Keywords: alkynes · allenes · butadienes · pericyclic reactions · rearrangements

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An Iron(III) – Catechol Complex as a Mushroom Pigment**

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Dedicated to Prof. Heinrich Nöth on the occasion of his 70th birthday

Cortinarius violaceus [(L.: Fr.) S. F. Gray][1] is a spectacular mushroom well known for its dark blue-violet color and its cedar-wood-like smell. Fries[2] described this type species of the genus *Cortinarius* as "species nobilissima, pulcherrima". Previous efforts to examine the chemical nature of the violet pigment failed because of its instability and polarity. The dark violet water extracts of fresh or freeze-dried fruit bodies became dark brown within minutes. We were able to suppress this decomposition by exhaustive extraction of the lyophilized mushrooms with methanol prior to the water extraction. After freeze-drying the resulting aqueous solution, the residue was purified by chromatography on a Sephadex LH-20 column with methanol/water (1/1). This procedure enabled us to enrich the highly sensitive pigment. The pigment's NMR spectra were inconclusive due to strong signal broadening by paramagnetic iron, which can be detected both in the extract and the mushrooms. Since the intensity of the violet color correlates with the concentration of iron, the presence of an iron complex as the coloring principle seems obvious.

Energy dispersive X-ray analysis[3] (EDX), atomic absorption spectroscopy[4] (AAS), and the thiocyanate test indicated that *C. violaceus* is capable of accumulating iron in a unique manner. The amount of iron in the mushroom is 4.5 – 7.5 mg g^{-1} (dry weight), which is about 100 times the average value of 0.06 mg g^{-1} determined for other basidiomycetes.[5, 6] The Mössbauer spectra[7] (Figures 1 and 2, Table 1) show that the iron in the pigment is trivalent, and the ESR spectra[8] indicate a high-spin Fe^{III} complex.[9] The spectra of the freeze-dried mushrooms and the water extracts are identical.

After addition of aqueous HCl to the enriched pigment (*R*)-*β*-dopa ((*R*)-**3**) can be identified as the complex ligand.[10] Chromatographic workup of the methanol extracts followed by recrystallization yields the analytically pure amino acid. The (*R*)-*β*-dopa amounts to 2% of the dry weight of the mushroom. *β*-Dopa is a new natural product that has been synthesized only as the racemate before.[11] We obtained

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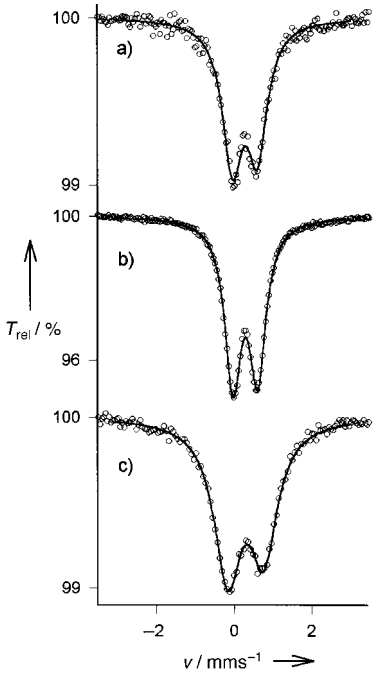


Figure 1. Mössbauer spectra at room temperature. a) Freeze-dried *C. violaceus*; b) water extract; c) synthetic 1:2 iron(III)–β-dopa complex at pH 6.2. T_{rel} = relative transmission.

