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Copper-mediated oxygenation of flavonolate in the presence of a tridentate N-ligand. Synthesis and crystal structures of [Cu(fla)(idpaH)]ClO_4 and [Cu(idpaH)(O-bs)]ClO_4, [fla = flavonolate, idpaH = 3,3′-iminobis(*N*,*N*-dimethylpropylamine), O-bs = O-benzoylsalicylate]

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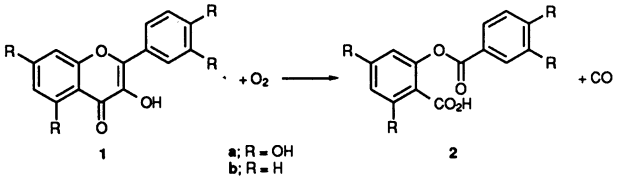
Abstract

The complexes [Cu(fla)(idpaH)]ClO_4 (**4**) and [Cu(idpaH)(O-bs)]ClO_4 (**5**) (fla = flavonolate, idpaH = 3,3′-iminobis(*N*,*N*-dimethylpropylamine), O-bs = O-benzoylsalicylate) have been synthesised and characterised. Complex **5** can be obtained also by the oxygenation of **4** and concomitant CO release. The structures of the compounds have been determined by X-ray diffraction. Complex **4** exhibits distorted trigonal-bipyramidal geometry around the copper(II) ion while complex **5** is distorted square-pyramidal. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Copper; Flavonolate complexes; Salicylate complexes

1. Introduction

The oxidative degradation of various organic compounds proceeds with the help of dioxygen utilizing oxygenases [1]. One of these metalloenzymes, the copper-containing quercetin 2,3-dioxygenase, converts quercetin (**1a**) to a depside (**2a**, carboxylic acid ester) with loss of carbon monoxide (Eq. (1)) [2–5].



(1)

Only limited data on quercetinase are available in the literature and the role of the copper ion at its active site is obscured. In the resting state of quercetinase, copper(II) ion has been found and the substrate quercetin is believed to coordinate to copper(II) through its 3-hydroxy and 4-carbonyl groups [6–8]. Investigations however, have been done on functional model systems on the parent compound flavonol (**1b**) [9–11] together with autoxidation reactions [12,13]. Our interest in flavonolato copper complexes as possible functional models for the active site of quercetinase has led us to synthesise a number of compounds with 3-hydroxyflavones. Copper(I) and copper(II) flavonolate (fla) complexes with simple ligands were prepared and successfully used in the oxygenation of flavonol [14–18]. These systems provide the first copper-containing functional models for quercetinase. As an extension of this work we intended to work out copper(I) and copper(II) flavonolate complexes with the tridentate ligand 3,3′-iminobis(*N*,*N*-dimethylpropylamine) (**3**, idpaH).

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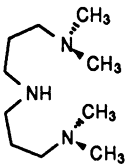


3, idpaH

Here we report the preparation and the crystal structure of a Cu(II) flavonolate complex with the ligand idpaH. Furthermore the oxygenation of the flavonolato copper(II) complex to the copper(II) complex of the corresponding depside (O-benzoylsalicylic acid, O-bsH) and CO. The X-ray structure of the latter is also reported.

2. Experimental

All preparations were carried out using standard Schlenck techniques [19]. Solvents used for the reactions were purified by literature methods and stored under argon. Flavonol [9], O-benzoylsalicylic acid [20], and tetrakis(acetonitrile)copper(I) perchlorate [21] were prepared by literature methods. The compounds 3,3′-iminobis(*N*,*N*-dimethylpropylamine) and $Cu(ClO_4)_2\cdot 6H_2O$ were obtained from Aldrich and used without further purification.

