Chromophores Encapsulated in Gold Complexes: DPP Dyes with Novel Properties

**Heinz Langhals,*[a] Michael Limmert,[b] Ingo-Peter Lorenz,*[b] Peter Mayer,[b]
Holger Piotrowski,[b] and Kurt Polborn[a]**

Dedicated to Prof. Dr. R. Huisgen on the occasion of his 80th birthday

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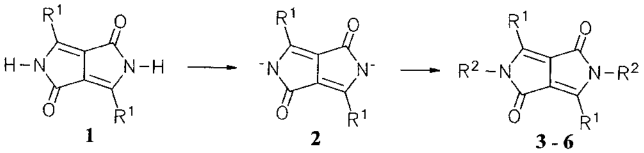
Colour pigments of the DPP type (R^2 = H) were deprotonated and coordinated to transition metals [R^2 = $M(PPh_3)_2$ (M = Cu, Ag) and $AuPPh_3$]. Dyes were obtained with novel properties such as high solubilities, high fluorescence quantum yields and bathochromic absorptions. The crystal structures indicate a torsion of the planes of the rings of the substituents R^1 with respect to the plane of the chromophore depending on the complex fragment.

Introduction

The diaryl DPP dyes **1**[1] (DPP = **d**iketo**p**yrrolo**p**yrrol) belong to the most recently developed classes of technical pigments. Their good properties as pigments are supported by the formation of intermolecular hydrogen bond structures. However, these hydrogen bonds are also a disadvantage for the use of **1** for fluorescence applications because they diminish fluorescence quantum yields in many cases. For example, the fluorescence quantum yield[2] of **1a** was found to be only 50%. The formation of hydrogen bonds can be inhibited by an alkylation[3] or an arylation[4] at the nitrogen atoms. The coordination of the nitrogen atoms to metal ions would be a further possibility for the blocking these positions. The elements of the first subgroup would be suitable for this purpose and the formation of polymeric networks should be prevented by the coordination of at least one further coordination site by bulky substituents such as in compounds **4−6** (Scheme 1). The entire chromophore would be thus shielded against external influences.



1 **2** **3 - 6**

R^1	C_6H_5	4-Cl-C_6H_4	3,5-di-*t*-bu.-C_6H_3
1 - 6	**a**	**b**	**c**

R^2	CH_3	$((C_6H_5)_3P)_2Cu$	$(C_6H_5)_3PAg$	$(C_6H_5)_3PAu$
	3	**4**	**5**	**6**

Scheme 1. Derivatives of DPP dyes

Results and Discussion

One mol DPP **(1a)** was allowed to react according to this concept with two mol hexamethyldisilazane sodium salt to give the dianion of DPP **(2a)**, and then with a mixture of two mol copper(I) chloride and two mol triphenylphosphane to obtain a violet, rather persistent, but absolutely insoluble material. A polymeric structure is probably responsible for the low solubility. An increase of the amount of triphenylphosphane to six mol or more results in partially soluble components in the reaction product. The filling of two coordination sites initially gave appreciably better results: bis(triphenylphosphane)copper(I) nitrate reacts with **2a** to give the complex **4a**. A substitution at the *p*-position of the phenyl groups in **1** with chloride **(1b)** results, after initial formation of **2b**, in the appreciably more-stable complex **4b**. Suitable single crystals of **4b** could be obtained for an X-ray single crystal structure analysis. Compound **1b** however, was preferred for the following synthesis because a higher stability was generally found for metal complexes with the chlorine derivative, see Scheme 2.

With silver(I) tetrafluoroborate and triphenylphosphane, compound **2a** forms the homogeneously soluble and brilliant violet complex **5b** with two triphenylphosphane ligands at each silver ion. However, no suitable single crystals could be obtained for a crystal structure analysis.

Even better results were obtained from the reaction of **2b** with triphenylphosphanegold(I) chloride: compound **6b** was obtained as a bright-red crystalline powder and well-

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[a] Department Chemie, Universität München,
Butenandtstr. 5−13 (Haus F), 81377 München, Germany
Fax: (internat.) +49-89/2180-7640
E-mail Langhals@lrz.uni-muenchen.de
[b] Department Chemie, Universität München,
Butenandtstr. 5−13 (Haus D), 81377 München, Germany
Fax: (internat.) +49-89/2180-7867
E-Mail: ipl@cup.uni-muenchen.de

