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Synthesis and characterization of copper(I) and copper(II) flavonolate complexes with phthalazine ligand, and their oxygenation and relevance to quercetinase

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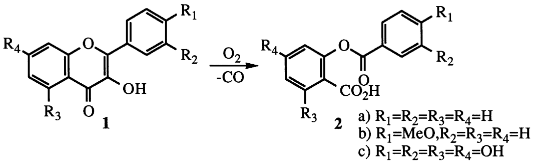
Abstract

Copper(I) and copper(II) flavonolate (fla) complexes with 1,4-(di-2′-pyridyl)aminophthalazine ligand ($PAPH_2$) have been prepared by the reaction of copper salts with flavonol and the ligand in acetonitrile or dichloromethane. The copper(II) centers are bound to the tetradentate phthalazine ligand resulting in both mononuclear and binuclear complexes. Flavonol is oxygenated to the corresponding depside catalyzed by flavonolato copper(II) phthalazine complexes.

Keywords: Copper complexes; Flavonolate complexes; Phthalazine complexes

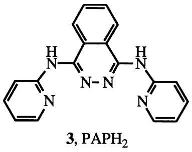
1. Introduction

The degradation of quercetin (**1c**, 3′,4′,5,7-tetrahydroxyflavonol) in living systems to the corresponding depside (**2c**) and carbon monoxide is performed by the dioxygenase quercetinase (Eq. (1)) [1–4].



(1)

The catalytic center of this enzyme contains copper(II) ion, but the ligand environment around Cu^{II} has not been encountered. Studies on structural and functional models have been carried out to elucidate the mechanism of the reaction. Base catalyzed oxygenation of quercetin and related 3-hydroxyflavones under aqueous [5] and non-aqueous [6] conditions, photosensitized oxygenations [7] and reaction with superoxide [8] have been investigated. Co(salen) proved a good catalyst in the oxygenation of flavonols [9,10]. Copper(I) [11] and copper(II) [12] flavonolate complexes with simple ligands were also successfully used for the oxygenation of flavonols. Aminophthalazines have been shown to form mononuclear and binuclear complexes with copper, cobalt, nickel and zinc salts [13–21]. Catecholase and phenolase activity was reported for some copper(II) phthalazine derivatives [13,14]. Here we report the preparation of some copper(I) and copper(II) flavonolate complexes with 1,4-(di-2′-pyridyl)aminophthalazine ($PAPH_2$, **3**) ligand and their catalytic activity in the oxygenation of flavonol.



3, $PAPH_2$

2. Experimental

Solvents used for the reactions were purified by literature methods [22] and stored under argon. 3-Hydroxyflavone [5], 3-hydroxy-4′-methoxyflavone [5], $PAPH_2$ [21], mesityl copper(I) [23], $Cu(OMe)_2$ [24] and $[Cu(CH_3CN)_4]ClO_4$ [25] were prepared by literature methods.

2.1. Preparation of $[Cu_2(ClO_4)_2(fla)_2(PAPH_2)]$ (4a)

$[Cu(CH_3CN)_4]ClO_4$ (0.328 g, 1 mmol) was dissolved in acetonitrile (20 ml). Flavonol (**1a**) (0.238 g, 1 mmol) and

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$PAPH_2$ (0.158 g, 0.5 mmol) were added and stirred under argon for 1 h and then under dioxygen for 4 h. A light yellow crystalline solid formed, which was filtered, washed with acetonitrile and dried in vacuum (0.48 g, 88%). The product was recrystallized from acetonitrile. Compound **4b** was prepared similarly using 4′-methoxyflavonol (**1b**). Attempts to obtain suitable single crystals of the compounds **4a** or **4b** for X-ray analysis failed and only thin needles could be obtained.

