Inorganic Chemistry

COMMUNICATION

pubs.acs.org/IC

Tuning of the Spin Distribution between Ligand- and Metal-Based Spin: Electron Paramagnetic Resonance of Mixed-Ligand Molybdenum Tris(dithiolene) Complex Anions

Ulrich Fekl,*,[†] Biprajit Sarkar,[‡] Wolfgang Kaim,[‡] Marco Zimmer-De Iuliis,[†] and Neilson Nguyen[†]

[†]University of Toronto, 3359 Mississauga Road N, Mississauga, Ontario, Canada L5L 1C6

[‡]Institut für Anorganische Chemie, Universität Stuttgart, D-70569 Stuttgart, Germany

Supporting Information

ABSTRACT: Electron paramagnetic resonance spectra of homoleptic and mixed-ligand molybdenum tris(dithiolene) complex anions $[Mo(tfd)_m(bdt)_n]^-$ ($n + m = 3$; bdt = $S_2C_6H_4$; tfd = $S_2C_2(CF_3)_2$) reveal that the spin density has mixed metal−ligand character with more ligand-based spin for $[Mo(tfd)_3]^-$ and a higher degree of metal-based spin for $[Mo(bdt)_3]^-$: the magnitude of the isotropic $^{95,97}Mo$ hyperfine interaction increases continuously, by a factor of 2.5, on going from the former to the latter. The mixed complexes fall in between, and the metal character of the spin increases with the bdt content. The experiments were corroborated by density functional theory computations, which reproduce this steady increase in metal-based character.

Metal tris(dithiolene) complexes[1] are very unusual coordination compounds, and one of the most intriguing features has been that both the ligands and the metal may be redox-active: the frontier orbitals contain significant ligand π character, in addition to metal d contributions. For molybdenum tris(dithiolene) complexes, a classic example known since the mid-1960s, recent in-depth electronic structure descriptions[2] and new reactivity studies (with water[3] and with alkenes[4]/alkynes[5]) as well as semiconductor applications (hole dopant)[6] have contributed to invigorating a research field that was once considered mature. The synthesis of new tris(dithiolene) complexes may be guided by insight into the electronic structure and has the potential to fine-tune the electronic properties for applications. The question of metal-based versus ligand-based redox activity has also been important for those molybdenum dithiolene complexes [mono(dithiolenes) and bis(dithiolenes)] that occur in nature in the form of the "molybdopterin" enzyme cofactor.[7] We have become interested in the tunable properties of molybdenum tris(dithiolene) complexes, in particular in the interplay of ligand and metal. The aliphatic molybdenum tris(dithiolene) complex $Mo(tfd)_3$ [tfd = $S_2C_2(CF_3)_2$] is known to display ligand-based reduction, to form $[Mo(tfd)_3]^-$.[8] An isotropic $^{95,97}Mo$ hyperfine coupling of 12.2 G was reported for the electron paramagnetic resonance (EPR) spectrum.[8b] In 2001, EPR data for the analogous complex $[Mo(bdt)_3]^-$ (bdt = $S_2C_6H_4$) were reported,[9] where large hyperfine coupling to molybdenum (26.6×10^{-4} cm^{-1} reported at the X band, corresponding to ca. 29 G) may suggest that a more metal-based radical may be formed. A very similar EPR spectroscopic signature [$A = 29(1)$ G] was observed in 1966 after reduction of the 3,4-toluenedithiolate complex $Mo(tdt)_3$ [tdt = $S_2C_6H_3(CH_3)$].[10] Consistent with this EPR-based indication of a significantly metal-based spin, Wieghardt et al.[2c] found the substituted analogue $[Mo(3,5\text{-di-}tert\text{-butyl-bdt})_3]^-$ to be a d^1-configured complex (metal-based radical), as concluded from S−K-edge X-ray absorption spectroscopy. The latter technique, in conjunction with density functional theory (DFT) computations, has been used by another group[2b] to identify $[Mo(3,5\text{-di-}tert\text{-butyl-bdt})_3]^-$ as a metal-based spin system, while the aliphatic analogue $[Mo(S_2C_2(CH_3)_2)_3]^-$ is best formulated as a d^2 complex with one ligand hole (ligand-centered radical). A very recent study, which includes EPR data on various molybdenum tris(dithiolene) complex anions with either aliphatic or bdt-type aromatic dithiolenes, consistently demonstrated that the radical is much more metal-based in the case of aromatic dithiolenes as opposed to the situation for aliphatic dithiolenes.[2a] All of this is consistent with the initial ligand-based radical interpretation of aliphatic $[Mo(tfd)_3]^-$. The question arises as to whether the transition from ligand- to metal-based reduction appears abruptly or smoothly in these systems. In order to address this question, we are presenting here the first EPR data on mixed tris(dithiolene) complexes that contain different dithiolenes in the same metal complex.

