Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.058$
$S = 1.129$
4079 reflections
262 parameters
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = -0.004$
$\Delta\rho_{\max} = 0.326$ e Å^{-3}
$\Delta\rho_{\min} = -0.776$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mo—C3	1.949 (3)	Mo—P	2.4994 (8)
Mo—C2	1.986 (2)	O1—C1	1.149 (4)
Mo—C1	2.012 (3)	O2—C2	1.151 (3)
Mo—C4	2.041 (3)	O3—C3	1.160 (4)
Mo—N	2.326 (2)	O4—C4	1.128 (4)
C3—Mo—C2	88.08 (10)	C3—Mo—P	99.42 (7)
C3—Mo—C1	89.89 (12)	C2—Mo—P	172.24 (6)
C2—Mo—C1	91.33 (11)	C1—Mo—P	90.66 (8)
C3—Mo—C4	91.74 (13)	C4—Mo—P	88.72 (8)
C2—Mo—C4	89.08 (11)	N—Mo—P	75.70 (5)
C1—Mo—C4	178.33 (11)	O1—C1—Mo	178.9 (2)
C3—Mo—N	175.00 (7)	O2—C2—Mo	178.3 (3)
C2—Mo—N	96.75 (8)	O3—C3—Mo	179.2 (2)
C1—Mo—N	91.28 (10)	O4—C4—Mo	178.6 (3)
C4—Mo—N	87.07 (11)		

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The final structural model used anisotropic displacement parameters for the non-H atoms. The H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to $1.2U_{eq}$ of their carrier atoms.

Data collection: local diffractometer software (Gomm, 1993). Cell refinement: local diffractometer software. Data reduction: local diffractometer software. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

This work was supported by the Fonds der Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1116). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bernal, I., Reisner, G. M., Dobson, G. R. & Dobson, C. B. (1986). *Inorg. Chim. Acta*, **121**, 199–206.
Cotton, F. A. & Wing, R. M. (1965). *Inorg. Chem.* **4**, 314–317.
Dahlenburg, L. & Herbst, K. (1997). *Chem. Ber.* **130**. In the press.
Dahlenburg, L., Herbst, K. & Kühnlein, M. (1997). *Z. Anorg. Allg. Chem.* **623**, 250–258.
Dahlenburg, L., Herbst, K. & Liehr, G. (1997). *Z. Kristallogr.* **212**. In the press.
Dahlenburg, L. & Kühnlein, M. (1997). *Acta Cryst.* C**53**, 1190–1192.
Gomm, M. (1993). *Single-Crystal Diffractometry – Hardware and Software. IUCr Crystallographic Symposia* 6 (*Crystallographic Computing*), edited by H. D. Flack, L. Párkányi & K. Simon, pp. 1–9. Oxford University Press.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Shiu, K.-B., Wang, S.-L. & Liao, F.-L. (1991). *J. Organomet. Chem.* **420**, 207–215.
Siemens (1990). *XP. Interactive Molecular Graphics Program.* Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Ueng, C.-H. & Leu, L.-C. (1991). *Acta Cryst.* C**47**, 725–728.

Acta Cryst. (1997). C**53**, 1547–1549

(2,2′-Bipyridine)(flavonolato)copper(II) Perchlorate,† [Cu(bpy)(fla)]ClO$_4$

ISTVÁN LIPPAI,[a] GÁBOR SPEIER,[a] GOTTFRIED HUTTNER[b] AND LÁSZLÓ ZSOLNAI[b]

[a]*Department of Organic Chemistry, University of Veszprém, 8201 Veszprém, Hungary, and* [b]*Anorganisch-Chemisches Institut, Ruprecht-Karls Universität, 69120 Heidelberg, Germany. E-mail: speier@almos.vein.hu*

(Received 25 November 1996; accepted 10 April 1997)

Abstract

3-Hydroxyflavone coordinates to Cu^{II} together with the auxiliary ligand 2,2′-bipyridine to form a stable cationic flavonolato–copper(II) complex, $[Cu(C_{15}H_9O_3)(C_{10}H_8N_2)]ClO_4$. The complex has distorted square pyramidal geometry. Two O atoms of the flavonol and the N atoms of the chelating bpy ligand are in the basal position, while a perchlorate O atom occupies the apical position.