2.2. Preparation of $[Cu_2(fla)_2(PAP)]$ (5a)

A mixture of $Cu(OMe)_2$ (0.126 g, 1 mmol), flavonol (0.238 g, 1 mmol) and $PAPH_2$ (0.158 g, 0.5 mmol) in dichloromethane (30 ml) was refluxed under argon for 4 h. The dark red solution was allowed to stand for one night. The red crystalline product was filtered, washed with dichloromethane and dried under vacuum. Compound **6a** was prepared in a similar manner reacting equimolar amounts of reagents at room temperature. Compounds **5b** and **6b** were prepared similarly from 4′-methoxyflavonol.

2.3. Preparation of $[Cu_2(fla)_2(OH)(PAPH)]$ (7a)

A mixture of $[Cu(mes)]_5$ (0.183 g, 0.2 mmol), flavonol (0.238 g, 1 mmol) and $PAPH_2$ (0.158 g, 0.5 mmol) in acetonitrile (30 ml) was stirred at room temperature under dioxygen for 2 h. The orange product was filtered, washed with acetonitrile and dried. Compound **8a** was prepared similarly, reacting equimolar amounts of reagents under argon. Compounds **7b** and **8b** were prepared in a similar way from 4′-methoxyflavonol.

2.4. Reaction of flavonol with dioxygen in the presence of copper flavonolate complexes

In a typical procedure, to a solution of $[Cu_2(ClO_4)_2(fla)_2(PAPH_2)]$ (0.111 g, 0.1 mmol) in DMF (20 ml) flavonol (0.119 g, 0.5 mmol) was added and the mixture stirred under dioxygen at 100°C for 8 h. GC analyses were made to determine the conversion of the substrate. GC analyses of the solution after treating with an ether solution of diazomethane gave the yields of the products. Products were identified by comparison of their mass spectra with reference spectra [12].

The catalytic reactions were also followed by electronic spectra in the range 50 000–20 000 cm^{-1}. In these experiments the copper complex and flavonol were dissolved under argon atmosphere in DMF, and the solution was heated to 100°C. The argon was then replaced with dioxygen and consumption of flavonol was analyzed periodically (about every 10 min) at 29 069 cm^{-1}.

2.5. Physical measurements

Electronic spectra were recorded with a Shimadzu UV-160 (Carl Zeiss) spectrometer, and IR spectra with a Specord IR-75 (Carl Zeiss) spectrometer. Magnetic susceptibilities were determined at room temperature with a Bruker B-E 10B8 magnetic balance. EPR spectra were obtained with a JEOL JES-FE3X spectrometer. Electrochemical measurements were carried out under argon atmosphere at room temperature in acetonitrile with 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte, using platinum working electrode, platinum auxiliary electrode and Ag/AgCl reference electrode with a BAS CV-1B cyclic voltammograph. Potentials are given relative to SCE referenced to the internal ferrocene/ferrocenium potential taken as 0.425 V [26]. GC analyses were performed on an HP 5830A gas chromatograph equipped with a flame ionization detector and CP SIL8CB column. GC-MS measurements were recorded on an HP 5890 II, 5971 GC/MSD at 75 eV. Analytical data for the complexes are given in Table 1.

3. Results and discussion

3.1. Characterization of the complexes

In a series of binuclear copper(I) and copper(II) complexes involving tetradentate aminophthalazine ligands the metal centers are bridged by a diazine entity (=N–N=).