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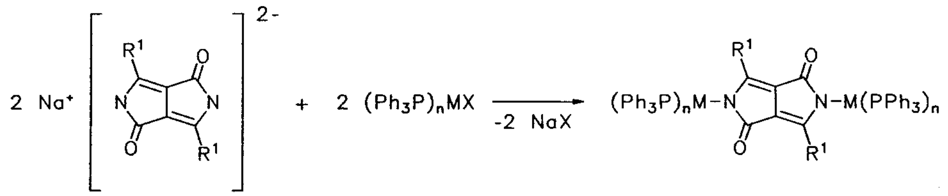

2b

4b – 6b

	4b	**5b**	**6b**
M	Cu^+	Ag^+	Au^+
l	2	2	1
X	NO_3^-	BF_4^-	Cl^-

Scheme 2

formed single crystals suitable for an X-ray crystal structure analysis were isolated. The X-ray structure shows a bond of one triphenylphosphane group with one gold(I) ion and a linear N1−Au1−P1 arrangement. Complex **6b** is completely stable under argon at room temperature and can even be stored in air for several days.

The single crystal structure analysis of **4b** (Figure 1) and **6b** (Figure 2) indicates the different composition and structures of the inversion symmetrical copper(I) and gold(I) compounds. The copper atoms in **4b** are trigonal planar, and are surrounded by the phosphorus atoms of the phosphane ligands and the N atom of the DPP dianion **2b**. The P_2CuN skeletons are planar and the Cu atoms pressed out-of-plane by 18°. The two P_2Cu planes and the planes of the rings R^1 are twisted by 70° and 25°, respectively, with respect to the central planes of the molecules. This indicates the enormous steric demand of the 12 covering phenyl groups.

The gold atoms in **6b** are linearly coordinated[5] to one N and one P atom so that a linear arrangement of all N, Au and P atoms results. The two phosphane ligands are staggered with their phenyl groups so that there is enough room

