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Bisaxially Coordinated (Phthalocyaninato)ruthenium(II) Compounds

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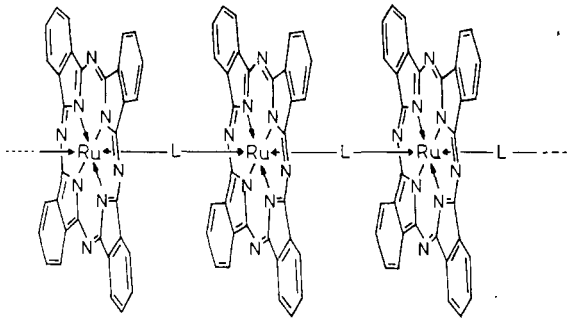
(Phthalocyaninato)ruthenium(II), PcRu, prepared by thermal decomposition of the bis(dimethyl sulfoxide) adduct PcRu-$(Me_2SO)_2 \cdot 2Me_2SO$ (**3**) is reacted with various N-donor ligands (L = pyrazine, substituted pyrazines, 4,4′-bipyridine, pyridazine, pyrimidine) to yield bisaxially coordinated monomeric derivatives of stoichiometry $PcRuL_2$ (**5–9**), which are structurally characterized mainly by ^1H NMR spectroscopy. Pyrazine and 4,4′-bipyridine can act as bidentate ligands as well, leading to one-dimensionally bridged polymer chain structures $[PcRuL]_n$ (**10** and **11**). With 1,4-diisocyanobenzene as a ligand to PcRu, both the monomer **12** and the polymeric compound **13** are obtained. Polymeric derivatives exhibit substantially higher dc conductivities compared to the corresponding monomeric complexes.

Introduction

Polymeric bridged macrocyclic metal complexes **1** are a new class of compounds, which we have under systematic investigation with respect to their properties as organic conductors.[1] The



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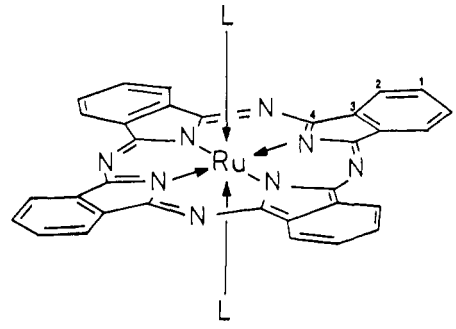
one-dimensional structure has three components: a planar, tetradentate macrocycle as exemplified in **1**: phthalocyaninate (Pc); a complexing transition-metal atom (e.g. Fe, Ru, Co, Cr, or Mn); and bridging linear bidentate π-electron-containing ligands L [e.g. pyrazine (pyz), bipyridine (bpy), 1,4-diisocyanobenzene (dib), or cyanide (CN)].

Examples for the polymers **1** are the (phthalocyaninato)iron and (tetrabenzoporphinato)iron compounds $[PcFe(pyz)]_n$, $[PcFe(dib)]_n$, $[PcFe(bpy)]_n$,[2] $[PcFe(tz)]_n$[3] (tz = tetrazine), and $[(TBP)Fe(dib)]_n$,[4] for which we have recently published the preparation, characterization, and conductivities.

We now report the characterization of the analogous (phthalocyaninato)ruthenium(II) polymers **1**, for which high complex stabilities were expected. As bidentate coordinatively binding bridging ligands L pyrazine, 4,4′-bipyridine, and 1,4-diisocyanobenzene were used.

The coordination behavior of the different ligands L has been studied with the corresponding bis-axial-substituted monomeric complexes **2**. To synthesize ruthenium compounds of types **1** and **2**, a suitable route for the preparation of pure (phthalocyaninato)ruthenium(II), PcRu, had to be developed first.



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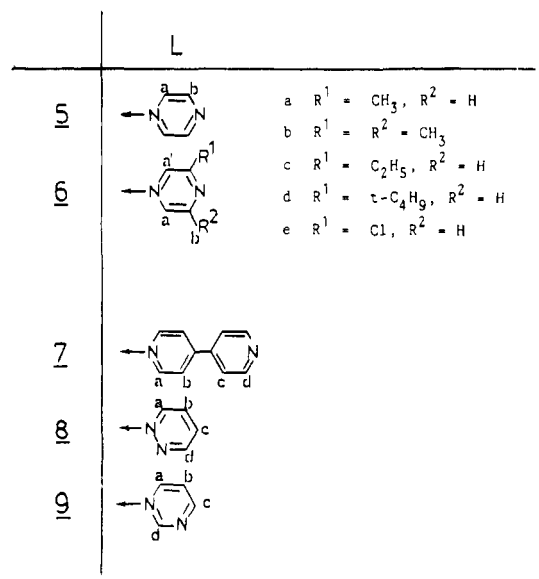

Results and Discussion

Synthesis and Characterization of (Phthalocyaninato)ruthenium(II). Several octahedrally coordinated (phthalocyaninato)ruthenium(II) complexes with various types of axial ligands (e.g. amines, pyridines, acetonitrile, CO, benzyl isocyanide, Me_2SO, tetrahydrofuran, and phosphines) have been reported in the literature.[5-12] In contrast to these well-characterized $PcRuL_2$ adducts no procedure has yet been described for the preparation of the analytically pure parent metallomacrocycle, (phthalo-

