Ligand additivity on the formal potential of Os$^{III}$–Os$^{II}$ couple in bidentate mixed-ligand complexes

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We have successfully synthesised a series of mixed-ligand complexes of type [OsQ$_3$–$_n$ L$_n$]$^{z+}$ (Q = deprotonated quinolin-8-ol, L = a set of (N, N), (N, O) and (O, O) neutral or anionic chelate ligands, n = 0 to 3 and z = overall charge depending on the nature of L). The compounds are electroactive and have a reversible Os$^{III}$–Os$^{II}$ couple. Using cyclic voltammetry, $E_{1/2}$ (average cathodic and anodic peak potentials) values of this couple have been determined. The potentials depend on the degree of substitution and nature of coligand L, and a wide range in potential (−1.3 to +1.9 V vs SCE) is covered by changing the donor sets. A particular potential value reflects the energy of metal $t_2$ level. Plots of $E_{1/2}$ vs. n give straight lines which intersect at $E_{1/2}$ value for [OsQ$_3$]. The slopes of these lines depend on the specific influence of L, which appears to be related to their π-acceptance or π-donation capacity. By compilation of these data, the interrelationship of one L with the other is delineated, and the concept of electrochemical series of ligands (at least in osmium frame) is made. The potential map ligand parameter ($P_L$) is very useful for prediction of the properties of the metal complexes and for the design of new systems of chemical interest. Above all, preassignment of metal oxidation level in tractable form with a given donor set can be ascribed from such results.

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