

## *trans*-Bis(3-aminoflavone- $\kappa^2N,O$ )-bis(perchlorato- $\kappa O$ )copper(II), a new potential antitumour agent

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The title compound, *trans*-bis(3-amino-2-phenyl-4*H*-1-benzopyran-4-one- $\kappa^2N,O^4$ )bis(perchlorato- $\kappa O$ )copper(II), [Cu(ClO<sub>4</sub>)<sub>2</sub>(C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub>)<sub>2</sub>], is composed of mononuclear units wherein the central Cu<sup>II</sup> cation occupies a crystallographic inversion centre. The cation is coordinated by two bidentate 3-aminoflavone ligands occupying the equatorial sites and by two perchlorate anions in the apical positions, thereby giving rise to a markedly elongated octahedral coordination geometry. Two symmetry-related intermolecular N—H...O hydrogen bonds link the molecules into chains of rings running parallel to the [100] direction, while intramolecular N—H...O hydrogen bonds help to determine the orientation of the apical perchlorate anions.

### Comment

Flavonoids have been shown to possess a variety of biological activities, including antitumour, antioxidative, antiviral, antibacterial and antimutagenic properties (Kośmider *et al.*, 2004, 2004*a*). This biological relevance of the flavanone system initiated the synthesis of a new analogue of cisplatin, *viz.* *cis*-bis(3-aminoflavone)dichloroplatinum(II) (Ochocki & Zyner, 2003), for which a possible application as an antitumour agent is conceived (Kośmider *et al.*, 2004*b*; Kośmider, Osiecka *et al.*, 2005; Kośmider, Wójcik *et al.*, 2005). This compound exhibits significant antitumour activity in the development of murine leukaemia L1210 (Zyner *et al.*, 1999). Given the biological activity of flavonoid derivatives involving a metal ion, we decided to synthesize the novel title complex, (I), of the 3-aminoflavone ligand, choosing Cu<sup>II</sup> as the metal ion because its complexes are considered to be potent antitumour agents (Gamez *et al.*, 2004).

The X-ray crystallographic study of (I) presented here was undertaken in order to determine the coordination number of the central Cu<sup>II</sup> ion and to obtain detailed information about

the molecular structure and coordination geometry of the complex. We were interested in the potential binding sites of the 3-aminoflavone ligand, in particular whether the N or O atoms, or both, are attached to the metal centre. Moreover, it was our intention to determine whether, in the absence of other potential ligands, the perchlorate anion participates in coordination to the central Cu<sup>II</sup> atom.

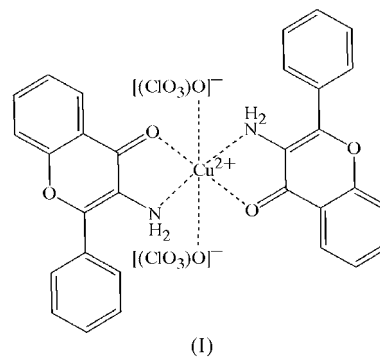
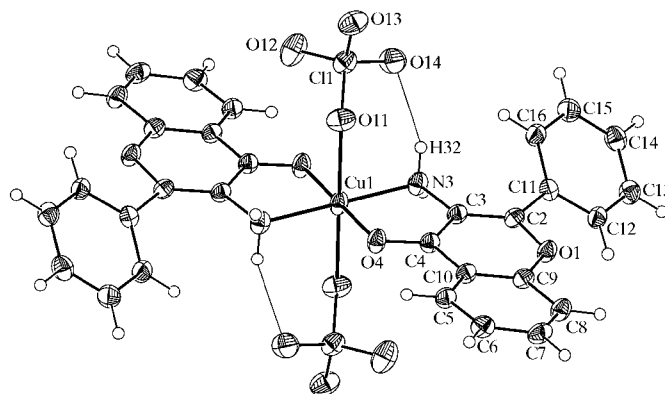
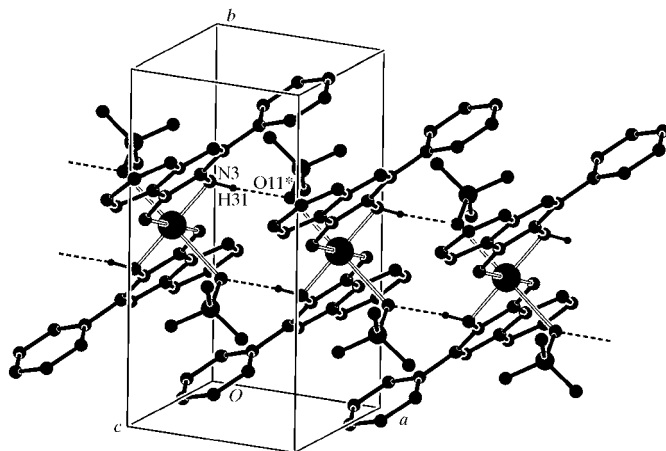


Fig. 1 shows a displacement ellipsoid plot of compound (I) with the atom-labelling scheme. Atom Cu1 lies on a crystallographic inversion centre and is six-coordinate: it is chelated by atoms N3 and O4 of two bidentate 3-aminoflavone ligands and by two perchlorate anions. The 3-aminoflavone ligands are bound to the Cu<sup>II</sup> centre in a mutually *trans* fashion. As a result of chelation, two inversion-related five-membered rings are formed [Cu1/N3/C3/C4/O4 and Cu1/N3<sup>i</sup>/C3<sup>i</sup>/C4<sup>i</sup>/O4<sup>i</sup>; symmetry code: (i)  $-x, 1 - y, 1 - z$ ] which, together with the benzopyran systems, generate the main equatorial plane of the molecule. The geometric parameters around atom Cu1 (Table 1) indicate a significant deformation from octahedral geometry towards a tetragonal bipyramid, in which perchlorate atoms O11 and O11<sup>i</sup> occupy the apical positions.