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cyaninato)ruthenium(II), PcRu. Reaction of $Ru_3(CO)_{12}$ with phthalonitrile[8] yields a "PcRu(CO)" complex with a strongly coordinated carbon monoxide ligand (as evidenced by IR spectroscopy), which cannot be completely removed in preparative scale, either by subsequent thermal treatment or by a conventional ligand-exchange reaction. From $RuCl_3 \cdot xH_2O$ and *o*-cyanobenzamide[5] or phthalonitrile[6,7] is obtained a chlorine-containing crude "PcRu" product, the nature of which (either a $PcRu^{III}Cl$ or a ring-chlorinated $ClPcRu^{II}$ species) is still controversal.[13] In our hands, the procedure given by Dolphin[9] using naphthalene as solvent and halogen acceptor turned out to be useful for the synthesis of a "PcRu" species of low chlorine content (after Soxhlet extraction with glacial acetic acid). We obtained an analytically pure, crystalline Me_2SO adduct $PcRu(Me_2SO)_2 \cdot 2Me_2SO$ (**3**)[14] by heating the above mentioned crude "PcRu" in Me_2SO[10,15] and then slowly cooling the hot filtrate.

Compound **3** was fully characterized by elemental analysis, simultaneous thermogravimetric/differential thermal analysis (TG/DTA), and ^1H NMR spectroscopy. Both ^1H NMR spectroscopy and TG/DTA clearly show that **3** contains two kinds of nonequivalently bonded Me_2SO molecules. Due to the ring current effect of the phthalocyanine system,[15] the NMR signal of the methyl protons of the axially coordinated Me_2SO ligands is shifted upfield to −1.18 ppm while the additional Me_2SO lattice solvent protons appear at 2.58 ppm. The different nature of the Me_2SO molecules in **3** is confirmed by TG/DTA experiments: the weakly bonded Me_2SO lattice solvent is split off between 145 and 190 °C with an endothermic DTA maximum at 175 °C (16.6% mass loss, calcd 16.8%); the loss of the two Me_2SO ligands coordinated to the (phthalocyaninato)ruthenium moiety is indicated by an endothermic DTA maximum at 330 °C (mass loss between 220 and 340 °C 16.2%, calcd 16.8%). The remaining blue-black residue was identified by means of elemental analysis and IR and mass spectroscopy as (phthalocyaninato)ruthenium(II) (**4**) free from chlorine or sulfur impurities. Thus, thermal decomposition of $PcRu(Me_2SO)_2 \cdot 2Me_2SO$ (**3**) either in an inert-gas stream or under high vacuum proved to be an efficient procedure for the purification of crude "PcRu" starting material.[13b]

Synthesis and Characterization of $PcRuL_2$ Complexes Containing Six-Membered N-Heterocyclic Donor Ligands. According to synthetic procedures for $PcRuL_2$ adducts (L = pyridine-type ligands),[7,9,10] PcRu (**4**) was reacted with a pyrazine (pyz) melt to yield, after removal of the excess ligand, the bisadduct $PcRu(pyz)_2$ (**5**). Similarly, upon treatment of **4** with 2-methylpyrazine (Mepyz), 2,6-dimethylpyrazine (Me_2pyz), 2-ethylpyrazine (Etpyz), 2-*tert*-butylpyrazine (*t*-Bupyz), 2-chloropyrazine (Clpyz), 4,4′-bipyridine (bpy), pyridazine (pdz), and pyrimidine (pym), the corresponding monomers $PcRu(Mepyz)_2$ (**6a**), $PcRu(Me_2pyz)_2$ (**6b**), $PcRu(Etpyz)_2$ (**6c**), $PcRu(t\text{-}Bupyz)_2$ (**6d**), $PcRu(Clpyz)_2$ (**6e**), $PcRu(bpy)_2$ (**7**), $PcRu(pdz)_2$ (**8**), and $PcRu(pym)_2$ (**9**), respectively, were obtained in good yields. The monomers **5–9**, isolated as blue to violet powders or fine crystals, are stable to oxygen and moisture. Although insoluble in common organic solvents such as alcohols, acetone, and ether, they dissolve readily in chloroform without any detectable degradation; $PcRu(t\text{-}Bupyz)_2$ (**6d**), as expected, exhibits the best solubility. In contrast to $PcFe(pyz)_2$, which in solution undergoes an immediate separation of one pyrazine ligand to form the insoluble polymeric coordination complex (μ-pyrazine)(phthalocyaninato)iron(II), $[PcFe(pyz)]_n$,[2] $PcRu(pyz)_2$ (**5**) is fairly stable in $CHCl_3$ solution. As evidenced by ^1H NMR spectroscopy, degradation of **5** leading to soluble, low molecular weight oligomeric complexes (pyz)-PcRu-[PcRu(pyz)]$_x$-PcRu(pyz) takes places only to a minor extent.

As observed for PcFe[2] and PcCo,[16] PcRu could not be reacted with pyrazine derivatives whose potential coordination sites are both sterically hindered by neighboring substituents (e.g. 2,5-dimethylpyrazine, 2,3,5,6-tetramethylpyrazine, and phenazine).

