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Ruthenium Phthalocyanine Chemistry: Synthesis and Properties of a Mixed-valence Nitrido-bridged Ruthenium Phthalocyanine Dimer†

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The synthesis and some properties of μ-nitrido-bis[(phthalocyaninato)ruthenium], [{Ru(pc)}$_2$N], are reported. Infrared spectra, structural, magnetic, and e.s.r. data identify this complex as a mixed-valence Ru^{III}–Ru^{IV} dimer. It represents the first example of a ruthenium phthalocyanine complex containing the metal atom in oxidation states higher than II.

Difficulties encountered with the synthesis and characterization of pure (phthalocyaninato)ruthenium(II), [Ru(pc)] (pc = phthalocyaninate dianion, $C_{32}H_{16}N_8^{2-}$), presumably influenced the development of ruthenium phthalocyanine chemistry, so far restricted to ruthenium(II) six-co-ordinate derivatives of formulae [Ru(pc)L$_2$] (L = neutral monodentate donor) or [{Ru(pc)L}$_n$] (L = bidentate N-base).[1] We recently described the synthesis of the first nitrido-bridged iron phthalocyanine dimer, *i.e.* [{Fe(pc)}$_2$N],[2] and compared its electrochemical behaviour in pyridine (py) with that of the analogous complex [{Fe(tpp)}$_2$N] (tpp = 5,10,15,20-tetraphenylporphyrinate dianion).[3] We report here the synthesis and characterization of a nitrido-bridged ruthenium phthalocyanine analogue of formula [{Ru(pc)}$_2$N], formally a mixed-valence Ru^{III}–Ru^{IV} dimer. To our knowledge, no other examples have been reported in the literature of similar N-atom-bridged ruthenium complexes containing N$_4$ porphyrin or porphyrin-like macrocycles.

Experimental

Preparation of [Ru(pc)], [Ru(pc)(dmso)$_2$]·2dmso, *and* [Ru(pc)(py)$_2$].—Based on the previously reported procedure by Dolphin *et al.*[4] [Ru(pc)] was prepared by reaction of RuCl$_3$·3H$_2$O with *o*-cyanobenzamide in naphthalene at 280—290 °C for 2 h. The suspension was then brought to room temperature and the solid material was extracted with glacial CH$_3$COOH in a Soxhlet apparatus for 36—48 h. The undissolved residual 'ground [Ru(pc)]' was subsequently purified by: (*a*) sublimation under vacuum (10^{-2}—10^{-3} mmHg) at 550 °C (Found: C, 62.4; H, 2.5; N, 18.5. Calc. for $C_{32}H_{16}N_8Ru$: C, 62.6; H, 2.65; N, 18.25%); (*b*) conversion into [Ru(pc)(dmso)$_2$]·2dmso (dmso = dimethyl sulphoxide) as described elsewhere,[1] followed by elimination of dmso by heating under vacuum (10^{-2}—10^{-3} mmHg) at 300 °C for 2 h (Found: C, 62.3; H, 2.5; N, 18.3%); (*c*) formation of [Ru(pc)(py)$_2$] by extracting 'ground [Ru(pc)]' with pyridine in a Soxhlet apparatus and then elimination of pyridine from the adduct by heating under vacuum (10^{-2}—10^{-3} mmHg) at 350—360 °C for 2 h (Found: C, 62.05; H, 2.70; N, 18.0%). Quantities of 50—100 mg of pure [Ru(pc)] could be easily obtained by method (*a*) whereas larger amounts (1—2 g) could be prepared by method (*b*), which is preferred to method (*c*) because of the lower temperatures required for the elimination of the adduct molecules and for more satisfactory elemental analyses on [Ru(pc)].

