(COD)Rh unit, yet we still lack understanding and rational control of such factors.

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Notes

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(Phthalocyaninato)osmium(II) and Bisaxially Coordinated (Phthalocyaninato)osmium(II) Compounds

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Bisaxially coordinated complexes MacML$_2$ and bridged systems [MacML]$_n$ with phthalocyanine (Pc) or 1,2- or 2,3-naphthalocyanine as the macrocycle (Mac) and transition metals, e.g. iron or ruthenium, as the central metal atom (M) have been systematically investigated by us regarding their semiconducting properties.[1,2] The third metal in the eighth group of the periodic table of elements, osmium, has rarely been used until today, however. On the other hand, (porphyrinato)osmium complexes with octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) as macrocyclic ligands have been much better studied than their analogous ruthenium complexes.[3–6]

Osmium phthalocyanine derivatives have been described several times in the literature.[7–15] The pure unsubstituted PcOs^{II} and bisaxially coordinated PcOsL$_2$ compounds with N-heterocyclic or isocyanide ligands or bridged PcOs compounds [PcOsL]$_n$ carrying bidentate ligands have not yet been reported.

Synthesis and Characterization of (Phthalocyaninato)osmium(II) (PcOs^{II})

All of the procedures that have been described so far for the

Table I. Electronic Absorption Maxima (nm) of $PcM(py)_2$ (M = Fe, Ru, Os) in Chloroform

complex	Q band			Soret band
PcFe(4-pic)$_2$[21,25]	656	594	410	328
PcRu(py)$_2$[21,24]	625	573	377	313
PcOs(py)$_2$[a]	616	563	369	308

[a] Bands also appear at 460, 436, and 416 nm.

synthesis of PcOs deliver only insufficiently characterized products and/or require the use of the highly poisonous OsO_4 as the starting metal compound. For the synthesis of pure PcOs^{II} we therefore followed the route that we have already described for the synthesis of pure PcRu^{II} [16] (Scheme I).

o-Cyanobenzamide[17] was reacted with $OsCl_3$ in molten naphthalene. After column chromatography a uniform product (TLC) is obtained. The FD mass spectrum does not show the expected molecular ion for PcOs (m/e = 702), but instead the peak for a dimeric molecule (m/e = 1407) with the characteristic isotopic pattern for osmium.[18] According to its IR spectrum, the crude product might actually be a bisaxially coordinated species, where derivatives of phthalic acid or the cyclized o-cyanobenzamide is axially coordinated. The crude PcOsL$_x$ is then heated slowly up to 400 °C under a stream of nitrogen, and this temperature is maintained for about 1 h. Reaction control is carried out by simultaneous thermogravimetry/differential thermal analysis (TG/DTA). Separation of the axially coordinated ligands is observed between 160 and 385 °C.

The FD mass spectrum of the resulting blue-black powder shows the expected molecular ion (m/e = 702) with the characteristic isotopic pattern for osmium. A signal for the dimeric [PcOs]$_2^+$ as for the crude PcOsL$_x$ cannot be detected. The infrared spectrum of PcOs is almost identical with that of PcRu[19–21] with only a few bands shifted to higher or lower frequencies, respectively.

This striking similarity can be explained by the nearly identical covalent radii of ruthenium(II) and osmium(II).[22] PcOs exhibits a dark conductivity of 2.5 × 10^{-5} S/cm (pressed powder, two-probe technique). This value is rather high compared with those of most metal phthalocyanines, but it is within the same range as the conductivity of PcRu.[19]

Bisaxially Coordinated (Phthalocyaninato)osmium(II) Complexes

Bis(pyridine)(phthalocyaninato)osmium(II) (PcOs(py)$_2$). PcOs(py)$_2$ can be synthesized from the crude PcOsL$_x$ or pure PcOs