2.1. Preparation of [Cu(fla)(idpaH)]ClO$_4$ (4)

$Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 1 mmol) and 3,3′-iminobis(*N*,*N*-dimethylpropylamine) (0.187 g, 1 mmol) in methanol (20 cm^3) were stirred under an atmosphere of N_2 for 1 h. The solution was then treated with flavonol (0.238 g, 1 mmol) and piperidine (0.085 g, 1 mmol) and the mixture stirred at room temperature (r.t.) under an atmosphere of N_2 for 2 h. A green solid which deposited was then filtered off and recrystallised from acetonitrile to give **4** as green crystals (0.53 g, 90%). M.p. 267°C. *Anal.* Calc. for $C_{25}H_{34}N_3O_7CuCl$: C, 51.10; H, 5.83; N, 7.10. Found: C, 50.32; H, 5.43; N, 7.02%. IR (Nujol): 3228 ν(NH), 1559 ν(CO), 1095, 1055, 631 $\nu(ClO_4)$ cm^{-1}. UV–Vis (λ_{max} DMF): 262 (log ε/dm^3 mol^{-1} cm^{-1} 4.271), 426.5 (4.287), 690 (2.232) nm. $\mu_B = 1.85$.

2.2. Preparation of [Cu(idpaH)(O-bs)]ClO$_4$ (5)

$[Cu(CH_3CN)_4]ClO_4$ (0.164 g, 0.5 mmol) and O-benzoylsalicylic acid (0.242 g, 1 mmol) were dissolved in 30 cm^3 of acetonitrile and stirred under an atmosphere of O_2 for 2 h, then 3,3′-iminobis(*N*,*N*-dimethylpropylamine) (0.093 g, 0.5 mmol) was added and the solution refluxed for 5 h. Diethyl ether was layered on the solution and left at −20°C for 5 days to afford blue crystals of **5** (0.24 g, 80%). M.p. 195°C. *Anal.* Calc. for $C_{24}H_{33}N_3O_8CuCl$: C, 48.73; H, 5.79; N,7.10. Found: C, 46.90; H, 5.47; N, 6.83%. IR (Nujol): 3198 ν(NH), 1717 ν(CO), 1572 and 1375 $\nu(CO_2)$, 1079, 1032, 655 $\nu(ClO_4)$ cm^{-1}. UV–Vis (λ_{max} DMF): 276 (log ε/dm^3 mol^{-1} cm^{-1} 3.979), 716 (2.445) nm. $\mu_B = 1.80$. $g_\perp = 2.05$, $g_\parallel = 2.22$.

2.3. Oxygenation of [Cu(fla)(idpaH)]ClO$_4$ in DMF

Complex **4** was dissolved in DMF under N_2 atmosphere in a thermostated reaction vessel with an inlet for taking samples. The solution was then heated to 100°C, and N_2 was replaced with dioxygen. The reaction was followed by electronic spectra in the range 200–500 nm. The consumption of [Cu(fla)(idpaH)]ClO$_4$ was analyzed periodically (about every 10 min) at 426.5 nm. In order to isolate **5**, 294 mg (0.5 mmol) of [Cu(fla)(idpaH)]ClO$_4$ was stirred in 50 cm^3 of DMF for 8 h, the solution was cooled to r.t. and diethyl ether was layered to afford blue powder of **5** (183 mg, 62%).

2.4. Physical measurements

Electronic spectra were recorded on a Shimadzu UV-160 (Carl Zeiss) spectrometer. IR spectra were taken as Nujol mulls using a Specord IR-75 (Carl Zeiss) spectrophotometer. Magnetic susceptibilities were determined at r.t. with a Bruker B-E 10B8 magnetic balance. EPR spectra were obtained with a Jeol JES-FE3X spectrometer. Microanalysis were carried out by Microanalytical Service of the University of Veszprém.

2.5. X-ray crystallography

Suitable crystals of **4** were obtained from acetonitrile solution upon standing at r.t. for a few days. Suitable crystals of **5** were grown by slow diffusion of diethyl ether into acetonitrile solution of the complex at −20°C. Data for both compounds were measured on a Siemens (Nicolet Syntex) R3m/V diffractometer with Mo Kα radiation using ω-scans. The data were corrected for Lorentz polarisation factors and experimental absorption (based on ψ-scans $\Delta\psi = 10°$) corrections were applied.