Experiments to prepare $PcRuL_2$ complexes by a ligand-exchange reaction starting from the bis(dimethyl sulfoxide) adduct **3** gave mixtures of complexes. Treatment of **3** with a 20-fold excess of pyrazine-type ligands at elevated temperature resulted in a product mixture, which was identified by NMR spectroscopy to consist of the desired $PcRuL_2$ adduct and the corresponding $PcRu(Me_2SO)L$ complex. According to ^1H NMR investigations (Table I), PcRu complexes **5–9** (i) are almost free from impurities, (ii) are diamagnetic (no paramagnetic line shifts detected), and (iii) have the stoichiometry $PcRuL_2$. Moreover, in the cases of the monomers **6a–e** containing 2- and 2,6-substituted pyrazine ligands, respectively, the NMR data unambiguously show that axial coordination to the central ruthenium atom takes place exclusively via the sterically nonhindered pyrazine nitrogen N-4.

Table I. ^1H NMR Data of **5–9**[a]

compd	H^a	H^b	$H^{a'}$	R^b	Pc[c]
$PcRu(pyz)_2$ (**5**)	2.35 4; m (4)[d]	6.43 4; m (4)[d]			9.20; 7.90
$PcRu(Mepyz)_2$ (**6a**)	2.15 2; d (3)	6.30 2; d (3)	2.17 2; s	1.09 6; s	9.19; 7.93
$PcRu(Me_2pyz)_2$ (**6b**)	1.98 4; s			1.03 12; s	9.19; 7.93
$PcRu(Etpyz)_2$ (**6c**)	2.20 2; d (3)	6.29 2; d (3)	2.17 2; s	1.35 4; q (7.5) 0.13 6; t (7.5)	9.20; 7.93
$PcRu(t\text{-}Bupyz)_2$ (**6d**)	2.27 2; d (3)	6.32 2; d (3)	2.25 2; s	0.16 18; s	9.18; 7.91
$PcRu(Clpyz)_2$ (**6e**)	2.15 2; d (4)	6.21 2; d (4)	2.27 2; s		9.23; 7.98

compd	H^a	H^b	H^c	H^d	Pc[c]
$PcRu(bpy)_2$ (**7**)	2.53 4; m (6)[d]	5.43 4; m (6)[d]	6.35 4; m (6)[d]	8.18 4; m (6)[d]	9.17; 7.90
$PcRu(pdz)_2$ (**8**)	2.89 2; m	5.31 2; m	5.70 2; m	6.82 2; m[e]	9.16; 7.87
$PcRu(pym)_2$ (**9**)	2.56 2; m	5.27 2; m	7.00 2; m	3.04 2; m[f]	9.16; 7.91

[a] Shifts are given in δ vs. $CHCl_3$ (7.24). For assignments see formulas **5–9**. Second line: integration; multiplicity (coupling constant in Hz). [b] **6a,b**: R = CH_3. **6c**: R = CH_2CH_3. **6d**: R = $C(CH_3)_3$. [c] AA′BB′ system. Multiplet near 9.2 ppm corresponds to inner Pc-ring protons (H^2); multiplet near 7.9 ppm to other Pc-ring protons. Integration = 8 throughout. [d] Part of an AA′XX′ system. Coupling constant corresponds to the separation between the two most intense signals of the multiplet. [e] J_{ab} = 6 Hz; J_{bc} = 8 Hz; J_{cd} = 5 Hz; J_{ac} = 1.5 Hz; J_{ad} = 1.2 Hz; J_{bd} = 2 Hz. [f] J_{ab} = 6 Hz; J_{bc} = 4.8 Hz; J_{cd} = 0 Hz; J_{ac} = 2.1 Hz; J_{ad} = 1 Hz; J_{bd} = 1.2 Hz.

Table II. UV/Vis Data of $PcRuL_2$ **5–9**[a]

compd	λ_{max}, nm					
$PcRu(pyz)_2$ (**5**)[b]	641	587	442	376 sh	314	268
$PcRu(Mepyz)_2$ (**6a**)	639	587	436	375 sh	313	273
$PcRu(Me_2pyz)_2$ (**6b**)	636	587 sh	431		313	273
$PcRu(Etpyz)_2$ (**6c**)	638	587	435		314	271
$PcRu(t\text{-}Bupyz)_2$ (**6d**)	637	588 sh	434		315	271
$PcRu(Clpyz)_2$ (**6e**)	641	585	462		315	
$PcRu(bpy)_2$ (**7**)[b]	626	575 sh	446	370	314	272
$PcRu(pdz)_2$ (**8**)	634	585 sh	453	375 sh	317	
$PcRu(pym)_2$ (**9**)	632	586 sh	425	377 sh	313	

[a] In $CHCl_3$. [b] In C_6H_5Cl for **5**: 638, 584, 439, 316. In C_6H_5Cl for **7**: 627, 575 sh, 450, 375, 368, 318.

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As expected, the shape of the UV/vis spectra of monomers **5–9** (Table II) is dominated by the intense Q (640-nm) and B (315-nm) transitions of the phthalocyaninato moiety. A weak absorption in the 450-nm range may be characteristic of the nature of the axial ligand. Although ascribed to the Fe → L CT transition in a similar $PcFeL_2$ adduct, this assignment is controversial[17] and thus cannot provide additional information for the structural characterization of $PcRuL_2$ complexes.

