Structural and Spectroelectrochemical Studies on (2,2′-Bidipyrrinato)copper(II) and -palladium(II) Complexes

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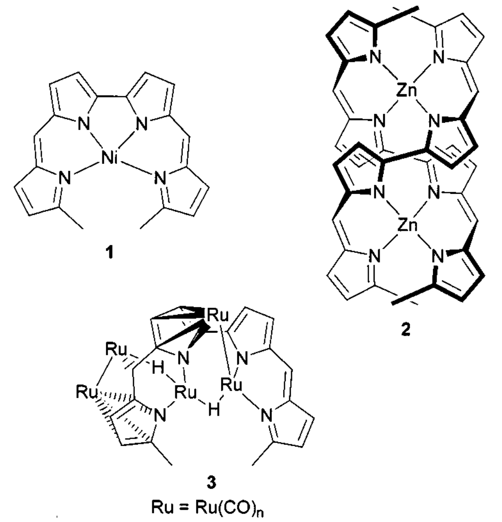
Copper(II) and palladium(II) complexes of two 2,2′-bidipyrrin ligands were prepared and examined, in comparison with the known nickel(II) complexes of these ligands, by means of X-ray crystallography, cyclic voltammetry, and spectroelectrochemistry. All compounds are of helical geometry with coordination environments of the metal centres displaying very small tetrahedral distortions for palladium and very large ones for copper complexes. Porphyrinoid behaviour was found for the one- and two-electron oxidations of all complexes studied, as well as for the reductions of the Pd^{II} species. On the other hand, the reduction of the Cu^{II} complexes shows some special features, which may be explained from the results of spectroelectrochemical studies as related to the particular non-planarity of these compounds.

Introduction

As part of an ongoing project to study the coordination chemistry of open-chain oligopyrrolic ligands, we recently became interested in the tetrapyrrolic 2,2′-bidipyrrins.[1,2] Topologically, 2,2′-bidipyrrins resemble the porphyrins both in their build-up (from two connected dipyrrin units) and their expected dianionic character when serving as ligands in metal complexes.[3] Our initial studies on a set of (2,2′-bidipyrrinato)nickel(II) complexes showed that this tetrapyrrole formed conformatively stable helicates, which may be resolved chromatographically into the separate enantiomers. In addition to this, the delocalized π system of 2,2′-bidipyrrin ligands largely determines the electrochemical behaviour of the Ni^{II} complexes, in that only ligand centred oxidation and reduction steps could be observed. This finding, in particular, qualifies 2,2′-bidipyrrins as open-chain analogues of the porphyrins.[4]

The higher flexibility of the 2,2′-bidipyrrin ligand with respect to the porphyrins, however, has tremendous impact on its coordination chemistry, as was recently shown by the X-ray crystallographic characterization of two non-porphyrinoid coordination modes (Scheme 1).[5,6] Therefore, a prediction of how this tetrapyrrole would interact with a given metal ion is not trivial. In the early 1960s, the Johnson group reported the first palladium and copper complexes of 2,2′-bidipyrrins. From molecular mass determination, the latter were deduced to exist in two different, interchangeable forms, namely the coordination modes displayed by **1** and **2** (Scheme 1).[7]



Scheme 1. Coordination modes of 2,2′-bidipyrrins

In this context, we had two important questions. Firstly, what is the impact of elongated M−N bonds of e.g. Pd^{II} vs. Ni^{II} complexes of 2,2′-bidipyrrins on the stability of the helical conformation? Secondly, how does the typical structural lability for Cu^{II} complexes influence the coordination mode, the ligand structure, and the redox behaviour of these complexes? In this paper we try to answer these questions using structural and electrochemical arguments.

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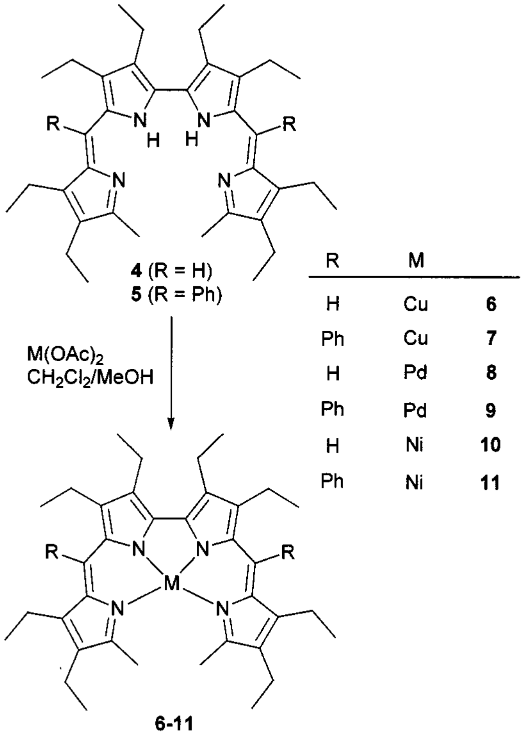
Results and Discussion

Preparation and Characterization of Complexes 6−9

The copper(II) and palladium(II) complexes **6−9** were prepared from the 2,2′-bidipyrrins **4** and **5** by treatment with a methanolic solution of excess metal acetate (Scheme 2). The complexation reactions were complete after 30 min at room temperature. The copper complexes **6** and **7** were purified by several washings of the resulting solutions with water, and recrystallization from dichloromethane/*n*-hexane. In the case of the palladium complexes **8** and **9**, convenient purification could be achieved by chromatographic filtration through silica and subsequent recrystallization from the above solvent mixture. The observed yields were good (78−92%). Only one copper(II) complex was formed from either ligand by this method, namely the M_1L_1 compound of type **1**.



R	M	
H	Cu	**6**
Ph	Cu	**7**
H	Pd	**8**
Ph	Pd	**9**
H	Ni	**10**
Ph	Ni	**11**

Scheme 2. Syntheses of (2,2′-bidipyrrinato)metal(II) complexes

All new compounds gave correct analyses, and were further characterized by EIMS. In addition, proton and carbon NMR measurements were carried out on the palladium derivatives **8** and **9**, showing the expected sharp signals for **8** and broadened resonances for **9** due to the steric encumbrance of the peripheral substituents. The same line broadening was observed earlier on a set of related (2,2′-bidipyrrinato)nickel(II) complexes like **11**.[3] The splitting of the signals of the *meso*-phenyl substituents indicates the expected helical conformation of **9** in solution at room temperature.

