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Phthalocyanine Complexes of Ruthenium(II)

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Continuing our studies of model complexes for biological systems, especially those relating to heme proteins [1], we have prepared some new complexes of ruthenium(II) containing phthalocyanine (Pc) as the macrocyclic N_4 ligand system.

Although there have been several previous reports on the preparation of ruthenium phthalocyanine complexes, most of these have not been well-characterized. Reaction of *o*-cyanobenzamide with $RuCl_3 \cdot 3H_2O$ in a naphthalene melt has been reported to give a complex "RuPc", which after extraction with aniline was said to give a crystalline complex $RuPc \cdot 6C_6H_5NH_2$ [2]. Complexes with the same stoichiometry resulted on using other amines such as n-butylamine and 4-methylpyridine [3]. Extraction of the same crude "RuPc" with dimethylsulphoxide and N,N′-dimethylformamide (dmf) is said to give analogous compounds [4]. Reaction of $RuCl_3 \cdot 3H_2O$ with 1,2-dicyanobenzene reportedly gives Cl-RuPc [5]. Interaction of "RuPc" with concentrated H_2SO_4 has been noted to give, without demetallation, a monoprotonated species $[RuPcH]^+$, with protonation occurring on a non-coordinating nitrogen atom [6]; no details of the preparation of the "RuPc" were given. Little has appeared on the catalytic properties of ruthenium phthalocyanines, but RuPc and ClRuPc, prepared by unspecified means, are reported in a patent to carbonylate aromatic nitro-compounds to isocyanates under high temperatures and pressures [7]:

$$ArNO_2 + CO \rightarrow ArN{=}C{=}O + O_2$$

Results and Discussion

Investigation of several possible methods for the preparation of ruthenium phthalocyanine complexes reveals that the reaction of $RuCl_3 \cdot 3H_2O$ with *o*-cyanobenzamide, using naphthalene as a dilutant, is the most effective. A method similar to that employed for synthesis of Ru(TPP)(CO) [8] (TPP = tetraphenylporphyrinato), namely by reacting $Ru_3(CO)_{12}$ with H_2Pc, gives a product which is probably RuPc(CO) [ν(CO) = 1945 cm^{-1}, Nujol] but the method was somewhat irreproducible, and sometimes additional weak i.r. bands were observed in the carbonyl region. Chemical analyses were also variable. Other methods similar to those employed for the preparation of ruthenium Schiff base complexes [9] using the dialkali metal salts of phthalocyanine, failed to yield any ruthenium-containing species.

The product formed by reaction of $RuCl_3 \cdot 3H_2O$ and *o*-cyanobenzamide is a blue-black powder which, when Soxhlet-extracted with aromatic amines, gives deep blue solutions. Chromatography of these solutions using alumina or florisil yields a blue ethereal eluate from which are isolated purple crystals of the complexes $RuPcL_2$ (L = py, 4-Mepy, 4-^{t}Bupy). A black residue left in the Soxhlet has been reported as pure RuPc [2], but the residue that we obtain contained excess *o*-cyanobenzamide and other impurities.

The prolonged carbonylation of $RuPcL_2$ in refluxing diglyme under 1 atm CO results in the replacement of one amine linand by a carbonyl to give the complexes RuPc(CO)L [ν(CO) = 1980 cm^{-1}, $CHCl_3$], which can be isolated as purple crystals following chromatography; these species are also generated by

TABLE I. Analytical Data.

Complex	Calculated %			Found %		
	C	H	N	C	H	N
$RuPc(4\text{-}Mepy)_2$	66.1	3.7	17.6	66.4	3.6	16.9
RuPc(CO)(4-Mepy)·0.25 diglyme	63.3	3.3	16.4	62.5	3.5	16.0
$RuPc(py)_2$	65.8	4.3	17.3	65.4	3.4	18.2
RuPc(CO)(py)·0.25 diglyme	62.8	3.4	16.7	62.9	3.3	16.7
$RuPc(4\text{-}^tBupy)_2$	68.0	4.8	15.9	68.3	4.6	15.0
$RuPc(CO)(4\text{-}^tBupy)$	65.6	4.2	16.4	64.9	3.7	16.2

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TABLE II. N.M.R. Spectra[a].

