Coordination Chemistry Reviews 254 (2010) 1397–1405

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Electronic characteristics of an extensive series of ruthenium complexes with the non-innocent *o*-benzoquinonediimine ligand: A pedagogical approach

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Contents

ARTICLE INFO

Article history:
Received 21 January 2010
Accepted 15 February 2010
Available online 20 February 2010

Keywords:
o-Benzoquinonediimine
bqdi
Density functional theory
DFT
Pedagogy
Molecular orbitals
Electrochemistry
Ligand electrochemical parameters

ABSTRACT

Density functional theory (DFT) calculations are carried out on an extensive series of ruthenium complexes with the non-innocent (redox active) *o*-benzoquinonediimine (bqdi) ligand, namely [Ru(WXYZ)(bqdi)]$^{n+}$ where WXYZ are a range of spectator ligands including ammonia, phosphines, 2,2′-bipyridine, 2,2′,2″-terpyridine, carbon monoxide, water, halide, acetonitrile, triazacyclononane, nitrosyl, cyclam, etc. In addition, a smaller series, Ru(acac)$_2$(R-bqdi) is explored, where acac = 2,4-pentanedionate, and R = H, Cl, Me, NO$_2$ and N-SO$_2$Me. A range of properties including Mulliken and Natural population analysis (NPA) charges, Mayer bond orders (Ru–N, C=N, C=C, etc.), net σ-donation and net π-back donation, and percentage Ru 4dπ in the LUMO, are derived and correlated with experimental properties including oxidation and reduction potentials and ligand electrochemical parameters, $E_L(L)$. The various properties are understood in terms of the primary involvement of π-back donation to the π^*-LUMO of bqdi. Net π-back donation is derived from the contribution of the π^*-LUMO (and higher virtual orbitals) of bqdi, to filled molecular orbitals of the complex. The question of whether these species should be considered exclusively as being represented as [Ru^{II}L$_4$(bqdi)] or [Ru^{III}L$_4$(sqdi)] (sqdi = *o*-benzosemiquinonediimine) is briefly considered and evidence presented for the former electronic structure. This is written as a pedagogical treatise rather than a detailed research discussion of the electronic properties of these molecules.

1. Introduction

An extensive group of complexes of general formula [Ru(WXYZ)(R-bqdi)]$^{n+}$ is available [1–23], where WXYZ, so-called spectator ligands, are a wide range of monodentate, bidentate and tridentate ligands filling, between them, four coordination sites on the molecule, and R-bqdi is *o-benzoquinonediimine* or a

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doi:10.1016/j.ccr.2010.02.022

Table 1
Some experimental and theoretically calculated data of $[(WXYZ)Ru(bqdi)]^{n+}$ species.

WXYZ[a]	ΣE_L(WXYZ) (V vs NHE)[b]	$E_{1/2}$[q/sq] (V vs NHE)	$E_{1/2}[Ru^{III/II}]$ (E_L(bqdi)) (V vs NHE)	Bqdi charge (Mulliken) (a.u.)	Bqdi charge (NPA) (a.u.)	Ru charge (NPA) (a.u.)	$h\nu$ MLCT[c] (10^3 cm^{-1})
$(NH_3)_2Cl_2$	−0.34	−0.96	$0.47(0.40_5)$	−0.14	−0.06	0.67	20.10
$(acac)_2$	−0.32	−0.96	$0.53(0.42_5)$	−0.12	−0.04	1.00	19.90
N_3-triazacyclononane	n.a.	−0.69	0.81	−0.10	0.02	0.72	19.38
I-triazacyclononane	n.a.	−0.67	1.01	0.00	0.10	0.58	18.87
Cl-terpy	0.51	−0.30	$1.18(0.32_5)$	0.02	0.10	0.71	19.65
$(dppb)Cl_2$	0.40	n.a.	n.a.	0.06	0.14	0.31	19.23
$(PPh_3)_2Cl_2$	0.30	−0.70	$0.91(0.30_5)$	0.06	0.14	0.31	20.53
$(PPh_3)_2(CH_3CN)Cl$	0.88	−0.41	1.42(0.27)	0.08	0.19	0.29	20.75
Cyclam	n.a.	n.a.	n.a.	0.08	0.15	0.70_5	21.01
H_2O-triazacyclononane	n.a.	n.a.	n.a.	0.14	0.21	0.75	19.34
CH_3CN–triazacyclononane	n.a.	−0.38	1.48	0.14	0.28	0.66	19.65
$(CH_3CN)_2(PPh_3)_2$	1.46	−0.24	$1.89(0.21_5)$	0.16_5	0.29	0.28	21.55
$(bpy)_2$	1.04	−0.21	1.61(0.28)	0.18	0.27	0.70	19.44
$(opda)_2$	n.a.	n.a.	n.a.	0.22	0.24	0.69	21.37
$(NH_3)_4$	0.28	n.a.	$1.10(0.19_5)$	0.25	0.28	0.69	21.28
$(PhCN)_2(H_2O)(PPh_3)$	1.17	n.a.	n.a.	0.26	0.35	0.50	n.a
$(CO)_2(PPh_3)Br$	2.15	0.10	n.a.	0.33	0.36	−0.05	n.a
(NO)-terpy	n.a.	n.a.	n.a.	0.69	0.67	0.76	n.a

[a] In order of increasing positive Mulliken charge on bqdi.

[b] Potentials are not available in the literature for all species; n.a.: not available. E_L parameters are generally not available for cyclic ligands. In the case of the opda species, oxidation occurs at opda and not Ru and so E_L(opda) cannot be easily measured. The nitrosyl group is non-innocent and does not have fixed E_L(NO) value.

[c] Most data recorded in organic phase, usually CH_3CN, and not solvatochromic.

substituted version thereof. R-bqdi is a so-called *non-innocent* [24], i.e. redox active, ligand. The complexes range from those containing fairly strongly electron donating chloride and acetylacetonate ions at one extreme to complexes with a highly electron withdrawing carbonyl or nitrosyl(1+) group at the other extreme. The detailed electronic interaction between Ru(II) and bqdi is known to vary quite dramatically as a function of the WXYZ ligands, as indicated, for example, by the electrochemical ligand parameter E_L(bqdi) [25–28] that varies from 0.20 to 0.43 V as a function of the spectator ligands (also see Table 1). Thus this large body of complexes provides an opportunity to probe this interaction in much greater depth than heretofore provided. Using density functional theory (DFT) we can derive a range of physical properties such as net charge on the various fragments, bond orders, σ-bonding and π-back bonding, mixing of Ru 4dπ orbitals into π* orbitals of bqdi, etc. and discuss how they depend on Ru(WXYZ) fragment interaction with bqdi. This information can be tied to experimental data specifically $E_{1/2}$[q/sq] reduction potentials, $E_{1/2}[Ru^{III/II}]$ oxidation potentials, E_L(WXYZ) and E_L(R-bqdi) parameters and MLCT transition energies. We restrict the study here to the parent oxidation state, formally Ru(II)-quinone. A comparison of the DFT predicted electronic structure with the aforementioned experimental observables provides a means to convince us that the theoretical analysis is meaningful.