The crystal structures were solved by direct methods and refined by the full-matrix least-squares on F^2. The weighting scheme was $w^{-1} = s^2(F_o^2) + (aP)^2$ where $3P = (F_o^2 + 2F_c^2)$ and $a = 0.0618$ for **4** and 0.0828 for **5**. Form factors were taken from the usual sources [22]. Computations were carried out using SHELXL-93 [23] and SHELXS-86 [24] programs. Further details are given in Table 1.

Table 1
Crystal data and details of data collection and structure refinement for complexes **4** and **5**

	4	**5**
Formula	$C_{25}H_{34}N_3O_7CuCl$	$C_{24}H_{33}N_3O_8CuCl$
Molecular weight	587.54	590.52
Crystal system	monoclinic	triclinic
Temperature (K)	200	200
Wavelength (Å)	0.71073	0.71073
Monochromator	graphite	graphite
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.248(2)	7.880(3)
b (Å)	18.273(2)	12.721(3)
c (Å)	14.264(2)	14.390(4)
α (°)	90.0	71.01(2)
β (°)	98.59(1)	77.84(2)
γ (°)	90.0	75.42(2)
Volume (Å^3)	2641.1(7)	1306.9(7)
Z	4	2
Crystal size (mm)	0.30 × 0.30 × 0.25	0.20 × 0.25 × 0.20
Colour	green	blue
D_{calc} (g cm^{-3})	1.478	1.501
F(000)	1228	616
μ (mm^{-1})	0.977	0.991
2θ Range (°)	4.5–48.0	3.9–50.1
Index ranges	$-11 \leq h \leq -14$, $-16 \leq k \leq 11$, $20 \leq l \leq 16$	$-9 \leq h \leq -14$, $-16 \leq k \leq 9$, $14 \leq l \leq 17$
Reflections collected	4395	4939
Independent reflections	4142	4567
Observed data [$I > 2\sigma(I)$]	3252	2658
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0498, 0.1212	0.0795, 0.1657
(all data)	0.0698, 0.1308	0.1534, 0.2139
Goodness-of-fit	1.115	1.311

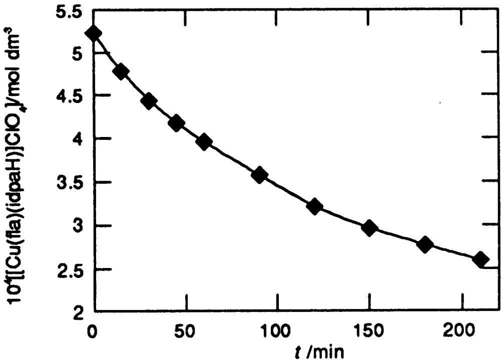


Fig. 1. Time course of the oxygenation of **4**. {[Cu(fla)(idpaH)]ClO$_4$}$_0$ = 10 × 10^{-4} M, [O$_2$] = 6.1 × 10^{-3} M, 50 cm^3 DMF, 120°C.

3. Results and discussion

3.1. Characterisation of the complex [Cu(fla)(idpaH)]ClO$_4$ (4)

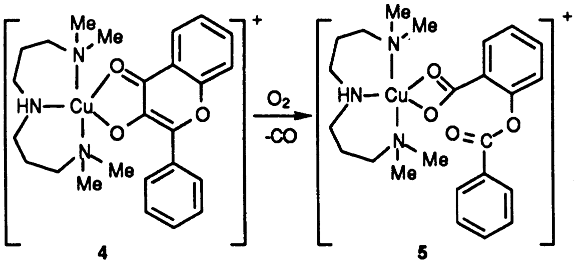
Complex **4** was isolated as a green solid by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, flavonol and 3,3′-iminobis(*N*,*N*-dimethylpropylamine) in the presence of piperidine at r.t. in methanol under an atmosphere of N_2, as summarised in Eq. (2):

$$Cu(ClO_4)_2 \cdot 6H_2O + flaH + idaH \xrightarrow[\text{piperidine}]{N_2,\ MeOH} \underset{\mathbf{4}}{[Cu(fla)(idpaH)]ClO_4} \quad (2)$$

