Halogen to metal π-donation in metalloporphyrins

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The ¹H NMR analysis of the paramagnetic *trans*-dihalo-geno-ruthenium(IV) and osmium(IV) porphyrins reveals that the halides have a pronounced effect on both the magnitude and the direction of charge transfer between the metal and the porphyrin, that the degree of covalency of metal–halide bonds increases in the order of Mn^{III} < Ru^{IV} < Os^{IV}, and that the relative strength of halogen-to-metal π-donation is Cl < Br < I.

The relative π-donation strength of halides has become a matter of dispute in recent years. While both early and recent *ab initio* calculations suggested that π-donation increases down the group, F < Cl < Br < I,[1] the conclusions from NMR chemical shift analysis of halomethyl cations (¹³C) and boron halides (¹¹B) are opposite.[2] A similar conflict seems to exist for halogeno-coordinated metalloporphyrins. The ¹H NMR spectra of halogeno-coordinated manganese(III) porphyrins were originally analyzed in terms of competition for π-donation to the metal by the halide (X → M CT) and the porphyrin (P → M CT), and the π-donation ability was proposed to decrease in the order of I < Br < Cl < F.[3] But, much more recent investigations of Mn^{III} and Fe^{III} porphyrins have shown that their metal–ligand bonds are predominantly charge rather than orbital controlled.[4,5] For (*trans*-dihalogeno)ruthenium(IV) tetraphenylporphyrins, the monotonic trend of decreasing upfield isotropic shifts of pyrrole-H down the halide group,[6] opposite to that in (halogeno)manganese(III) porphyrins, led to the conclusion that the order of π-donation ability is Cl < Br < I.[7] But, while Ke *et al.* analyzed the isotropic shifts in terms of P → M CT, M → P CT was indicated by investigation of a (*trans*-dibromo)ruthenium(IV) porphyrin.[8] Obviously, without a definite conclusion about the direction of the CT process in these complexes, the relative π-donation ability of the halides cannot be determined.

The contradictory NMR analyses of the *trans*-dihalogeno-ruthenium(IV) tetraphenylporphyrins calls for the examination of a larger range of porphyrin structures, as well as of the analogous osmium(IV) complexes.[9] These tetragonally distorted octahedral complexes are exceptionally well suited for the current investigation owing to their stability, high symmetry, well resolved NMR spectra, and because the metal ion is confined to the porphyrin's plane and only the d$_π$ orbitals are

singly occupied.[10] Accordingly, we have prepared a large series of dihalogeno-ruthenium(IV) and -osmium(IV) complexes with both pyrrole-unsubstituted and *meso*-unsubstituted porphyrins (Scheme 1),[11] taking advantage of our recently introduced synthetic method for their preparation.[12] The detailed ¹H NMR analysis leads to the conclusion that the relative π-donation ability of the halides is Cl < Br < I for all metalloporphyrins, and that the main difference between the metal complexes is an icnrease of σ-covalency of their bonds with axial ligands in the order of Mn^{III} < Ru^{IV} < Os^{IV}.

The first concern in the NMR analysis is the separation of the isotropic shifts into contributions from dipolar (pseudocontact, through field) and contact (through σ and/or π orbitals) shifts.[3b] Examination of Table 1 clearly shows that the *meso*-aryls of the (por)Os^{IV}X$_2$ complexes experience only dipolar shifts, as all isotropic shifts are shifted downfield and they decrease as a function of their distance from the metal exactly as predicted by eqn. (1), which is relevant for purely dipolar shifts.[3b]

$$(\Delta H/H)_i^{\text{dip}} : (\Delta H/H)_j^{\text{dip}} = [(3\cos^2\theta - 1)/r_i^3] : [(3\cos^2\theta - 1)/r_j^3] \quad (1)$$

$$(\Delta H/H)_i^{\text{iso}} = (\Delta H/H)_i^{\text{dip}} + (\Delta H/H)_i^{\text{con}} \quad (2)$$