Complex	$\tau_{\mathrm{aromatic(py)}}$		τ_{X}, N⌬–X	$\tau_{\mathrm{phthalocyanine}}$[b]
	H_α	H_β		
$RuPc(py)_2$	7.53[c]	4.53[d]	3.94[e]	0.83, 2.07
RuPc(CO)py	7.99[e]	4.65[f]	3.99[g]	0.59, 1.88
$RuPc(4\text{-}Mepy)_2$	7.66[h]	4.96[h]	8.84[i]	0.85, 2.11
RuPc(CO)(4-Mepy)	8.17[h]	4.92[h]	8.85[i]	0.65, 1.95
$RuPc(4\text{-}^{t}Bupy)_2$	7.62[h]	4.80[h]	9.69[i]	0.84, 2.10
$RuPc(CO)(4\text{-}^{t}Bupy)$	8.18[j]	4.80[j]	9.79[i]	0.67, 1.97

[a] Measured in $CDCl_3$ relative to tetramethylsilane = 10τ. [b] Two pairs of doublets. [c] Doublet of triplets $J_{H\gamma-H\beta}$ = 7Hz, $J_{H\gamma-H\alpha}$ ≈ 2Hz. [d] Doublet of triplets $J_{H\alpha-H\beta} \approx J_{H\beta-H\gamma}$ = 5Hz. [e] Doublet of doublets $J_{H\alpha-H\beta}$ = 5 Hz, $J_{H\alpha-H\gamma}$ = 2Hz. [f] Doublet of triplets $J_{H\alpha-H\beta} \approx J_{H\alpha-H\beta}$ = 6Hz. [g] Doublet of triplets $J_{H\alpha-H\beta}$ = 7Hz, $J_{H\alpha-H\gamma}$ = 2Hz. [h] Doublet $J_{H\alpha-H\beta}$ = 6Hz. [i] Singlet. [j] Doublet $J_{H\alpha-H\beta}$ = 7Hz.

TABLE III. Visible Spectra in CH_2Cl_2.

Complex	λ_{max} nm ($\epsilon \times 10^{-4}$, l mol^{-1} cm^{-1})
$RuPc(4\text{-}Mepy)_2$	622 (6.7), 560 (2.8), 375 (2.8)
RuPc(CO)(4-Mepy)	640 (15.2), 618 (4.5), 580 (4.1), 342 (2.9)
$RuPc(py)_2$	622 (7.4), 567 (2.9), 375 (2.6)
RuPc(CO)(py)	637 (16.5), 614 (4.5), 578 (3.7), 342 (2.8)
$RuPc(4\text{-}^{t}Bupy)_2$	621 (6.5), 567 (2.8), 375 (2.7)
$RuPc(CO)(4\text{-}^{t}Bupy)$	640 (17.0), 615 (3.9), 579 (3.5), 345 (2.8)

reaction of RuPc(CO) with the amine ligands. The spectral and analytical data for these complexes are given in Tables I–III.

Photolysis of the RuPc(CO)L or RuPc(CO) complexes in the presence of excess amine generates the bis amine species in solution as identified by visible spectra. We also find that the complex believed to be $RuPc(dmf)_2$ [4] is in fact RuPc(CO)(dmf) [ν(CO) = 1943 cm^{-1}, Nujol], and only on photolysis of this complex in dmf is the bis amide complex formed. The Figure shows the visible spectral changes observed generally for photolysis of RuPc(CO)L complexes; for the L = pyridine system shown, isosbestic points occur at 302, 339, 356, 444, 517, 574, 598, 630 and 664 nm. The photolysis product in dmf is thought to be RuPc(dmf)L rather than $RuPc(dmf)_2$, although the visible spectra are likely to be indistinguishable. However, the final solutions on exposure to CO or O_2 show reactivity different (in terms of rates, *etc.*) to that shown by solutions of $RuPc(dmf)_2$ [10], and are thus considered to contain the mixed ligand species.