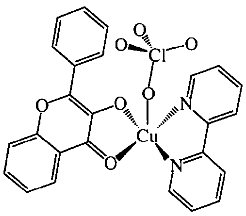
Comment

Quercetin 2,3-dioxygenase is a Cu^{II}-containing enzyme which catalyses the degradation of quercetin and related compounds into a depside (phenolic carboxylic acid ester) (Westlake, Talbot, Blakely & Simpson, 1959; Takamura & Ito, 1977). Quercetin coordinates to the copper(II) ion and flavonol forms stable Cu^{I} and Cu^{II} compounds (Speier, Fülöp & Párkányi, 1990; Balogh-Hergovich, Speier & Argay, 1991). Simple flavonolato–copper complexes have been used as model compounds and in model reactions (Utaka, Hojo, Fujii & Takeda, 1984; Utaka & Takeda, 1985). Following this, we report here the molecular structure of a cationic mixed-

---

† Alternative name: (2,2′-bipyridyl-*N*,*N*′)(4-oxo-2-phenyl-4*H*-chromen-3-olato-*O*^{3},*O*^{4})copper(II) perchlorate.

ligand flavonolato–Cu^{II} complex, (I), in order to gain information about the possible structure of the active site of the enzyme and its role in the catalytic process.



(I)

Compound (I) has a distorted square-pyramidal geometry around the copper(II) ion. Flavonol coordinates through its 3-hydroxy and 4-carbonyl groups with the O atoms occupying the basal positions together with the N atoms of the chelating bpy ligand. One of the perchlorate O atoms occupies the apical position. The Cu—O bond distance of the 4-carbonyl O atom is longer [Cu1—O1 1.970 (3) Å] than that found in [Cu(fla)$_2$] [1.944 (3) Å], and that of the 3-hydroxy O atom is shorter [Cu1—O2 1.897 (3) Å] than in [Cu(fla)$_2$] [1.901 (2) Å]. The apical Cu—O distance [Cu1—O6 2.425 (4) Å] is considerably longer than those in the basal position and as observed in a Cu^{II} perchlorate compound with *P,P,N,N*-coordination (Pilloni, Bandoli, Tisato & Corain, 1996). The O—Cu—O and N—Cu—N angles differ only slightly from the ideal 90°.

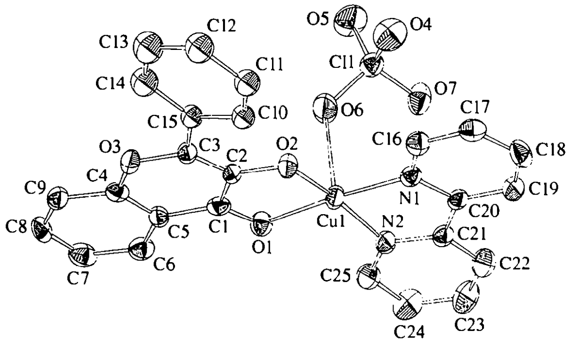


Fig. 1. The molecular structure showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complex was prepared by stirring $[Cu(CH_3CN)_4]ClO_4$ with equimolar amounts of flavonol and 2,2′-bipyridine in acetonitrile at room temperature under a dioxygen atmosphere. The resulting green precipitate was crystallized from acetonitrile.