The phenyl substituents defined by atoms C11–C16 and C11<sup>i</sup>–C16<sup>i</sup> lie out of the equatorial plane defined by atoms Cu1, O4, N3, O1 and C2–C10 and the symmetry-related atoms



**Figure 1**  
A view of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Unlabelled atoms are related to labelled atoms by an inversion centre at  $(-x, 1 - y, 1 - z)$ . Intramolecular N—H...O hydrogen bonds are shown as thin lines.



**Figure 2**

A chain of molecules linked by hydrogen bonds running parallel to [100]. Intermolecular N—H...O interactions are shown as dashed lines. H atoms have been omitted for clarity, except for those taking part in hydrogen bonding. [Symmetry code: (ii)  $1 + x, y, z$ .]

of the same molecule. The dihedral angle between this plane and least-squares phenyl plane is  $39.6(1)^\circ$ .

Protonated atom N3 of the amino group is hydrogen bonded to the O atoms of two perchlorate anions, leading to the formation of one intramolecular and one intermolecular interaction. As a result of the N3—H31...O14 hydrogen bond (Fig. 2 and Table 2), there is an intramolecular  $S(6)$  ring motif (Etter *et al.*, 1990). This interaction plays an important role in stabilizing the orientation of the apical perchlorate anions.

The effects of the intermolecular hydrogen-bonding network are more complex. N3—H32...O11 hydrogen bonds connect molecules related by translation along the  $a$  axis of the unit cell, forming a chain motif with graph-set symbol  $C(4)$  and an  $R_2^2(8)$  ring pattern. When both types of hydrogen bonds are considered, the complete notation is  $C(4)[S(6)][R_2^2(8)]$ .

The variations in bond length for the perchlorate anion are worth mentioning. The longest, at  $1.456(2)$  Å, is for Cl—O11, corresponding to the O atom which is involved in coordination to the metal centre. Of the remaining three Cl—O bonds, the longest is Cl1—O14 [ $1.440(2)$  Å], where atom O14 participates in the intramolecular hydrogen bond. These observations are consistent with bond valence (BV) number rules, namely that covalent bonds become longer when atoms are involved in intermolecular interactions (Grabowski, 2004). In comparison, the two shortest Cl—O distances (Cl1—O12 and Cl1—O13) are the same length within one s.u.

## Experimental

The title compound was prepared by the reaction of two equivalents of 3-aminoflavone with one equivalent of copper(II) perchlorate in water-methanol (1:1 v/v). The reaction mixture was stirred at room temperature for 24 h and the solvent partly removed by evaporation. The resulting solution was cooled and light-blue crystals of (I) suitable for X-ray diffraction analysis appeared after a few days.

## Crystal data

$[\text{Cu}(\text{ClO}_4)_2(\text{C}_{15}\text{H}_{11}\text{NO}_2)_2]$	$\gamma = 98.332(9)^\circ$
$M_r = 736.95$	$V = 705.88(15) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.4957(6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.6909(14) \text{ \AA}$	$\mu = 1.04 \text{ mm}^{-1}$
$c = 11.7435(14) \text{ \AA}$	$T = 193(2) \text{ K}$
$\alpha = 103.142(10)^\circ$	$0.25 \times 0.08 \times 0.06 \text{ mm}$
$\beta = 101.398(9)^\circ$	

## Data collection

Stoe IPDSII image-plate diffractometer	6559 measured reflections
Absorption correction: Gaussian (WinGX; Farrugia, 1999)	2503 independent reflections
$T_{\min} = 0.781, T_{\max} = 0.940$	1851 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.048$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
$S = 0.96$	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
2503 reflections	
222 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Cu1—N3	1.989(3)	Cl1—O12	1.426(3)
Cu1—O4	1.952(2)	Cl1—O13	1.424(3)
Cu1—O11	2.453(2)	Cl1—O14	1.440(2)
Cl1—O11	1.456(2)		
O4—Cu1—N3	85.2(1)	O11—Cu1—N3	88.8(1)
O4—Cu1—O11	83.2(1)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H31...O11 <sup>ii</sup>	0.79(4)	2.21(4)	2.941(4)	155(3)
N3—H32...O14	0.87(4)	2.17(4)	2.996(4)	160(3)

Symmetry code: (ii)  $x + 1, y, z$ .

Aromatic H atoms were introduced in calculated positions with idealized geometry and refined using a rigid body model, with  $C-H = 0.93$  Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The amine H atoms were located in a difference Fourier map and were subsequently refined freely; N—H distances are  $0.79(4)$  and  $0.87(4)$  Å.

Data collection: X-Area (Stoe & Cie, 2000); cell refinement: X-Area; data reduction: X-Area; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3030). Services for accessing these data are described at the back of the journal.

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