We have been able to obtain isotropic solution EPR spectra for $[Mo(tfd)_2(bdt)]^-$ and $[Mo(bdt)_2(tfd)]^-$,[11] in addition to reproducing the spectra of $[Mo(tfd)_3]^-$ and $[Mo(bdt)_3]^-$ (Figure 1 and Table 1). Most significantly, the magnitude of isotropic hyperfine coupling to $^{95,97}Mo$ increases by a factor of 2.5 on going from all-tfd to all-bdt, where the values for the mixed dithiolenes fit almost linearly between the values of the homoleptic ones, thus mapping out a sector between mostly ligand-based and more metal-based reduction (Figure 2, left-hand scale).

It is observed that the g value decreases steadily with increasing metal character, from 2.009 for $[Mo(tfd)_3]^-$ to 2.003 $[Mo(bdt)_3]^-$ (Figure 2, right-hand scale). Standard errors for g were estimated to be within 0.001. The decrease in g with increasing metal character is consistent with a value $g \approx 1.95$ for the extreme case of a Mo^V d^1 system.[12] For all species studied, the g anisotropies are small, within 0.013 (see the Supporting Information for frozen solution spectra).

The transition from ligand-based to more metal-based reduction has also been probed using computational (DFT) methods (using the B3LYP functional with 6-31G for H and 6-31G* for C,

Received: May 18, 2011
Published: August 19, 2011

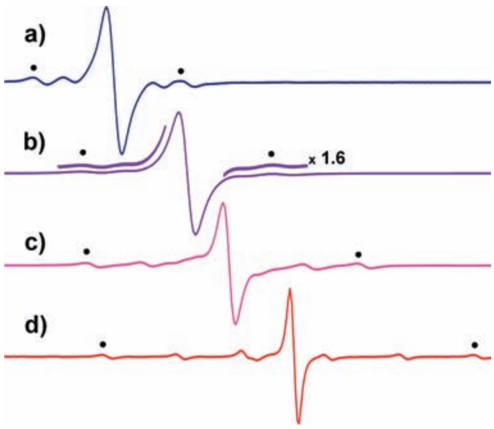

Figure 1. Solution (298 K, CH_2Cl_2 solvent) X-band EPR spectra for (a) $[Mo(tfd)_3]^-$, (b) $[Mo(tfd)_2(bdt)]^-$, (c) $[Mo(bdt)_2(tfd)]^-$, and (d) $[Mo(bdt)_3]^-$. The spectra are to scale but horizontally offset for clarity purposes (*g* values can be found in Table 1). The black dots denote the outermost satellites of the molybdenum satellites' sextet pattern, due to molybdenum isotopes having $S = {}^5/_2$ (25.5% natural abundance for ^{95}Mo and ^{97}Mo combined).