In addition, the monomers **5**, **7**, and **9** containing potentially bidentate ligands were investigated by thermal analysis. While the pyrimidine molecules in $PcRu(pym)_2$ (**9**) are split off in a single step between 270 and 400 °C (DTA: T_{max} = 360 °C, endothermic; Δm observed 20.3%, calculated for $PcRu(pym)_2 \rightarrow PcRu$ 20.7%), loss of the axially coordinated pyrazine ligands from $PcRu(pyz)_2$ (**5**) is clearly divided into two well-resolved steps. Upon heating **5**, two endothermic DTA maxima near 285 and 560 °C are observed, each corresponding to the separation of one pyrazine molecule from the parent monomer **5**. The total mass loss up to 560 °C (found 20.0%) is in reasonable agreement with the calculated loss for the decomposition $PcRu(pyz)_2 \rightarrow PcRu$ (20.7%). Similar behavior is observed for $PcRu(bpy)_2$ (**7**). After separation of one bpy ligand (DTA: T_{max} = 350 °C, endothermic; Δm observed 16.6%, calculated 16.9%), a continuous mass loss is detected upon further heating of the sample.

Polymeric (Phthalocyaninato)ruthenium(II) Complexes with Pyrazine and 4,4′-Bipyridine. As described previously,[2] polymeric (phthalocyaninato)iron(II) complexes $[PcFeL]_n$ (L = pyz, bpy) are readily available by (i) refluxing the parent metallomacrocycle PcFe in chlorobenzene with a slight (1:1.1) excess of the respective ligand and (ii) thermal decomposition of the monomer $PcFeL_2$ (L = pyz) in a high-boiling solvent.

Attempts to apply these procedures to the analogous phthalocyaninato)ruthenium system failed to yield homogeneous polymeric complexes $[PcRuL]_n$ (L = pyz (**10**), bpy (**11**)). Upon reaction of PcRu (**4**) with a 1.1-fold excess of pyrazine and 4,4′-bipyridine in boiling chlorobenzene, considerable amounts of the monomers $PcRu(pyz)_2$ (**5**) and $PcRu(bpy)_2$ (**7**), respectively, were detected by IR spectroscopy (vide infra).

Taking into account the PcRu:L stoichiometry (1:1.1) chosen, the residue (after extraction of the soluble $PcRuL_2$ monomers) of the above reaction cannot consist of pure, if any, $[PcRuL]_n$ polymers but is likely to contain unknown amounts of unreacted PcRu (**4**) starting material.

Similarly, refluxing $PcRu(pyz)_2$ (**5**) in chlorobenzene does not result in a quantitative separation of one pyrazine ligand from **5**, although the monomer concentration gradually decreases. Thus, depending on the reaction time, mixtures with varying contents of polymer **10** and monomer **5** were obtained. As revealed by elemental analysis, the insoluble polymer residue still contains some chlorobenzene that cannot be removed either by washing with alcohol or by drying under vacuum at 100 °C.

However, according to the results of the TG/DTA investigations, PcRu:L = 1:1 complexes should be accessible by slowly heating $PcRu(pyz)_2$ (**5**) and $PcRu(bpy)_2$ (**7**) to a final temperature characteristic of the end of the first step in the respective TG curves. The thus obtained 1:1 adducts, isolated as deep blue powders, are insoluble in organic solvents. A pentacoordinated PcRuL monomer structure with one terminal pyz or bpy ligand can be ruled out for these products from their IR spectra, by applying the symmetry considerations outlined in a previous paper on PcFe and PcCo complexes:[18] the transition from monomeric $PcRu(pyz)_2$ (**5**) with terminal ligands to the one-dimensionally bridged polymer complex $[PcRu(pyz)]_n$ (**10**) containing bidentate pyrazine is associated with an increase in the local symmetry of the axial pyrazine ligand ($C_{2v} \rightarrow D_{2h}$). In consequence, some C_{2v}-allowed vibrational modes of the pyz ligand present in the IR spectrum of $PcRu(pyz)_2$ (**5**) (1581 cm^{-1}, ν_{8a}, centrosymmetric ring stretch; 1227 cm^{-1}, ν_{9a}, in plane C–H bending; 698 cm^{-1}, ν_{6b}, ring deformation)[19] are IR-restricted for bidentate (D_{2h}) pyrazine and accordingly are no longer observed in the spectrum of $[PcRu(pyz)]_n$ (**10**). Similar to the case of the corresponding PcFe complexes, the out-of-plane C–H vibration (ν_{11}), which is IR-allowed in adducts both with terminal and with bridging pyrazines molecules, is shifted from 807 cm^{-1} in $PcRu(pyz)_2$ (**5**) to 815 cm^{-1} in the polymeric compound **10**.

Assuming a coplanar arrangement of the pyridyl groups in 4,4′-bipyridine,[20] the most predominant spectral changes observed when $PcRu(bpy)_2$ (**7**) is polymerized to $[PcRu(bpy)]_n$ (**11**) can be explained by similar symmetry considerations. Due to the increasing local symmetry, the in-plane vibrations ($\nu_{8a,b}$, ν_{9a}) of the terminal bpy ligand in **7** at 1589 and 1214 cm^{-1} disappear upon polymerization. Again, the out-of-plane C–H vibration (ν_{11}) is shifted to higher energy in the polymeric derivative **11** (830 cm^{-1}) in comparison to that of the parent monomer **7** (807 cm^{-1}). In addition, the shift of the out-of-plane C–H mode of the equatorial phthalocyaninato ligand to lower energy (729 cm^{-1} (**5**) → 720 cm^{-1} (**10**); 732 cm^{-1} (**7**) → 722 cm^{-1} (**11**)), which was found to be characteristic of the analogous PcFe monomer/polymer systems,[18] provides evidence for a polymeric structure of the (phthalocyaninato)ruthenium complexes **10** and **11**.