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Scheme I
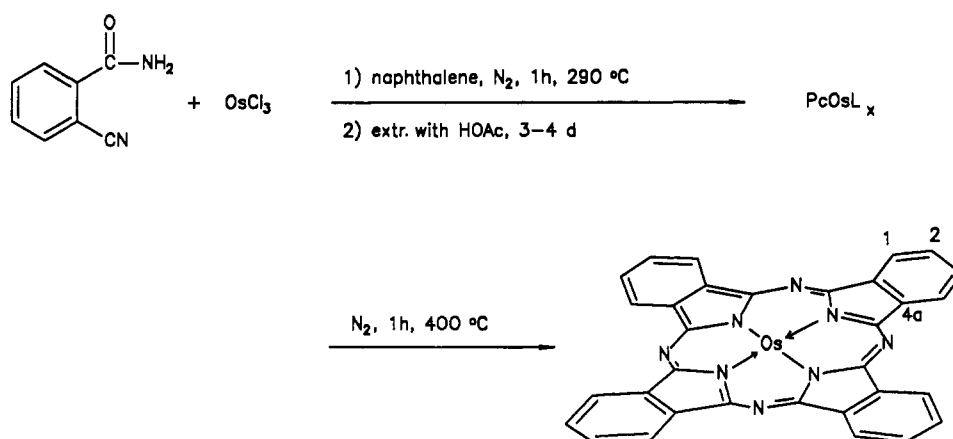
Table II. ^{1}H NMR Data for Iron, Ruthenium, and Osmium Phthalocyanines[a]

compd	Pc		py or pyz		py
	H[1]	H[2]	H[a]	H[b]	H[c]
PcFe(4-pic)$_2$[21]	9.27	7.92	1.95	4.78	
PcRu(py)$_2$[21,27]	9.13	7.87	2.43	5.21	6.02
PcOs(py)$_2$	8.83	7.71	3.24	5.27	6.20
PcFe(pyz)$_2$[23]	9.35	8.00	1.92	6.01	
PcRu(pyz)$_2$[16]	9.20	7.90	2.35	6.43	
PcOs(pyz)$_2$	8.93	7.81	2.99	6.46	

[a]Shifts are given δ (ppm) vs CHCl$_3$. Data for the free ligands (ppm): pyrazine H (8.63); pyridine H[a] (8.60), H[b] (7.25), H[c] (7.64).

by heating either compound in pyridine for several days; the product is precipitated by adding hexane. The infrared spectra of bis(pyridine) phthalocyaninato complexes of iron,[23] ruthenium,[21] and osmium look very much alike.

The electronic influence of the central metal atom on the macrocycle can be shown very well by comparing the absorption spectra of PcM(py)$_2$ with M = Fe, Ru, Os (Table I). The maxima of the absorption bands of the bis(pyridine) complexes are blue shifted from iron to ruthenium and to osmium. This is also true for other (phthalocyaninato)metal complexes of this group[21] and can be correlated to the d$_x$-donor ability of the central metal atom. Depending on the axial ligand, this shift is more or less pronounced.

The bands at 410, 377, and 369 nm for the iron, ruthenium, and osmium bis(pyridine) phthalocyaninato complexes, respectively, are assigned to charge-transfer transitions between the metal and the axial ligand.[26]

The solubility of bisaxially coordinated complexes PcML$_2$ (M = Fe, Ru, Os; L = py, pyz, tBuNC) in chloroform is sufficient to measure ^{1}H NMR spectra. A change in the central metal atom causes a shift for the protons of the phthalocyanine system (Table II). To underline the effect of the central metal atom, the ^{1}H NMR data of PcM(pyz)$_2$ complexes are also given in Table II.

As one goes from PcFeL$_2$ via PcRuL$_2$ to PcOsL$_2$ (Table II), the phthalocyanine protons H[1] and H[2] are shifted to higher field, caused by the increasing back-donation of the central metal atom, which leads to an increase in the electron density in the π orbitals of the macrocycle.[28] The protons of the axially coordinated

Table III. ^{13}C NMR Data for the C Atoms of the Phthalocyanine Ring in PcM(tBuNC)$_2$ (M = Fe, Ru, Os) and PcM(py)$_2$ (M = Ru, Os)[a]

compd	C$_1$	C$_2$	C$_{4a}$	N=C—N
PcFe(tBuNC)$_2$[29]	120.8	127.5	141.1	146.9
PcRu(tBuNC)$_2$[29]	121.7	127.7	140.5	143.6
PcOs(tBuNC)$_2$	121.8	128.0	140.1	145.2
PcRu(4-pic)$_2$[21]	121.2	127.8	140.8	143.6
PcOs(py)$_2$	121.9	128.2	139.9	148.4

[a]Shifts are given in δ (ppm) vs CDCl$_3$.

