(W2)		
	86.1 (6)	—
N(9)—Cu—N(11)		
	88.1 (6)	96.2 (5)
N(9)—Cu—N(12)		
	94.5 (5)	88.5 (5)
N(9)—Cu—N(13)		
	—	90.4 (6)
N(9)—Cu—O(W1)		
	95.8 (5)	—
N(9)—Cu—O(W2)		
	92.2 (6)	—
N(11)—Cu—N(12)		
	171.9 (5)	101.2 (5)
N(11)—Cu—N(13)		
	—	95.6 (5)
N(11)—Cu—O(W1)		
	98.4 (4)	—
N(11)—Cu—O(W2)		
	92.2 (7)	—
N(12)—Cu—N(13)		
	—	163.2 (5)
N(12)—Cu—O(W1)		
	88.9 (5)	—
N(12)—Cu—O(W2)		
	80.1 (7)	—
N(13)—Cu—O(W1)		
	—	—
N(13)—Cu—O(W2)		
	—	—
O(W1)—Cu—O(W2)		
	166.9 (7)	—

0.48 × 0.37 × 0.25 mm was used for data collection. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method and variable scan speed (0.87–5.5° min⁻¹) using monochromatized radiation in the range 2 < θ < 24°. The intensities of three standard reflections decreased by 38.8% linearly over the course of data collection; this decay was corrected for by appropriate scaling. Intensities of 4889 unique reflections were measured (h 0 → 13, k 0 → 13, l -24 → 24), of which 2390 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization effects and empirically for absorption (North, Phillips & Mathews, 1968); maximum and minimum transmission coefficients were 1.00 and 0.81, respectively.

The structure was solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement of the structure was by full-matrix least-squares calculations on F^2 's with anisotropic temperature factors for the non-H atoms except those of ethylamino, O atoms of the water ligands and furan groups which were allowed isotropic thermal motion. A difference map showed only a few maxima corresponding to the positions of H atoms; H atoms were ignored. Refinement converged with $R = 0.064$ and $wR = (\sum w\Delta^2 / \sum F_o^2)^{1/2} = 0.083$, where $w = [\sigma^2(F_o) + (0.060F_o)^2]^{-1}$; max. Δ/σ in the last cycle < 0.02 and $S = 1.648$. Scattering factors were taken from Cromer & Mann (1968) and allowance was made for

anomalous dispersion (Cromer & Liberman, 1970). A difference map calculated at the conclusion of the refinement had no chemically significant features, $\Delta\rho$ being $\pm 0.49 \text{ e } \text{Å}^{-3}$. All computer programs used were part of the Enraf-Nonius *Structure Determination Package* (B. A. Frenz & Associates, Inc., 1982), and the figures were plotted using ORTEPII (Johnson, 1976).

Discussion. The final fractional coordinates and isotropic equivalent thermal parameters of selected

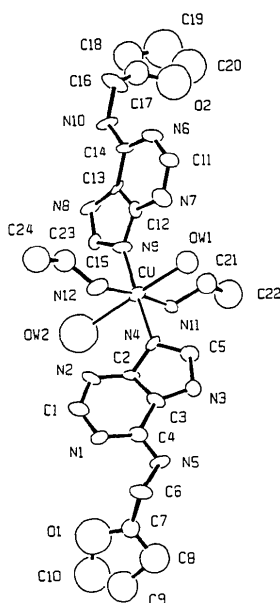


Fig. 1. ORTEP drawing of $[\text{Cu}(\text{kin})_2(\text{EtNH}_2)_2(\text{H}_2\text{O})_2]$, *A*.

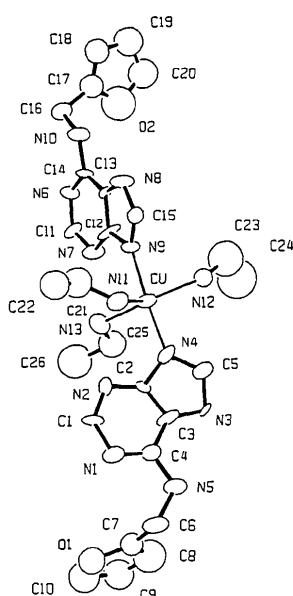


Fig. 2. ORTEP drawing of $[\text{Cu}(\text{kin})_2(\text{EtNH}_2)_3]$, *B*.