Molecular Structures of 6 and 8

Crystals of **6** and **8** were obtained from slow concentration of the respective solutions in dichloromethane/*n*-hexane. As in the case of the nickel(II) complex **10** of the same ligand, complexes **6** and **8** crystallized in the monoclinic system, space group $P2_1/c$, with $Z = 4$. Both compounds show helically distorted ligand frameworks in the solid, and both enantiomers co-crystallize in the same unit cell. Figures 1 and 2 show the molecular structures of **8** and **6**, and Table 1 summarizes structural parameters of **6**, **8**, and **10**.

For the palladium derivative **8**, the Pd−N bond lengths of 1.956(3)−2.045(3) Å appear in the range found for other (tetrapyrrole)palladium(II) complexes,[8−12] and indicate a larger N_4 core as compared with the Ni^{II} derivative **10**. As a consequence of these elongations, the coordination sphere of the metal ion becomes significantly more trapezoidal. This is clearly visible in the reduced internal N−M−N angles (by 1.37−2.05° with respect to **10**), and a widened N(1)−Pd−N(4) angle of 105.44°. The ligand itself was found to expand upon coordination of the Pd^{II} ion. This

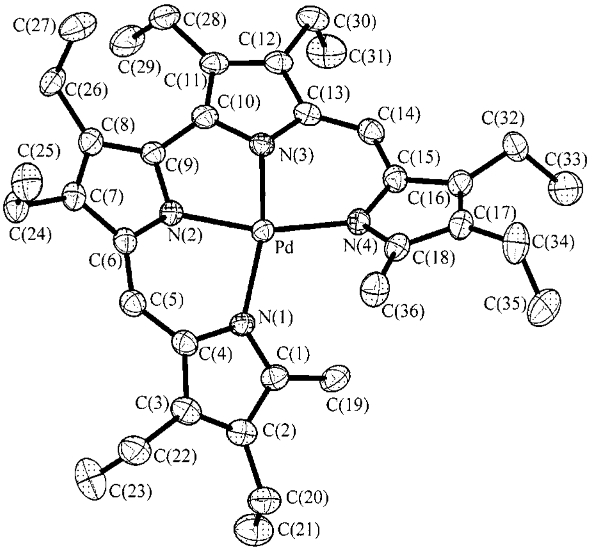


Figure 1. ORTEP plot of the molecular structure of **8** (50% probability)

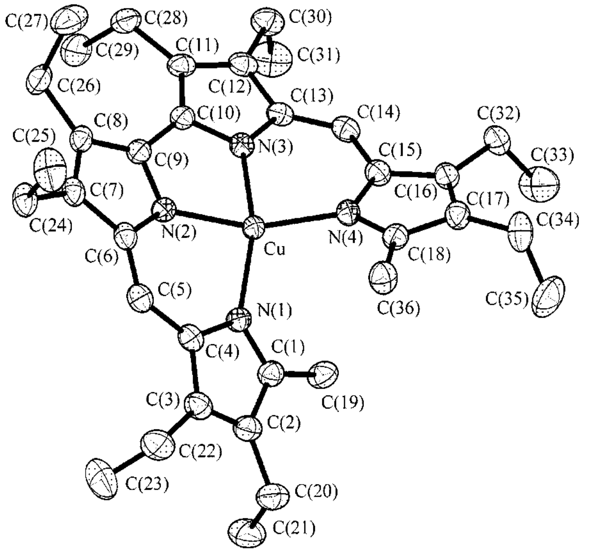


Figure 2. ORTEP plot of the molecular structure of **6** (50% probability)

Table 1. Selected bond lengths, distances [Å] and angles [°] for **6**, **8**, and **10**

	M = Cu (**6**)	M = Pd (**8**)	M = Ni (**10**)
M−N(1)	1.9782(16)	2.044(3)	1.9088(15)
M−N(2)	1.9291(16)	1.959(3)	1.8451(15)
M−N(3)	1.9250(17)	1.956(3)	1.8498(14)
M−N(4)	1.9794(16)	2.045(3)	1.9068(15)
N(1)−C(1)	1.332(3)	1.337(4)	1.341(2)
N(1)−C(4)	1.407(3)	1.404(4)	1.409(2)
N(2)−C(6)	1.366(3)	1.372(4)	1.371(2)
N(2)−C(9)	1.348(3)	1.356(4)	1.349(2)
N(3)−C(10)	1.349(3)	1.351(4)	1.353(2)
N(3)−C(13)	1.360(3)	1.360(4)	1.373(2)
N(4)−C(15)	1.405(3)	1.407(4)	1.409(2)
N(4)−C(18)	1.340(3)	1.338(4)	1.340(2)
C(1)−C(2)	1.429(3)	1.432(5)	1.432(3)
C(2)−C(3)	1.370(3)	1.372(5)	1.372(3)
C(3)−C(4)	1.433(3)	1.432(5)	1.432(3)
C(4)−C(5)	1.392(3)	1.388(5)	1.380(3)
C(5)−C(6)	1.393(3)	1.390(5)	1.391(3)
C(6)−C(7)	1.429(3)	1.430(5)	1.426(3)
C(7)−C(8)	1.385(3)	1.387(5)	1.386(3)
C(8)−C(9)	1.430(3)	1.427(5)	1.428(3)
C(9)−C(10)	1.464(3)	1.463(5)	1.457(3)
C(10)−C(11)	1.435(3)	1.430(5)	1.425(3)
C(11)−C(12)	1.389(3)	1.387(5)	1.382(3)
C(12)−C(13)	1.427(3)	1.425(5)	1.430(3)
C(13)−C(14)	1.397(3)	1.398(5)	1.386(3)
C(14)−C(15)	1.389(3)	1.378(5)	1.383(3)
C(15)−C(16)	1.435(3)	1.444(5)	1.435(3)
C(16)−C(17)	1.379(3)	1.364(5)	1.365(3)
C(17)−C(18)	1.430(3)	1.434(5)	1.427(3)
$C_{term}\cdots C_{term}$	3.58	3.48	3.34
N(1)−M−N(2)	88.92(7)	89.02(11)	90.39(7)
N(1)−M−N(3)	159.28(7)	164.02(11)	161.72(7)
N(1)−M−N(4)	107.69(7)	105.44(11)	101.76(7)
N(2)−M−N(3)	78.86(8)	78.73(12)	80.72(7)
N(2)−M−N(4)	157.97(7)	162.69(11)	163.08(7)
N(3)−M−N(4)	88.80(7)	88.50(11)	90.55(6)
N(2)−C(9)−C(10)	111.15(16)	111.8(3)	109.57(15)
N(3)−C(10)−C(9)	110.75(17)	111.2(3)	109.99(15)
C(4)−C(5)−C(6)	126.22(19)	127.9(3)	125.45(18)
C(13)−C(14)−C(15)	126.03(19)	127.0(3)	125.33(17)