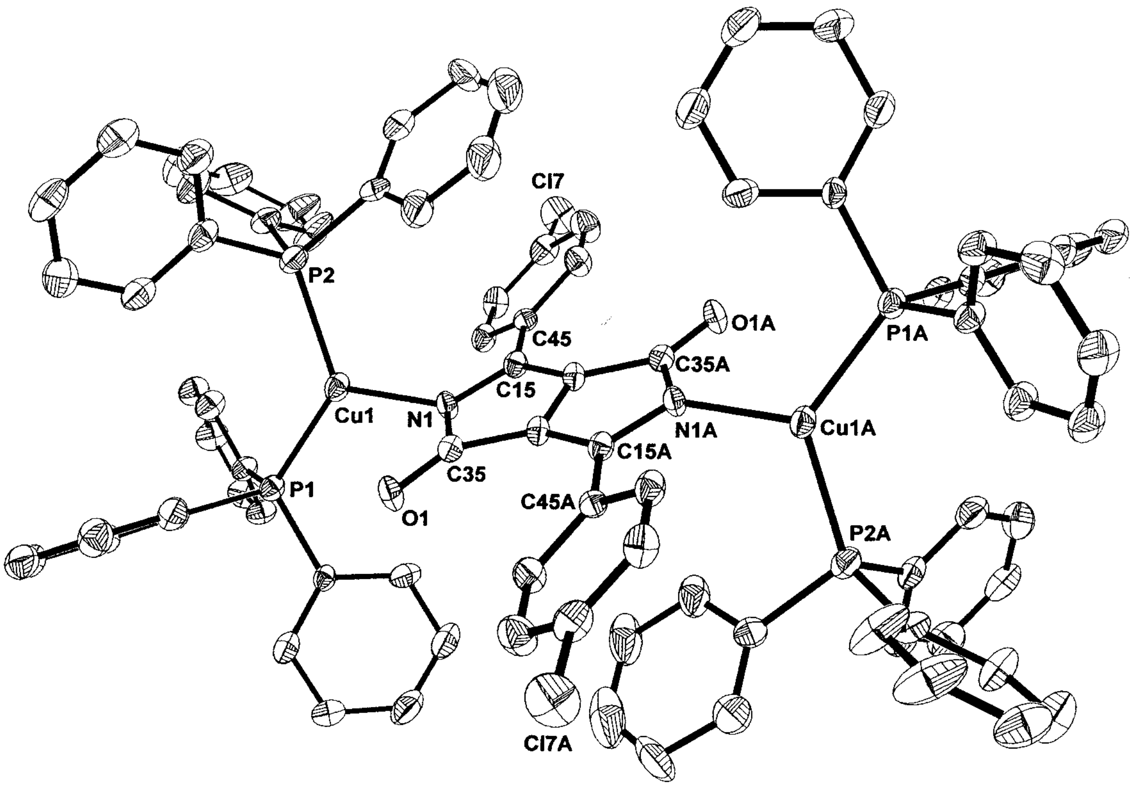

Figure 1. Crystal structure of **4b**; selected bond lengths [Å] and angles [°]: Cu1−N1 1.984(5), Cu1−P1 2.229(2), Cu1−P2 2.253(2), C15−C45 1.478(9), N1−Cu1−P1 118.7(2), N1−Cu1−P2 113.7(2), P1−Cu1−P2 127.48(7); sum of angles at N = 355.52°, sum of angles at Cu = 360°

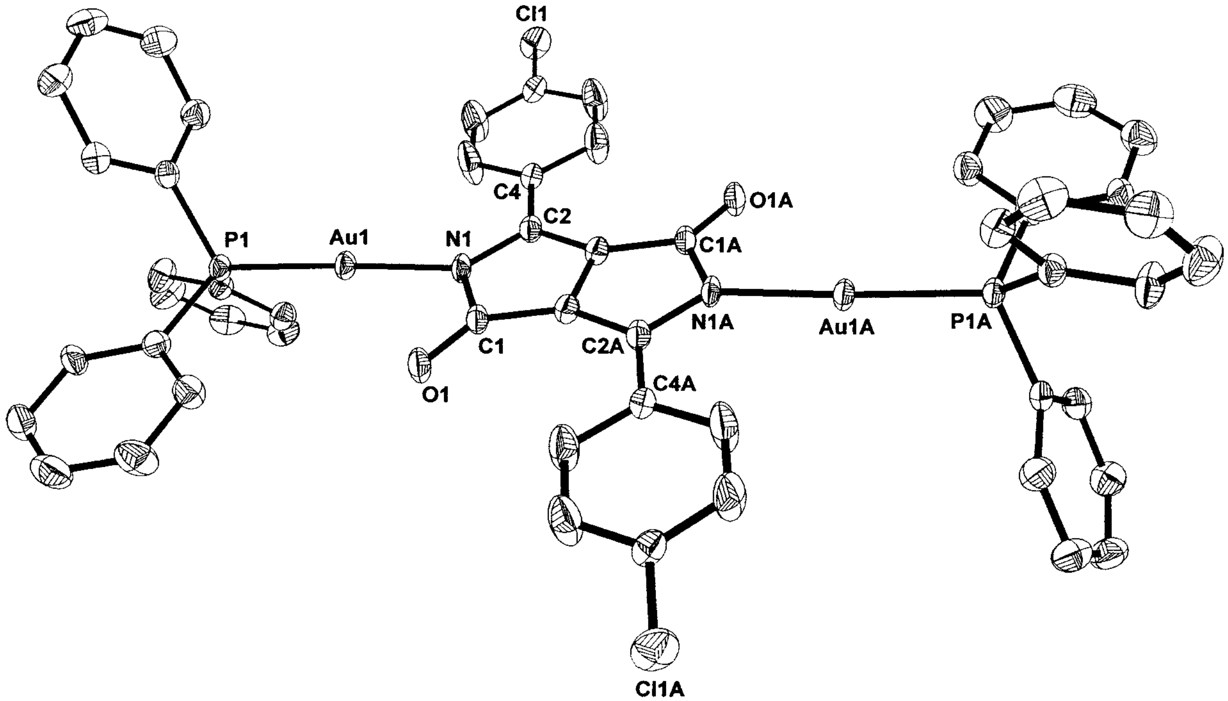

Figure 2. Crystal structure of **6b**; selected bond lengths [Å] and angles [°]: Au1−N1 2.047(5), Au1−P1 2.230(2), C2−C4 1.467(10), N1−Au1−P1 175.3(2); sum of angles at N1 = 360°

for the planarization of R^1 into the plane of the chromophore; this geometry is also preferred for electronic reasons.

Dye **1c** was used as a reference for the UV/Vis spectra of **4b−6b**, because of its sufficiently high solubility caused by the four solubilising *tert*-butyl groups in the *m*-positions of the phenyl groups.[6,7] Compound **1c** exhibits a structured UV/Vis absorption spectrum in chloroform solution (λ_{max} = 507 nm) and a mirror-type fluorescence spectrum (λ_{max} = 513 nm), see Figure 3.