Table 1. Isotropic ^{95,97}Mo Hyperfine Coupling (Gauss) and *g* Values for $[Mo(tfd)_m(bdt)_n]^-$, Sorted by the Number of bdt Ligands (*n*)

	bdt # (*n*)			
	0	1	2	3
A	12.1	16.5	23.1	30.0
g	2.0092	2.0051	2.0041	2.0030

S, and F and the LANL2DZ basis set with an effective core potential for Mo). Full geometry optimizations were performed, using an open-shell formalism, for all four species $[Mo(tfd)_m(bdt)_n]^-$. Vibrational analyses were carried out on all optimized structures to verify that true minima had been located (no negative frequencies). The geometry of each ion was optimized using two different starting geometries: a more octahedral one (based on X-ray crystal structure data of the complex $[Mo(bdt)_3]^-$)[13] and an approximately trigonal-prismatic one. No exact 180°/90° angles or torsion angles were given, and no symmetry was used. Formally, two different stable minima were found for each complex anion. For $[Mo(tfd)_3]^-$, the differences between the two structures, energetically (identical within 0.2 kcal) and structurally (twist angle and chelate fold angle; see the Supporting Information for definition, identical within 1° and 4°, respectively), are small and probably not chemically significant. A similar observation is made for $[Mo(tfd)_2(bdt)]^-$. Of the four structures optimized, only two that were started with an "octahedral" geometry maintained such a deviation from trigonal-prismatic after optimization, namely, $[Mo(bdt)_3]^-$ and $[Mo(tfd)(bdt)_2]^-$. The free energy difference (ΔG, 298 K, 1 atm, gas phase) between the octahedral and trigonal-prismatic structures is minimal, with the octahedral geometry being favored by 2.1 kcal/mol for $[Mo(bdt)_3]^-$ and 1.3 kcal/mol for $[Mo(tfd)(bdt)_2]^-$. The more stable computed structure for $[Mo(bdt)_3]^-$ is in excellent agreement with the experimental crystal structure.[13]

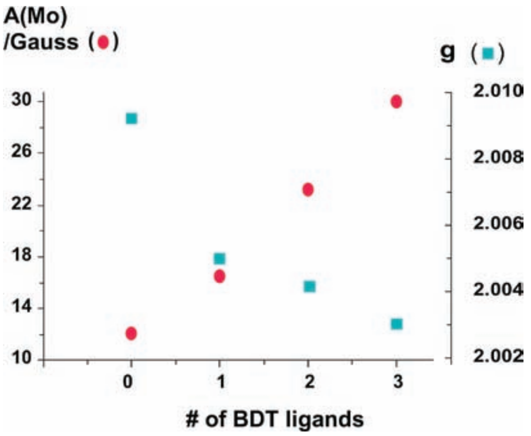

Figure 2. Variation of the molybdenum hyperfine coupling and isotropic *g* factor as a function of the number of bdt ligands.

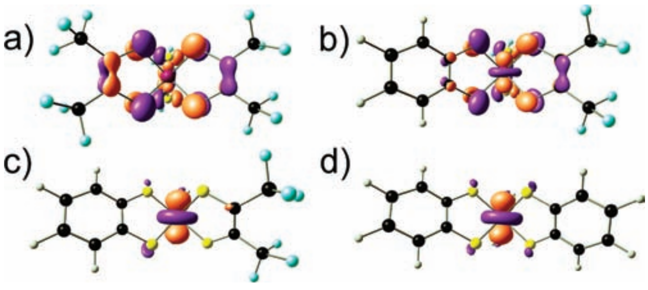

Figure 3. SOMOs (0.05 isovalue), demonstrating increasingly metal-based character if the bdt content is increased: (a) $[Mo(tfd)_3]^-$; (b) $[Mo(tfd)_2(bdt)]^-$; (c) $[Mo(bdt)_2(tfd)]^-$; (d) $[Mo(bdt)_3]^-$.

The spin population ($\alpha-\beta$, Mulliken) at molybdenum increases with increasing bdt content, from 0.004 ($[Mo(tfd)_3]^-$) via 0.184 ($[Mo(tfd)_2(bdt)]^-$) to 0.757 ($[Mo(bdt)_2(tfd)]^-$) and 0.745 ($[Mo(bdt)_3]^-$). This effect also becomes clear from Figure 3, where the singly occupied molecular orbitals (SOMOs; Kohn—Sham orbitals from DFT) of all four complexes are shown.