By reacting molar quantities of $[Cu(CH_3CN)_4]ClO_4$, flavonol or 4′-OMe-flavonol and a half mole quantity of $PAPH_2$ in acetonitrile with dioxygen at room temperature the complexes $[Cu_2(ClO_4)_2(fla)_2(PAPH_2)]$ (**4a**) and $[Cu_2(ClO_4)_2(4'\text{-MeOfla})_2(PAPH_2)]$ (**4b**) were obtained. Compounds **4a** and **4b** have very similar IR and electronic spectra. The presence of a π–π^* charge transfer absorption above 26 000 cm^{-1} has been used to indicate the presence of neutral $PAPH_2$, while the observation of a single band below 26 000 cm^{-1} implies an anionic ligand [21]. Compound **4a** and **4b** have charge transfer absorption at 30 200 and 29 400 cm^{-1} (Table 2), implying the presence of the neutral $PAPH_2$ ligand. The band at 24 783 cm^{-1} indicates the presence of the flavonolate ligand [12]. The very weak band at 12 000 cm^{-1} can be assigned to a d–d transition in the copper(II) centers. In the IR spectra single NH stretching absorption occurs at 3315 and 3340 cm^{-1}, suggesting the presence of one type of NH group. The ligand is therefore expected to exist in the tautomeric form **3**. Two bands associated with CN stretching frequencies of the neutral ligand are observed above 1600 cm^{-1}. Similar absorptions were obtained for copper tetrafluoroborate $PAPH_2$ complexes [18]. Previous studies have shown that the presence of an IR band above 1000 cm^{-1}, associated with the ring breathing mode of the pyridine ring in $PAPH_2$, indicates the coordination of this group to the metal centers [21]. Absorptions at 1011 and 1020 cm^{-1} indicate the tetradentate coordination of the $PAPH_2$ ligand in both complexes. The strong absorption at 1557 cm^{-1} in **4a** can be assigned to ν_{CO} of the coordinated flavonolate ligand. The decrease of ~ 40 cm^{-1} of the ν_{CO} band compared to that of flavonol is due to chelation and formation of a stable five-membered ring [12]. Two major

Table 1
Characterization of flavonolato copper phthalazine complexes

Complex	M.p. (°C)	Color	Yield (%)	Analytical data [a] (%)		
				C	H	N
4a [Cu$_2$(ClO$_4$)$_2$(fla)$_2$(PAPH$_2$)]	298–300	yellow	88	51.80	2.79	7.65
				(51.71)	(2.89)	(7.54)
4b [Cu$_2$(ClO$_4$)$_2$(4′MeOfla)$_2$(PAPH$_2$)]	290–294	yellow	84	50.72	3.04	6.99
				(51.11)	(3.08)	(7.15)
5a [Cu$_2$(fla)$_2$(PAP)]	300–304	red	75	62.97	3.19	9.25
				(63.08)	(3.31)	(9.19)
5b [Cu$_2$(4′MeOfla)$_2$(PAP)]	305–308	red	72	59.45	3.33	8.67
				(60.69)	(3.61)	(8.84)
6a [Cu(fla)(PAPH)]	193–195	orange	73	64.40	3.40	13.40
				(64.53)	(3.61)	(13.68)
6b [Cu(4′MeOfla)(PAPH)]	196–198	orange	68	63.20	3.90	12.81
				(63.39)	(3.75)	(13.05)
7a [Cu$_2$(fla)$_2$(OH)(PAPH)]	245–250	orange	74	61.77	3.47	8.94
				(61.86)	(3.46)	(9.02)
7b [Cu$_2$(4′MeOfla)$_2$(OH)(PAPH)]	235–240	orange	76	60.30	3.66	8.61
				(60.53)	(3.65)	(8.47)
8a [Cu(fla)(PAPH$_2$)]	190–195	yellow	82	64.21	3.57	13.32
				(64.44)	(3.76)	(13.65)
8b [Cu(4′MeOfla)(PAPH$_2$)]	205–210	yellow	85	62.97	3.78	12.83
				(63.29)	(3.90)	(13.02)

[a] Theoretical values in parentheses.

IR absorptions are observed at 1103 and 1060 cm^{-1} associated with the perchlorate group, suggesting that the anion is coordinated to copper [20]. For complexes **4a** and **4b** slightly reduced room temperature magnetic moments are observed (Table 2), indicative of systems involving weak antiferromagnetic exchange between the metal centers. Efficient bridging exchange groups are therefore considered to be absent in these complexes. EPR spectra recorded on solid samples