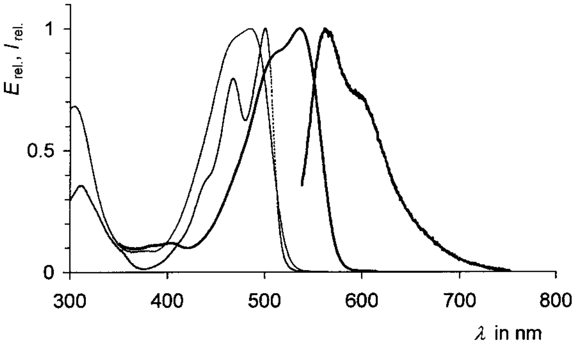

Figure 3. UV/Vis absorption and fluorescence spectrum of **6b** (—) and the absorption spectra of **1c** (···) and **3c** (—) in chloroform

A methylation of the nitrogen atoms **(3c)** will block the formation of hydrogen bonds and thus increase the fluorescence quantum yields by several percent and induce a hypsochromic shift of the UV/Vis absorption with a substantial loss of spectral structure (see Figure 3). A blocking of the nitrogen atoms by complexation with AuP(C_6H_5)$_3$ also increases the fluorescence quantum yield; however, in contrast to the former, a bathochromic shift is obtained (absorption: λ_{max} = 535.4 nm; fluorescence: λ_{max} = 561 nm; **6a** absorbs at 530 nm, see Figure 3). The changes in the UV/Vis spectra can be explained in terms of changes in the torsion angles of the aryl substituents. A torsion angle of 15° was calculated (AM1) for the phenyl groups in **1a**. This angle is probably representative of the dissolved dye. An *N*-methylation increases the torsion angle to 30° in **3c** and induces a hypsochromic shift because of the decoupling of the two π-systems. In contrast to this, the phenyl groups in the more bathochromically absorbing gold complex **6b** are completely turned into the plane of the chromophore. This corresponds to the bathochromic absorption of the planar blue dianion **2a**; a planar structure was also calculated for **2a** (AM1).

The fluorescence quantum yield of **1a** was found to be 50%. A complexation with copper **(4b)** decreases the quantum yield to 20%; this corresponds to the well-known fluorescence quenching effect of copper ions. The fluorescence quantum yield is further diminished in the silver complex **5b** to 17%. Surprisingly, the fluorescence quantum yield is strongly increased by coordination with gold ions so that 99% was obtained for **6b**. Solutions of **6b** in chloroform are bright yellow in daylight and purple in transmitted light. All complexes **4b**, **5b** and **6b** exhibit a red, solid-state fluorescence.

The high fluorescence quantum yield of **6b** indicates the efficient supporting effect of the bulky gold substituents for fluorescence. Interestingly, in contrast to alkyl groups the gold substituents allow the complete planarization of the chromophore, including the phenyl substituents (R^1 = **b**). This is a further indicator for the efficient shielding of the chromophore against aggregation because such a large planar π-system would otherwise exhibit a very high tendency for aggregation. Furthermore, the fluorescence quantum yield of **6b** of nearly 100% excludes a notable intersystem crossing rate to triplet states. This is remarkable because one might expect a pronounced heavy-atom effect on the I.S.C.-rate by gold because of its high atomic weight. This will be the subject of further investigations.

Experimental Section

2b: Addition of $NaN(SiMe_3)_2$ (0.30 mL, 1.00 M solution in THF) to a well-stirred suspension of **1b** (50 mg, 0.14 mmol) in 10 mL of DMF (cf. ref [8]) yielded a blue solution of **2b**, which was used in all further reactions.

