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^{2n+1} configuration bridged by ligands u-L, giving rise to the phenomenon of "superexchange" in (M[•])(µ-L)(M[•]) species.^[1] More recently,^[2] the reverse situation $(L^{\cdot})(M)(L^{\cdot})$ 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 ligand L⁻⁻ and two mixed-valent metal centers.

$$(\mathbf{M}^{\cdot})(\mathbf{L}^{\cdot-})(\mathbf{M}) \leftrightarrow (\mathbf{M})(\mathbf{L}^{\cdot-})(\mathbf{M}^{\cdot})$$

$$\tag{1}$$

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^[3] and, by implication, of metal centers in the coordination compounds. Prominent examples include the bidentate 1,2-dioxolene chelate ligands $Q/Q^{-}/Q^{2-}$ for which structure-valency correlations were reported^[4,5] and applied, and simple diatomic ligands such as the potentially metal-metal bridging redox system $O_2/O_2^{-1}/O_2^{-2}$, a textbook case.^[6] Related to the latter by the relation O = NR are

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organic azo compounds (NR)2 which in the E configuration can act as reducible bis-bidentate bridges if R is a coordinating group, such as 2-pyridyl to form 2,2'-azobispyridine (abpy).^[7]



Abpy was first described by Lever and co-workers as a strongly π accepting but otherwise normal bridging ligand,^[7b] a special feature of its complexes being the relatively short metal-metal distance of about 5 Å.^[7a,c,e]

As with the O_2^{n-} system,^[6] 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^[8] to approximately 1.42 Å for single bonds in the two-electron-reduced forms (Scheme 1).^[9]

$$E=E \xrightarrow{+e^{-}}_{-e^{-}} (E=E)^{\bullet^{-}} \xrightarrow{+e^{-}}_{-e^{-}} (E-E)^{2^{-}}$$

$$E=O: 1.21 \text{ Å} 1.23-1.35 \text{ Å} 1.40-1.50 \text{ Å}$$

$$E=NR: 1.23-1.30 \text{ Å} ca. 1.35 \text{ Å} 1.40-1.45 \text{ Å}$$

Scheme 1. Bond lengths in E_2^{n-} systems.

E=0

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,^[7a] the lengthening caused by successive electron addition is so large and well documented through supporting spectroscopic data^[8] 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^[10] we have now obtained the compound $[(\mu-abpy){Ru(acac)_2}_2]$ from abpy^[7] and the neutral precursor [Ru(acac)₂(CH₃CN)₂] $(acac^- = 2, 4$ -pentanedionate),^[11] separated the *meso* and *rac* isomers^[12] by chromatography, characterized them by ¹H NMR spectroscopy,^[13] and identified them by crystalstructure analysis (Figure 1, Table 1).^[14]

The molecules show the expected "S-frame" configurations^[7a] with the bis-chelating abpy variably twisted; the C-N-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,^[7a] 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.^[8] A reduced N-N bond order of 1.5 would be compatible with the ease of twisting around the central CNNC backbone of abpy.

The abpy and related ligands are known to effect rather short metal-metal distances of about 5 Å.^[7a,c] The unusual $ly^{[7a,c]}$ short metal-metal distances observed for *rac* (4.664 Å)

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Figure 1. Crystal structures of *rac* (top) and one of the *meso* forms (bottom) of $[(\mu-abpy)\{Ru(acac)_2\}_2]$.

diamagnetism. As noted previously,^[7d] 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)].^[16]

$$[\mathbf{M}^{n}(\mu-\mathbf{L})\mathbf{M}^{n}] \xrightarrow{h\nu} [\mathbf{M}^{n+1}(\mu-\mathbf{L}^{-})\mathbf{M}^{n}] \text{ or } *[\mathbf{M}^{n+0.5}(\mu-\mathbf{L}^{-})\mathbf{M}^{n+0.5}]$$
(2)