Table 2
Spectroscopic data of flavonolato copper phthalazine complexes

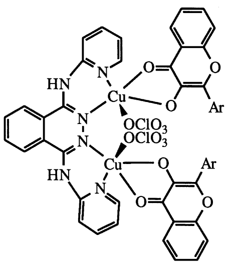
Complex	Infrared (cm^{-1}) (Nujol)	UV–Vis (cm^{-1}) (DMF)	μ_{eff} [b] (BM) (r.t.)	g [c]
4a	3315(NH), 1634, 1612(CN), 1557(CO) 1103, 1068(ClO$_4$), 1011(py)	38240(61960), 30211(28870), 24783(32160)	1.56	2.1263
4b	3340(NH), 1637, 1605(CN), 1556(CO) 1107, 1060(ClO$_4$), 1020(py)	38610(75060), 29411(30780), 24570(31220)	1.65	2.1346
5a	1614(CN), 1541(CO), 1012(py)	37878(48709), 30120(28058), 24154(32828), 23068(34900), 21367(26094), 12836(67) [a]	1.83	2.1132
5b	1608(CN), 1549(CO), 1004, 1020(py)	38314(27183), 29673(15020), 24096(17890) 23063(18670), 21505(12670)	1.74	2.1265
6a	3360(NH), 1614(CN), 1541(CO), 1024w, 1004s(py)	37593(30676), 27173(15527), 25445(19896), 24509(20065), 23255sh(13800)	1.71	2.0787 [d]
6b	3400(NH, 1608(CN), 1548(CO), 1028s, 1008s(py)	37593(26639), 26954(16149), 25773(16770) 24509(15596), 23207sh(11042)	1.65	2.0958
7a	3310(NH), 1614(CN), 1545(CO) 1028w, 1003s(py)	37593(41887), 30211(25000), 24242(32244) 23174(31580)	1.41	2.1170
7b	3330(NH), 1608(CN), 1545(CO) 1031s, 1003w(py)	37593(44857), 29717(26250), 23809(34642) 23014(37178)	1.39	2.1273
8a	3227(NH), 1614(CN), 1558(CO) 1016w, 988s(py)	38161(37887), 29325(18616), 27359(18926) 25641(20236), 24509(20581)	diam.	
8b	3231(NH), 1621(CN), 1548(CO) 1028s, 994s(py)	37593(28952), 28571(16544), 25773(18805) 24390(19944)	diam.	

[a] CH_2Cl_2.
[b] μ_{eff} per copper atom.
[c] Solid sample.
[d] In CH_3CN, $g_{\perp} = 2.0504$, $g_{\parallel} = 2.2384$, $A_{\mathrm{N}} = 16.5$ G.

show isotropic spectra, which are not very informative; they are listed in Table 2. Cyclic voltammetry of complex **4a** (−0.295 and −0.635 V versus SCE) and of **4b** (−0.325 and −0.725 V versus SCE) gave two redox waves at negative potentials, which may be associated with two-step, one-electron transfers. Similar results were obtained for binuclear copper(II) complexes with a macrocyclic ligand (−0.52 and −0.91 V versus SCE) [27]. Spectroscopic and other data indicate complexes **4a** and **4b** to be binuclear involving two five-coordinate copper(II) centers bound to the same $PAPH_2$ ligand, two flavonolate ligands, and two monodentate perchlorates (Fig. 1). The involvement of the perchlorate anion in the coordination is not unusual. Five-coordinate copper(II) centers and a monodentate perchlorate were proposed for the $[Cu_2(PAPH)(OH)_2(H_2O)(ClO_4)]$ [20] and $[Cu(bpy)(fla)(ClO_4)]$ [28] complexes.

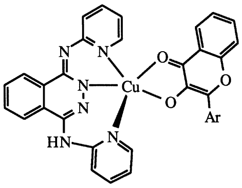
Compund **5a** has charge transfer bands at 23 068 and 21 367 cm^{-1}, suggesting the presence of the deprotonated PAP ligand. The band at 24 154 cm^{-1} is associated with flavonolate. The presence of a weak d–d band at 12 800 cm^{-1} is structurally not very informative. The pyridine ring breathing absorption in the IR spectrum at 1012 cm^{-1} is characteristic of tetradentate coordination of the PAP ligand. The IR band for ν_{CO} of the flavonolate is at 1541 cm^{-1}. A four-coordinate, binuclear structure is expected for this compound. The magnetic moment supports this structure. Cyclic voltammetry of the complex shows a one-step redox process at positive potential (0.675 V versus SCE). Positive redox potentials have been obtained for binuclear copper(II) complexes of cryptate ligands [29,30] and other ligands with NS donor sets [31], which have magnetically isolated metal centers without an oxygen bridging group. The binuclear, hydroxo-bridged copper(II) complexes of some quadridentate pyridazine and phthalazine thioether ligands exhibit two-electron transfer at positive potentials as well [14,15]. For the other complexes rather poorly defined cyclic voltammograms were obtained. Compound **5b** is suggested to have a similar structure.