Table IV. NC Valence Frequencies of PcM(tBuNC)$_2$ (M = Fe, Ru, Os)[a]

ν_{NC}, cm^{-1}	2150	2142	2122
M	Fe[29]	Ru[29]	Os

[a]Nujol mull; ν_{NC} = 2134 cm^{-1} (film) for free tBuNC.

ligands are shifted to lower field in this series (Table II).

The solubilities of only a few (phthalocyaninato)metal complexes are sufficient to obtain ^{13}C NMR spectra. Because of the lack of data for the corresponding PcFe(py)$_2$ complex, in Table III are also listed the data of PcM(tBuNC)$_2$ complexes for comparison of the signals of the phthalocyaninato carbon atoms.

The influence of the central metal atom on the position of the ^{13}C nuclei in the ^{13}C NMR spectra is much smaller than that for the ^{1}H NMR spectra. The paramagnetic shielding term which comprises the nonspherical charge distribution of the electrons is the dominating shift[30] for the ^{13}C nuclei. Except for H, this is the same for all nuclei (Table III).

Significant differences concerning the thermal stabilities of PcM(py)$_2$ complexes (M = Fe, Ru, Os) are found as well.[21] PcOs(py)$_2$ shows an increased thermal stability compared with the corresponding iron compound.

Bis(dimethyl sulfoxide)(phthalocyaninato)osmium(II) (PcOs-(dmso)$_2$), Bis(pyrazine)(phthalocyaninato)osmium(II) (PcOs-(pyz)$_2$), and Bis(tert-butyl isocyanide)(phthalocyaninato)osmium(II) (PcOs(tBuNC)$_2$). Bis(dimethyl sulfoxide)(phthalocyaninato)osmium(II) (PcOs(dmso)$_2$) is synthesized by heating crude PcOsL$_x$ in dimethyl sulfoxide under a nitrogen atmosphere, analogous to the synthesis of pure PcRu.[16] After the mixture is cooled, dark purple crystals with the stoichiometry PcOs-(dmso)$_2$·dmso are obtained.

Bis(pyrazine)(phthalocyaninato)osmium(II) (PcOs(pyz)$_2$) and bis(tert-butyl isocyanide)(phthalocyaninato)osmium(II) (PcOs-(tBuNC)$_2$) are synthesized by reacting PcOs with excess pyrazine or tert-butyl isocyanide, respectively. Excess pyrazine is removed from the pulverized melt, and PcOs(pyz)$_2$ remains as a purple powder. PcOs(tBuNC)$_2$ is obtained as a purple powder after

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Table V. ^{1}H NMR Data for PcM(tBuNC)$_2$ (M = Fe, Ru, Os)^a

| M | Pc | | |
	H^1	H^2	CH$_3$
Fe^{29}	9.31	7.96	−0.51
Ru^{29}	9.25	7.94	−0.49
Os	9.11	7.87	−0.44

^{a}Shifts are given in δ (ppm) vs CHCl$_3$. Data for free tBuNC: CH$_3$, 1.44 ppm (1:1:1).[34]

Table VI. ^{13}C NMR (100.6 MHz) Data for the C Atoms of the Axially Coordinated tBuNC in PcM(tBuNC)$_2$ (M = Fe, Ru, Os)^a

M	C≡N	C(CH$_3$)$_3$	CH$_3$
Fe^{29}	143.0	55.0	28.7
Ru^{29}	133.9	54.5	28.7
Os	116.8	54.5	28.8

^{a}Shifts are given in δ (ppm) vs CDCl$_3$. Data for free tBuNC (ppm):[35] C≡N (153.2), C(CH$_3$)$_3$ (54.1), CH$_3$ (30.2).

washing the mixture with methanol at the end of the reaction. Both pyrazine and *tert*-butyl isocyanide do not react with crude PcOsL$_x$; i.e., they are not able to substitute the coordinated impurity in PcOsL$_x$.

As observed for the pyridine complexes, infrared spectra of PcOs(dmso)$_2$·dmso, PcOs(pyz)$_2$, and PcOs(tBuNC)$_2$ are almost indistinguishable from those of their corresponding ruthenium compounds.[16,20,21,29] The infrared spectrum of PcOs(pyz)$_2$ shows an intense band at 1578 cm^{-1}, which is assigned to the centrosymmetric vibrational mode of the axially coordinated pyrazine ligand.