Reversible oxidation and reduction processes of both the meso and rac forms of $[(\mu-abpy){Ru(acac)_2}_2]$ 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,^[17a] and thus suggesting a {Ru^{II}(abpy⁻)Ru^{II}} 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 Ru^{III} center,^[17b] which would be compatible with a {Ru^{III}(abpy⁻⁻)Ru^{III}} or {Ru^{II}-(abpy)Ru^{III}} formulation. Absence of the near infrared band expected for a conventional mixed-valent compound^[10,12,15] suggests the {Ru^{III}(abpy⁻)Ru^{III}} alternative, implying metalbased electron transfer within the redox system [(µ-abpy)- ${\rm Ru}({\rm acac})_{2}^{1/0/-}$ as befits a mixed-valency situation for the neutral form $\{Ru^{2.5}(abpy^{-})Ru^{2.5}\}$.

The UV/Vis spectra of the neutral compounds are characterized by very intense bands ($\varepsilon = 29000 \text{ M}^{-1} \text{ cm}^{-1}$) 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.^[18a] 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 singlettriplet 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 iso-

Table 1: Comparison of experimental and computed (DFT^[a]) structural parameters^[b] for different isomers of $[(\mu-abpy)\{Ru(acac)_2\}_2]$.

Parameter	Experimental ^[c]			DFT			
	rac	mesol	meso2	¹ rac	³ rac	¹ meso	³ meso
C-N=N-C ^[d]	26.1	15.5	0.0	18.3	24.8	0.0	0.0
N=N	1.372(4)	1.374(11)	1.352(17)	1.344	1.410	1.339	1.408
C-N _{azo}	1.390(5)	1.382(12)	1.420(12)	1.390	1.365	1.391	1.365
	1.390(5)	1.391(12)					
Ru-N _{azo}	1.963(3)	1.961(8)	1.962(9)	2.014	2.000	2.029	2.015
	1.954(3)	1.997(8)					
Ru-N _{py}	2.008(3)	1.995(8)	2.027(9)	2.027	2.055	2.021	2.046
	2.007(3)	2.001 (8)					

[a] Optimized parameters for singlet and triplet states obtained at the B3LYP/SDD/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 $Ru^{II}Ru^{III}$ 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, $Ru^{2.5}Ru^{2.5})^{[15]}$ with strong antiferromagnetic coupling between metal- and ligand-based spins in accord with the observed

mers, 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.^[18f,g] The $\pi_{(N=N)}$ occupancies for both *rac* and *meso* isomers are about 1.87 e while $\pi^*_{(N=N)}$ 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



 π^* 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 π back-donation 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 $\pi^*_{(N=N)}$ 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 stereoisomeric compounds *rac*- and *meso*-[(μ -abpy){Ru(acac)₂}₂] must be formulated as [Ru^{2.5}(abpy⁻)Ru^{2.5}] 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 molecules such as O₂^{--[6]} or CO₂^{--[20]} or as larger entities,^[2,4,5] has thus been extended to yield unprecedented electronic structures, using the rather simple inorganic complex fragment {Ru(acac)₂}. The additional feature of two separable stereoisomers will stimulate further investigations into configurational aspects of intramolecular interactions in these unconventional mixed-valent species.