In the reaction between equimolar amounts of $Cu(OMe)_2$, flavonol and $PAPH_2$ in dichloromethane an orange product, **6a**, is formed. Compound **6a** contains the deprotonated PAPH ligand and flavonolate (Table 2). The very weak band at 11 100 cm^{-1} can be assigned to a d–d transition. The IR band at 1004 cm^{-1} can be assigned to coordinated pyridine. $PAPH_2$ exhibits a pyridine ring breathing absorption at 987 cm^{-1}. Thus both pyridine residues of the ligand are coordinated to copper. The strong absorption at 1541 cm^{-1} shows coordination of the flavonolate [12]. A five-coordinate structure is suggested for compound **6a**, with deprotonated PAPH and one flavonolate ligand (Fig. 2). This structure requires the PAPH ligand to be tridentate [21]. The ambient temperature EPR spectrum is isotropic, whilst in acetonitrile at low temperature an axial spectrum was obtained, very similar to that obtained for pentacoordinate copper complexes of nitrogen-donor ligands [32]. Compound **6b** is believed to have a similar structure.



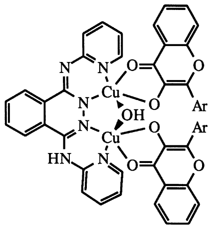
4a, Ar = Ph
4b, Ar = 4-MeOPh

Fig. 1. Proposed structure for complexes **4a** and **4b**.



6a, Ar = Ph
6b, Ar = 4-MeOPh

Fig. 2. Proposed structure for complexes **6a** and **6b**.



7a, Ar = Ph
7b, Ar = 4-MeOPh

Fig. 3. Proposed structure for complexes **7a** and **7b**.

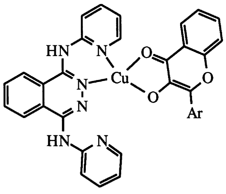
Compound **7a** was prepared by the reaction of $[Cu(mes)]_5$, flavonol and $PAPH_2$ in acetonitrile. The charge transfer region of the electronic spectra exhibits bands of an anionic PAPH and a flavonolate ligand. The weak d–d band at 11 400 cm^{-1} is structurally not very informative. The IR band at 1545 cm^{-1} shows the coordination of the flavonol. The band at 1003 cm^{-1} indicates the tetradentate coordination of PAPH. For complex **7a** a reduced room temperature magnetic moment was observed, due to antiferromagnetic exchange between copper(II) centers. Considerably reduced magnetic moments are observed for $PAPH_2$ complexes where the copper centers are bridged by oxygen groups, e.g. methoxide or hydroxide [15]. A rather broad weak absorption around 3600 cm^{-1} is associated with the hydroxide bridge. Considering all the data, complex **7a** can be represented as a binuclear system involving two five-coordinate copper(II) centers, a tetradentate PAPH, two flavonolate and a hydroxide bridge (Fig. 3). Compound **7b** is assumed to have a similar structure.