Preparation of [{Ru(pc)}$_2$N].—The compounds [Ru(pc)] or [Ru(pc)(py)$_2$] were used as starting materials for the preparation of this μ-nitrido dimeric species: [Ru(pc)] (300 mg), or [Ru(pc)(py)$_2$] (350 mg), and NaN$_3$ (300 mg) were suspended in α-chloronaphthalene and heated, with stirring, at 280—290 °C for 20 h. Brought to room temperature, the suspension was filtered and the bluish solid [{Ru(pc)}$_2$N] was washed with H$_2$O and acetone and heated for 30 min at 250 °C under vacuum (10^{-2}—10^{-3} mmHg) to give the product (Found: C, 60.7; H, 2.45; N, 18.8. Calc. for $C_{64}H_{32}N_{17}Ru$: C, 61.9; H, 2.6; N, 19.2%). The complex, indefinitely stable to air, is practically insoluble in non-donor or weakly donor solvents and very scarcely soluble (*ca.* 10^{-5} mol dm^{-3}) in heterocyclic N-bases (pyridine, 4-methylpyridine, *etc.*). Like [{Fe(pc)}$_2$N], [{Ru(pc)}$_2$N] shows no tendency further to co-ordinate N-base molecules at the external axial sites of the ruthenium atoms within the dimer.

Preparation of [{Ru(pc)}$_2$^{15}N].—This ^{15}N isotopically labelled species was prepared from [Ru(pc)] (30 mg) and Na^{15}N$_3$ (30 mg) (99% in ^{15}N) in α-chloronaphthalene following a procedure identical to that used for [{Ru(pc)}$_2$N].

Preparation of [Fe(pc)], [Fe(pc)(dmso)$_2$]·2dmso, *and* [Fe(pc)(py)$_2$].—The compound [Fe(pc)] was an Eastman Kodak product purified by sublimation under vacuum (10^{-2} mmHg) at 400—450 °C. [Fe(pc)(dmso)$_2$]·2dmso was obtained from a hot solution of [Fe(pc)] in dmso under nitrogen.[5] [Fe(pc)(py)$_2$] was prepared by dissolving [Fe(pc)] in hot pyridine from which the bis-adduct reprecipitates on cooling.

Physical Measurements.—Infrared spectra were taken on a Perkin-Elmer 983 spectrophotometer using Nujol mulls on NaCl discs, or KBr pellets. Visible solution spectra in pyridine were run on a Perkin-Elmer 330 instrument. *X*-Ray powder patterns were obtained with a Debye powder camera (114.6 mm diameter) with a Cu-K_α (Ni-filtered) radiation. Magnetic

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† *Non S.I.-units employed:* mmHg ≈ 133 Pa, B.M. ≈ 9.274×10^{-24} J T^{-1}.

susceptibilities were measured on a Gouy balance. E.s.r. spectra (*X*-band) were run on a Varian E9 instrument.

Results and Discussion

[Ru(pc)] *and its Adducts*.—Following the method previously outlined by Dolphin *et al.*,[4] and recently re-examined by Kobel and Hanack,[1] pure [Ru(pc)] (**1**) was obtained from 'ground [Ru(pc)]' (**2**) (see Experimental section) and then converted into the adduct [Ru(pc)(dmso)$_2$]·2dmso (**3**). This adduct was previously formulated as [Ru(pc)(dmso)$_2$][4] and [Ru(pc)(dmso)$_6$],[6] though it was apparently obtained under similar experimental conditions. The formulation [Ru(pc)(dmso)$_2$]·2dmso, as given by Kobel and Hanack,[1] is definitely the correct one, as also verified by us by elemental and thermogravimetric analyses. Elimination of dmso from (**3**) under drastic conditions (see Experimental section) leads to (**1**). The structural similarity between (**3**) and its iron analogue has been already considered and the presence of S-bonded dmso to ruthenium was also suggested,[4] as found by *X*-ray analysis of [Fe(pc)(dmso)$_2$]·2dmso.[5]

We have now established that (**3**) is strictly isomorphous with the corresponding iron species, a fact which lends more support to the hypothesis of dmso being S-bonded to the metal atom in the ruthenium complex.[4] We could also obtain (**1**) from (**2**) by extraction with pyridine and subsequent elimination of the pyridine molecules from the adduct [Ru(pc)(py)$_2$] (**4**). Finally, microcrystalline purple (**1**) was obtained by sublimation of (**2**) or (**4**) under vacuum (550 °C, 10^{-2} mmHg).