1,4-Diisocyanobenzene as a Ligand to PcRu. Coordination of various unidentate isocyanides CNR (R = alkyl, aryl) to the PcRu moiety leading to a series of well-characterized $PcRu(CNR)_2$ adducts has been reported by us elsewhere.[21] With this experience at hand, 1,4-diisocyanobenzene (dib), containing two active coordination sites, was reacted with PcRu (**4**) to yield, depending on the reaction conditions, both the monomer complex $PcRu(dib)_2$ (**12**) and the dib-bridged 1:1 polymer $[PcRu(dib)]_n$ (**13**). The monomer **12** is readily precipitated from a chloroform solution containing **4** and a 50-fold excess of the dib ligand upon treatment with *n*-hexane, while the polymer **13** is obtained by refluxing a PcRu:dib = 1:1.1 mixture in acetone for 24 h.

According to ^1H NMR investigations, the monomer **12** is not analytically pure but is likely to contain a dimeric species, as evidenced by the appearance of a set of low-intensity AA′BB′ signals near 9.14 and 7.89 ppm besides the Pc-ring proton resonances of **12** near 9.32 and 8.01 ppm, respectively.[22] These additional absorptions are suppressed if an excess of 1,4-diisocyanobenzene is added to the $CDCl_3$ solution, the remaining NMR lines being fully coincident with the $PcRu(dib)_2$ monomer structure. The exact nature of the dimeric species remains elusive. The stoichiometry of the blue-black powder **13** isolated from the 1:1.1 reaction of PcRu with dib in acetone is confirmed by thermal analysis. The axially coordinated dib ligand is split off at temperatures above 210 °C (DTA: T_{max} = 295 °C, endothermic). The total mass loss up to 500 °C (17.6%) agrees with the separation of one dib ligand per (phthalocyaninato)ruthenium moiety (17.3%); the infrared spectrum of the thermal residue is indistinguishable from that of an authentic sample of PcRu (**4**).

In analogy with the case for PcRu pyz and bpy complexes, conclusions on the structure of **13** can be drawn from a comparison of the IR characteristics of the respective dib adducts with regard to both the $C_{2v} \rightarrow D_{2h}$ symmetry restriction of the centrosymmetric ring stretch ($\nu_{8a,b}$)[23] and the shift of the intense N≡C stretching

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(19) For assignments see ref 18 and literature cited therein.

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(22) (a) Similar Pc-ring proton shifts have been reported for stacked-ring (phthalocyaninato)silicon derivatives RO–$(PcSiO)_x$–PcSi–OR (x = 1.2). E.g.: Mezza, T. M.; Armstrong, N. R.; Ritter, G. W.; Iafalice, J. P.; Kenney, M. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *137*, 227. (b) In solutions of pure $PcRuL_2$ with L = 1,4-diisocyano-2,3,5,6-tetramethylbenzene, the formation of the dimer $L(PcRuL)_2$ and the trimer $L(PcRuL)_3$ was detected by ^1H NMR spectroscopy: Keppeler, U.; Hanack, M., unpublished results.

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Table III. Pressed-Powder Electrical Conductivity Data for Monomeric and Polymeric PcRu Complexes at Room Temperature

compd	σ_{RT}, Ω^{-1} cm^{-1}
PcRu(pyz)$_2$ (**5**)	2×10^{-11} [b]
PcRu(bpy)$_2$ (**7**)	1×10^{-11} [b]
PcRu(CNPh)$_2$[a]	3×10^{-11} [b]
[PcRu(pyz)]$_n$ (**10**)	1×10^{-7} [b,c]
[PcRu(bpy)]$_n$ (**11**)	2×10^{-8} [b]
[PcRu(dib)]$_n$ (**13**)	2×10^{-6} [c]

[a] CNPh = phenyl isocyanide; for preparation see ref 21. PcRu(CNPh)$_2$ was chosen to serve as a monomeric reference system rather than PcRu(dib)$_2$ (**12**), as **12** (i) is not free from (dimeric) impurities and (ii) seems to decompose under pressure to form the polymer **13** as evidenced by IR investigations on KBr pellets. [b] Two-probe technique. [c] Four-probe technique.

vibration of the axially coordinated dib ligand. Again, the absence of $\nu_{8a,b}$ in the IR spectrum of the 1:1 adduct **13**, which is however present in the spectrum of PcRu(dib)$_2$ (**12**) at 1592 cm^{-1}, gives evidence for a polymeric structure of **13** with 1,4-diisocyanobenzene acting as a bidentate ligand. A slight shift of the Pc out-of-plane C–H mode, characteristic of pyz and bpy polymers **10** and **11**, is also observed for the dib system (**12**, 731 cm^{-1}; **13**, 728 cm^{-1}).