Reacting molar quantities of $[Cu(mes)]_5$, flavonol and $PAPH_2$ in acetonitrile under argon a diamagnetic compound, **8a**, was obtained. The π–π^* transition at 25 641 cm^{-1} indicates the presence of the neutral $PAPH_2$ ligand. The band at 24 509 cm^{-1} is associated with flavonolate. The IR band at 1016 cm^{-1} can be assigned to the ring breathing absorption of coordinated pyridine. The band at 988 cm^{-1} shows that one pyridine ring of the $PAPH_2$ ligand is not coordinated. The coordination of the flavonol is expected from the ν_{CO} at 1558 cm^{-1}. A mononuclear structure with four-coordinate

Table 3
Oxygenation of flavonol by flavonolato copper(II) phthalazine complexes

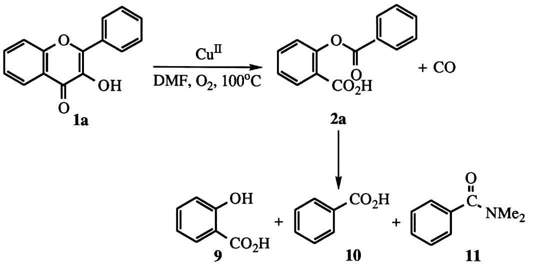
Complex	Time (h)	Solvent	Conversion [a] (%)	Products [a] (%)			
				2a	**9**	**10**	**11**
[$Cu_2(ClO_4)_2(fla)_2(PAPH_2)$] (**4a**)	8	DMF	87	4	48	18	30
[$Cu_2(fla)_2(PAP)$] (**5a**)	8	DMF	100	27	36	20	17
[$Cu_2(fla)_2(PAPH)(OH)$] (**7a**)	8	DMF	69	32	34	25	9
[Cu(fla)(PAPH)] (**6a**)	8	DMF	27	48	26	18	8

[a] Determined by GLC.



8a, Ar = Ph
8b, Ar = 4-MeOPh

Fig. 4. Proposed structure for complexes **8a** and **8b**.



Scheme 1.

copper(I) is expected for complex **8a** (Fig. 4). A similar structure is suggested for compound **8b**.

3.2. Dioxygenation of flavonol by flavonolato copper(II) phthalazine complexes

Catalytic oxygenation of flavonol was carried out using the flavonolato copper(II) phthalazine complexes discussed before. Conversions and composition of the products are shown in Scheme 1 and Table 3.

We find now that the oxygenation of flavonol using flavonolato copper(II) phthalazine catalysts results in oxidative cleavage of the heterocyclic ring to give depside (**2a**) and CO as primary products. Secondary products derived from **2a** such as salicylic acid (**9**), benzoic acid (**10**) and *N,N*-dimethylbenzamide (**11**) due to hydrolysis and amidation of **2a** by DMF were also formed. The oxidation is selective, no other products were obtained. Different products were obtained in the oxidation of flavonol catalyzed by CuCl and $CuCl_2$ [33,34]. It can be seen from these results that binuclear complexes are better and more selective catalysts than mononuclear ones. The time dependence of the consumption of flavonol in some of the oxygenation reactions was followed also spectroscopically (Fig. 5). Preliminary kinetic measurements of the oxygenation reactions show that the flavonolato copper(II) phthalazine complexes have a different behavior (**6a** versus **4a**, **5a, 7a**) which may be explained by mononuclear or binuclear catalysis. However a detailed kinetic investigation is necessary to disclose these mechanistic differences in the catalytic processes. These are now in progress in our laboratory. The oxygenation results show however that copper flavonolate complexes containing phthalazine N-donor ligands catalyze the oxidative cleavage of 3-hydroxyflavone leading to identical products to those found in the enzyme reaction.

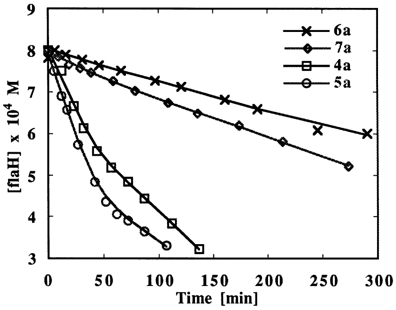


Fig. 5. Time dependence of the consumption of flavonol during the catalytic oxidation with flavonolato copper phthalazine complexes. $[Cu]_0 = 0.5 \times 10^{-4}$ M, $[flaH]_0 = 8 \times 10^{-4}$ M, $p_{O_2} = 1$ bar, 100°C, DMF.

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