A series of mixed ligand ruthenium(II) complexes $[Ru(pdto)(diimine)](ClO_4)_2/(PF_6)_2$ **1–3** and $[Ru(bbdo)(diimine)](ClO_4)_2$ **4–6**, where pdto is 1,8-bis(pyrid-2-yl)-3,6-dithiooctane, bbdo is 1,8-bis(benzimidazol-2-yl)-3,6-dithiooctane and diimine is 1,10-phenanthroline (phen), dipyrido-[3,2-*d*:2′,3′-*f*]-quinoxaline (dpq) and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), have been isolated and characterised by analytical and spectral methods. The complexes $[Ru(pdto)(phen)](PF_6)_2$ **1a**, $[Ru(pdto)(dpq)(Cl)](PF_6)$ **2a**, $[Ru(bbdo)(phen)](PF_6)_2$ **4a** and $[Ru(bbdo)(dpq)](ClO_4)_2$ **5** have been structurally characterized and their coordination geometries around ruthenium(II) are described as distorted octahedral. In **1a**, **4a** and **5** the two thioether sulfur and two py/bzim nitrogen atoms of the tetradentate pdto/bbdo ligand are folded around Ru(II) to give predominantly a "*cis*-α" configuration. ^1H NMR spectral data of the complexes support this configuration in solution. In $[Ru(pdto)(dpq)Cl](PF_6)$ **2a** with a distorted octahedral coordination geometry, one of the two py nitrogens of pdto is not coordinated. The DNA binding constants (K_b: **2**, $2.00 \pm 0.02 \times 10^4$ M^{-1}, $s = 1.0$; **3**, $3.00 \pm 0.01 \times 10^6$ M^{-1}, $s = 1.3$) determined by absorption spectral titrations of the complexes with CT DNA reveal that **3** interacts with DNA more tightly than **2** through partial intercalation of the extended planar ring of coordinated dppz with the DNA base stack. The DNA binding affinities of the complexes increase with increase in the number of planar aromatic rings in the co-ligand, and on replacing both the py moieties in pdto complexes (**1–3**) by bzim moieties to give bbdo complexes (**4–6**). Upon interaction with CT DNA the complexes **1**, **2**, **5** and **6** show a decrease in anodic current in the cyclic voltammograms. On the other hand, interestingly, **3** and **4** show an increase in anodic current suggesting their involvement in electrocatalytic guanine oxidation. Interestingly, of all the complexes, only **6** alters the superhelicity of DNA upon binding with supercoiled pBR322 DNA. The cytotoxicities of the dppz complexes **3** and **6**, which avidly bind to DNA, have been examined by screening them against cell lines of different cancer origins. It is noteworthy that **6** exhibits selectivity with higher cytotoxicity against the melanoma cancer cell line (A375) than other cell lines, potency approximately twice that of cisplatin and toxicity to normal cells 3 and 90 times less than cisplatin and adriamycin respectively.