Crystal data

$[Cu(C_{15}H_9O_3)(C_{10}H_8N_2)]$-$ClO_4$
$M_r = 556.40$
Monoclinic
$P2_1/c$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.0$–$14.0°$

$a = 10.305\,(3)$ Å
$b = 22.511\,(7)$ Å
$c = 9.641\,(3)$ Å
$\beta = 83.25\,(2)°$
$V = 2221.0\,(12)$ Å^3
$Z = 4$
$D_x = 1.664$ Mg m^{-3}
D_m not measured

$\mu = 1.157$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.30 × 0.30 × 0.20 mm
Green

Data collection

Siemens (Nicolet Syntex) diffractometer
ω scan
Absorption correction: ψ scan (*XDISK*; Siemens, 1990)
$T_{min} = 0.573$, $T_{max} = 0.793$
3481 measured reflections
3282 independent reflections

2960 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 23.5°$
$h = -5 \rightarrow 11$
$k = -7 \rightarrow 25$
$l = -10 \rightarrow 10$
3 standard reflections every 50 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.053$
$wR(F^2) = 0.162$
$S = 1.911$
3282 reflections
328 parameters
H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.058$
$\Delta\rho_{max} = 2.764$ e Å^{-3}
$\Delta\rho_{min} = -0.857$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O2	1.897 (3)	O2—C2	1.323 (5)
Cu1—N2	1.961 (4)	O3—C4	1.362 (5)
Cu1—O1	1.970 (3)	O3—C3	1.378 (5)
Cu1—N1	1.978 (4)	C1—C5	1.444 (6)
Cu1—O6	2.425 (4)	C1—C2	1.448 (6)
O1—C1	1.271 (5)	C2—C3	1.362 (6)
O2—Cu1—N2	170.29 (13)	C2—O2—Cu1	110.7 (3)
O2—Cu1—O1	85.64 (12)	Cl1—O6—Cu1	125.5 (2)
N2—Cu1—O1	95.64 (13)	C16—N1—Cu1	125.5 (3)
O2—Cu1—N1	96.12 (13)	C20—N1—Cu1	114.5 (3)
N2—Cu1—N1	82.07 (14)	C21—N2—Cu1	114.4 (3)
O1—Cu1—N1	176.29 (13)	C25—N2—Cu1	127.2 (3)
O2—Cu1—O6	93.68 (14)	O1—C1—C5	123.1 (4)
N2—Cu1—O6	96.01 (14)	O1—C1—C2	118.1 (4)
O1—Cu1—O6	85.82 (13)	O2—C2—C3	124.8 (4)
N1—Cu1—O6	97.30 (13)	O2—C2—C1	116.1 (4)
C1—O1—Cu1	109.4 (3)	C2—C3—O3	121.5 (4)

The low θ_{max} value (23.5°) is related to the low reflectivity beyond 24°. The high value of S (1.911) is probably a result of the somewhat higher rest density near the Cu atom. Despite the experimental absorption correction (ψ scan), the high value of $\Delta\rho_{max}$ (2.764 e Å^{-3}) could not be reduced (0.9 Å from Cu).

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

This research was supported by the Hungarian Research Found (OTKA T02326 and T016285) and COST (CIPECT926093, 12160).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1079). Services for accessing these data are described at the back of the journal.

References

Balogh-Hergovich, É., Speier, G. & Argay, G. (1991). *J. Chem. Soc. Chem. Commun.* pp. 551–552.

Pilloni, G., Bandoli, G., Tisato, F. & Corain, B. (1996). *J. Chem. Soc. Chem. Commun.* pp. 433–434.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1990). *SHELXTL-Plus.* Release 4.11/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Speier, G., Fülöp, V. & Párkányi, L. (1990). *J. Chem. Soc. Chem. Commun.* pp. 512–513.

Takamura, K. & Ito, M. (1977). *Chem. Pharm. Bull.* **25**, 3218–3225.

Utaka, M., Hojo, M., Fujii, Y. & Takeda, A. (1984). *Chem. Lett.* pp. 635–638.

Utaka, M. & Takeda, A. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1824–1826.

Westlake, D. W. S., Talbot, G., Blakely, E. R. & Simpson, F. J. (1959). *Can. J. Microbiol.* **5**, 621–629.