4b: Compound **2b** was added dropwise to $(PPh_3)_2CuNO_3$ (195 mg, 0.30 mmol) in 5 mL of DMF at ambient temperature and left stirring for two hours. The solvent was removed under vacuum at 60 °C, the residue dissolved in 10−15 mL $CHCl_3$ and filtered (P3). The solution was carefully diluted with *n*-hexane and stored at −20 °C for some days, after which time **4b** had precipitated as violet crystals. To improve the yield the solution can be layered with some more *n*-hexane. Yield: 111 mg (42%) of **4b** as violet crystals, m.p. 165 °C. − IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1}, 3035, 1607, 1598, 1579, 1556, 1521, 1481, 1435, 1408, 1342, 1300, 1277, 1262, 1214, 1182, 1157, 1121, 1093, 1070, 1027, 1011, 998, 837, 828, 820, 773, 741, 694, 642, 628, 618, 527, 516, 507, 490, 442, 431. − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.15−7.37 (m, 68 H, Ph, 4-Cl−C_6H_4). − $^{31}P\{^1H\}$ NMR (109.37 MHz, $CDCl_3$): δ = −2.4 (s, PPh_3). − UV ($CDCl_3$): λ_{max} (ε) = 547.7 nm (1), 572 sh (0.91). − Solid-state fluorescence: λ_{max} (I_{rel}) = 642. − FAB-MS: *m/z* = 1007 [M^+ − 2PPh_3], 587 [$Cu(PPh_3)_2$], 325 [$CuPPh_3$], 262 [PPh_3]. − $C_{90}H_{68}Cu_2Cl_2N_2O_2P_4 \cdot 4CHCl_3$ (1890): calcd. C 54.93, H 3.52, N 1.33; found C 55.49, H 3.66, N 1.46.

5b: Compound **2b** was added to a stirred solution of $AgBF_4$ (58 mg, 0.30 mmol) and PPh_3 (236 mg, 0.90 mmol) in 5 mL of DMF. After 1 hour **5b** was formed as a violet solid. The solvent was removed and the residue washed with acetone (25 mL, three times) and diethyl ether (25 mL) and dried in vacuum. Soxhlet extraction of the crude product with 200 mL CH_2Cl_2 in the dark and covering the solution with a layer of *n*-hexane gave **5b** as a violet powder. Yield: 134 mg (59%), m.p. 223 °C. − IR (KBr) $\tilde{\nu}$ = 3082 cm^{-1}, 3053, 1597, 1577, 1553, 1522, 1480, 1435, 1408, 1337, 1300, 1278, 1213, 1180, 1158, 1122, 1092, 1027, 1011, 998, 839, 818, 772, 743, 715, 694, 644, 630, 618, 513, 504, 490, 437. − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.15−7.45 (m, 68 H, Ph, 4-ClC_6H_4). − $^{31}P\{^1H\}$ NMR (109.37 MHz, $CDCl_3$): δ = 8.56 (s, PPh_3) . − UV ($CDCl_3$): λ_{max} (ε) = 525.8 nm (0.81), 560.1 (1.00). − Solid-state fluorescence: λ_{max} (I_{rel}) = 662. − FAB-MS: *m/z* = 1096 [M^+ − 2 PPh_3], 631 [$Ag(PPh_3)_2$], 369 [$AgPPh_3$]. − $C_{90}H_{68}Ag_2Cl_2N_2O_2P_4$ (1620): calcd. C 66.73, H 4.20, N 1.73; found C 65.09, H 4.27, N 1.93.

6b: Addition of **2b** to a stirred solution of Ph_3PAuCl (148 mg, 0.30 mmol) in 5 mL of DMF gave **6b** as a red solid. The product was purified analogously to **5b**; it was dissolved in 50 mL of warm $CHCl_3$, filtered (P3) and layered with *n*-hexane to give red crystals of **6b**. Yield: 135 mg (64%) of **6b** as a red powder, m.p. > 300 °C. − IR (KBr) $\tilde{\nu}$ = 3082 cm^{-1}, 3053, 1699, 1673, 1615, 1574, 1484, 1436, 1405, 1330, 1302, 1277, 1200, 1183, 1119 1102, 1092, 1027, 1011, 996, 836, 743, 711, 694, 545, 509, 484, 451, 440. − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.71 [d, ^3J (H,H) = 8.62 Hz, 4H, 4-Cl−C_6H_4], 7.45−7.60 (m, 30 H, Ph_3P), 7.26 [d, ^3J (H,H) = 8.88 Hz, 4H, 4-Cl−C_6H_4]. − $^{31}P\{^1H\}$ NMR (109.37 MHz, $CDCl_3$): δ = 33.01 (s, PPh_3). − $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ = 170, 134.99, 134.39, 134.19, 131.91, 131.86, 131.45, 129.78, 129.62, 129.39, 129.25, 128.71, 128.27. − FAB-MS: *m/z* = 1274 [M^+], 814 [M^+ − $AuPPh_3$], 721 [$Au(PPh_3)_2$], 459 [$AuPPh_3$]. − UV ($CDCl_3$): λ_{max} (ε) = 512.5 nm sh (23400), 535.4 (26000). − Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 561 nm (1.0), 597 (0.72); solid-state fluorescence: λ_{max} (I_{rel}) = 633 nm (1.0), 690 sh (0.4). − $C_{54}H_{38}Au_2Cl_2N_2O_2P_2 \cdot 2CHCl_3$ (1512): calcd. C 44.72, H 2.66, N 1.86; found C 43.91, H 2.67, N 1.93.