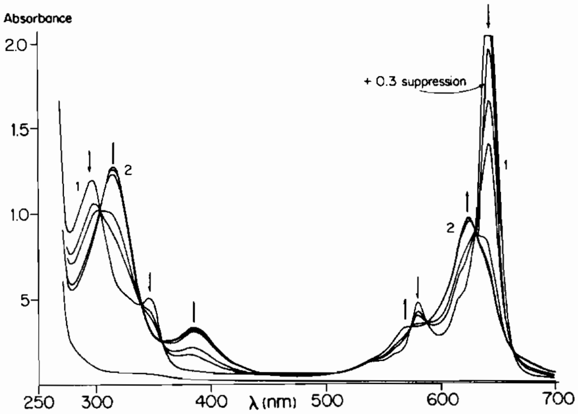

Figure. Visible spectral changes as a function of time for the photolysis of RuPc(CO)(py), *1*; half-life is ~2h at 20 °C. In pyridine, the product *2* is $RuPc(py)_2$; in dmf, *2* is probably RuPc(dmf)(py) (see text).

Experimental

All preparations were carried out under argon atmosphere using standard Schlenk techniques, unless noted otherwise.

Dmf was distilled from anhydrous $CuSO_4$ prior to use. Other solvents were reagent grade and were used without further purification. *o*-Cyanobenzamide was prepared by a standard procedure [11].

Photolysis experiments were carried out under vacuum using a 650 W visible photo-flood lamp.

Spectra were recorded on a Varian XL-100 operating in the Fourier transform mode (^{1}H nmr) a Cary

17D (uv, vis), and a Perkin Elmer 457 (ir). Microanalyses were carried out by P. Borda of this department.

Bis(pyridine)phthalocyaninatoruthenium(II)

A mixture of $RuCl_3 \cdot 3H_2O$ (1.0 g, 3.8 mmol), *o*-cyanobenzamide (10 g, 68 mmol) and naphthalene (4g, 31 mmol) was heated at 290 °C for *ca* 1 h and the mixture then allowed to cool. Ethanol (10 cm^3) was added to the residues and the resulting suspension filtered and the solid dried at 100 °C.

The dried residues were Soxhlet-extracted with glacial acetic acid (50 cm^3) until the washings were colourless (*ca.* 24 h). The remaining blue-black solid residues were dried in an oven at 120 °C to remove traces of acetic acid. The solid was then Soxhlet-extracted with the required amine (50 cm^3) until the washings were clear (*ca.* 12 h). The resulting blue solution was then added to an alumina chromatography column containing hexane, and the column was then eluted with hexane until all the excess pyridine had been removed. The column was then eluted with diethyl ether, and a deep blue eluate was obtained which on evaporation to low volume yielded purple crystals of the complexes. Yield *ca.* 5%.

Carbonyl(pyridine)phthalocyaninatoruthenium(II)

$RuPc(py)_2$ (0.2 g, 0.3 mmol) was dissolved in diglyme (50 cm^3) and carbon monoxide bubbled through the refluxing solution until the visible spectrum showed that all the reactant had been carbonylated (*ca.* 5 h). The resulting blue solution was chromatographed as above. Yield *ca.* 30%.

$Ru_3(CO)_{12}$ (1.0 g, 1.6 mmol) and phthalocyanine were refluxed together in benzonitrile for 1½h yielding a deep blue solution. Chromatography of this solution using alumina and Et_2O as elutant yielded a dark blue solid which was probably RuPc(CO), Soxhlet extraction of the dark blue solid with the pyridines, followed by work-up as described above, yielded a product identical with that prepared by the preceding method. Yield *ca.* 10%.

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References

1 D. Dolphin, N. P. Farrell and B. R. James, *J. Am. Chem. Soc., 100,* 324 (1978).

2 P. C. Krueger and M. E. Kenney, *J. Inorg. Nucl. Chem., 25,* 305 (1963); J. W. van Eek, private communication.

3 J. E. Maskasky, *Ph.D. Thesis,* Case Western Reserve University (1974).

4 C. K. Choy and M. E. Kenney, private communication.

5 I. M. Keen and B. W. Malerbi, *J. Inorg. Nucl. Chem., 27,* 1311 (1965).

6 B. D. Berezin, *Zh. Obshch. Khim., 43,* 2738 (1973).

7 M. Hiraoka and M. Ito, Japan Pat. 7,414,731; through *Chem. Abs., 81,* 120195 (1974).

8 J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc., 95,* 2141 (1973).

9 J. R. Thornback and G. Wilkinson, *J. Chem. Soc. Dalton,* 110 (1978).

10 To be published.

11 G. T. Byrne, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.,* 1017 (1934).