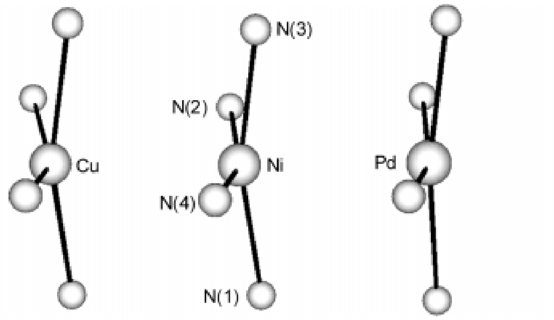


Figure 3. Comparison of coordination geometries found in **6**, **8**, and **10**

was deduced from the fact that the inner bond angles of the bipyrrole linkage N(2)−C(9)−C(10) and N(3)−C(10)−C(9) as well as those at the *meso* carbon atoms C(4)−C(5)−C(6) and C(13)−C(14)−C(15) became larger. In summary, the changes result in reduced overlap of the terminal methyl groups, and thus in diminished helicity of the ligand and enhanced planarity of the metal centre {rms deviation of MN_4 fragments from planarity: Pd 0.151 Å, Ni 0.203 Å; angle between the planes [N(2),N(3),M] and [N(1),N(4),M]: for **8** 14.0°, for **10** 19.9°; angles N(1)−M−N(3) and N(2)−M−N(4): Pd 164.02(11) and 162.69(11)°, Ni 161.72(7) and 163.08(7)°; Figure 3}. The distance between the terminal methyl groups, however, increased in the Pd^{II} complex from 3.34 to 3.48 Å. Obviously, this value is not a good indicator for the helical topology of the tetrapyrrole perimeter in chelates with different metal ions. Despite the more open structure of **8** with respect to **10**, the helical arrangement is still quite pronounced and stable. Further support to this statement is provided by the fact, that the diphenyl derivative **9** of (2,2′-bidipyrrinato)palladium(II) could be separated into the enantiomers by HPLC on an analytical scale, and by the observation, that in the ^1H NMR spectrum the splitting of the signals of the *meso*-phenyl groups of **9** remained unchanged up to 90 °C.

The Cu−N bond lengths of the copper(II) complex **6** of 1.9250(17)−1.9794(16) Å are normal for copper(II) complexes of tetrapyrrolic ligands,[9,13−16] and are therefore again longer than the Ni−N bond length of **10**. The same conclusions as with the palladium derivative **8** above can thus be drawn concerning the changes found for the inner bond angles and the overlap of the terminal methyl groups of the tetrapyrrole ligand. In contrast to **8**, however, the more open structure of complex **6** results in enhanced helicity of the ligand and reduced planarity of the metal coordination sphere. This difference is caused by the pronounced tetrahedral distortion imposed by the metal centre as measured by the N(1)−Cu−N(3) and N(2)−Cu−N(4) angles of 159.28(7) and 157.97(7)°, respectively. The difference could be monitored in the enlarged deviation of the CuN_4 fragment from planarity (0.234 Å) as well as in the angle between the planes [N(2),N(3),Cu] and [N(1),N(4),Cu] of 22.0° (Figure 3). The flexibility of 2,2′-bidipyrrin ligands thus allows different metal centres to accommodate the coordination geometry within some range, even if the same coordination mode is established.

Cyclic Voltammetry

As we have shown earlier, the redox characteristics of (2,2′-bidipyrrinato)nickel(II) complexes resemble those of porphyrinoid nickel(II) complexes. In both cases, two one-electron transfer steps occurred upon oxidation or reduction, and all could be shown to be ligand centred.[4] The values detected for the potentials of (2,2′-bidipyrrinato)nickel(II) complex oxidations and reductions, however, are more closely related to those of the chlorinato- and bacteriochlorinato complexes than to the metalloporphyrins themselves.[17,18]

Cu^{II} and Pd^{II} complexes **6−9** were studied in benzonitrile with 0.1 M nBu_4NPF_6, and gave well-defined signals (Fig-

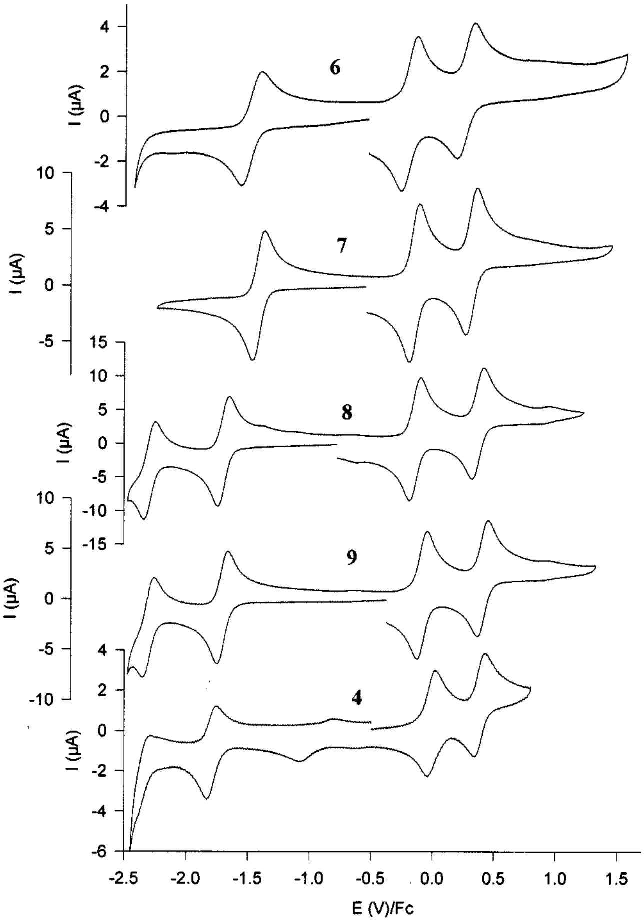


Figure 4. Cyclic voltammetry of **4**, **6**, **7**, **8**, and **9** in PhCN with 0.1 M Bu_4NPF_6 on a platinum working electrode; sweep rate: v = 0.2 V s^{-1}