We use the B3LYP functional with the LANL2DZ basis set since this has proven reliable for the study of Ru(II) bqdi complexes in the past [3,29–33]. Other functionals and basis sets were briefly explored but did not offer any advantages over the ones chosen. The inclusion of solvent using the polarized continuum model (PCM) was also explored but offered no real advantage and so was not implemented. The intent is not to perfectly fit experimental data but to extract a greater insight into the electronic structures of these molecules, and to show how their properties are influenced by the spectator ligands WXYZ.

The primary pieces of information that will be extracted from the computational analysis include:

(i) Natural population analysis (NPA) and Mulliken charges on Ru and on R-bqdi overall as well as individual NPA charges on the coordinating ligand atoms.
(ii) Mayer Ru–N bond orders [34,35] and C=C and C=N bond orders within the Ru-bqdi-metallocycle ring and within the C_6 ring of bqdi.
(iii) Mayer bond orders between the R-bqdi and Ru(WXYZ) (and $Ru(acac)_2$) fragments.
(iv) Percent mixing of the Ru 4dπ into the bqdi localized π* LUMO of the complex.
(v) Mixing of filled Ru 4d orbitals with ligand orbitals.
(vi) Factorization of σ-donation and π-back donation between Ru and bqdi.
(vii) How the E_L(R-bqdi) parameter varies with R and with spectator ligand.

This article is written with a pedagogical tone since it offers the opportunity to test some simple ideas that might seem fairly obvious but which have probably been rarely proven. For example, a major component of the behavior of these species is an increasing degree of π-back donation to R-bqdi as WXYZ become stronger donors, in a kind of push–pull mechanism. One may suppose that this ought then to increase the Ru–N(bqdI) bond order and the bond order between R-bqdi and Ru(WXYZ) fragments. Does this occur by enhancement of the π-bond or both σ- and π-bonds? Further, placing negative charge into R-bqdi should affect the bond orders of other bonds in a predictable fashion depending on the bonding and anti-bonding behavior of the orbital(s) involved. This group of complexes is sufficiently large to probe this behavior in a statistically meaningful fashion. One may also expect to gain other insights. For example if π-back donation to bqdi increases, do the charges on N and on bqdi overall, also become more negative or does the ligand become a stronger σ-donor to offset this charge build-up? These, and other, considerations can be probed by the DFT analysis.

2. Computation

2.1. DFT Calculations

Density functional theory (DFT) calculations utilized the *Gaussian 03* (Revision C.01) program and Gaussian 09 program [36]. Optimized geometries were calculated using the B3LYP exchange-correlation functional [37] with the LANL2DZ basis set [38–41]. Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Vibrational frequency calculations were performed to ensure that the stationary points were minima. Molecular orbital (MO) compositions and the overlap populations between molecular fragments were calculated using the *AOMix* package of programs [12,42] using the Mulliken scheme [43–46]. Atomic charges were calculated using the Mulliken [43–46] and natural population analysis [47] methods (MPA and NPA, respectively) as implemented in *Gaussian 03/09*. The analysis of the MO compositions, and the charge decomposition analysis was performed using *AOMix-CDA* [48]. The CHIMERA program [49] was used to extract bond order data. Bond distances were generally well reproduced (by comparison with relevant X-ray data).

2.2. Complexes

Data were taken from the literature, as cited: $[Ru(NH_3)_2Cl_2(bqdi)]$ [2], $[Ru(acac)_2(bqdi)]$ [3], $[RuN_3(triazacyclononane)(bqdi)]^+$ [4], $[Ru(PPh_3)_2Cl_2(bqdi)]$ [6,50], $[RuI(triazacyclononane)(bqdi)]^+$ [4], $[RuCl(terpy)(bqdi)]^+$ [5], $[Ru(dppb)Cl_2(bqdi)]$ [7], $[RuCl(PPh_3)_2(CH_3CN)(bqdi)]^+$ [6,51], $[Ru(cyclam)(bqdi)]^{2+}$ [8], $[Ru(H_2O)(triazacyclononane)(bqdi)]^{2+}$ [4], $[Ru(CH_3CN)(triazacyclononane)(bqdi)]^{2+}$ [4], $[Ru(bpy)_2(bqdi)]^{2+}$ [11–13,19], $[Ru(opda)_2(bqdi)]^{2+}$ [17], $[Ru(CH_3CN)_2(PPh_3)_2(bqdi)]^{2+}$ [6,52], $[Ru(NH_3)_4(bqdi)]^{2+}$ [18–20,53], $[Ru(PhCN)_2(H_2O)(PPh_3)(bqdi)]^{2+}$, [50] $[RuBr(CO)_2(PPh_3)(bqdi)]^+$ [21], $[Ru(NO)(terpy)(bqdi)]^{3+}$ [23,54,55] dppb = 1,4-bis(diphenylphosphine)butane; bpy = 2,2′-bipyridine; terpy = 2,2;,2″-terpyridine; opda = *o*-phenylenediamine]. The complexes are displayed in the tables using the WXYZ acronym to identify them, without noting the overall charge on the molecule; however this is defined immediately above.

3. Correlation of DFT with experimental data

3.1. Net charge on bqdi and coordinating N(H) atoms. (R-bqdi, R = H)

We explore first the group of complexes that contain the unsubstituted parent bqdi ligand. Table 1 provides experimental $E_{1/2}$[q/sq] and $E_{1/2}[Ru^{III/II}]$ potentials (vs NHE) where available and calculated net charge on bqdi according to the Mulliken and Natural population analysis models [55]. Fig. 1 illustrates that there is a fairly good linear correlation between the experimental reduction $E_{1/2}$[q/sq] and oxidation $E_{1/2}[Ru^{III/II}]$ potentials and the Mulliken charge on bqdi; specifically, as the net charge residing on bqdi, becomes more negative, it become more difficult to reduce the complex, and easier to oxidize it, as would be expected [56]. The linearity of the relationships is encouraging. A similar, but not quite so good linear correlation with the NPA charge is also seen. There is some scatter that arises for a variety of reasons. The experimental data come from several different laboratories and used different reference electrodes that have been adjusted to NHE. Some errors can be expected. There is also no *a priori* reason that the correlation be linear. The $E_{1/2}$[q/sq] and $E_{1/2}[Ru^{III/II}]$ potentials are a measure of the relative stabilities of the oxidized and reduced components but the aforementioned Mulliken charge is a property solely of the $Ru^{II}Q$ species. Generally in a homologous series of complexes, a linear relationship is observed between electrochemical potentials and DFT derived data such as HOMO or LUMO energies of just one component of the redox pair (e.g. [57–66]). In Fig. 1 and some other figures there are outliers that were excluded from the least squares lines; they are noted in the figure or legend; the reasons for the anomalies are generally not obvious but may simply be due to experimental error.

