**Mixed-Valent Complexes**

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**Theoretical and Experimental Evidence for a New Kind of Spin-Coupled Singlet Species: Isomeric Mixed-Valent Complexes Bridged by a Radical Anion Ligand**

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Singlet species composed from clearly identified odd-electron components have long been known in the form of antiferromagnetically spin–spin coupled transition-metal centers (M) of d^{n+1} configuration bridged by ligands μ-L, giving rise to the phenomenon of “superexchange” in (M)(μ-L)(M) species. More recently, the reverse situation (L')(M)L' with a bridging diamagnetic metal center was described and referred to in terms of “singlet diradical” species. Herein we present another alternative [Eq. (1)], involving the strong intramolecular interaction between a bridging anion radical L− and two mixed-valent metal centers.

\[
(M)(L')(M) \rightarrow (M)(L')(M)
\]  

Evidence for the formulation in Equation (1) comes from structure determination in conjunction with density functional theory (DFT) calculations. Structural criteria have been increasingly used to establish the oxidation states of “non-innocent” ligands and, by implication, of metal centers in the coordination compounds. Prominent examples include the bidentate 1,2-dioxolene chelate ligands Q/Q for which structure–valency correlations were reported and applied, and simple diatomic ligands such as the potentially metal–metal bridging redox system O2/O2, a textbook case. Related to the latter by the relation O = NR are organic azo compounds (NR), in which the E configuration can act as reducible bis-bidentate bridges if R is a coordinating group, such as 2-pyrrol to form 2,2'-azobispyridine (abpy).

Abpy was first described by Lever and co-workers as a strongly π accepting but otherwise normal bridging ligand, a special feature of its complexes being the relatively short metal–metal distance of about 5 Å.

As with the O_2^- system, the addition of electrons to abpy causes a lengthening of the central N-N bond from double-bond values of about 1.25 Å via approximately 1.35 Å in the anion radicals to approximately 1.42 Å for single bonds in the two-electron-reduced forms (Scheme 1).

\[
E=E \quad +e^- \quad (E=E)^+ \quad +e^- \quad (E=E)^{2+}
\]  

Whereas coordination of π back-donating metal centers can result in a slight increase of the double-bond length relative to that in the free ligand, the lengthening caused by successive electron addition is so large and well documented through supporting spectroscopic data that these criteria can be unequivocally applied to establish the bonding situation.

In the search for unusual mixed-valent configurations involving ruthenium and other platinum metals we have now obtained the compound [(μ-abpy)[Ru(acac)2]2] from abpy and the neutral precursor [Ru(acac)2(CH3CN)2] (acac = 2,4-pentanedionate) separated the meso and rac isomers by chromatography, characterized them by 1H NMR spectroscopy and identified them by crystal-structure analysis (Figure 1, Table 1).

The molecules show the expected “S-frame” configuration with the bis-chelating abpy variably twisted; the C-N-C torsional angles are 26.1° in the rac form but only 15.5° and 0.0° for the two crystallographically independent molecules of the meso form. As expected, the bonds from the metal centers to the stronger π-accepting azo nitrogen atoms (ca. 1.965 Å) are shorter than those to the pyridine N centers (average 2.010 Å). Most remarkably, the central N-N bonds of the abpy ligand are considerably lengthened to 1.372(4) Å in the rac form and to 1.374(11) Å and 1.352(17) Å in the meso form whereas the adjacent C-N bonds are slightly shortened to about 1.395 Å. The average N-N distance of 1.366 Å lies in the same range as the 1.345(7) Å determined for a structurally and electronically well identified dicopper(i) complex containing the radical anion of the closely related 2,2'-bis(5-chloropyrimidine) (abcp) ligand. A reduced N–N bond order of 1.5 would be compatible with the ease of twisting around the central CNCN backbone of abpy.

The abpy and related ligands are known to effect rather short metal–metal distances of about 5 Å. The unusually short metal–metal distances observed for rac (4.664 Å)
Communications

Comparison of experimental and computed (DFT [a]) structural parameters [b] for different metal- and ligand-based spins in accord with the observed