ure 4). All derivatives underwent two reversible one-electron oxidations at rather low potentials. In reduction, the first reduction step (one-electron reversible step) was well resolved, whereas the second reduction step occurred close to the electrolyte discharge for the Pd^{II} complexes and could not be observed for the Cu^{II} complexes. The potentials of all accessible electron transfers are collected in Table 2.

Table 2. Electrochemical data for free base **4** and complexes **6−11**

Compound[a]	Red. 2	Red. 1	Ox. 1	Ox. 2	HLG[b]	EN[c]
4 (H_2, R = H)	−2.37	−1.82	−0.02	0.37	1.80	–
6 (Cu, R = H)	–[d]	−1.50	−0.22	0.25	1.28	1.9
7 (Cu, R = Ph)	–[d]	−1.42	−0.15	0.31	1.27	1.9
8 (Pd, R = H)	−2.30	−1.70	−0.15	0.32	1.55	2.2
9 (Pd, R = Ph)	−2.30	−1.71	−0.08	0.41	1.63	2.2
10 (Ni, R = H)	−2.35	−1.71	−0.18	0.31	1.53	1.8
11 (Ni, R = Ph)	−2.36	−1.75	−0.13	0.36	1.62	1.8

[a] Measured on a platinum electrode in PhCN solution with 0.1 M nBu_4NPF_6. Values are given in V relative to the Fc^+/Fc couple. [b] HOMO−LUMO gap (= $E_{Ox.\ 1} - E_{Red.\ 1}$). [c] Electronegativity values taken from ref.[19] [d] Not observed.

The redox behaviour of the palladium complexes **8** and **9** is similar to that of the respective nickel complexes **10** and **11**, and all four redox waves were in analogy assigned to ligand-centred electron transfer processes. The phenyl substituents of **9** and **11** shifted the oxidation potentials to more positive values, whereas the first reduction became slightly more negative. Such shifts are not expected for donor substitution. It seems much more likely that the electronic effect of the phenyl moiety is superimposed by a structural one. X-ray crystallographic work on *meso*-aryl-substituted nickel(II) complexes shows a reduced bite angle of both dipyrrin units due to the higher congested periphery. This structural difference may be responsible for the effect in **9** and **11**.

For the two one-electron oxidation steps of the copper(II) derivatives **6** and **7**, the above discussion still holds true, and both electron transfers are therefore assigned to ligand-centred processes. The interpretation of the reduction behaviour of **6** and **7**, however, is more difficult. A comparison of the obtained data clearly shows, that the potentials of the first reduction step of the copper complexes are at less negative values than those of the nickel and palladium species. However, even if the first reduction is facilitated, the second reduction step is not observed in the available potential range. This peculiar behaviour is again probably due to geometric reasons, since Cu^{II} can more easily adopt and support the non-planar coordination geometry imposed by the ligand, in contrast to Ni^{II} or Pd^{II}, which prefer square-planar environments. The easier reduction of the copper complexes **6** and **7** is most likely a consequence of strain release, and does not seem to result from a possible reduction of the metal ion. Spectroelectrochemical studies discussed below further strengthen this conclusion.

Since structural effects have a strong impact on the redox characteristics of 2,2′-bidipyrrinato complexes, it is obvious that metal-dependent trends known from metalloporphyrin electrochemistry cannot be expected to hold true for the open-chain analogues. Correlations like the potential evolution vs. metal electronegativity,[19] or the energy of the HOMO−LUMO gap vs. the potential difference between the first oxidation and first reduction potential,[20−22] which are typical for metalloporphyrins and other rigid porphyrinoid complexes, strongly depend on structural factors and are therefore not valid for complexes **6−11** (Table 2).

Spectroelectrochemical Investigations

Spectroelectrochemical studies were carried out on the complexes **7**, **9**, and **11**, as well as on the free base **4**. The time-resolved UV/Vis spectra recorded during spectroelectrochemical studies are given in Figures 5 and 6, and the UV/Vis data for all species are summarized in Table 3. It has to be mentioned that in all cases after the first reduction, as well as after the first oxidation, the initial spectrum could be recovered quantitatively. After the second oxidation step, the reduction to regenerate the radical cation was not quantitative, and only 60 to 75% of the radical cation could be recovered for the studied complexes. The second oxidation step of the free base was irreversible on the time scale of spectroelectrochemistry.

Table 3. UV/Vis data from spectroelectrochemical studies on **4**, **7**, **9**, and **11**

Compound	
4 (H_2)	336, 600, 628 sh
7 (Cu)	310, 422, 495, 842
9 (Pd)	347, 436, 528, 843
11 (Ni)	310, 356, 436, 545, 630, 894
$\mathbf{4}^{+\cdot}$	434, 629, 718 sh, 972
$\mathbf{7}^{+\cdot}$	308, 348, 464, 820
$\mathbf{9}^{+\cdot}$	342, 418, 482, 830
$\mathbf{11}^{+\cdot}$	356, 439, 567, 843, 887 sh
$\mathbf{4}^{2+}$	447, 599
$\mathbf{7}^{2+}$	403, 689, 788
$\mathbf{9}^{2+}$	344, 861
$\mathbf{11}^{2+}$	348, 516, 609
$\mathbf{4}^{-\cdot}$	553, 637, 696, 772
$\mathbf{7}^{-\cdot}$	319, 448, 524 sh, 556, 706, 973
$\mathbf{9}^{-\cdot}$	332, 478, 502, 821 sh, 899
$\mathbf{11}^{-\cdot}$	339, 487, 635, 713, 932

Since the UV/Vis spectra and redox potentials of free base 2,2′-bidipyrrins **4** differ significantly from those of the respective metal complexes, the spectroelectrochemical data of **4** are only of limited value as a reference. One important trend, however, is easily seen in Figure 5: the one-electron oxidised and reduced ligand species are both characterized by new and quite narrow bands in the optical spectra. For the two-electron oxidised species, on the other hand, only broad absorptions were detected.