Thus the spectator ligands, WXYZ, do dramatically influence the net charge on bqdi and also thereby tune the electron density on the ruthenium atom. Data are presented in Fig. 2 and Table 1. There is a large difference of 0.83 a.u. between the donors $(NH_3)_2Cl_2$ and acceptor nitrosyl complexes. This large change is, of course, derived from the significant difference in π-back donation in these species (Table 1). Yet, the charge on the donating N(H) atoms (Fig. 2) is essentially constant through the series whether it be calculated by the Mulliken or NPA models. We return to this result below.

3.2. π-back donation

A first, zero-order, measure of the extent of π-back donation is afforded by the calculated percent Ru 4dπ contribution to the LUMO of the complex. This molecular orbital is formed from an anti-bonding interaction between 4dπ and the π* LUMO of bqdi. This percentage will, qualitatively, reflect the mixing of the LUMO into filled orbitals of the complex, to which we will return below. The effect of the WXYZ ligands upon the electron density at Ru can be modeled either by $E_{1/2}[Ru^{III/II}]$ if available, and more generally by ΣE_L(WXYZ), the sum of the ligand electrochemical parameters [25,67,68]. Both these parameters, which will differ by $2E_L$(bqdi)

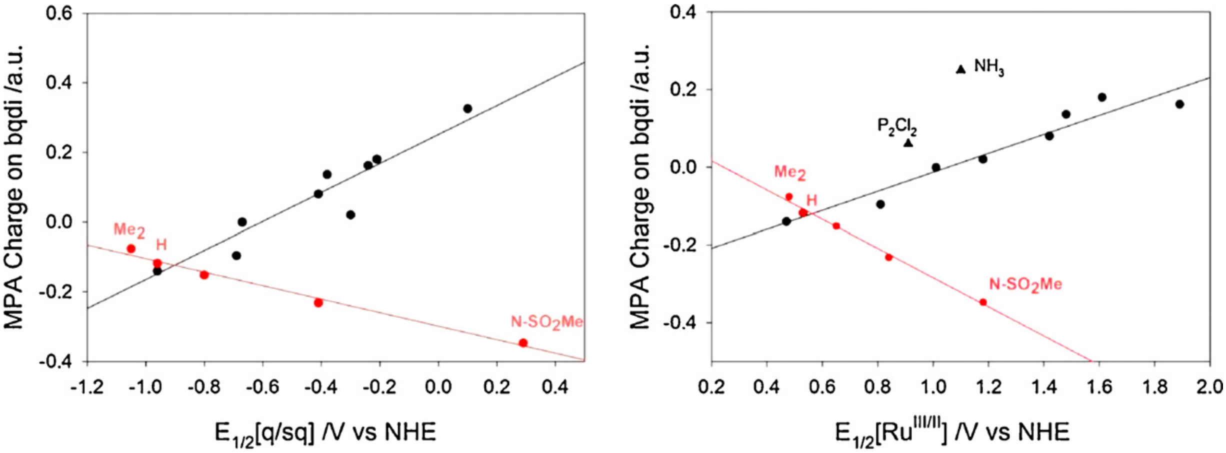

Fig. 1. (Left) Plot of the net Mulliken charge on bqdi vs $E_{1/2}$[q/sq] potential of the (WXYZ)Ru(bqdi) species (black). The least squares line is drawn. Data in red in these, and subsequent, figures are the corresponding plots for $Ru(acac)_2$(R-bqdi) and are discussed in Section 4; R = 4-H, 4-Cl, 4-NO_2, 4,5-di-CH_3 and di-N-SO_2Me. NB The red R = H exactly overlays the black $Ru(acac)_2$(bqdi) entry. The almost overlapping black entry is $Ru(NH_3)_2Cl_2$(bqdi). Charges here, and in subsequent figures are expressed as electrons and written as atomic units, a.u. (Right) Plot of the net Mulliken charge on bqdi vs the $E_{1/2}[Ru^{III/II}]$ oxidation potential of the (WXYZ)Ru(bqdi) species. The least squares line is drawn.

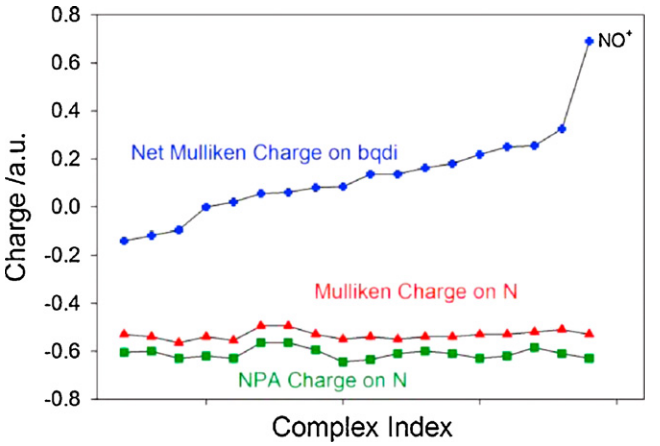

Fig. 2. Net Mulliken charge on bqdi and Mulliken and NPA charges on the ligating N(H) atoms, of the [Ru(WXYZ)(bqdi)]$^{n+}$ species, ordered in increasing order of net Mulliken positive charge on bqdi. The connecting lines are intended to draw the eye and have no intrinsic meaning.

which is variable (see Section 5), are directly based upon experimental data, and so a correlation with %Ru in the LUMO is another check of the DFT calculation. Fig. 3 shows good linear correlations with few exceptions off the line.