Table 1: Comparison of experimental and computed (DFT [a]) structural parameters [b] for different isomers of [(µ-abpy)(Ru(acac))₂]₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental [b]</th>
<th>meso₁</th>
<th>meso₂</th>
<th>'rac</th>
<th>'rac</th>
<th>'meso</th>
<th>'meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N=N-C≡C</td>
<td>26.1</td>
<td>15.3</td>
<td>0.0</td>
<td>18.3</td>
<td>24.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N=N</td>
<td>1.372(4)</td>
<td>1.374(11)</td>
<td>1.352(17)</td>
<td>1.344</td>
<td>1.410</td>
<td>1.339</td>
<td>1.408</td>
</tr>
<tr>
<td>C-N_N₁₁₂</td>
<td>1.390(5)</td>
<td>1.382(12)</td>
<td>1.420(12)</td>
<td>1.390</td>
<td>1.365</td>
<td>1.391</td>
<td>1.365</td>
</tr>
<tr>
<td>Ru-Nₐ₁₆</td>
<td>1.963(3)</td>
<td>1.961(8)</td>
<td>1.962(9)</td>
<td>2.014</td>
<td>2.000</td>
<td>2.029</td>
<td>2.015</td>
</tr>
<tr>
<td>Ru-N₉₉</td>
<td>1.954(3)</td>
<td>1.997(8)</td>
<td>1.997(8)</td>
<td>1.997(8)</td>
<td>2.000</td>
<td>2.029</td>
<td>2.015</td>
</tr>
<tr>
<td>Ru-N₉₉</td>
<td>2.008(3)</td>
<td>1.995(8)</td>
<td>2.027(9)</td>
<td>2.027</td>
<td>2.055</td>
<td>2.021</td>
<td>2.046</td>
</tr>
<tr>
<td>Ru-N₉₆</td>
<td>2.007(3)</td>
<td>2.001(8)</td>
<td>2.001(8)</td>
<td>2.001(8)</td>
<td>2.000</td>
<td>2.029</td>
<td>2.015</td>
</tr>
</tbody>
</table>

[a] Optimized parameters for singlet and triplet states obtained at the B3LYP/6-31G° level.
[b] Bond lengths [Å] and angles [°].
[c] Two independent molecules in the unit cell of the crystallized meso isomer.
[d] Torsional angle.

and meso forms (4.698 and 4.780 Å) are partly caused by the CNNC twisting. The structural data thus clearly indicate the presence of a one-electron reduced (i.e. radical anion) ligand bridge, leaving a Ru²⁺Ru¹⁻ mixed-valent formulation for the metal centers. Since structural and spectroscopic results for this diamagnetic compound point to a symmetrical situation, this mixed valency would then have to be described as a Class III system (fully valence delocalized, that is, Ru²⁺Ru¹⁻) [c] with strong antiferromagnetic coupling between metal- and ligand-based spins in accord with the observed diamagnetism. As noted previously, [d] mixed-valent complexes with radical anion bridging ligands (L⁻⁻) can be invoked as metal-to-ligand charge transfer (MLCT) excited states of symmetrical dinuclear complexes [Eq. (2)]. [e]

\[ [M⁺(µ-L)M⁺]^{−0.5}_{\text{MLCT}} \cdot [M⁺(µ-L⁻)M⁺] \text{ or } [M⁺(µ-L⁻)M⁺]^{−0.5} \]  

(2)

Reversible oxidation and reduction processes of both the meso and rac forms of [(µ-abpy)(Ru(acac))₂]₂ occur at 0.05 (oxidation) and −1.03 V (reduction; versus saturated calomel electrode (SCE) in CH₃CN/0.1m Bu₄NClO₄), yielding a very large comproportionation constant \( K_c \) of \( 10^{18.3} \). Reduction produces EPR signals at \( g = 1.990 \) that are indicative of a radical,[f] and thus suggesting a [Ru¹⁺(abpy⁻)Ru¹⁺] configuration. Oxidation produces EPR signals at \( g = 2.25, 2.14 \) and 1.98 (rac isomer) or \( g = 2.35, 2.15 \) and 1.81 (meso isomer) that are indicative of the presence of an Ru¹⁺ center,[g] which would be compatible with a [Ru¹⁺(abpy⁻)Ru¹⁺] or [Ru¹⁻(abpy⁻)Ru¹⁻] formulation. Absence of the near infrared band expected for a conventional mixed-valent compound[9,12,15] suggests the [Ru¹⁺(abpy⁻)Ru¹⁺] alternative, implying metal-based electron transfer within the redox system [(µ-abpy)Ru(acac)₂] as befits a mixed-valency situation for the neutral form [Ru¹⁺(abpy⁻)Ru¹⁺].

The UV/Vis spectra of the neutral compounds are characterized by very intense bands (\( \epsilon = 29000 \text{ M}^{-1} \text{ cm}^{-1} \)) at 835 (rac) and 848 nm (meso) which are assigned to MLCT/MMCT (metal-to-ligand/metal-to-metal charge transfer) transitions between a metal-based occupied molecular orbital and a mixed abpy/metal LUMO.