Upon coordination of aromatic isocyanides (e.g. phenyl isocyanide) to the PcRu moiety, the intense $\nu_{N\equiv C}$ absorption of the free ligand is shifted to lower energy,[21] due to a distinct metal → ligand π back-donation. The same is true for the dib complexes **12** and **13**, the polymer system **13** exhibiting a larger shift of the N≡C frequency as compared to the monomer **12** (dib, 2130 cm^{-1}; **12**, 2095 cm^{-1}; **13**, 2087 cm^{-1}). Interestingly, a shoulder near 2130 cm^{-1}, indicative of a terminal, noncoordinating isocyano group, cannot be detected in the spectrum of **12**, suggesting a complete delocalization of the charge, transferred from the central metal to the π-electronic system of the axially coordinated ligand. In accordance with this model, the $\nu_{N\equiv C}$ frequency must exhibit an additional decrease in a [PcRu(dib)]$_n$ polymer chain, where π-electron density from two metal centers is transferred to the now-bidentate dib ligand.

Conductivity Measurements. Monomeric PcRuL$_2$ and polymeric [PcRuL]$_n$ complexes were tested for their dc dark conductivities (Table III).

In accordance with that of the analogous PcFe complexes,[2] polymerization of PcRu via the bidentate bridging ligands pyz, bpy, and dib resulting in the one-dimensional linear-chain structure is paralleled by a significant increase in conductivity as compared to the respective monomeric PcRuL$_2$ derivatives. Albeit slightly reduced, the conductivities of the (phthalocyaninato)ruthenium polymers **10**, **11**, and **13** (Table III) reflect the same characteristics with regard to the axial bridging ligand (dib > pyz > bpy) as their iron analogues ([PcFe(dib)]$_n$, 2×10^{-5} Ω^{-1} cm^{-1}; [PcFe(pyz)]$_n$, 10^{-6} Ω^{-1} cm^{-1}; [PcFe(bpy)]$_n$, 2×10^{-8} Ω^{-1} cm^{-1})[2].

As in the case of [PcFe(pyz)]$_n$ and [PcFe(dib)]$_n$,[1a,24] the PcRu polymers **10** and **13** are doped with weighed amounts of iodine in the presence of a few drops of benzene, to form blue-black powders [PcRuLI$_x$]$_n$. As evidenced by IR spectroscopy, the doping is not likely to affect the polymeric structure of the parent systems. The doped ruthenium polymers show distinct conductivity enhancements up to 10^{-2} and 10^{-1} Ω^{-1} cm^{-1} at the maximum dopant level and are fairly stable under ambient conditions. A detailed report about the doping experiments and the electrical properties of [PcRuLI$_x$]$_n$ will be published elsewhere.[25]

Experimental Section

Starting Materials and Instrumentation. Pyrazine, the substituted pyrazines, 4,4′-bipyridine, pyridazine, and pyrimidine were commercially available. 1,4-Diisocyanobenzene was prepared according to a given procedure.[26] Crude "PcRu" was prepared by a method described previously.[9]

Infrared spectra were recorded on a Perkin-Elmer 398 as Nujol mulls. ^{1}H NMR spectra were obtained on a Bruker WH 90 and WM 400, respectively, using $CDCl_3$ as solvent and internal standard.

Thermogravimetric measurements and differential thermal analyses were carried out simultaneously on a Netzsch STA Model 429 under a flow of nitrogen (20 mL/min), with a heating rate of 2 K/min. UV/vis spectra were recorded in purified chloroform or chlorobenzene on a Beckman Acta M-VII.

Dc conductivity measurements were performed on pressed pellets (13-mm diameter, 1 kbar) with home-build setups using either standard two-point or four-probe techniques.[27,28]

Bis(dimethyl sulfoxide)(phthalocyaninato)ruthenium(II) (3). A 4-g sample of "PcRu" was suspended in 60 mL of dimethyl sulfoxide, and the mixture was heated under N_2 protection for 3 h at 130 °C. Upon cooling of the hot filtrate, violet crystals of the stoichiometry PcRu(Me$_2$SO)$_2$·2Me$_2$SO (**3**) were obtained, which were washed with methanol and dried in vacuo at 70 °C. Yield: 1.3 g (18.5%).

Anal. Calcd for $C_{40}H_{40}N_8O_4S_4Ru$ (M_r = 926.1): C, 51.87; H, 4.35; N, 12.10; S, 13.84. Found: C, 51.44; H, 5.05; N, 11.91; S, 13.80. ^{1}H NMR: δ 9.32 m (Pc H^2), 8.02 m (Pc H^1), 2.58 s (Me$_2$SO uncoordinated), −1.18 s (Me$_2$SO coordinated). UV/vis λ_{max}, nm ($CHCl_3$): 641, 580, 545 sh, 313.

(Phthalocyaninato)ruthenium(II) (4). PcRu(Me$_2$SO)$_2$·2Me$_2$SO (**3**) was slowly heated (5 K/min) under high vacuum to a final temperature of 330 °C, which was maintained for 5 h. After cooling, PcRu (**4**) was obtained as a blue-black powder in quantitative yield.

Anal. Calcd for $C_{32}H_{16}N_8Ru$ (M_r = 613.6): C, 62.63; H, 2.63; N, 18.26; Ru, 16.47. Found: C, 62.69; H, 2.59; N, 18.23; Ru, 16.2. Mass spectrum: m/e 614 (40, M$^+$), 128 (100, [C$_6$H$_4$(CN)$_2$]$^+$).