The results of eqn. (1) were also used in eqn. (2), which allows the calculation of the contact shifts at the pyrrole protons,
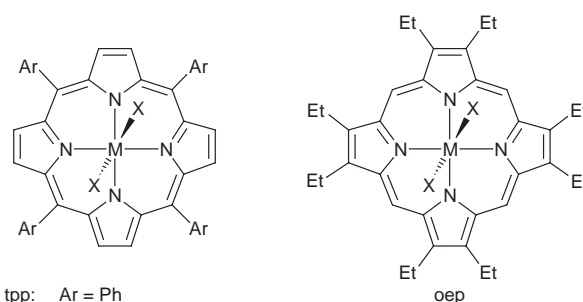
tpp: Ar = Ph
ttp: Ar = C$_6$H$_4$Me-4
tdmp: Ar = C$_6$H$_3$Me$_2$-2,6
tmp: Ar = C$_6$H$_2$Me$_3$-2,4,6

oep

M = Ru, Os; X = Cl, Br, I

Scheme 1

Table 1 ¹H NMR isotropic shifts (ppm, CDCl₃, 23 °C) of the (por)OsX₂ complexes, and their separation into contributions from dipolar and contact shifts^a

	Phenyl				Pyrrole			
	o-H	*m*-H	*o*-Me	*p*-Me	H	α-CH$_2$	β-Me	*meso*-H
Geometric factor^b	10.0	4.63	3.90	3.01	20.10	10.5	6.40	30.00
$(\Delta H/H)_{\text{iso}}$, X = Cl	2.66	0.90	0.79	0.67	−13.99	15.18	2.27	11.73
X = Br	2.42	0.90	0.81	0.64	−13.30	15.08	2.21	11.22
X = I	2.07	0.94	0.91	0.60	−12.02	14.55	2.05	10.40
$(\Delta H/H)_{\text{dip}}$, X = I^c	2.07	−0.96	0.81	0.62	4.16	2.17	1.32	6.21
$(\Delta H/H)_{\text{con}}$, X = I^d	0.00	−0.02	0.10	0.02	−16.8	12.38	0.73	4.19

^{a} $(\Delta H/H)_{\text{iso}}$, the difference in chemical shifts between identical protons in the paramagnetic osmium(IV) and diamagnetic *trans*-dioxo osmium(VI) complexes. ^{b} Calculated from the crystal structure of (tmp)OsI₂ and normalized to *o*-H = 10. ^{c} Calculated by eqn. (1), starting with the isotropic shift of *o*-H in (ttp)OsI₂. ^{d} Calculated by eqn. (2). The pyrrole-H contact shifts for X = Cl and X = Br are −19.3 and −18.6 ppm, respectively.

Table 2 ^{1}H NMR isotropic shifts (ppm, $CDCl_3$, 23 °C) of the (por)RuX_2 complexes^a

	Phenyl					Pyrrole			
	o-H	o-Me	m-H	p-H	p-Me	H	α-CH$_2$	β-Me	$meso$-H
X = Cl	−1.6	2.33	5.27	−1.5	1.49	−63.8	55.46	4.66	−2.41
X = Br	−3.49	2.74	7.75	−2.28	1.61	−53.75	55.85	5.05	−7.08
X = I	−4.06	2.64	10.33	−1.96	1.53	−32.55	54.12	5.18	−28.61

^{a} Referenced against the diamagnetic dioxoruthenium(VI) complexes. An isotropic shift of −0.95 ppm was reported for *meso*-H of (oep)RuF_2: C. Sishta, M. Ke, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1986, 787.

and a fair estimate of its contribution to the *meso*-H and pyrrole-CH_2CH_3 isotropic shifts in the (oep)$Os^{IV}X_2$ complexes. Large and alternating contact shifts of protons (−16.18 ppm) and methylene groups (+12.38 ppm) attached to the β-pyrrole carbons together with the relatively small downfield shifts at *meso*-H (+4.19 ppm) are clearly evident from Table 1. This pattern is fully consistent with π-contact shifts due to P (3e, filled) → M (d_π, singly occupied) CT, but not with M → P (4e, LUMO) CT.^{3b} We may safely conclude that the decrease of P → M CT in the order of I < Br < Cl, as reflected by the pyrrole-H contact shifts of δ −16.8, −18.6, and −19.4, respectively, is a result of an increase in X → M CT, *i.e.* the relative π-donation ability in the (por)$Os^{IV}X_2$ complexes is I > Br > Cl.