Depending on the corresponding σ-donor and π-acceptor contribution, coordination to an isocyanide can either raise or lower the value of the NC frequency.[31–33] When isocyanides are coordinated to divalent metals, as is the case for most metal phthalocyanines, generally the σ-donor contribution dominates. The NC valence frequency is then shifted to higher wavenumbers. With increasing π-donor ability of the metal, however, this shift decreases. The pronounced π-back-bonding ability of the osmium ion even lowers the NC valence frequency compared to that of the free isocyanide (Table IV).

The electronic influence of the central metal ion on the macrocycle can also be seen in the UV–vis spectra. When PcOs(dmso)$_2$·dmso, PcOs(pyz)$_2$, and PcOs(tBuNC)$_2$ are compared with the corresponding ruthenium compounds, the Q band and the Soret band are found shifted to shorter wavelengths.[16,20,29]

The ^{1}H NMR spectrum of PcOs(dmso)$_2$·dmso confirms the stoichiometry of the compound. PcOs(pyz)$_2$ is also sufficiently soluble in CDCl$_3$ to allow the measurement of a ^{1}H NMR spectrum (Table II). The singlet of the free pyrazine (8.57 ppm) is split into an AA′XX′ pattern (H^a, 2.99 ppm; H^b, 6.46 ppm) by coordination to the (phthalocyaninato)osmium system. PcOs(pyz)$_2$ is thermally more stable than the corresponding ruthenium compound. The separation of the axial ligand in PcOs(pyz)$_2$ starts at about 260 °C with an endothermic maximum at 310 °C. Tables V and VI show some ^{1}H and ^{13}C NMR data of PcM(tBuNC)$_2$ for M = Fe, Ru, and Os.

Experimental Section

(Phthalocyaninato)osmium(II)(PcOs). A mixture of OsCl$_3$ (1 g, 3.4 mmol), o-cyanobenzamide (15 g, 0.1 mol), and naphthalene (10 g, 78 mmol) was heated under nitrogen at 290 °C for 1 h and then allowed to cool. The melt was crushed with a pestle and a mortar, washed with ethanol, and extracted with glacial acetic acid for 3–4 days. The residue was dried in vacuo at 120 °C and chromatographed on an aluminum oxide column (neutral, I) by eluting with CHCl$_3$: yield 400 mg of crude PcOsL$_x$: purple powder; analytically impure.

The product was heated slowly to 400 °C under an inert-gas stream (2 K/min), and this temperature was maintained for 1 h: yield 270 mg (11%); blue-black powder; pure PcOs. Anal. Calcd for C$_{32}$H$_{16}$N$_8$Os (M$_r$ = 702.7): C, 54.69; H, 2.29; N, 15.95. Found: C, 54.35; H, 2.49; N, 15.65.

Registry No. PcOs^{II}, 47823-18-7; PcOs(py)$_2$, 123775-08-6; PcOs-(dmso)$_2$, 123775-09-7; PcOs(pyz)$_2$, 123775-10-0; PcOs(*t*-BuNC)$_2$, 123775-11-1; o-cyanobenzamide, 17174-98-0.

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Mixed-Ligand Complexes of Tetravalent Metal Ions with Amine-N-polycarboxylates and Fluoride

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Formation of the mixed-ligand complexes of metal ions with amine-N-polycarboxylates and fluoride has recently been studied to examine the affinities of highly hydrolizable metal ions to fluoride and to estimate the solution structures of the parent and the mixed-ligand complexes.[1,2] Such equilibrium data are also of analytical importance, since the extent of formation of the mixed-ligand complexes defines the efficiency of masking reagents for metal ions in the determination of fluoride with ion-selective electrodes.[3] In this paper, we have made a systematic study on the formation of the mixed-ligand complexes of tetravalent metal ions (M = Ge, Sn, Ti, Zr, Hf, Th) with amine-N-polycarboxylates (L)^4 and fluoride and have found in the Th–EGTA–F$^-$ system an exceptionally large stability constant, which is ascribed to a mode of formation of mixed-ligand complexes different from that of the others.

The tetravalent metal complexes with EDTA were isolated as described in literature.[5] Thorium complexes with other ligands were prepared in solution without isolation. All these complexes hydrolyze even in an acidic medium, and the resultant mixed-ligand complexes with a hydroxo or oxo group generally have much lower affinities to fluoride.[2] The −log [H$^+$] ranges for existence of ML were estimated as shown in Table I from the equilibrium data in literature.[6–9] Several solutions containing a metal complex

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