X-ray Crystal Structure Analysis: 4b: $C_{96}H_{74}Cl_{14}Cu_2N_2O_6P_4$, M_r = 2098.94, single crystal 0.30 × 0.10 × 0.10 mm^3, space group *P*1(bar), *a* = 12.683 (2), *b* = 13.247 (3), *c* = 16.676 (3) Å, α = 112.67 (2), β = 106.301 (19), γ = 86.86 (2), *V* = 2477.0 (8) $Å^3$, *Z* = 1, $\rho_{ber.}$ = 1.407 g·cm^{-3}. − Technical data: 2Θ-range 3−48°, radiation: Mo-K_α (λ = 0.71073 Å), area-detection at 200 K. − Data collection: a total of 13688 reflections, 7050 unique and 2752 observed [$I \geq 2\sigma(I)$]. Absorption correction: numerical, μ = 0.924 mm^{-1}, min./max. transmission 0.7943/0.9353. − Structure solution and refinement: SHELXS-97 (Sheldrick, 1997) and SHELXL-97 (Sheldrick, 1997), the structure was solved by direct methods and refined by full-matrix least-squares on F^2, H-atoms and inserted formic acid molecules were refined isotropically, all others were refined anisotropically. 542 Parameters, *R* = 0.0524, *wR*2 = 0.0921 for [$I \geq 2\sigma(I)$], largest peak and hole ρ = −0.313/0.663 e·$Å^{-3}$.
6b: $C_{56}H_{40}Au_2Cl_8N_20_2P_2$, M_r = 1512.37, single crystal 0.47 × 0.40 × 0.1 mm^3, space group *P*1(bar), *a* = 10.285(2), *b* = 11.8523 (13), *c* = 12.835 (2) Å, α = 90.569 (10), β = 106.128 (14), γ = 113.774 (13)°, *V* = 1362.2 (4) $Å^3$, *Z* = 1, $\rho_{calcd.}$ = 1.844 g·cm^{-3}. − Technical data: 2Θ-range: 5−48°, radiation: Mo-K_α (λ = 0.71073 Å), ω-2θ-scan at 293 (2) K. − Data collection: a total of 4529 reflections, 4259 unique and 3764 observed [$I \geq 2\sigma(I)$]. Absorption correction: semiempirical μ = 5.874 mm^{-1}, min./max. transmission 0.4598/0.9980. − Structure solution and refinement: SHELXS-86 (Sheldrick, 1990) and SHELXL-93 (Sheldrick, 1993), the structure was solved by direct methods and refined by full-matrix least-squares on F^2, H-atoms were refined isotropically, all others were refined anisotropically. 325 Parameters, *R* = 0.0359, R_w = 0.0887 for [$I \geq 2\sigma(I)$], largest peak and hole ρ = −1.015/2.035 e·$Å^{-3}$.
Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137742 (**6b**) and -137784 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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[1] Review: A. Iqbal, M. Jost, R. Kirchmayr, J. Pfenninger, A. Rochat, O. Wallquist, *Bull. Soc. Chim Belg.* **1988**, *97*, 615−634.
[2] Determined according to: H. Langhals, J. Karolin, L. B.-Å. Johansson, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2919−2922.
[3] T. Potrawa, H. Langhals, *Chem. Ber.* **1987**, *120*, 1075−1078.
[4] H. Langhals, T. Grundei, T. Potrawa, K. Polborn, *Liebigs Ann.* **1996**, 679−682.
[5] See similar metal complexes with biologically active ligands: D. Koch, K. Sünkel, W. Beck, *Z. Naturforsch. B* **1999**, *546*, 92−102, and references therein.

[6] H. Langhals, *Ger. patent* 3016764 (April 30, **1980**); *Chem. Abstr.* **1982**, *96*, P70417x.

[7] H. Langhals, *Nachr. Chem. Tech. Lab.* **1980**, *28*, 716−718; *Chem. Abstr.* **1981**, *95*, R9816q.

[8] M. Poppe, Dissertation München, **1998**; M. Limmert, planned dissertation München, **2000**.

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