The UV/Vis spectra of the metal complexes **7**, **9**, and **11** also changed dramatically upon reduction or oxidation, and the different electrogenerated species show the same trends within the series (Figure 6). As for the free base ligand **4**, rather sharp absorptions were found after one-electron oxidation and reduction, and only broad bands were observed for the two-electron oxidised members. These similarities are best explained by the assumption of ligand-centred redox reactions throughout the series. The reduction of the copper(II) complex **7**, however, produced an extra distinct band at 706 nm, which was missing in the spectra of the other chelates. This band inhibits a simple comparative analysis of the data. We believe that a ligand-centred one-electron step occurs also in the case of Cu^{II} rather than a reduction to Cu^{I}, since upon reduction of **7** the other bands evolve in a similar fashion to those of **9** and **11**, and because these bands obviously belong to transitions of the tetrapyrrole ligand π system.

In order to identify the site of the one-electron reduction of the copper complexes **6** and **7**, further electrochemical experiments were performed. Upon changing the solvent from benzonitrile to dichloromethane very similar results were obtained for **6**, and all redox processes remained perfectly reversible. On the time scale of spectroelectrochemistry (i.e. ca. 20 min), however, the one-electron reduced $\mathbf{6}^{-\cdot}$ reacted irreversibly with the solvent, leading to a different UV/Vis spectrum with respect to the one obtained in benzonitrile. In fact, by cyclic voltammetry, in the presence of a large excess of the better electrophile *n*-propyl bromide (1000 equiv.), the first reduction step of **6** remained reversible at sweep rates higher than 1 V/s and became irreversible, and dielectronic at sweep rates lower than 0.1 V/s. Such a behaviour is characteristic for an ECE mechanism (*E*lectrochemical *C*hemical *E*lectrochemical) in the presence of a sufficient amount of an electrophile. The generated anion (electrochemical step) is reacting with *n*-propyl bromide (chemical step) to generate a new species, which is again one-electron reduced in another electrochemical step. Since four-coordinate Cu^{I} is a poor nucleophile, the outcome of this experiment strongly supports the hypothesis of a ligand radical anion character of $\mathbf{6}^{-\cdot}$. Similar experiments have been performed before on metalloporphyrins.[23]

In addition to the electrochemical investigations, chemical reduction of **6** using NaHg was attempted and was monitored by proton NMR and EPR spectroscopy. In THF (or [D_8]THF) the one-electron reduction of **6** proceeded slowly at room temperature and could be conveniently followed through the colour change from orange-red to red-violet. In NMR spectroscopy, the reduction of **6** was accompanied by an additional line broadening and the entire loss of any residual signal fine structure, which was detected even in the spectrum of **6** for the most distant CH_3 groups only.[24] This observation is again indicative of the presence of a π-radical on $\mathbf{6}^{-\cdot}$ that has no magnetic coupling with the

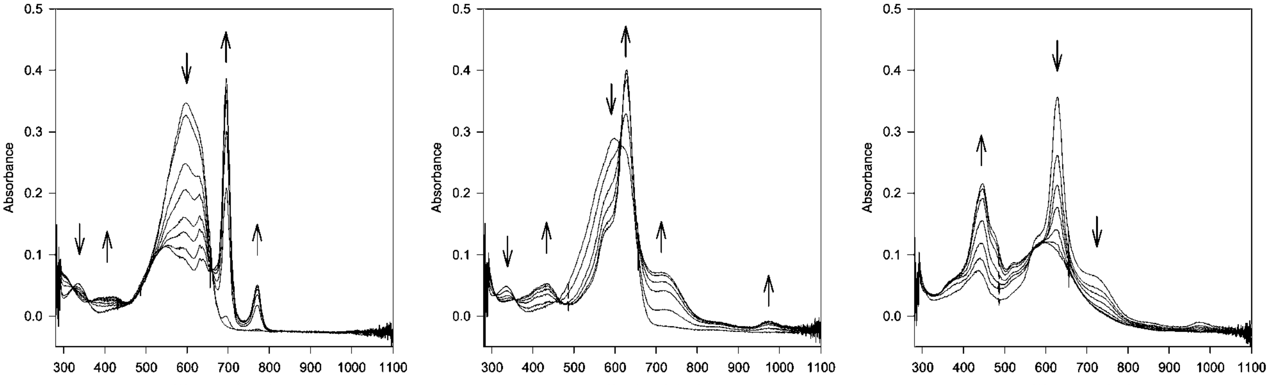


Figure 5. Time-resolved UV/Vis spectroelectrochemical measurements of free base 2,2′-bidipyrrin **4** in PhCN with 0.1 M Bu_4NPF_6; first column: Red. 1, second column Ox. 1, third column Ox. 2