The spectral analysis of the ruthenium(IV) complexes is less straightforward, since large contact shifts mask any possible contribution by the dipolar shift, even at the aryl protons. This is evident from the alternation of the isotropic shifts for the *meso*-aryl substituents (*ortho*- *vs.* *meta*- *vs.* *para*-H, as well as *ortho*-H *vs.* *ortho*-Me, and *para*-H *vs.* *para*-Me) and the exceptionally large pyrrole-H and *meso*-H shifts (Table 2). The large upfield shifts of both pyrrole-H and *meso*-H are consistent only with a simultaneous action of P → M (upfield pyrrole-H) and M → P (upfield *meso*-H) π charge transfer mechanisms. This explains the earlier mentioned contradictory analyses about the direction of the CT process in the *meso*-substituted (tpp)$Ru^{IV}X_2$ complexes. The most illuminating observation is that the relative importance of M → P CT clearly changes from very low in the dichloro complexes (small shifts of the *meso*-H and *meso*-aryls) to highly significant in the diiodo complexes [Δδ(*meso*-H) ≈ Δδ(pyrrole-H)]. This phenomenon suggests a π-donation strength series in the order of I > Br > Cl, since as more electron density is transferred from the axial ligand to the metal, M → P CT should indeed increase at the expense of P → M CT.

Finally, we suggest that the relatively small isotropic shifts and the lack of M → P CT in the osmium(IV) porphyrins reflect the well known phenomenon of increased σ-covalency of metal–ligand bonds in post-lanthanide transition metals relative to their 4d analogs.^{13} This proposal is supported by the exceptionally large substitution inertness of the (por)OsX_2 complexes.^{14} An additional consequence is that halogeno–metal bonds in osmium(IV) porphyrins are not expected to be unusually short, in contrast to the analogous ruthenium complexes with their very strong π-bonding component.^{7} Comparison of the bond lengths in (tmp)OsI_2 (Os–I 2.655 Å, this study)^{11} and (ttp)Os(Cl$_2$ (Os–Cl 2.294 Å)^{9c} with EXAFS data for *trans*-dihalogeno osmium(IV) complexes of a non-porphyrinic ligand (Os–I 2.627 Å, Os–Cl 2.227 Å),^{15} clearly supports this prediction. We conclude that the binding of axial ligands to d^4-metalloporphyrins changes from predominantly covalent for Os^{IV} through intermediate in Ru^{IV} to predominantly ionic in Mn^{III}.^{4} In all cases, the extent of P → M CT is a sensitive probe of the energy difference between the singly occupied d_π orbitals and the low-energy 3e orbitals of the porphyrin. In the ionic halogeno–Mn^{III} bonds, the energy of the d_π orbitals is reduced as the bond lengths increase (Mn–I >

Mn–Br > Mn–Cl).^{16,17} However, the decrease of P → M CT in the order of I < Br < Cl for the osmium(IV) and ruthenium(IV) porphyrin clearly reflects an increase in the energy of the d_π orbitals due to X → M CT, *i.e.* the relative π-donation ability is I > Br > Cl.

Notes and References

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10 For establishment of the $S = 1$ ground state of these derivatives by magnetic susceptibility studies, and for the temperature dependence of their NMR spectra, see refs. 7–9 and 12.

11 Supplementary material: synthetic procedures for all complexes, Tables S1–S4 with the full NMR data, on ORTEP drawing of (tmp)OsI_2, and Tables C1–C5 with the full data of its X-ray crystal structure (CCDC 182/830) (13 pp.). See http://www.rsc.org./suppdata/cc/1998/1105.

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