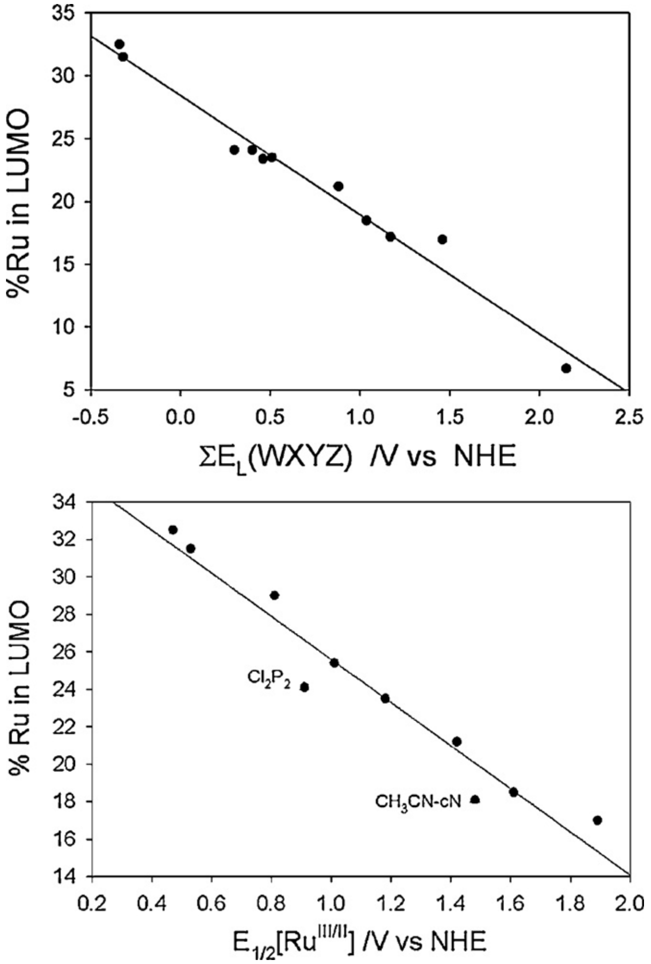

Fig. 3. (Upper) Plot of the percentage Ru 4dπ contribution to the complex LUMO, localized primarily on bqdi, vs ΣE_L(WXYZ). The nitrosyl species is omitted since $E_L(NO^+)$ is unknown (and variable). (Lower) Plot of the percentage Ru 4dπ contribution to the LUMO localized primarily on bqdi vs $E_{1/2}[Ru^{III/II}]$. (cN = triazacyclononane).

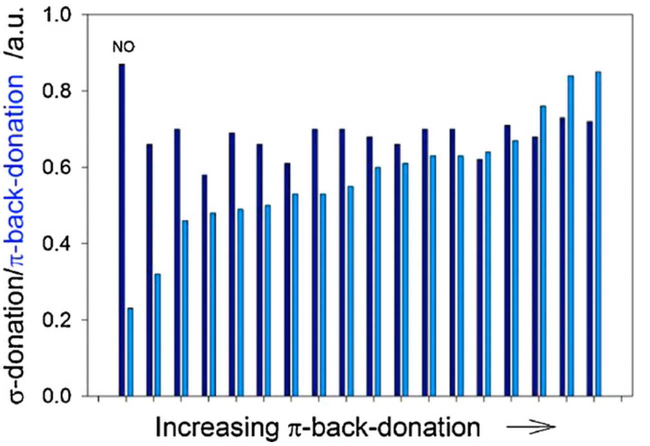

Fig. 4. A plot of σ, π-donation (dark blue) (from bqdi to Ru(WXYZ)) and π-back donation (light blue) (from Ru(WXYZ) to bqdi) ordered with respect to the latter, for the series [Ru(WXYZ)(bqdi)]$^{n+}$.

The linearity of these correlations provides a degree of confidence that the DFT calculation, using B3LYP/LANL2DZ, is meaningful. The degree of mixing of the Ru 4dπ orbital into the LUMO and other ligand MOs varies quite considerably across this series from strong donor to strong acceptor. This mixing, greater than 30% in the more strongly donating WXYZ species, is very much more significant in these non-innocent ligands than, for example in ruthenium complexes of bipyridine (bpy) (e.g. ca. 5% 4dπ Ru) yet bpy is generally regarded as a 'good π-acceptor'; here we observe values of %Ru 4dπ in the LUMO approaching an order of magnitude greater!

The LUMO of the complex is virtual and empty. A more direct measure of π-back donation is given by the mixing (contribution) of the π*-LUMO and other virtual orbitals of bqdi into filled orbitals of the complex. The three t_{2g} orbitals lie with a σ, π and δ relationship to the molecular plane of bqdi e.g. [11]. The 4dσ orbital remains fairly pure, except where it can couple significantly to orbitals on WXYZ. The 4dδ and especially 4dπ orbital can mix dramatically with virtual orbitals of appropriate symmetry on bqdi. Thus, there will be a bonding interaction between the π* LUMO of bqdi with the filled 4dπ and this provides the direct mechanism for π-back donation into bqdi. The filled orbital resulting from this interaction is usually the HOMO-1 or HOMO-2 of the complex. Depending on symmetry, the bqdi π* LUMO may also contribute to lower lying filled orbitals, and higher virtual orbitals of bqdi can also mix with lower lying filled orbitals. These interactions sum to provide a total figure for charge back donated to bqdi. The total σ-donation, also comprising some π-donation, is arrived at from the corresponding mixing of virtual orbitals of the Ru(WXYZ) fragment, into filled orbitals of the complex. To extract these numerical data, we make use of the charge decomposition analysis (CDA) as initially developed by Dapprich and Frenking [69–71] and augmented by Gorelsky as the extended CDA, or ECDA [48,72,73].

Table 2 and Fig. 4 provide values for the σ, π-donation and π-back donation in each complex as derived from the ECDA method. They do not exactly correspond to the difference in charge transfer in 'each direction' (difference between σ-donation and π-back donation) since they also include electronic polarization [48]. Nevertheless the polarization term is relatively small and one can treat the data in Table 2 in a relative sense. The first surprising result is that the net σ-donation (from bqdi to Ru(WXYZ)) varies little with the donor or acceptor power of the spectator ligands, with few exceptions. Thus for arguably the most donating system, acetylacetonate (acac), σ, π-donation is 0.73 a.u., while for the best acceptor systems it is 0.66 a.u for dicarbonyl species, and

Table 2
Charge decomposition analysis and bond orders in $[(WXYZ)Ru(bqdi)]^{n+}$ species[a].

WXYZ	σ-donation[b] (a.u.)	π-back donation[b] (a.u.)	Ru-N[c] bond order	C═N[d] bond order	C═C[e] bond order	Mayer[f] bond order	%Ru[g] in LUMO
$(NH_3)_2Cl_2$	0.72	0.85	0.76	1.19	1.61	2.22	32.5
$(acac)_2$	0.73	0.84	0.77	1.19	1.61	2.21	31.1
N_3-triazacyclononane	0.68	0.76	0.68	1.21	1.61_5	2.03	29.0
$(PPh_3)_2Cl_2$	0.70	0.63	0.64	1.28	1.64	2.01	24.1
I-triazacyclononane	0.71	0.67	0.68	1.25_5	1.63	2.01	25.4
Cl-terpy	0.62	0.64	0.63	1.24	1.63	1.93	23.5
$(dppb)Cl_2$	0.70	0.63	0.64	1.28	1.64	2.01	24.1
$(PPh_3)_2(CH_3CN)Cl$	0.68	0.60	0.78	1.31	1.68	1.97	21.2
Cyclam	0.66	0.61	0.65	1.26	1.63_5	1.93	24.1
H_2O-triazacyclononane	0.61	0.53	0.62	1.29_5	1.64	1.79	22.0
CH_3CN-triazacyclononane	0.58	0.48	0.58	1.32	1.65	1.68	18.1
$(bpy)_2$	0.66	0.50	0.61	1.29	1.64	1.80	18.5
$(opda)_2$	0.70	0.53	0.70	1.27	1.64	1.90	22.4
$(CH_3CN)_2(PPh_3)_2$	0.70	0.55	0.62_5	1.25	1.64	1.95	17.0
$(NH_3)_4$	0.69	0.49	0.67_5	1.30	1.64	1.83	20.6
$(PhCN)_2(H_2O)(PPh_3)$	0.70	0.46	0.59_5	1.40	1.67_5	1.80	17.2
$(CO)_2(PPh_3)Br$	0.66	0.32	0.44_5	1.36	1.67_5	1.48	6.7
(NO)-terpy	0.87	0.23	0.51	1.33	1.64	1.48	11.4