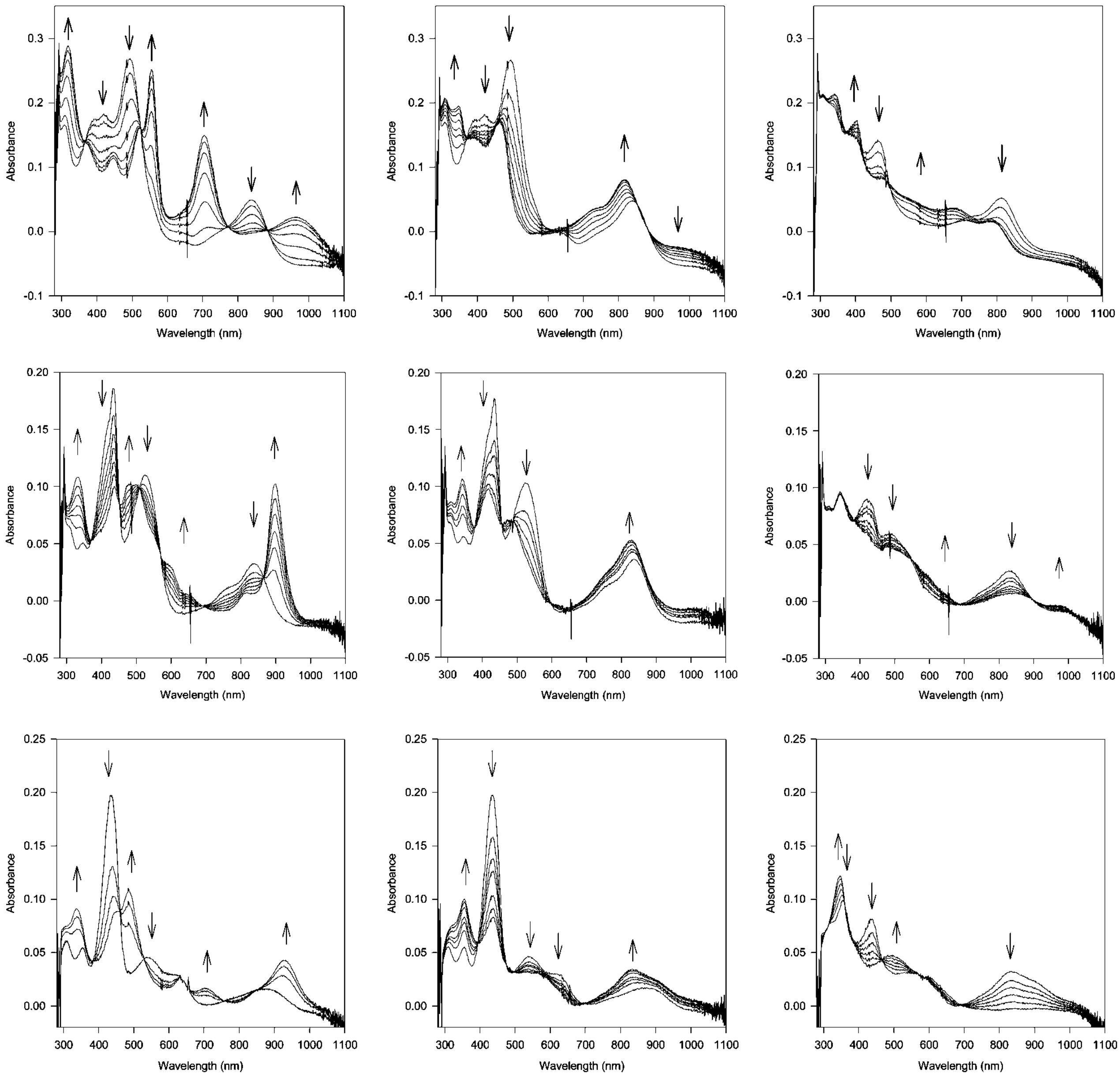


Figure 6. Time-resolved UV/Vis spectroelectrochemical measurements of 2,2′-bidipyrrinato complexes **7** (first row), **9** (second row), and **11** (third row) in PhCN with 0.1 M Bu_4NPF_6; first column: Red. 1, second column Ox. 1, third column Ox. 2

d-electron of the metal centre.[25] The EPR spectroscopic investigation of the reduction of **6** (X-band at 9.76 GHz, room temperature) gave the spectra depicted in Figure 7. Complex **6** shows an EPR spectrum similar to that of a related (porphyrinato)copper(II) complex,[26] with a g_0 value of 2.092 and a Cu hyperfine splitting of 82.6 G. The expected splitting of the signals by the nitrogen donors was not resolved. After chemical reduction, the signal for the Cu^{II} ion was still present and found shifted to $g_0 = 2.073$ with an enlarged splitting of 104.6 G. For $\mathbf{6}^{-\cdot}$ the hyperfine splitting by the nitrogen atoms is well resolved (line distance 16.6 G), and the theoretically possible nine lines (assuming, that all four nitrogen atoms are equivalent) can be found in two overlapping sets. The signal for the π-radical, however, is broad and heavily obscured by the signals of the single 3d-electron. The *g* value for this electron of ca. 2.00 is close to that of a free electron, which is expected for a porphyrinoid π-radical.[27]

Conclusion

(2,2′-Bidipyrrinato)copper(II) and -palladium(II) complexes belong to the same structural type as the respective nickel(II) complexes. The porphyrinoid M_1L_1 coordination mode generally leads to a helical distortion of the ligand scaffold, which is stable to helix inversion in all cases studied. The open-chain tetrapyrrolic ligand, however, is sufficiently flexible to accommodate different bonding situ-

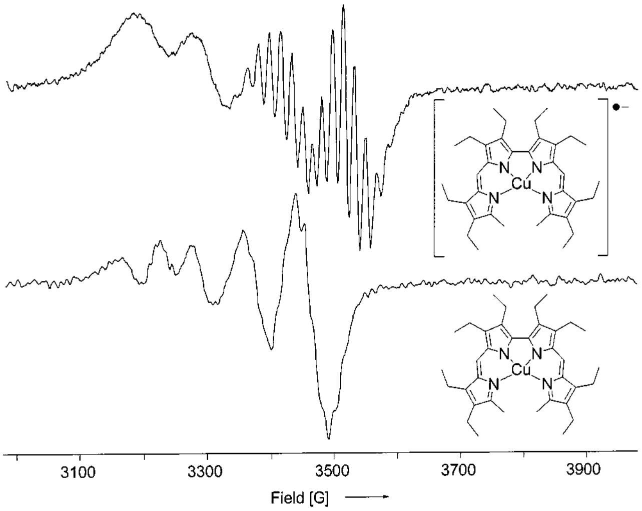


Figure 7. Solution EPR spectra of **6** and **6**$^{-\cdot}$ in THF at X-band (9.76 GHz)

ations for metal ions with square-planar or distorted tetrahedral coordination preferences. Electrochemically, 2,2′-bidipyrrinato complexes are enormously robust, so that even spectroelectrochemical analyses of electrogenerated oxidised and reduced species could be performed. The electrochemical behaviour of these complexes is strongly dependent on structural parameters, which almost always superimpose the electronic effects typical for the electrochemistry of metalloporphyrins.