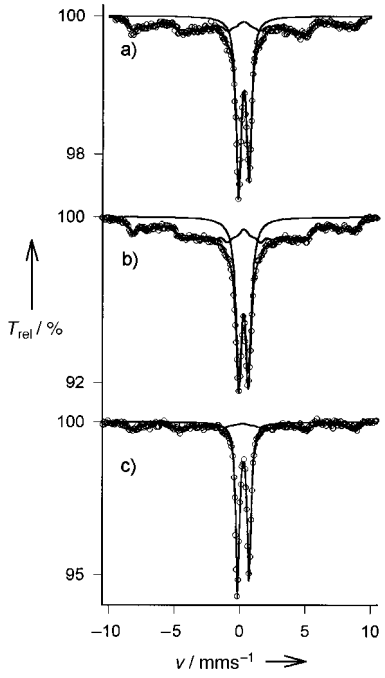


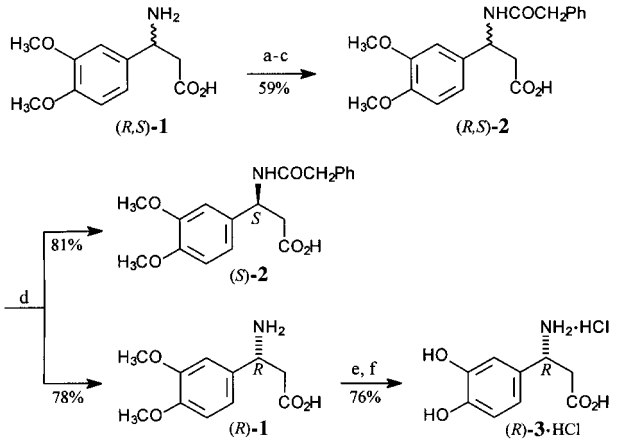
Figure 2. Mössbauer spectra at 4.2 K. a) Freeze-dried *C. violaceus*; b) water extract; c) synthetic 1:2 iron(III)–β-dopa complex at pH 6.2.

(*R*)-**3** from racemic (*R*,*S*)-3-amino-3-(3,4-dimethoxyphenyl)-propionic acid (**1**), which is easily accessible by Rodionov's procedure.[12] After conversion of (*R,S*)-**1** into the *N*-phenylacetyl derivative **2**, the action of penicillin acylase[13] yields optically pure (*R*)-**1**. Ether cleavage with 48% HBr affords (*R*)-β-dopa hydrobromide, which can be converted into the corresponding hydrochloride by ion exchange (Scheme 1).

Table 1. ^{57}Fe Mössbauer parameters[21] for the quadrupole doublets at room temperature and at 4.2 K. Quadrupole splitting *QS*; isomer shift *IS*; line width *LW*.

Sample	*T* [K]	QS [mm s^{-1}]	*IS*[a] [mm s^{-1}]	*LW* [mm s^{-1}]	Area[b] [%]
(a) freeze-dried	4.2	0.80(1)	0.38(1)	0.45(1)	50(1)
C. violaceus	294	0.64(1)	0.39(1)	0.62(2)	100
(b) water extract	4.2	0.74(1)	0.38(1)	0.53(1)	43(1)
	294	0.64(1)	0.40(1)	0.51(1)	100
(c) synthetic 1:2 Fe^{III}–	4.2	0.89(1)	0.40(1)	0.33(1)	70(1)
β-dopa complex (pH 6)	294	0.94(2)	0.41(1)	0.85(3)	100

[a] The isomer shifts refer to α-Fe. [b] The spectra recorded at 4.2 K show (in addition to the quadrupole doublet with the given fractional area) a magnetically split component with a distribution of hyperfine fields between 52.5(2) and 13.5(3) T, an effective quadrupole splitting of QS = 0.02(2) mm s^{-1} and an isomer shift of IS = 0.38(2) mm s^{-1}.



Scheme 1. Synthesis of (*R*)-**3**. a) MeOH, cat. HCl, reflux; b) $PhCH_2COCl$, CH_2Cl_2, NEt_3, cat. DMAP; c) LiOH, H_2O/MeOH (1/1); d) penicillin acylase, pH 7.5, phosphate buffer, 25 °C, 12 h; e) 48% HBr, 145 °C, 4 h; f) Dowex 50 WX8. DMAP = 4-dimethylaminopyridine.

Since comparison of the specific optical rotations of the natural and the synthetic products was ambiguous, the absolute configuration and optical purity of the natural ligand were determined by GC/MS.[14] For this purpose, natural β-dopa was O-methylated with diazomethane and subsequently acylated with Mosher's (*R*)-acid chloride.[15] The derivatives obtained from the natural and the synthetic amino acid were identical.[16] Within the scope of this method the natural product was enantiomerically pure.