The IR spectrum of complex **4** shows the principal band corresponding to the coordinated flavonolate at 1559 cm^{-1}. The decrease of approximately 40 cm^{-1} of the ν(CO) band compared to that of flavonol (ν(CO) 1602 cm^{-1}) is due to chelation and formation of a stable five-membered ring [25]. The absorption bands at 1095, 1055 and 631 cm^{-1} can be assigned to the perchlorate anion. The weak band at 3228 cm^{-1} can be rendered to the ν(NH) of the 3,3′-iminobis(*N*,*N*-dimethylpropylamine) ligand. The charge transfer region of the electronic spectrum of the complex exhibits band of the coordinated flavonolate ligand at 426.5 nm. The band at 690 nm is associated with the d-d transition of the complex. R.t. magnetic measurements yielded a value of $\mu_B = 1.85$ for **4** consistent with a copper(II) ion.

3.2. Oxygenation of complex [Cu(fla)(idpaH)]ClO$_4$

Treatment of the flavonolato copper complex **4** with dioxygen in DMF solution at elevated temperature leads to the corresponding O-benzoylsalicylato copper complex, [Cu(idpaH)(O-bs)]ClO$_4$, **5**. The oxygenation of **4** was followed by UV–Vis spectroscopy. The time course of the variation of [Cu(fla)(idpaH)]ClO$_4$ in DMF solution at 100°C is shown in Fig. 1. Plots of log[Cu(fla)(idpaH)]ClO$_4$ versus time showed a linear dependence under pseudo-first-order conditions (constant dioxygen pressure) in agreement with a rate equation of first-order dependence with respect to the complex **4**. The pseudo-first-order rate constant *k* was found to be $6.13 \pm 0.16 \times 10^{-3}$ mol^{-1} dm^3 s^{-1} at 100°C.



4 **5**

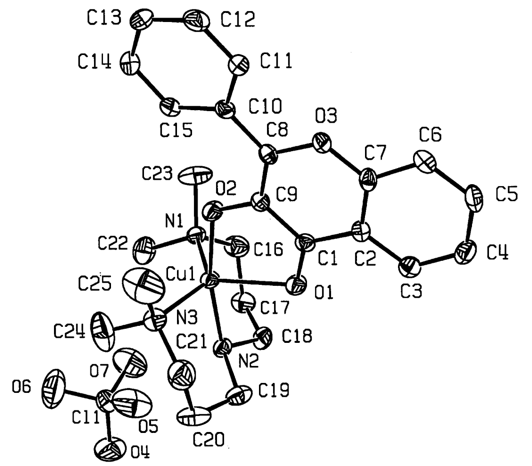


Fig. 2. Molecular structure of $[Cu(fla)(idpaH)]ClO_4$ (**4**).

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Cu(fla)(idpaH)]ClO_4$

Cu(1)–O(2)	1.918(3)	N(1)–C(22)	1.482(6)
Cu(1)–N(2)	2.006(4)	N(1)–C(16)	1.489(6)
Cu(1)–N(3)	2.112(4)	N(1)–C(23)	1.491(6)
Cu(1)–N(1)	2.137(3)	N(2)–C(18)	1.474(5)
Cu(1)–O(1)	2.210(3)	N(2)–C(19)	1.487(5)
O(1)–C(1)	1.260(5)	N(3)–C(24)	1.443(6)
O(2)–C(9)	1.320(5)	N(3)–C(25)	1.454(6)
O(3)–C(7)	1.365(5)	N(3)–C(21)	1.501(6)
O(3)–C(8)	1.369(5)	N(2)–H(2)	0.75(6)
C(1)–C(9)	1.436(6)	C(1)–C(2)	1.449(5)
C(2)–C(7)	1.378(6)	C(8)–C(9)	1.386(5)
O(2)–Cu(1)–N(2)	169.14(13)	C(1)–O(1)–Cu(1)	107.3(2)
O(2)–Cu(1)–N(3)	92.61(13)	C(9)–O(2)–Cu(1)	115.3(2)
N(2)–Cu(1)–N(3)	92.78(14)	C(22)–N(1)–Cu(1)	108.3(3)
O(2)–Cu(1)–N(1)	91.41(13)	C(16)–N(1)–Cu(1)	112.1(3)
N(2)–Cu(1)–N(1)	91.90(13)	C(23)–N(1)–Cu(1)	113.0(3)
N(3)–Cu(1)–N(1)	132.41(14)	C(18)–N(2)–Cu(1)	110.6(3)
O(2)–Cu(1)–O(1)	80.18(11)	C(19)–N(2)–Cu(1)	111.6(3)
N(2)–Cu(1)–O(1)	89.14(12)	C(24)–N(3)–Cu(1)	110.3(3)
N(3)–Cu(1)–O(1)	109.38(12)	C(25)–N(3)–Cu(1)	112.2(3)
N(1)–Cu(1)–O(1)	118.02(12)	C(21)–N(3)–Cu(1)	109.6(3)
Cu(1)–N(2)–H(2)	104.00(5)		