DFT calculations at the B3LYP level were performed for both isomers.[18j] The calculated bond characteristics for the singlet ground states (Table 1) are in reasonable agreement with the experimental values, in addition, triplet states with longer N–N and shorter C–N distances (Table 1) were found comparatively close (rac: 840 cm⁻¹; meso: 1535 cm⁻¹) to the singlet ground states. The higher singlet–triplet gap for the meso isomer reflects the invariant coplanar CNNC backbone structure. Conversely, the energy difference between the singlet isomers is only 330 cm⁻¹ whereas it increases to 1026 cm⁻¹ between the triplet isomers, in both cases in favor of the rac form.

The wave functions were further analyzed using the natural bond orbital (NBO) method to probe the electron occupancies of the key orbitals as well as the extent of delocalization.[18k] The \( \tau_{\text{N-N}} \) occupancies for both rac and meso isomers are about 1.87 e while \( \tau_{\text{C-N}} \) was found to have a substantial population of 0.73 e. The corresponding values for the neutral ligand are 1.90 and 0.16 e, respectively. Although the change in occupancy is negligible for the π orbital on complex formation, it is significantly higher for the
\[ \pi^* \] molecular orbital, reflecting a substantial metal-to-ligand charge shift in the ground state. The donor–acceptor interaction energies obtained from the NBO analysis suggest that the cumulative effects of ligand-to-metal donation and \( \pi \) backonation make the azo nitrogen atoms slightly better donors than pyridyl nitrogen atoms. This result is in agreement with the experimental differences in the Ru–N bond lengths. The high values for the metal-to-ligand donation together with the substantial population of \( \pi^* \) clearly justify a description of the bridging ligand as a radical anion.

In summary, X-ray structure, spectroscopy, and DFT calculations have clearly established that the new stereo-isomeric rac- and meso-\([\mu\text{-}abpy]\)[Ru(acac)\(_3\)] complexes, must be formulated as \([\text{Ru}^2\text{a}(\text{abpy}^\text{b})\text{Ru}^2\text{b}]^2\) complexes, thus constituting both a new kind of unconventional mixed-valent compound and a new class of singlet species composed from metal/ligand/metal intramolecular spin-spin coupling. The occurrence of radical anions as ligands,}\(^{[19]}\) either as small metal/ligand/metal intramolecular spin-spin coupling. The compound and a new class of singlet species composed from donors than pyridyl nitrogen atoms. This result is in agreement with the experimental differences in the Ru–N bond lengths. The high values for the metal-to-ligand donation together with the substantial population of \( \pi^* \) clearly justify a description of the bridging ligand as a radical anion.

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13. \([\text{Ru(acac)}_2(\text{CH}_2\text{CN})_2]\)^{2+} (0.10 g, 0.26 mmol) and abpy^{2+} (0.022 g, 0.12 mmol) were combined in ethanol (10 mL) and heated to reflux for 4 h under a dinitrogen atmosphere.
14. a) Single crystals of the isomers \(\text{C}_3\text{H}_6\text{N}_2\text{O}_4\text{Ru}_2\) (M = 782.77) were measured using MoK\(_\alpha\) radiation, (0.7107 Å). The structures were solved and refined by full-matrix least-squares on \(F^2\) using SHELX-97 (SHELXTL).\(^{[21]}\) Hydrogen atoms were included in the refinement process as per the riding model. CCDC-265479 and CCDC-266238 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. b) rac Isomer: Single crystals grown by slow evaporation of a dichloromethane solution, crystal size 0.35 × 0.30 × 0.03 mm\(^3\), monoclinic, space group \(P2_1/c\), \(a = 20.5490(10), b = 11.8440(8), c = 25.695(3)\), \(\alpha = 94.004(8)\), \(V = 3217(14)\), \(T = 293(2)\) K, \(Z = 4\), \(\rho_{\text{calc}} = 1.616 \text{ g} \cdot \text{cm}^{-3}\), \(\mu = 0.993 \mu\text{m}\). \(2\theta_{\text{max}} = 58.15\), 4898 independent reflections (R(int) = 0.0000), \(R = 0.0328, wR_2 = 0.0758\) for 2000 reflections, \(\rho_{\text{calc}} = 1.616 \text{ g} \cdot \text{cm}^{-3}\), \(\mu = 0.993 \mu\text{m}\). \(2\theta_{\text{max}} = 58.15\), 4898 independent reflections (R(int) = 0.0000), R = 0.0328, wR2 = 0.0758 for 2000 reflections.