Experimental Section

General: All reagents and solvents were purchased from commercial sources and used as received. NMR spectra were obtained in $CDCl_3$ solution with a Bruker AC 200 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^1H spectra) or to chloroform (^{13}C). Mass spectra (EI, 70 eV or FAB) were recorded with a Finnigan 90 MAT instrument; *m/z* values are given for the most abundant isotopes only. Melting points were measured by DTA with a Thermoanalyzer DuPont 9000. Elemental analyses (C, H, N) were effected at the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg. Solution EPR spectra were measured in THF at ambient temperature with a Bruker ESP 300 spectrometer at X-band (9.76 GHz). Chiral HPLC was performed with a Pirkle-type column (D-phenylglycine on spherical silica gel; 25 cm × 4.6 mm, 5 μ particle size), using a Latek P402 chromatographic system and 2% acetone in *n*-hexane as the eluent. The fractions were detected by single point UV absorption at 400 nm. Electrochemical studies were carried out in benzonitrile containing $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte (0.1 M). Benzonitrile (Aldrich) was dried with anhydrous $CaCl_2$ for 2 d, and further distilled from P_2O_5 under a reduced pressure of argon. $n\mathrm{Bu_4NPF_6}$ (Fluka, electrochemical grade) was dried under vacuum at 65 °C. Before use, the 0.1 M solution of $n\mathrm{Bu_4NPF_6}$ in benzonitrile was purified in a glove box on activated neutral alumina (Merck). The measurements were carried out in the glove box using a classical three-electrode cell. The working electrode was a platinum disk (2 mm in diameter), the pseudo reference electrode and the counter electrode being platinum wires. All potentials are given against the ferrocene/ferrocenium couple used as internal standard. The cell was connected to an EG&G PAR potentiostat (Model 273) interfaced with a computer (type PC). The studies were carried out by cyclic voltammetry (CV), at sweep rates ranging from 0.02 to 5 V/s, and by steady state voltammetry (SSV), on a platinum rotating disk electrode. Spectroelectrochemical measurements were performed in an air-tight closed quartz cell (1 mm) through an optically transparent thin-layer electrode (OTTLE) made of a Pt mini-grid (1000 mesh). The auxiliary electrode and the pseudo-reference electrode were Pt wires placed in separate compartments. The cell was filled with the electrolyte and the species to be studied, and hermetically closed in the glove-box. The cell was then removed from the glove-box and placed in a Hewlett Packard diode-array UV/Vis spectrometer model 8453. The OTTLE cell was connected to a Bruker potentiostat (model EI30M) for control and measurement of the electrochemical parameters.

Preparation of Complexes

(2,2′-Bisdipyrrinato)copper Complexes 6 and 7. − General Procedure: 2,2′-Bidipyrrin **4** or **5** (0.1 mmol) in 30 mL of dichloromethane was treated with a solution of copper(II) acetate hydrate (399 mg, 2 mmol) in 30 mL of methanol, and the resulting solution was stirred for 30 min (colour change from deep blue to brownish-orange). The reaction mixture was extracted four times with 100 mL of water, dried with sodium sulfate, and the solvent removed in vacuo. Recrystallization from dichloromethane/methanol yielded the title compounds as dark green, shiny crystals.

(3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-2,2′-bidipyrrinato)copper (6): Yield 48.6 mg (81%); m.p. 192 °C (decomp.). MS (70 eV, EI): *m/z* = 599 [M$^+$]. $C_{36}H_{48}CuN_4$ (600.34): C 72.02, H 8.06, N 9.33; found C 71.88, H 8.04, N 9.20.

Crystallographic Data for 6: $C_{36}H_{48}CuN_4$, green plates obtained by slow concentration of a CH_2Cl_2/*n*-hexane solution, crystal size: 0.40 × 0.40 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 12.580(3), b = 20.030(4), c = 13.316(3) Å, β = 108.721(4)°, V = 3177.8(11) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.255 g cm^{-3}, Z = 4, $2\theta_{\max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, scan mode: ω-scans, T = 173(2) K, 44776 measured, 5576 independent reflections, 5019 reflections observed for $I > 2\sigma(I)$, μ = 0.718 mm^{-1}, solved by Patterson method (SHELXS-97: G. Sheldrick, University of Göttingen), refined with full-matrix least squares on F^2 (SHELXL-97: G. Sheldrick, University of Göttingen), 380 parameters, H atoms refined with isotropic temperature factors. R = 0.0379, wR = 0.0964, residual electron density ρ = 0.438/−0.207 e Å^{-3}. CCDC-170387 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

(3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6,6′-diphenyl-2,2′-bidipyrrinato)copper (7): Yield 58.7 mg (78%); m.p. 249 °C (decomp.). MS (70 eV, EI): *m/z* = 751 [M$^+$]. $C_{48}H_{56}CuN_4$ (752.54): C 76.61, H 7.50, N 7.45; found C 76.28, H 7.29, N 7.19.

(2,2′-Bisdipyrrinato)palladium Complexes 8 and 9. − General Procedure: 2,2′-Bidipyrrin **4** or **5** (0.1 mmol) in 30 mL of dichloromethane was treated with a solution of palladium(II) acetate (80 mg, 0.4 mmol) in 30 mL of methanol, and the resulting solution was stirred for 30 min (colour change from deep blue to deep red). The reaction mixture was extracted with 100 mL of water, dried with sodium sulfate, and the solvent removed in vacuo. Chromatographic filtration with dichloromethane on silica gave the product as a red, major band. Recrystallization from dichloromethane/methanol yielded the title compounds as green, shiny crystals.

(3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-2,2′-bidipyrrinato)palladium (8): Yield 59.2 mg (92%); m.p. 212 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 1.03 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 1.06 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 1.08 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 2.11 (q, $^3J = 7.5$ Hz, 4 H, 2×CH_2CH_3), 2.31−2.39 (m, 12 H, 6×CH_2CH_3), 2.59 (s, 6 H, terminal CH_3), 6.18 (s, 2 H, H_{meso}). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3, 16.7, 16.8, 17.2, 17.3, 17.6, 17.7, 18.1, 18.4, 120.1, 128.1, 130.9, 131.6, 136.1, 138.5, 148.0, 150.1, 165.8. MS (70 eV, EI): m/z = 642 [M^+]. $C_{36}H_{48}N_4Pd$ (643.22): C 67.22, H 7.52, N 8.71; found C 67.21, H 7.50, N 8.51.