atoms with e.s.d.'s are given in Table 1* and the geometry for the first coordination sphere of Cu atoms in Table 2. The crystal consists of two types of molecules, $[\text{Cu}(\text{kin})_2(\text{EtNH}_2)_2(\text{H}_2\text{O})_2]$ (*A*) and $[\text{Cu}(\text{kin})_2(\text{EtNH}_2)_3]$ (*B*), as shown in Figs. 1 and 2, respectively. The two molecules are separated by normal van der Waals distances and do not show any unusual intermolecular contacts. The coordination of the Cu atom in *A* is distorted octahedral. It is bound to two kinetin ligands *via* mutually *trans* equatorial Cu—N bonds [both 1.99 (1) Å and N—Cu—N 176.0 (6)°], two *trans* axial aminoethyl groups [Cu—N 2.04 (1) and 2.05 (1) Å and N—Cu—N 171.9 (5)°] and two *trans* axial water molecules [Cu—O 2.47 (1) and 2.65 (2) Å and O—Cu—O 166.9 (7)°]. The Cu coordination sphere in *B* is trigonal bipyramidal where the kinetin ligands are *trans* [Cu—N both 2.01 (1) Å and N—Cu—N 171.7 (5)°] and the three aminoethyl groups occupy equatorial positions [Cu—N 2.32 (1), 2.09 (2) and 2.04 (2) Å]. The Cu—N distances involving kinetin in each molecule are in excellent agreement with the corresponding distances found in Cu complexes of purine bases, *e.g.* theophylline [2.004 (13) Å] (Biagini Cingi, Manotti Lanfredi & Tiripicchio, 1983), guanine (1.976 Å) (Carrabine & Sundaralingam, 1970) and guanosine [2.012 (7) and 2.052 (7) Å] (Sheldrick, 1981). The Cu—O distances involving water ligands in *A* are rather long. However, Cu—O distances of 2.474 (8) Å [$\text{Cu}(\text{guanosinemonophosphate})_2(\text{H}_2\text{O})_3$] (Sheldrick, 1981) and 2.43–2.47 Å [$\text{Cu}(\text{purine})(\text{H}_2\text{O})_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$] (Vestues & Sletten, 1981) are known. The bond lengths and bond angles in the ligands are unexceptional.

* Lists of structure factors, anisotropic thermal parameters, final fractional coordinates and molecular dimensions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52869 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Tetranuclear Uranium(IV) Compound: Hemiaquatetrakis(trifluoroacetato)uranium(IV)–4,7,13,16,21,24-Hexaoxa- 1,10-diazabicyclo[8.8.8]hexacosane (4/2)

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Abstract. $4[\text{U}(\text{CF}_3\text{COO})_4(\text{H}_2\text{O})_{0.5}]_2\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$, $M_r = 3549$, triclinic, $P\bar{1}$, $a = 13.003$ (5), $b = 13.338$ (7), $c = 16.738$ (4) Å, $\alpha = 84.36$ (3), $\beta = 68.71$ (2), $\gamma = 87.19$ (4)°, $V = 2691$ (4) Å³, $Z = 1$, $D_x = 2.190$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.853$ mm⁻¹, $F(000) = 1680$, $T = 295$ K, $R = 0.038$ for 3534 unique observed reflections. Four U^{IV} atoms are connected by bridging trifluoroacetate ligands and water molecules to form a centrosymmetric tetrameric neutral unit in which the four U atoms are 4.0769 (4) and 3.5969 (6) Å apart at the corners of a lozenge. The trifluoroacetato group behaves as either a unidentate or a bridging group. Two water molecules, located inside the uranium tetranuclear unit, are triply shared by U atoms. The two cryptand molecules, related by an inversion center, have an *endo-endo* type configuration: no significant contacts exist between the tetramer and cryptand units.

Introduction. The ¹H NMR spectra of complexes of U^{IV} salts with crown ethers and cryptands in solvents with high electric constants have given evidence for direct coordination of the U atoms to the O atoms of the macrocyclic ligands; in the solid state, a structural determination has confirmed the U^{IV} insertion as the UCl₃⁺ cation in dicyclohexyl-18-crown-6 (de Villardi, Charpin, Costes, Folcher, Plurien, Rigny & de Rango, 1978). Attempts to isolate such complexes

with cryptands have led to crystals which could not be handled. However, when a solution of U^{IV} trifluoroacetate and ⟨222⟩ cryptand (⟨222⟩ = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in acetonitrile was evaporated in air particularly stable crystals were formed. We report here the structure of the compound so obtained.

Experimental. Green crystal approximately 0.5 × 0.45 × 0.3 mm; Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation; ω–2θ scan, ω-scan width: (0.8 + 0.35tanθ)°; determination of the lattice parameters from 25 reflections (8 < θ < 12°); three standard reflections ($\bar{3}\bar{1}\bar{4}$, 321, $\bar{1}\bar{1}\bar{3}$) were monitored every hour, decay of 1.6% in 55 h, not corrected; 5479 reflections measured, 4715 unique ($R_{\text{int}} = 0.023$), 3534 observed with $I > 3\sigma(I)$ which were used in the refinement; $2 \leq \theta \leq 20^\circ$, $0 \leq h \leq 12$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$; Lp corrections; absorption correction using the program *DIFABS* (Walker & Stuart, 1983), max. and min. corrections 1.16 and 0.82; the structure was solved by the Patterson function, for U, and the remaining atoms were located by the difference Fourier technique; full-matrix least-squares refinement on F_o ; anisotropic thermal parameters for U and F, isotropic for O and the rest due to lack of data. The F atoms in one CF₃ group [belonging to the monodentate carboxylate C(71)–C(72)], which showed high thermal motion,