[a] DFT B3LYP/LANL2DZ.
[b] Between bqdi and Ru(WXYZ) fragments; subject to polarization, see [48].
[c] Ru-N bqdi-metallocycle. Average bond order values are provided for asymmetrically bound bqdi.
[d] Intra-bqdi-metallocycle.
[e] 3,4 and 5,6 C═C bonds.
[f] Bond order between bqdi and Ru(WXYZ) fragments.
[g] May include a very small contribution of Ru 4s and/or 4p orbitals.

0.87 a.u. for the nitrosyl. This is consistent with the calculated, almost unchanging, charge on the ligating N(H) atoms as WXYZ changes (Fig. 2). On the other hand, π-back donation is clearly significantly dependent on E_L(WXYZ), being greatest for $(NH_3)_2Cl_2$ (0.85 a.u.) and $(acac)_2$ (0.84 a.u.) and much smaller for the dicarbonyl (0.32 a.u.) and the nitrosyl species (0.23 a.u.) (Fig. 4, Table 2). Thus increasing π-back donation is not offset by a strengthening of the basicity of the ligand or an increase in σ-bond strength. The extra negative charge delocalizes into the metallocycle and C_6 ring. Relatively good linear correlations exist between the total calculated π-back donation and the experimental ΣE_L(WXYZ), $E_{1/2}$[q/sq] and $E_{1/2}[Ru^{III/II}]$ values. Given that σ-donation is almost constant, and polarization is small, there is necessarily also a fairly good linear relationship between net charge on bqdi and π-back donation. We comment in passing that the atypically large σ-donation from bqdi to $[Ru(NO^+)(terpy)]^{3+}$ is a consequence of the strong Lewis acidic character of this nitrosyl species. The Ru–N bond order *trans* to (NO^+) is 0.59 while that *trans* to the central N atom of terpy is only 0.44.

3.3. Bond orders

The π-back donation occurs primarily via the 4dπ-LUMO(bqdi) bonding interaction as noted above. In the case of $[Ru(NH_3)_4(bqdi)]^{2+}$, this is the HOMO-2 and is responsible for approximately 76% of the total π-back donation. The bonding orbital shown in Fig. 5 for $[Ru(NH_3)_4(bqdi)]^{2+}$ is basically very similar for all the species. In this MO, Ru–N, C4–C5 and C1–C2 are bonding, C═N (metallocycle) is anti-bonding and C3–C4 and C5–C6 are likely only peripherally involved. Thus we can predict how changing the donation strength of WXYZ will influence the bond orders of these various bonds. Fig. 6 displays how decreasing E_L(WXYZ) (i.e. increasing donation to Ru) which will increase π-back donation, leads to increasing Ru–N bond order.

Fig. 7 (upper) reveals how increasing π-back donation is associated with a decrease in the C═N (metallocycle) bond order (green) and in increase in the C4–C5 bond order. The correlation with the C4–C5 bond order is especially good because this bond is fairly far removed from areas of asymmetry which likely cause scatter in the C═N correlation (green) [74]. Fig. 7 (lower) shows an example of a corresponding correlation with net MPA charge comparing the C4–C5 and C1–C2 bonding interactions, probably, within experimental error, of the same slope. The C3–C4 and C5–C6 bond orders are essentially constant, 1.63 ± 0.02, for the entire series. Thus these data show nicely how the mixing of the bqdi π*-LUMO with the filled Ru 4dπ orbital can be tuned with variation in WXYZ and provide changes in bond order in agreement with the simple predictions based on the nodal pattern of the bqdi localized π*-LUMO.

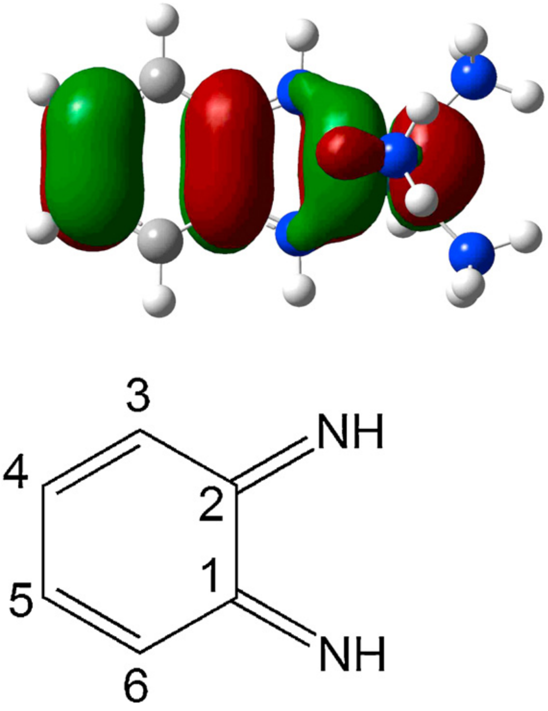

Fig. 5. (Upper) The filled HOMO-2 (MO# 53) of $[Ru(NH_3)_4(bqdi)]^{2+}$ showing the π-bonding interaction between 4dπ and π* LUMO of bqdi. Assuming the bqdi lies in the *xz* plane, then the dπ orbital is dyz. (Lower) Numbering scheme for bqdi.

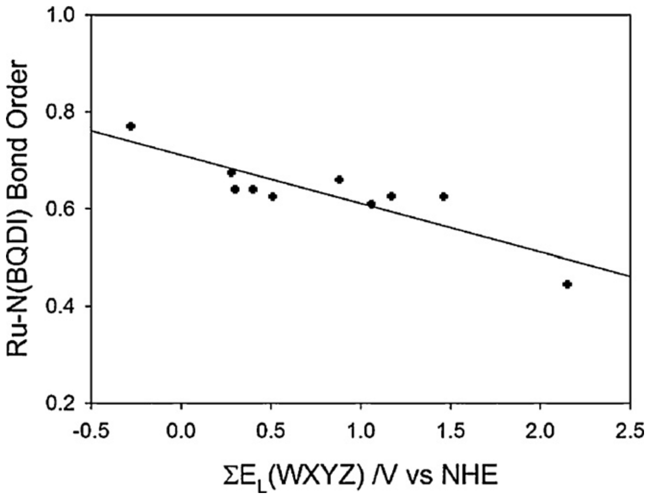

Fig. 6. Plot of the Ru-N(bqdi) (Mayer) bond order vs ΣE_L(WXYZ).