Crystallographic Data for 8: $C_{36}H_{48}N_4Pd$, green plates obtained by slow concentration of a CH_2Cl_2/n-hexane solution, crystal size: 0.40 × 0.40 × 0.24 mm, monoclinic, space group $P2_1/c$, a = 12.6786(19), b = 19.954(3), c = 13.3074(19) Å, β = 108.546(3)°, V = 3191.8(8) Å^3, $\rho_{calcd.}$ = 1.338 g cm^{-3}, Z = 4, $2\theta_{max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, scan mode: ω-scans, T = 173(2) K, 45066 measured, 5603 independent reflections, 5351 reflections observed for $I > 2\sigma(I)$, μ = 0.612 mm^{-1}, solved by direct methods (SHELXS-97: G. Sheldrick, University of Göttingen), refined with full-matrix least squares on F^2 (SHELXL-97: G. Sheldrick, University of Göttingen), 380 parameters, H atoms refined with isotropic temperature factors. R = 0.0456, wR = 0.1012, residual electron density ρ = 0.872/−0.900 e Å^{-3}. CCDC-170388 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

(3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6,6′-diphenyl-2,2′-bidipyrrinato)palladium (9): Yield 69.2 mg (87%); m.p. 267 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.55 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 0.58 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 0.83 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 0.96 (t, 6 H, $^3J = 7.5$ Hz, 2×CH_3), 1.04−1.36 (m, 8 H, 4×CH_2CH_3), 2.01, 2.26 (2×br.s, 14 H, terminal CH_3 and 4×CH_2CH_3), 7.19−7.61 (m, 10 H, H_{phenyl}). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.9, 16.2, 17.0, 17.1, 17.6, 17.8, 18.0, 18.5, 19.5, 127.4, 127.5, 128.1, 129.7, 130.1, 132.1, 137.9, 141.1, 142.0, 149.7, 151.3, 151.9, 165.6. MS (70 eV, EI): m/z = 794 [M^+]. $C_{48}H_{56}N_4Pd$ (795.41): C 72.48, H 7.10, N 7.04; found C 72.33, H 7.18, N 6.96.

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[1] M. Bröring, *Synthesis* **2000**, 1291−1294.
[2] M. Bröring, D. Griebel, C. Hell, A. Pfister, *J. Porph. Phthal.* **2001**, *5*, 708−714.
[3] A. W. Johnson, R. Price, *J. Chem. Soc.* **1960**, 1649−1653.
[4] M. Bröring, C. D. Brandt, J. Lex, H.-U. Humpf, J. Bley-Escrich, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2001**, 2549−2556.
[5] Y. Zhang, A. Thompson, S. J. Rettig, D. Dolphin, *J. Am. Chem. Soc.* **1998**, *120*, 13537−13538; for related structures, see also: R. G. Khoury, L. Jaquinod, K. M. Smith, *Tetrahedron* **1998**, *54*, 2339−2346.
[6] M. Bröring, A. Pfister, K. Ilg, *Chem. Commun.* **2000**, 1407−1408.
[7] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, I. T. Kay, J. Leng, *J. Chem. Soc. C* **1966**, 98−106.
[8] P. A. Lord, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **2000**, *39*, 1128−1134.
[9] R. G. Khoury, M. O. Senge, J. E. Colchester, K. M. Smith, *J. Chem. Soc., Dalton Trans.* **1996**, 3937−3950.
[10] A. J. Golder, K. B. Nolan, D. C. Povey, L. R. Milgrom, *Acta Crystallogr., Sect. C* **1988**, *44*, 1916−1917.
[11] M. Currie, J. D. Dunitz, *Helv. Chim. Acta* **1971**, *54*, 98−112.
[12] E. B. Fleischer, C. K. Miller, L. E. Webb, *J. Am. Chem. Soc.* **1964**, *86*, 2342−2347.
[13] R. Koerner, M. M. Olmstead, A. Ozarowski, S. L. Phillips, P. M. Van Calcar, K. Winkler, A. L. Balch, *J. Am. Chem. Soc.* **1998**, *120*, 1274−1284.
[14] A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1993**, *115*, 12206−12207.
[15] L. D. Sparks, C. J. Medforth, M.-S. Park, J. R. Chamberlain, M. R. Ondrias, M. O. Senge, K. M. Smith, J. A. Shelnutt, *J. Am. Chem. Soc.* **1993**, *115*, 581−592.
[16] M. O. Senge, C. J. Medforth, L. D. Sparks, J. A. Shelnutt, K. M. Smith, *Inorg. Chem.* **1993**, *32*, 1716.
[17] G. Peychal-Heiling, G. S. Wilson, *Anal. Chem.* **1971**, *43*, 550−556.
[18] D. Chang, T. Malinski, A. Ulman, K. M. Kadish, *Inorg. Chem.* **1984**, *23*, 817−824.
[19] J.-H. Fuhrhop, K. M. Kadish, D. G. Davis, *J. Am. Chem. Soc.* **1973**, *95*, 5140−5147.
[20] K. M. Barkigia, M. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1993**, *113*, 3627−3635.
[21] C. Bernard, J.-P. Gisselbrecht, M. Gross, E. Vogel, M. Lausmann, *Inorg. Chem.* **1994**, *33*, 2393−2401.
[22] J. Wytko, V. Berl, M. McLaughlin, R. R. Tykwinski, M. Schreiber, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1998**, *81*, 1964−1977.
[23] Y. J. Deng, X. H. Mu, P. Tagliatesta, K. M. Kadish, *Inorg. Chem.* **1991**, *30*, 1957−1960.
[24] G. M. Godziela, H. M. Goff, *J. Am. Chem. Soc.* **1986**, *108*, 2237−2243.
[25] For a discussion, see: A. L. Balch, *Coord. Chem. Rev.* **2000**, *200−202*, 349−377; L. Latos-Grazynski, J. Wojaczynski, R. Koerner, J. J. Johnson, A. L. Balch, *Inorg. Chem.* **2001**, *40*, 4971−4977.
[26] E. M. Roberts, W. S. Koski, *J. Am. Chem. Soc.* **1960**, *82*, 3006−3010.
[27] J. Seth, D. F. Bocian, *J. Am. Chem. Soc.* **1994**, *116*, 143−153.

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