An oxidative cleavage of the C_2–C_3 double bond of the pyranone ring of the coordinated flavonolato ligand takes place in a similar fashion as in the enzymatic reaction.

3.3. *Characterisation of the complex $[Cu(idpaH)(O\text{-}bs)]ClO_4$ (5)*

The O-benzoylsalicylato complex was also prepared by the reaction of $[Cu(CH_3CN)_4]ClO_4$, O-benzoylsalicylic acid and 3,3′-iminobis(*N*,*N*-dimethylpropylamine) in acetonitrile under an atmosphere of O_2 at r.t.

The infrared (IR) spectrum of the complex shows bands corresponding to the coordinated O-benzoylsalicylate at 1717 ν(CO), 1572 and 1375 $\nu(CO_2)$ cm^{-1}. Absorption bands at 1079, 1032 and 655 cm^{-1} may be assigned to the perchlorate anion. The electronic spectrum of the complex **5** shows an absorption band at 716 nm due to d–d transition. A higher energy band at 276 nm is associated with charge transfer transition. R.t. magnetic measurements yielded a value of $\mu_B = 1.80$ for the complex consistent with a copper(II) ion. The solid state EPR spectrum of **5** is typical of a square pyramidal Cu(II) ion exhibiting an axial spectrum with $g_\perp = 2.05$ and $g_\parallel = 2.22$.

3.4. *X-ray crystal structures of complexes **4** and **5***

The molecular structure and atom numbering scheme for the crystalline complex **4** is shown in Fig. 2, and selected bond distances and angles are listed in Table 2. The geometry around the copper ion is distorted trigonal bipyramidal with $\tau = 0.61$. For perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity respectively, τ being an index of the degree of trigonality within the structural continuum between square pyramidal and trigonal bipyramidal geometries [26]. Two nitrogen atoms of the tridentate ligand idpaH (Cu(1)–N(1) 2.137(3), Cu(1)–N(3) 2.112(4) Å), and one oxygen atom of the flavonolate ligand (Cu(1)–O(1) 2.210(3) Å) occupy basal positions. The other oxygen atom of the flavonolate (Cu(1)–O(2) 1.918(3) Å), and one nitrogen of the 3,3′-iminobis(*N*,*N*-dimethylpropylamine) ligand (Cu(1)–N(2) 2.006(4) Å) are in apical positions. The Cu–O bond distances are comparable with those of the [Cu(fla)(ind)] (1.942(5), 2.206(5) Å) [27]. They are however longer than those in $[Cu(fla)_2]$ (1.901(2), 1.944(3) Å) [15]. The Cu–O(1) bond length is 0.29 Å longer than the Cu–O(2) bond. The C(9)–O(2) distance is shorter while the C(1)–O(1) distance is longer than those in the uncoordinated flavonol (1.357(3) and 1.232(3) Å) [28]. Due to coordination to the copper ion there are changes in the bond lengths of the pyranone ring too. The O(3)–C(8) (1.369(5) Å), C(7)–C(2) (1.378(6) Å) bond distances become longer, and the C(1)–C(9) bond distance (1.436(6) Å) is somewhat shorter which may be assigned to delocalisation of the π-system over the whole molecule. There is a weak N–H···O hydrogen bonding between the O(8) of the perchlorate anion and the N(2) of the idpaH ligand.