General Directions for the Preparation of (Phthalocyaninato)bis(pyrazine)ruthenium(II) (5), Bis(2-methylpyrazine)(phthalocyaninato)ruthenium(II) (6a), Bis(2,6-dimethylpyrazine)(phthalocyaninato)ruthenium(II) (6b), Bis(2-ethylpyrazine)(phthalocyaninato)ruthenium(II) (6c), Bis(2-*tert*-butylpyrazine)(phthalocyaninato)ruthenium(II) (6d), Bis(2-chloropyrazine)(phthalocyaninato)ruthenium(II) (6e), (Phthalocyaninato)bis(pyridazine)ruthenium(II) (8), and (Phthalocyaninato)bis(pyrimidine)ruthenium(II) (9). A 1-mmol sample of PcRu (**4**) was suspended in 20 mmol of the liquid or melted ligand, and the mixture was heated for 24 h at 80 °C. After cooling, the reaction mixture was treated with methanol to remove the excess ligand. The remaining residue was vacuum-dried at 80 °C. Yields: 65–95%.

Anal. Calcd for **5** (violet powder), $C_{40}H_{24}N_{12}Ru$ (M_r = 773.8): C, 62.09; H, 3.13; N, 21.72. Found: C, 61.63; H, 2.91; N, 21.47. Calcd for **6a** (violet powder), $C_{42}H_{28}N_{12}Ru$ (M_r = 801.8): C, 62.91; H, 3.52; N, 20.97. Found: C, 62.43; H, 3.41; N, 20.79. Calcd for **6b** (fine, violet crystals), $C_{44}H_{32}N_{12}Ru$ (M_r = 829.9): C, 63.68; H, 3.89; N, 20.26. Found: C, 62.53; H, 3.90; N, 19.64. Calcd for **6c** (fine, violet crystals), $C_{44}H_{32}N_{12}Ru$ (M_r = 829.9): C, 63.68; H, 3.89; N, 20.26. Found: C, 63.34; H, 3.78; N, 20.04. Calcd for **6d** (dark blue powder), $C_{48}H_{40}N_{12}Ru$ (M_r = 886.0): C, 65.07; H, 4.55; N, 18.97. Found: C, 63.90; H, 4.69; N, 18.72. Calcd for **6e** (blue-violet powder), $C_{40}H_{22}Cl_2N_{12}Ru$ (M_r = 842.7): C, 57.01; H, 2.63; Cl, 8.42; N, 19.95. Found: C, 55.95; H, 2.33; Cl, 8.39; N, 19.78. Calcd for **8** (fine, dark violet crystals), $C_{40}H_{24}N_{12}Ru$ (M_r = 773.8): C, 62.09; H, 3.13; N, 21.72. Found: C, 61.98; H, 3.10; N, 21.87. Calcd for **9** (blue-violet powder), $C_{40}H_{24}N_{12}Ru$ (M_r = 773.8): C, 62.09; H, 3.13; N, 21.72. Found: C, 61.69; H, 3.25; N, 21.47.

Bis(4,4′-bipyridine)(phthalocyaninato)ruthenium(II) (7). A 1-mmol sample of PcRu (**4**) was suspended in 30 mmol of melted 4,4′-bipyridine, and the mixture was heated for 24 h at 120 °C. Excess ligand was removed either by washing of the reaction mixture with ethanol or by high-vacuum sublimation at 90 °C. Yield: quantitative, violet powder.

Anal. Calcd for $C_{52}H_{32}N_{12}Ru$ (M_r = 926.0): C, 67.45; H, 3.48; N, 18.15. Found: C, 66.40; H, 3.57; N, 18.12.

(Phthalocyaninato)(μ-pyrazine)ruthenium(II) (10). **10** was obtained by slowly heating (2 K/min) (phthalocyaninato)bis(pyrazine)ruthenium(II) (**5**) in an inert-gas stream to a final temperature of 300 °C. Yield: quantitative, deep blue powder.

Anal. Calcd for [$C_{36}H_{20}N_{10}Ru$]$_n$ (M_r = 693.7): C, 62.33; H, 2.91; N, 20.19; Ru, 14.57. Found: C, 60.84; H, 2.68; N, 19.76; Ru, 14.3. UV/vis (C_6H_5Cl) λ_{max}, nm: 796, 620.

(μ-4,4′-Bipyridine)(phthalocyaninato)ruthenium(II) (11). **11** was obtained analogously by heating the corresponding monomeric compound **7** to a final temperature of 400 °C. Yield: quantitative, blue-violet powder.

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Anal. Calcd for $[C_{42}H_{24}N_{10}Ru]_n$ (M_r = 769.8): C, 65.53; H, 3.14; N, 18.20. Found: C, 65.17; H, 3.21; N, 18.07. UV/vis (C_6H_5Cl) λ_{max} = 693 nm.

Bis(1,4-diisocyanobenzene)(phthalocyaninato)ruthenium(II) (12). A 0.2-g (0.33-mmol) sample of PcRu (**4**) and 2 g (15.6 mmol) of 1,4-diisocyanobenzene were heated in 100 mL of chloroform under reflux for 1 h. After cooling to room temperature, the reaction mixture was filtered; the deep blue filtrate was concentrated to one-third of its parent volume and subsequently treated with 50 mL of *n*-hexane. The precipitate was suction-filtered, washed with methanol, and dried in vacuo at 70 °C. Yield: 0.24 g (85%), violet powder.