The UV/Vis spectrum of the enriched pigment at pH 6.2, the physiological pH value of the mushroom, exhibited a ligand-to-metal charge-transfer (LMCT) absorption of λ_{max} = 571 nm, which is typical for iron(III)–catechol complexes. At pH 9.0 a hypsochromic shift to λ_{max} = 487 nm is observed. The blue-violet solution changes to bordeaux and decomposes quickly. Addition of KCN or ethylenediaminetetraacetic acid (EDTA) to the original solution causes discoloration.

The behavior of the pigment is consistent with that of other iron(III)–catechol complexes, in which the cation:ligand ratio depends on the pH value. An increase in the pH value leads to the typical color changes from green (pH 3, 1:1)[17] to blue-violet (pH 6, 1:2) and finally bordeaux (pH 9, 1:3; Figure 3). The UV/Vis data of iron(III)–dopamine[18] and iron(III)–

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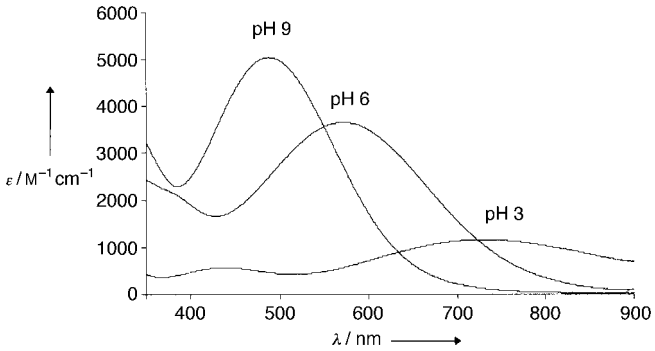
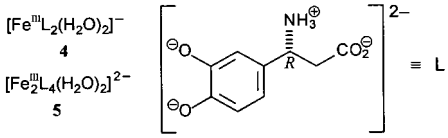


Figure 3. UV/Vis spectra of the synthetic iron(III)–β-dopa complex in water.

catechol complexes[19, 20] at various pH values are in close agreement with those of our pigment.

The experimental evidence indicates that the pigment from *C. violaceus* is an iron–ligand 1:2 complex; however, it cannot be determined if it is mono- or binuclear (**4** or **5**, Scheme 2).



Scheme 2. Proposals for the blue-violet 1:2 iron(III)–β-dopa complex species present in *C. violaceus* at pH 6.2.

The Mössbauer spectra[21] of the pigment are in good agreement with those of a binuclear 1:2 iron(III)–catechol complex,[22] whose structure has been established by X-ray analysis.[22] Neither mass spectroscopic methods nor chiroptical measurements led to a more detailed insight into the structure of the natural complex. The analogy of our pigment to an iron ink is clear. To the best of our knowledge, pigments of this type have not yet been discovered in nature.[23, 24]

Experimental Section

Isolation of (*R*)-**3**: Powdered, freeze-dried fruit bodies (12.7 g) of *C. violaceus* (collected in September 1996 in a spruce forest near Gilching, Oberbayern, Germany) were defatted with CH_2Cl_2 (200 mL) for 2 d and then extracted exhaustively with MeOH. After concentration of the extracts, the residue (5.1 g) was purified by chromatography on a Sephadex LH-20 column (40 × 8 cm) with MeOH. Fractional recrystallization of the crude material from dry MeOH removed sugar impurities and yielded analytically pure (*R*)-**3** (41 mg, 0.3 % of dry weight).

Isolation of (*R*)-**3**·HCl: The MeOH extracts (see the isolation of (*R*)-**3**) were purified by chromatography on a cation-exchange column (Dowex 50 WX8, H^+ form). After washing with water (300 mL) the ligand was eluted with 4 N HCl (100 mL). Further purification on Dowex 50 WX8 yielded (*R*)-**3**·HCl as a hygroscopic, beige foam (0.27 g, 2 % of dry weight).