The molecular structure and atom numbering scheme for the crystalline complex **5** is shown in Fig. 3, and selected bond distances and angles are listed in Table 3. The molecule is monomeric in the solid state. The copper(II) centre is in distorted square-pyramidal environment ($\tau = 0.16$) with basal planes defined by three nitrogen atoms derived from the tridentate 3,3′-imino-

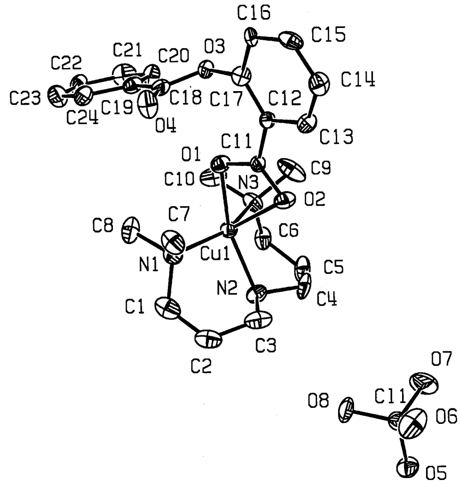


Fig. 3. Molecular structure of [Cu(idpaH)(O-bs)]ClO_4 (**5**).

Table 3
Selected bond lengths (Å) and bond angles (°) for [Cu(idpaH)(O-bs)]ClO_4

Cu(1)–O(1)	1.995(5)	N(1)–C(7)	1.477(10)
Cu(1)–N(2)	1.996(7)	N(1)–C(8)	1.497(10)
Cu(1)–N(1)	2.036(7)	N(2)–C(4)	1.481(10)
Cu(1)–N(3)	2.044(7)	N(2)–C(3)	1.497(11)
Cu(1)–O(2)	2.344(6)	N(3)–C(6)	1.466(10)
O(1)–C(11)	1.308(9)	N(3)–C(10)	1.476(11)
O(2)–C(11)	1.236(9)	N(3)–C(9)	1.480(11)
O(1)–Cu(1)–N(2)	159.5(3)	N(3)–Cu(1)–O(2)	101.9(2)
O(1)–Cu(1)–N(1)	91.1(3)	C(1)–N(1)–Cu(1)	111.2(5)
N(2)–Cu(1)–N(1)	94.9(3)	C(7)–N(1)–Cu(1)	115.3(5)
O(1)–Cu(1)–N(3)	90.1(3)	C(8)–N(1)–Cu(1)	104.7(5)
N(2)–Cu(1)–N(3)	94.4(3)	C(4)–N(2)–Cu(1)	107.6(6)
N(1)–Cu(1)–N(3)	149.9(3)	C(3)–N(2)–Cu(1)	105.2(5)
O(1)–Cu(1)–O(2)	60.3(2)	C(6)–N(3)–Cu(1)	110.6(5)
N(2)–Cu(1)–O(2)	99.2(2)	C(10)–N(3)–Cu(1)	102.7(5)
N(1)–Cu(1)–O(2)	104.7(2)	C(9)–N(3)–Cu(1)	116.3(5)

bis(*N*,*N*-dimethylpropylamine) ligand and one oxygen atom of the bidentate carboxylate group (Cu(1)–O(1) 1.995(5) Å). The apical position is occupied by the other oxygen atom of the O-benzoylsalicylate (Cu(1)–O(2) 2.344(6) Å). The copper–nitrogen bond distances (Cu(1)–N(1) 2.036(7), Cu(1)–N(2) 1.996(7), Cu(1)–N(3) 2.044(7) Å), are similar to values obtained for **4**. The Cu–O distance in the basal plane is 0.349 Å shorter than the distance of Cu to apical O. The Cu–O(1) distance is shorter while the Cu–O(2) length is longer than those in [Cu(O-bs)$(PPh_3)_2$] (2.148(2) and 2.280(2) Å) [29].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 142157, 142158. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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