All samples of [Ru(pc)] obtained by the different methods used were found to be isomorphous with one another. However, [Ru(pc)] is not isomorphous with the crystallographic β-form of many first transition series metal phthalocyanines, including [Fe(pc)], which is known from *X*-ray work.[7]

[{Ru(pc)}$_2$N] (**5**).—The μ-nitrido dimeric species (**5**) was obtained from (**1**) or (**4**) by a method similar to that used for [{Fe(pc)}$_2$N].[2,3] The compound [Ru(pc)(N$_3$)] is very likely formed as an intermediate of the reaction. Samples of [{Ru(pc)}$_2$N] obtained from different preparations show essentially identical *X*-ray powder patterns. The complex is indefinitely stable in air. Thermogravimetric analysis indicates that the complex can be heated, under N$_2$, up to temperatures of 350—400 °C without significant decomposition. Its visible absorption spectrum in pyridine solution shows a main band with maximum intensity at a wavelength lower (600 nm) than that found for (**1**) (620 nm) in the same solvent. Noticeably, the observed spectral variations in going from (**1**) to (**5**) are similar in direction and magnitude to those observed by changing [Fe^{II}(pc)] (main absorption at 653 nm) into [{Fe(pc)}$_2$N] (630 nm). In contrast to what is observed for the μ-oxo dimer [{Fe(pc)}$_2$O], no breaking of the μ-nitrido species (**5**) and reduction to the Ru^{II} monomeric species [Ru(pc)(py)$_2$] is produced by standing for a long time in contact with pyridine, as was also the case for [{Fe(pc)}$_2$N], compound (**5**) being recovered unchanged even from pyridine solutions kept at the boiling point for several hours. Under experimental conditions identical to those used for the oxidation of [{Fe(pc)}$_2$N] to the corresponding monocation [{Fe(pc)}$_2$N]$^+$,[2,3] compound (**5**) remains unchanged.

Compound (**5**) shows an i.r. spectrum which differs from that of (**1**) essentially in the presence of a broad medium-strong absorption at 1 040 cm^{-1} [Figure (*a*)]. This absorption falls in the range (1 150—1 000 cm^{-1}) where a number of μ-nitrido binuclear ruthenium cationic and anionic species of formulae [Ru$_2$N(NH$_3$)$_8$X$_2$]$^{3+}$ (X = Cl, Br, or NO$_3$) and [Ru$_2$NX$_8$(H$_2$O)$_2$]$^{3-}$ (X = Cl, NCS, or NO$_2$) all exhibit strong and sharp bands assigned as ν_{asym}(Ru–N–Ru).[8] All these complexes are expected to have a linear Ru–N–Ru bond system, as has been shown by *X*-ray diffraction for two of them.[9] Thus, the band at 1 040 cm^{-1} in the i.r. spectrum of (**5**) is also assigned as ν_{asym}(Ru–N–Ru) and leads to an assumption of a linear (or quasi-linear) Ru–N–Ru moiety in this complex. The assignment of this band has been confirmed by ^{15}N isotopic enrichment using Na^{15}N$_3$ (99% ^{15}N) as starting material. The i.r. spectrum of [{Ru(pc)}$_2$^{15}N] [Figure (*b*)] exhibits ν_{asym}(Ru–^{15}N–Ru) at 1 023 cm^{-1}, *i.e.* 27 cm^{-1} lower than for [{Ru(pc)}$_2$^{14}N], in good agreement with expectation.[8] Finally, [{Ru(pc)}$_2$N] shows an *X*-ray powder spectrum identical to those of the already known [{Fe(pc)}$_2$O][10] and [{Fe(pc)}$_2$N],[2,3] both characterized as linear or quasi-linear single-atom bridged dimeric Fe–X–Fe species (X = O or N). This structural relationship is of relevant support to (**5**) as being a dimeric species having a Ru–N–Ru bridging moiety.

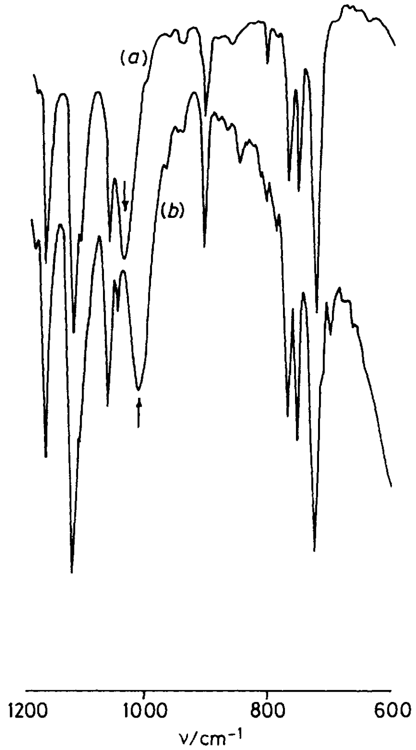

Figure. Nujol mull i.r. spectra: (*a*) [{Ru(pc)}$_2$^{14}N]; (*b*) [{Ru(pc)}$_2$^{15}N]. The arrows indicate bands assigned as ν_{asym}(Ru–N–Ru)