Enrichment of the blue-violet pigment: After the treatment with MeOH, the mushroom residues were extracted with H_2O (200 mL) at 25 °C for 20 min under argon. The resulting deep blue-violet solution was freeze-dried and purified by chromatography repeatedly on Sephadex LH-20 (H_2O/MeOH/0.1 % KOH 25/25/1). Yield of pigment 15 mg, 0.1 % of dry weight.

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[10] (*R*)-**3**: M.p. 194 °C; $[\alpha]_{589}^{23} = -12.1$ ($c = 0.5$ in 6 N HCl); R_f: 0.45 (*n*BuOH/EtOH/AcOH/H_2O 4/1/1/1); IR (KBr): $\tilde{\nu} = 3400$ (br), 3043 (s), 1608 (m), 1571 (s, CO_2^-), 1531 (s), 1466 (s), 1392 (s), 1361 (m), 1281 (m), 1250 (s), 1197 (w), 1173 (m), 1126 (m), 1042 (w), 986 (w), 948 (w), 929 (w), 868 (w), 818 (w), 792 (w), 775 (w), 696 (w), 650 (w), 595 (w), 573 (w), 460 cm^{-1} (w); ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 2.30$ (dd, $J = 16.1$, 3.9 Hz, 1H; CH^{α}H$^{\beta}$), 2.41 (dd, $J = 16.0$, 10.0 Hz, 1H; CH$^{\alpha}H^{\beta}$), 4.14 (dd, $J = 9.6$, 3.8 Hz, 1H; ArCHN), 6.65 (dd, $J = 8.0$, 1.7 Hz, 1H; 6-H), 6.69 (d, $J = 8.0$ Hz, 1H; 5-H), 6.83 (s, 1H; 2-H); ^{13}C NMR (151 MHz, [D$_6$]DMSO): $\delta = 40.83$ (CH_2), 51.90 (ArCHN), 114.81 (C-2), 115.75 (C-5), 117.94 (C-6), 130.27 (C-1), 145.59 (C-4), 145.61 (C-3), 173.68 (CO_2H); EI-MS (decomposition, 70 eV): *m*/*z* (%): 180 (7) [$M - NH_3$]$^+$, 136 (100) [$M - NH_3 - CO_2$]$^+$; FAB-MS (glycerol): *m*/*z* (%): 198 (45) [M+H]$^+$, 181 (56), 171 (100), 153 (58), 136 (35); ESI-MS: *m*/*z* (%): 220 (8) [M+Na]$^+$, 198 (34) [M+H]$^+$, 181 (100), 171 (5), 163 (4), 139 (61); ESI-HR-MS: calcd for $C_9H_{12}NO_4$: 198.0766; found: 198.0767; elemental analysis calcd for $C_9H_{11}NO_4 \cdot \frac{1}{3}H_2O$: C 53.20, H 5.79, N 6.89; found: C 53.29, H 5.74, N 7.02. Tris(trimethylsilyl)-(*R*)-β-dopa: GC: $R_i = 2105$; GC/MS (70 eV): *m*/*z* (%): 413 (8) [M^+], 398 (2) [$M - CH_3$]$^+$, 396 (2) [$M - NH_3$]$^+$, 381 (1), 282 (100) [$M - CH_2CO_2Si(CH_3)_3$]$^+$, 268 (5), 210 (6), 194 (5), 167 (3), 147 (3), 117 (3), 75 (20) [$HOSi(CH_3)_2$]$^+$, 73 (49) [$Si(CH_3)_3$]$^+$; HR-GC/MS: calcd for $C_{18}H_{35}NSi_3O_4$: 413.1874, found: 413.1889.
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[21] At 4.2 K the Mössbauer spectra of the natural samples show, in addition to the quadrupole doublet, a broad background caused by magnetic hyperfine splitting. The magnetic component is assigned to iron hydroxides, and it increases with the ageing of the mushrooms. The strongly broadened Mössbauer spectra observed at room temperature are caused by a superposition of the quadrupole doublet of the iron hydroxides, which do not show magnetic order yet, and the quadrupole doublet of the iron(III) – catechol complex. Differences in the line width and quadrupole splitting of the doublet observed at 4.2 K are attributable to badly crystallized iron hydroxides, which are not ordered even at 4.2 K. The higher Lamb – Mössbauer factor of the iron hydroxides causes an overrepresentation of the iron hydroxides in comparison to the iron(III) – catechol complex, especially at room temperature.
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The First Coordinatively Saturated, Quadruply Stranded Helicate and Its Encapsulation of a Hexafluorophosphate Anion.**