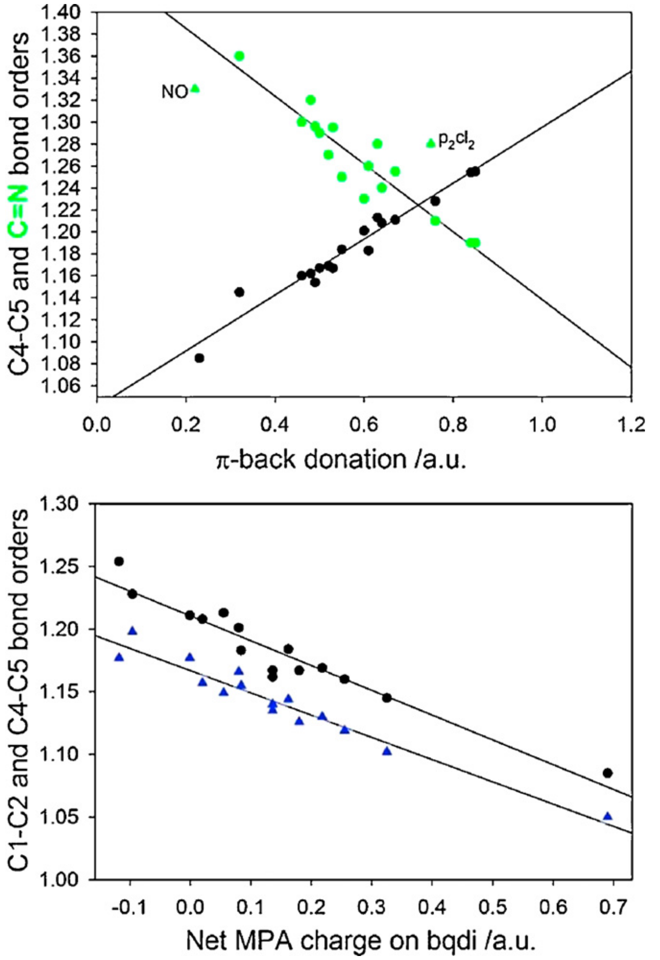

Fig. 7. (Upper) A plot of π-back donation vs the C4–C5 bond order (black) and C═N bond order (green) in the $[\text{Ru(WXYZ)(bqdi)}]^{n+}$ series. The use of average values for the C═N bond order in asymmetric complexes will contribute to the scatter (see text). (Lower) A plot of the C4–C5 (black circles) and C1–C2 (blue triangles) bond order vs net MPA charge on bqdi.

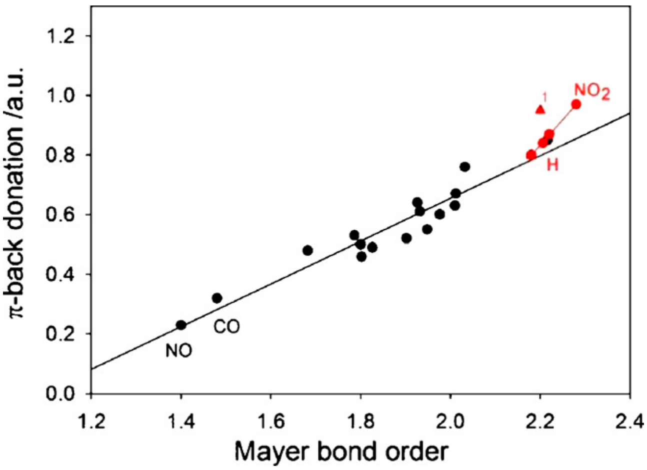

Fig. 8. Plot of the total π-back donation (a.u.) (Ru(WXYZ) to bqdi) vs Mayer bond order between the bqdi and Ru(WXYZ) fragments. The corresponding data for Ru(acac)_2(R-bqdi) are in red (Ru(acac)_2 to R-bqdi). Outlier '1′ is R = N-SO_2Me. 'NO' and 'CO' refer to the nitrosyl and carbonyl complexes in the WXYZ group.

It is useful also to consider the Mayer bond order [34,35] between the two fragments themselves since this takes into account additional interactions that are possible between the bqdi and Ru(WXYZ) fragments over and above the direct Ru–N interaction. This total Mayer bond order correlates nicely with the calculated π-back donation (Fig. 8) and the experimental $E_{1/2}$[q/sq] potential (Fig. 9). The $E_{1/2}$[q/sq] potential is, of course, an experimental reflection of the increasing π-back donation and the bond order is seen to increase as the complex becomes more difficult to reduce. Thus the bonding and anti-bonding interactions between the Ru(WXYZ) and bqdi fragments can be clearly understood in terms of a dominant π-back donation via the bqdi LUMO.

3.4. *Optical spectra; charge transfer transitions*

The transition between the bonding 4dπ + bqdi(π*) and the anti-bonding bqdi(π*) 4dπ molecular orbital is expected to be the most intense of the 4d(t_{2g}) to LUMO transitions. There is a well developed model to relate the energy of metal to ligand charge transfer transitions (MLCT) to the difference between the (first) oxidation potential localized at the metal and the (first) reduction potential, localized at the bqdi ligand. This difference in potential is usually referred to as Δ*E*(redox), and Eq. (1) is frequently used with the assumption that constant *C* is small [11,18,75–84]. For a large number of ruthenium complexes *C* has a value of approximately 0.2 eV [84].

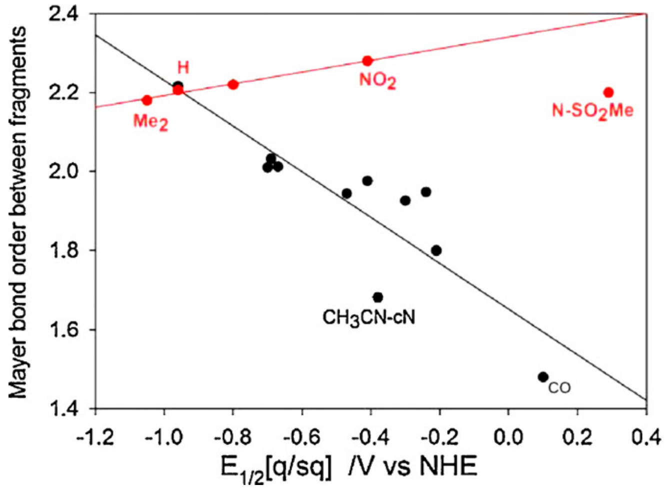

Fig. 9. Plot of Mayer bond order between the bqdi and Ru(WXYZ) fragments vs the experimental $E_{1/2}$[q/sq] potential. The corresponding data for Ru(acac)_2(R-bqdi) are in red. NB The red R = H exactly overlays the black Ru(acac)_2(bqdi) entry. The overlapping black entry is $\text{Ru(NH}_3)_2\text{Cl}_2$(bqdi). (cN = triazacyclononane).