It has been shown recently by visible spectroscopy that a one-electron oxidation of [Ru^{II}(pc^{2-})] complexes can lead to the formation of a monocationic species containing the ligand radical monoanion pc$^{\bullet -}$.[11] The presence of this paramagnetic species in (**5**) can certainly be excluded for a number of reasons. (*a*) The i.r. data discussed above preclude the assignment of the band at 1 040 cm^{-1} as being due to the presence of the radical anion,[12] as is also suggested by the general appearance of the spectrum in the region explored (4 000—600 cm^{-1}), which does not exhibit the dramatic changes associated with the formation of that species.[12] (*b*) The visible absorption spectrum of (**5**) in pyridine does not show the typical absorption between 500 and 550 nm associated with the formation of the radical anion.[11,12] (*c*) The presence of a low-intensity signal at $g = 2$ in the e.s.r. spectrum (−180 °C) of (**5**) is also not indicative of this species within the dimer, since a signal of comparable intensity and position, due probably to an impurity, is already detectable in the e.s.r. spectra of the precursors (**1**) and (**4**).

The conclusion drawn is that in (**5**) the positive charge is entirely localized on the Ru atoms. Thus, the dimer is formally identified as a mixed-valence $\mathrm{Ru^{III}}$–$\mathrm{Ru^{IV}}$ species. Attempts to oxidize $[\mathrm{Ru^{II}(pc^{2-})}]$ complexes have apparently so far led to $[\mathrm{Ru^{II}(pc^{\bullet -})}]^{+}$,[4,11] and not to $[\mathrm{Ru^{III}(pc^{2-})}]^{+}$ species. Hence, (**5**) appears to be the first well established ruthenium phthalocyanine complex containing Ru in oxidation states higher than II. The room-temperature magnetic moment of (**5**) is 1.8 ± 0.15 B.M., consistent with the presence of one unpaired electron per dimer, as might be expected. Further work is being carried out in order to establish whether (**5**) can be described by the formula $[\mathrm{(pc)Ru^{III}}$–N–$\mathrm{Ru^{IV}(pc)}]$, or, rather more appropriately, as $[\mathrm{(pc)Ru^{3.5+}}$–N–$\mathrm{Ru^{3.5+}(pc)}]$, as, indeed, has been suggested for $[\{\mathrm{Fe(pc)}\}_2\mathrm{N}]$.[3]

References

1 W. Kobel and M. Hanack, *Inorg. Chem.*, 1986, **25**, 103 and refs. therein.

2 V. L. Goedken and C. Ercolani, *J. Chem. Soc., Chem. Commun.*, 1984, 378.

3 L. A. Bottomley, J.-Noel Gorce, V. L. Goedken, and C. Ercolani, *Inorg. Chem.*, 1985, **24**, 3733.

4 D. Dolphin, B. R. James, A. J. Murray, and J. R. Thornback, *Can. J. Chem.*, 1980, **58**, 1123.

5 F. Calderazzo, G. Pampaloni, D. Vitali, I. Collamati, G. Dessy, and G. Fares, *J. Chem. Soc., Dalton Trans.*, 1980, 1965.

6 C. K. Choy, J. R. Mooney, and M. E. Kenney, *J. Magn. Reson.*, 1979, **35**, 1.

7 R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, 1936, 1736.

8 M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 1970, 1117.

9 M. Ciechanowicz and A. C. Skapski, *J. Chem. Soc. A*, 1971, 1792; R. J. D. Gee and H. M. Powell, *ibid.*, p. 1795.

10 C. Ercolani, M. Gardini, K. S. Murray, G. Pennesi, and G. Rossi, *Inorg. Chem.*, 1986, **25**, 3972.

11 T. Nyokong, Z. Gasyna, and M. J. Stillmann, *Inorg. Chim. Acta*, 1986, **112**, 11.

12 J. F. Myers, G. W. Rayner Canham, and A. B. P. Lever, *Inorg. Chem.*, 1975, **14**, 461.

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