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The use of metal ions to control the self-assembly of discrete supramolecular species has been an area of intense interest for some years,[1] with helicates having received particular attention.[2, 3] This interest has been driven, at least in part, by the potential use of helicates as functional components of molecular devices.[2] Although single-, double- and triple-stranded helicates have been well-documented,[2, 4] to our knowledge the only example of a quadruply stranded helicate is the recent report of pentanuclear metal complexes bridged by a pentadentate ligand.[5] These species contain metal – metal bonds with terminal ancillary ligands on octahedral metal centers and, as such, can be classified as unsaturated helicates.[2] It was predicted[2] that the synthesis of a saturated quadruply stranded helicate might be achieved by employing a combination of square-planar metal centers with oligomonodentate bridging ligands. We now report the successful realization of this challenge, with the synthesis and X-ray crystal structure of a quadruply stranded helicate that encapsulates a hexafluorophosphate anion.

We have previously reported that reaction of 1,4-bis(2-pyridyloxy)benzene with silver nitrate results in the self-assembly of a M_2L_2 dimetalloparacyclophane with intimate $\pi - \pi$ stacking of the central benzene rings,[6] whilst replacement of the central *p*-phenylene ring with a 2,7-naphthylene spacer results in the formation of a M_2L_4 molecular box.[7] In order to change the topology of the ligand so as to enlarge the cavity within such metallosupramolecular species we have begun to examine the coordination chemistry of the 3-pyridyl analogues. Thus, the ligand 1,4-bis(3-pyridyloxy)benzene (**1**) was prepared (Scheme 1) by reaction of 3-hydroxypyridine with 1,4-dibromobenzene in the presence of potassium carbonate and copper bronze.[8] Reactions of **1** with $[PdCl_2(PPh_3)_2]$ and $[PdI_2(py)_2]$ (py = pyridine), in the presence of silver triflate, gave what we believe to be the dimeric complexes **2** and **3**, respectively, the formulations of which are supported by their elemental analyses, ^{1}H NMR and FAB mass spectra (see Experimental Section). Diffusion of diethyl ether into an acetonitrile solution of **3** containing ammonium hexafluorophosphate resulted in a reorganization of the components and the assembly of a M_2L_4 species (**4**), which deposited from the solution as a tetrakis(hexafluorophosphate) salt and as a bis(acetonitrile) solvate. This latter species was prepared more efficiently, in 70% yield, when the appropriate 2:1 ligand:metal stoichiometry was employed.

A single crystal X-ray structure determination was carried out to determine the structure of this compound unambiguously.[9] The compound crystallizes in the centrosymmetric space group $P2_1/n$, the asymmetric unit of which contains a full M_2L_4 helical cage (**4**) that has each square-planar palladium atom coordinated to the four bridging ligands and within which resides a well-ordered PF_6^- ion (Figure 1). External to the cage are three other PF_6^- anions (two of which are disordered) and two acetonitrile solvate molecules (not shown). The dimensions of the cage are defined by the Pd···Pd separation [8.8402(8) Å] and the distance between the centroids of the cofacial benzene rings [8.849(7) and 8.925(7) Å].

Figure 2 shows the cage viewed down the Pd – Pd axis, which serves to emphasize its approximate D_4 symmetry and the helical disposition of the ligands. The helical pitch is defined by the approximate 45° angle subtended by each ligand about the helical axis. The planes of the pyridine rings are all approximately orthogonal to the planes of the linking benzene rings. This cage can be classified as a saturated,

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