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- $[Ru(acac)_2(CH_3CN)_2]^{[11]}$ (0.10 g, 0.26 mmol) and $abpy^{[7a]}$ [13] (0.022 g, 0.12 mmol) were combined in ethanol (10 mL) and heated to reflux for 4 h under a dinitrogen atmosphere. The color of the solution gradually changed from orange to dark brown. The solvent was removed and the residue was subjected to chromatography on a silica gel column. Initially, a red compound corresponding to [Ru(acac)₃] was eluted with CH₂Cl₂/CH₃CN (10:1). With CH₂Cl₂/CH₃CN (5:1), a green band corresponding to a mixture of rac and meso isomers was eluted. The rac and meso isomers were separated on a silica gel preparatory thin layer chromatography (TLC) plate using CH₂Cl₂/CH₃CN (7:1). rac Isomer: Yield 20 mg (20%); elemental analysis (%) calcd for $C_{30}H_{36}N_4O_8Ru_2$ (782.77): C 45.91, H 4.63, N 7.14; found: C 46.54, H 4.36, N 7.51; ESI MS (CH₂Cl₂): m/z: 783.08 [M⁺] (calcd m/z 782.78). meso Isomer: Yield 25 mg (25%); Calcd: C 45.91, H 4.63, N 7.14; found: C 45.62, H 4.99, N 7.28; ESI-MS (CH₂Cl₂): m/z: 784.19 [M⁺] (calculated m/z 782.78). ¹H NMR ((CD₃)₂SO; 300 MHz) for rac Isomer: $\delta =$ 8.55 (d, J=8.5 Hz, H3), 7.97 (d, J=6.3 Hz, H6), 7.70 (t, J=7.2 and 8.1 Hz, H4), 7.56 (t, J=6.4 and 7.2 Hz, H5), 5.31 (s, CH(acac)), 4.74 (s, CH(acac)), 2.11 (s, CH₃(acac)), 1.97 (s, CH₃(acac)), 1.64 (s, CH₃(acac)), 1.52 ppm (s, CH₃(acac)). meso-Isomer: $\delta = 8.32$ (d, J = 5.1 Hz, H6), 8.26 (d, J = 8.4 Hz, H3), 7.75 (t, J = 6.9 and 7.2 Hz, H4), 7.44 (t, J = 6.3 and 6.6 Hz, H5), 5.47 (s, t)CH(acac)), 5.39 (s, CH(acac)), 2.28 (s, CH₃(acac)), 2.09 (s, CH₃(acac)), 1.78 (s, CH₃(acac)), 1.69 ppm (s, CH₃(acac)).
- [14] a) Single crystals of the isomers $C_{30}H_{36}N_4O_8Ru_2$ ($M_r = 782.77$) were measured using $Mo_{K\alpha}$ radiation (0.71073 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 $0.35 \times 0.30 \times 0.30$ mm³, monoclinic, space group $P2_1/c$, a = 20.5490(10), b = 11.8440(8), c = 25.695(3) Å, $\beta = 149.040(8)^{\circ}$, V = 3217.1(4) Å³, T = 293 (2) K, Z = 4, $\rho_{\text{calcd}} = 1.616$ g cm⁻³, $\mu =$ 0.993 mm^{-1} , $2\theta_{\text{max}} = 49.86^{\circ}$, 4898 independent reflections (R-(int) = 0.0000), R1 = 0.0328, wR2 = 0.0758 $[I > 2\sigma(I)]$, R1 = 0.03280.0431, wR2 = 0.0814 (all data), GOF $(F^2) = 1.044$, data/ restraints/parameters = 4898/0/397, largest differential peak and hole 0.394 and -0.647 e Å⁻³. c) meso Isomer: Single crystals grown by slow evaporation of an acetonitrile solution, crystal size $0.85 \times 0.85 \times 0.40$ mm³, monoclinic, space group $P2_1/c$, a =26.296(9), b = 12.593(6), c = 15.018(7) Å, $\beta = 104.20(4)^{\circ}$, V =4821(4) Å³, T = 173(2) K, Z = 6 (1.5 independent molecules), $\rho_{\text{calcd}} = 1.618 \text{ g cm}^{-3}, \ \mu = 0.994 \text{ mm}^{-1}, \ 2\theta_{\text{max}} = 52.02^{\circ}, \ 9434 \text{ inde-}$ pendent reflections (R(int) = 0.0885), R1 = 0.0852, wR2 = 0.1947[for 6659 reflections with $I > 2\sigma(I)$], R1 = 0.1272, wR2 = 0.2146(all data), GOF $(F^2) = 1.653$, data/restraints/parameters = 9434/ 0/609, largest differential peak and hole 9.556 and $-2.613 \text{ e} \text{ Å}^{-3}$.
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