Acta Cryst. (1997). C**53**, 1549–1551

[*N*,*N*-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane](3,5-dimethylpyrazole)copper(II) Diperchlorate†

Peter D. W. Boyd,[a] Anthony K. Burrell[b] and Clifton E. F. Rickard[a]

[a]*Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand, and* [b]*Department of Chemistry, Massey University, Palmerston North, New Zealand. E-mail: pdw.boyd@auckland.ac.nz*

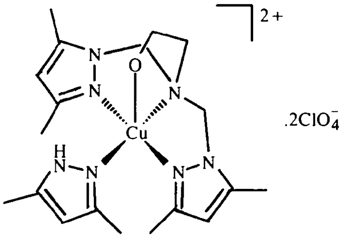
(*Received 10 February 1997; accepted 27 May 1997*)

Abstract

The title compound, $[Cu(C_5H_8N_2)(C_{14}H_{23}N_5O)](ClO_4)_2$, consists of a five-coordinate square-pyramidal copper(II) complex as its perchlorate salt. The copper(II) ion is coordinated in the basal plane by azole and amine N atoms of the *N*,*N*-bis[(3,5-dimethyl-1-pyrazolyl)methyl]-1-hydroxy-2-aminoethane (bpmhe) ligand and 3,5-dimethylpyrazole, and in the apical position by an alcohol O atom.

Comment

Copper(II) complexes of the tripodal ligand bpmhe (Driessen, 1982) of the type [Cu(bpmhe)*L*]*X* (*L* = Br, Cl, NO_3, N_3; *X* = Cl, Br, BF_4) have been reported as mononuclear five-coordinate complexes (Malachowski, Davidson & Hoffman, 1989). The ligand bpmhe may act as a tetradentate ligand with two pyrazole nitrogen, one tertiary amine and one alcohol oxygen donor. We have been interested in the formation of such complexes with *L* as a neutral donor ligand and have isolated the title compound $[Cu(bpmhe)L](ClO_4)_2$, where *L* is 3,5-dimethylpyrazole.



(I)

The coordination geometry around the copper(II) ion consists of two pyrazole N atoms, an alcohol O atom and an amine N atom of the bpmhe ligand and one N atom of the 3,5-dimethylpyrazole molecule in a square-pyramidal environment. The four N atoms form the base of the pyramid with the alcohol O atom at the apex. The Cu—N bond distances and angles are similar to those found in other *N*,*N*-bis(pyrazol-1-ylmethyl)amine complexes of copper(II) (Blonk, Driessen & Reedijk, 1985; Driessen, De Graaff & Wiesmeijer, 1987). The

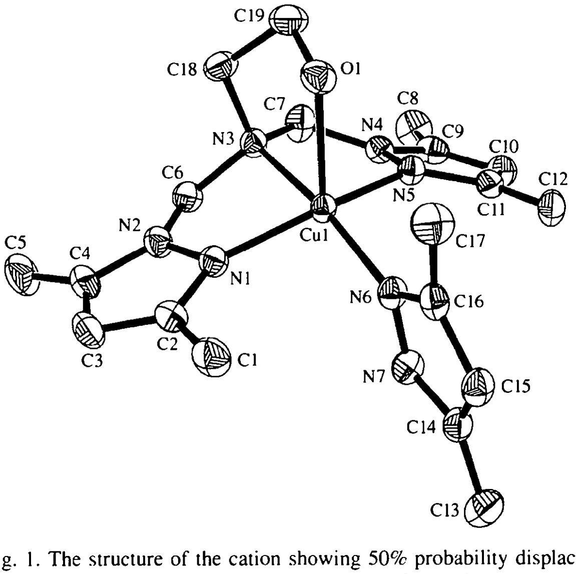


Fig. 1. The structure of the cation showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

---

† Alternative name: {2-{*N*,*N*-bis[(3,5-dimethylpyrazol-1-yl-N^2)methyl]amino-*N*}ethanol-*O*}(3,5-dimethylpyrazole-N^2)copper(II) diperchlorate.