Table 3
Selected data for the Ru(acac)$_2$(R-bqdi) series.

R[a]	$E_{1/2}$[q/sq] (V vs NHE)	$E_{1/2}$ [Ru$^{III/II}$] (E_L(R-bqdi)) (V vs NHE)	σ-donation (a.u.)	π-back donation (a.u.)	Net charge (a.u.)	Mayer Bond order[b]	%Ru in LUMO
4,5-Me$_2$	−1.05	0.48(0.40)	0.73	0.80	−0.08	2.18	30.0
Cl	−0.80	0.65(0.49)	0.73	0.87	−0.15	2.22	32.4
NO$_2$	−0.41	0.84(0.58)	0.74	0.97	−0.23	2.28	31.8
di(N-SO$_2$Me)	0.29	1.18(0.75)	0.60	0.95	−0.35	2.20	29.3

[a] R = H can be found in Tables 1 and 2.
[b] Between Ru(acac)$_2$ and R-bqdi fragments.

$$h\nu(\mathrm{MLCT}) = \Delta E(\mathrm{redox}) + C(\mathrm{eV}) \qquad (1)$$

The lesson to be learned here is that C may not be small when non-innocent ligands are concerned as can be discerned from the data in Tables 1 and 2. The energies of this transition, in the entire range of WXYZ complexes, fall in the narrow range of $(18.0 \pm 1.5) \times 10^3\ \mathrm{cm}^{-1}$ $(2.23 \pm 0.2\ \mathrm{eV})$. ΔE(redox) varies from 1.43 to 2.13 eV and constant C (Eq. (1)) from 0.48 to 1.15 eV. Not unexpectedly, there is a trend with the smaller values of C being associated with the complexes with a lesser degree of π-back donation, and larger values of C with greater values of π-back donation, e.g. [Ru(CH$_3$CN)$_2$(PPh$_3$)$_2$(bqdi)]$^{2+}$ C = 0.48 eV, net charge +0.16 a.u. and Ru(NH$_3$)$_2$Cl$_2$(bqdi) C = 1.15 eV, net charge = −0.14 a.u. The simple, small C model fails basically because the donor and acceptor orbitals are not localized on different parts of the molecule but involve a pair of orbitals where the same metal and ligand functions are significantly mixed together; there is therefore little charge transfer character. The constant C encompasses many terms [84] including solvation and reorganization energies and may include energy differences within the t$_{2g}$ subshell when, as is common, the MO involved in the electrochemical oxidation is not the same as the MO involved in the optical transition. We may note in passing, that we do expect very weak MLCT transitions arising from the other two 4d(t$_{2g}$) to the LUMO and these can sometimes be observed in these highly mixed, non-innocent ligand systems, more readily than in the less mixed species [3,67].

4. Ru(acac)$_2$(R-bqdi) complexes [3] (R = H, Cl, NO$_2$, 4,5-Me$_2$, di-N-SO$_2$Me)

Here we briefly explore keeping WXYZ constant as (acac)$_2$ and changing a substituent on bqdi. A similar set of correlations can be derived from this, albeit rather small, dataset and some relevant correlations are shown in red in Figs. 1, 8 and 9 with data in Table 3. Because of the asymmetry of the non-innocent ligand, it is not useful to look at the individual bond orders in these cases. We observe (Fig. 1) a nice linear correlation between the net charge on the R-bqdi ligand and both the oxidation and reduction potentials, but with a slope inverse to that of the WXYZ series. The difference in behavior between the two series (opposite slopes) can be understood in terms of a push-pull mechanism. In the [Ru(WXYZ)(bqdi)]$^{n+}$ series, the pull is constant (by bqdi) and the push increases with increasing net donor character of WXYZ. With increasing push, the net charge on bqdi becomes more negative and it becomes more difficult to reduce it electrochemically and the $E_{1/2}$[q/sq] reduction potential becomes more negative (and $E_{1/2}$[Ru$^{III/II}$] becomes less positive). In the Ru(acac)$_2$(R-bqdi) series, the push is constant and the pull increases with increasing acceptor character of R. Thus, increasing acceptor power of R causes R-bqdi to be more easily reduced resulting in both $E_{1/2}$[q/sq] and E$_{1/2}$[Ru$^{III/II}$] to shift positively.

Indeed it is interesting to note, for example, that a species Ru(WXYZ)(bqdi) with a net charge of zero on the bqdi will reduce at ca. −0.6 V vs NHE, while a substituted Ru(acac)$_2$(R-bqdi) having zero net charge would be predicted to reduce at ca. −1.5 V vs NHE ! This information can be used to design species with particular properties by making use of the Hammett parameters [85], for substituent R, which linearly correlate with the redox potentials of these R-bqdi species [3,67,86]. Figure 8 reveals that the Mayer bond orders, for the two fragments, correlate nicely with the extent of π-back donation. One might question whether the 'red' data in Fig. 8 actually lie on the same line as for the WXYZ data.

Fig. 9 shows a very nice, related, correlation of Mayer bond order (between fragments) with $E_{1/2}$[q/sq]. Here one should reflect that the increasing value of the Mayer bond order occurs with increasing net MPA negative charge on R-bqdi (R = H, etc.). The opposite slopes arise because for the WXYZ group, increasing net negative charge is from right to left, while for the (acac)$_2$ group, it is left to right.

Interestingly, the amount of π-donation in the C-substituted R-bqdi species is almost the same as the roughly constant amount seen for the WXYZ species. It is substantially reduced, however when the NH proton is replaced by methanesulfonyl (N-SO$_2$Me species). The variation in %Ru in the LUMO is too small to usefully correlate, in this very limited dataset (Table 3).

5. E_L(R-bqdi)

Unlike the $E_L(L)$ parameter of innocent ligands, the $E_L(L)$ parameter [25,67] of a non-innocent ligand is not a constant. It can be expected to vary with the extent of π-back donation. Thus, increasing Ru 4dπ back donation into bqdi will cause an increasingly positive potential to oxidize Ru^{II} to Ru^{III} which will be recognized as an apparent increase in E_L(R-bqdi). This is seen to be the case, and indeed in a fairly linear fashion (Tables 1 and 3, Fig. 10).