^{1}H NMR: δ 9.32 m (8 Pc H^2); 8.01 m (8 Pc H^1); 5.21 m (4 H^a), 6.45 m (4 H^b) (for nomenclature see Table I). UV/vis (C_6H_5Cl) λ_{max}, nm: 644, 619 sh, 583, 357, 310.

(μ-1,4-Diisocyanobenzene)(phthalocyaninato)ruthenium(II) (13). A 0.61-g (1-mmol) sample of PcRu (**4**) and 0.14 g (1.1 mmol) of 1,4-diisocyanobenzene were heated in 70 mL of acetone under reflux for 24 h. After cooling to room temperature, the reaction mixture was centrifuged; the residue was washed with 200 mL of acetone and then dried in vacuo at 70 °C. Yield: 95%, blue-black powder.

Anal. Calcd for $[C_{40}H_{20}N_{10}Ru]_n$ (M_r = 741.7): C, 64.77; H, 2.72; N, 18.89. Found: C, 63.60; H, 2.80; N, 17.95. UV/vis (C_6H_5Cl) λ_{max}, nm: 639, 619 sh, 582, 395, 360, 309.

Doping of [PcRu(pyz)]$_n$ (10) and [PcRu(dib)]$_n$ (13) with Iodine. Weighed quantities of polymers **10** and **13** and appropriate amounts of iodine were rigorously ground together (10–15 min) in a mortar in the presence of a few drops of benzene. After evaporation of the solvent at elevated temperature (50–70 °C) in an inert-gas stream, finely divided blue-black solids $[PcRuLI_x]_n$ (L = pyz, dib; x = 1.5, 2) were obtained. Stoichiometries of the iodine-doped polymers were confirmed by elemental analysis.

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Interaction of Copper(II) with *N*-(2-Hydroxyethyl)piperazine-*N*′-ethanesulfonic Acid (HEPES)

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The widespread use of HEPES as the biochemical buffer of choice at neutral pH is predicted on the assumption of its lack of binding affinity and reactivity with metal ions. In fact, under conditions encountered in studying Cu(II) reactions, complexation with and oxidation of HEPES by the metal was observed. The redox reaction only occurs in presence of ligands that stabilize Cu(I). The reduction of Cu(II) is first order in HEPES and second order in Cu(II). The pH profile suggests a direct interaction between HEPES and Cu(II). Several alcohols were tested for their ability to reduce Cu(II). In the absence of a N ligand the reaction is very slow or zero. Caution in the use of HEPES to study Cu reactions is advised.

Introduction

The selection of proper buffers for investigating the chemistry and biochemistry of trace metals in a variety of systems is a significant problem. Every buffer provides a potential ligand for cations. The use of hydrogen phosphate or hydrogen carbonate, e.g., is severely restricted because of the insolubility of many trace metal phosphates and carbonates. The application of amine buffers such as tris(hydroxymethyl)aminomethane (Tris) seemed to obviate these problems. However, it was soon recognized that Tris could form complexes with some of the trace metals.[1] The search for a more "innocent" buffer led to *N*-(2-hydroxyethyl)-piperazine-*N*′-ethanesulfonic acid (HEPES) (Figure 1). This buffer has become widely accepted and applied.[2-5] In the course of experiments concerning the reduction of Cu(II) by heme proteins,[6] we found a weak but significant interaction between HEPES and Cu(II). The nature of the Cu(II) reaction with HEPES and other related compounds, in particular the structurally related compound dimethylethanolamine (DMEA) (Figure 1), is reported here.

It has been long known that Cu(II) is able to oxidize certain organic compounds, if the resultant Cu(I) can be held in a stabilized form. For example, acetonitrile binds Cu(I) and enhances oxidation reactions. In the Fehling reaction, aldehydes are oxidized and the Cu(I) is stabilized in form of the insoluble copper(I) oxide.[7] Bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and its disulfonated derivative (batho) stabilize Cu(I) because of their peculiar steric properties. The redox potential $E°$(Cu(II)/Cu(I)) in the presence of batho is 0.62 V compared to 0.167 V for the aqua ion.[8,9] We have carried out kinetic studies of the oxidation reaction of HEPES and other alcohols by Cu(II) in the presence of batho, and have characterized the significant interaction of the Cu^{II}-$(batho)_2$ complex with HEPES.

Experimental Section

Copper(II) sulfate pentahydrate (Mallinckrodt, analytical reagent), HEPES (Sigma), and disodium bathocuproinedisulfonate (Sigma) were used. All solutions with batho were kept in the dark prior to use. All other chemicals were of reagent grade quality. The copper complexes were prepared by mixing aqueous solutions of copper sulfate and the ligands at the concentrations indicated. All reactions were carried out at an ionic strength of 1.0 M NaCl. The reduction of Cu(II) was measured spectrophotometrically. The alcohol was present in 3.0 mL of 1.0 M NaCl. Following equilibration to the desired temperature, 30 μL of 0.1 mM Cu(II) aqua complex or Cu(II) complex solution was added and rapidly mixed. In the case of DMEA, 20 mM phosphate buffer was used

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