In fact, in the Ru(WXYZ) series, there is quite a dramatic increase in E_L(bqdi) as negative charge is moved onto the bqdi ligand by the WXYZ ligands. Bearing in mind the value is per nitrogen atom,

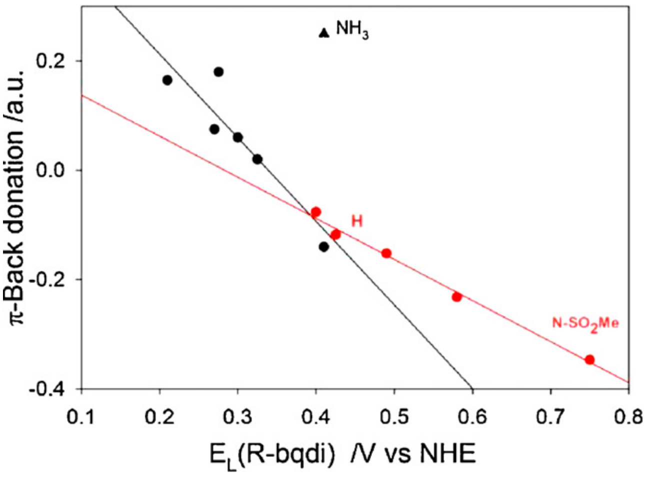

Fig. 10. Net MPA charge on R-bqdi vs E_L(R-bqdi). The Ru(WXYZ) series are in black and the Ru(acac)$_2$ series in red. The R = H datum applies to both lines.

the effect of this, from bqdi alone, is to shift the $Ru^{III/II}$ oxidation potential by approximately 0.80 V between the two extreme values noted in the table. However if we achieve a higher E_L(bqdi) by replacing one or more spectator ligands with more strongly donating ligands we have to consider that their *decreasing* ΣE_L value will offset the net result. Indeed ΣE_L(WXYZ) also correlates (not shown) fairly linearly with E_L(bqdi). The slope of this correlation leads to the conclusion that decreasing E_L(WXYZ) by 1.0 V will only increase $2 \times E_L$(bqdi) by about 0.25 V. However, it is an intriguing inverted procedure, use a donor rather than an acceptor, to achieve similar objectives.

A good linear correlation is also seen in the $Ru(acac)_2$(R-bqdi) series (Fig. 10) though here we are indeed changing the ligand as R is varied. However we might consider a modification of R, causing a change in net π-back donation, is just another procedure to tune π-back donation. There is another dramatic increase in E_L(R-bqdi) with increasing negative charge. The E_L(N-SO_2Me-bqdi) parameter is approaching that of carbon monoxide. This increase in E_L(R-bqdi) is achieved without changing the spectator ligand and so is potentially a more useful procedure to tune desired potentials. Since the potentials shown in Table 3 do correlate also with the Hammett parameter of R, this parameter can also be used as a design tool.

6. $Ru^{II}L_4$(bqdi) or $Ru^{III}L_4$(sqdi)?

We explore briefly whether these species ought to be considered as resonance hybrids of two canonical forms, $[Ru^{II}(WXYZ)(bqdi)]^{n+}$ and $[Ru^{III}(WXYZ)(sqdi)]^{n+}$ (sqdi = *o*-benzosemiquinone diimine) as has been suggested frequently in the past, e.g. [87]. In this model one might argue that we move from regarding these species as primarily $[Ru^{II}(WXYZ)(bqdi)]^{n+}$ to primarily $[Ru^{III}(WXYZ)(sqdi)]^{n+}$ as WXYZ become more donating and the π-back donation increases. Indeed π-back donation would not have the same significance in this model. Such a model in no way invalidates the correlations cited above between DFT derived data and experimental data but would require a somewhat different interpretation. Oxidation states are physically meaningless [24,88] since it is our choice how we define each component of the molecule, e.g. Ru^{II} with bqdi or Ru^{III} with sqdi(1−) (in this case, spin coupled Ru^{III} with sqdi).

However *it is meaningful* to ask if these species have a spectroscopic signature of Ru^{II} or Ru^{III} [88] or a geometric signature for a quinone or semiquinone. The fact that the bond order of the C3–C4 and C5–C6 ‘double bonds’ (1.63) is independent of the donor strength of WXYZ, would argue for the ligand remaining in the same oxidation state throughout the series i.e. to remain as a quinone. The C_6 ring bond distances retain the alternating values expected for a quinonoid species albeit the difference, between largest and smallest, is slightly greater for the better WXYZ donors than for the weaker ones.

The C3–C4, C5–C6 bond orders in the free bqdi ligand are calculated to be 1.75 while those in the free sqdi ligand are 1.57. In $Rh^{III}(NH_3)_2Cl_2$(sqdi) the corresponding bond order is also 1.57, while in $[Ru^{II}(NH_3)_2Cl_2(sqdi)]^-$ it is 1.48; thus we can speculate that in a true $Ru^{III}(NH_3)_2Cl_2$(sqdi) species, the C3–C4,C5–C6 bond order would lie between these two values, i.e. ca. 1.52. In fact it is 1.63. Thus these data argue for the $Ru^{II}L_4$(bqdi) model with increasing π-back donation, with no clear evidence that $Ru^{III}L_4$(sqdi) plays a significant role.

7. Summary

The DFT calculation using the commonly employed B3LYP functional and LANL2DZ basis set appears to provide an excellent assessment of the experimental properties of these non-innocent ligand complexes. The degree of π-back donation in these species is very significantly greater, approaching an order of magnitude more, than the extent of back donation to so-called good π-acceptor ligands such as 2,2′-bipyridine. Importantly, the extent of π-back donation primarily via mixing of the LUMO of bqdi into filled orbitals of the complex, can be nicely tuned by variation of WXYZ or the R-substituent of R-bqdi. This tuning can be dictated linearly through the ligand electrochemical parameters, $E_L(L)$ of WXYZ and, in the latter case, via the Hammett parameter of R. Our chemical intuition is validated by the increasing degree of back donation caused when the WXYZ ligands move charge onto Ru, as measured through $E_L(L)$ or the oxidation or reduction potentials of the complexes. Unexpectedly this negative charge is delocalized over the bqdi ligand with the exclusion of the coordinating N atoms whose charge remains essentially constant. This then leads to the extent of σ-donation remaining constant as π-back donation increases quite dramatically. π-Back donation occurs dominantly by the mixing of the bqdi π*-LUMO with metal 4dπ. The effect of increasing π-back donation on the bond orders of the C-C, C=C and C=N and Ru–N bonds, in the complexes, can be elegantly correlated with experimental parameters simply on the basis of the nodal pattern of this 4dπ + π*-LUMO (bqdi) bonding molecular orbital (Fig. 5). The increasing strength of the Ru–N bond with increasing donicity of WXYZ arises primarily through the π not σ-interaction. The E_L(R-bqdi) parameter can be tuned over a large range, as much as 0.5 V, either by varying ΣE_L(WXYZ) or by C- or N-substitution of bqdi. This provides a useful procedure to design species with desired properties.

Overall, the benzoquinonediimine system offers some important insights into chemical bonding; it is a fascinating area which has a lot to teach us.

Acknowledgements

The author is indebted to the Natural Sciences and Engineering Research Council (NSERC, Ottawa) for financial support. This work was made possible by the facilities of the *Shared Hierarchical Academic Research Computing Network* (SHARCNET: www.sharcnet.ca).

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