This qualitative behavior is observed with different functionals; however, the degree of the effect is strongly functional-dependent. The spin-population values for the above series are 0.090, 0.260, 0.718, and 0.707 if the M06-L functional is used.[14] The experimental trend is very well reproduced by DFT computations, with the exception that the metal-based character of the radical is experimentally still increasing from $[Mo(bdt)_2(tfd)]^-$ to $[Mo(bdt)_3]^-$, while computations indicate that it reaches saturation already at $[Mo(bdt)_2(tfd)]^-$.

In conclusion, the transition between ligand- and metal-based reduction is a relatively smooth one for molybdenum tris(dithiolene) complexes. The EPR data of the mixed-ligand species $[Mo(tfd)_2(bdt)]^-$ and $[Mo(bdt)_2(tfd)]^-$ indicate mixed metal—ligand character for the radical; the metal character increases and the ligand character decreases with increasing bdt content. This first study on the EPR properties of heteroleptic tris(dithiolene) complexes having different dithiolenes yields results consistent with those previously obtained from homoleptic tris(dithiolene) complexes (aromatic *or* aliphatic), where the presence of bdt also lowered the ligand-based character of the radical. Because the ligands are coupled, a behavior is obtained that is in stark contrast to expectations from organic free-radical chemistry, where aromatic radicals are generally associated with higher stability. A further message from this work is that an isotropic *g* factor close to the free electron value can be consistent with a largely metal-based radical.

ASSOCIATED CONTENT

Supporting Information. Details for the sample preparation and equipment used, isotropic spectra with curve fits, frozen solution spectra, and pictures and coordinates for DFT work. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ulrich.fekl@utoronto.ca.

ACKNOWLEDGMENT

Funding by the Natural Science and Engineering Research Council (NSERC) of Canada is gratefully acknowledged. N.N. and M.Z.-D.I. were, in part, supported from an Early Researcher Award (Province of Ontario) to U.F. Computations were performed on the GPC supercomputer at the SciNet HPC Consortium. SciNet is funded by the Canada Foundation for Innovation under the auspices of Compute Canada, the Government of Ontario, the Ontario Research Fund—Research Excellence, and the University of Toronto.

REFERENCES

(1) (a) Dithiolene Chemistry: Synthesis, Properties, and Applications. In *Progress in Inorganic Chemistry*; Stiefel, E. I., Ed.;John Wiley and Sons: Hoboken, NJ, 2004; Vol. 52. (b) Eisenberg, R. *Coord. Chem. Rev.* **2011**, *255*, 825.

(2) (a) Sproules, S.; Banerjee, P.; Weyhermüller, T.; Yan, Y.; Donahue, J. P.; Wieghardt, K. *Inorg. Chem.* **2011**, *50*, 7106. (b) Tenderholt, A. L.; Szilagyi, R. K.; Holm, R. H.; Hodgson, K. O.; Hedman, B.; Solomon, E. I. *Inorg. Chem.* **2008**, *47*, 6382. (c) Kapre, R. R.; Bothe, E.; Weyhermüller, T.; DeBeer George, S.; Wieghardt, K. *Inorg. Chem.* **2007**, *46*, 5642.

(3) (a) Cervilla, A.; Pérez-Pla, F.; Llopis, E.; Piles, M. *Inorg. Chem.* **2006**, *45*, 7357. (b) Cervilla, A.; Pérez-Pla, F.; Llopis, E.; Piles, M. *Dalton Trans.* **2004**, 1461.

(4) (a) Harrison, D. J.; Lough, A. J.; Nguyen, N.; Fekl, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 7644. (b) Harrison, D. J.; Fekl, U. *Chem. Commun.* **2009**, 7572.

(5) Nguyen, N.; Harrison, D. J.; Lough, A. J.; De Crisci, A. G.; Fekl, U. *Eur. J. Inorg. Chem.* **2010**, 3577.

(6) Qi, Y.; Sajoto, T.; Kröger, M.; Kandabarow, A. M.; Park, W.; Barlow, S.; Kim, E.-G.; Wielunski, L.; Feldman, L. C.; Bartynski, R. A.; Brédas, J.-L.; Marder, S. R.; Kahn, A. *Chem. Mater.* **2010**, *22*, 524.

(7) Hine, F. J.; Taylor, A. J.; Garner, C. D. *Coord. Chem. Rev.* **2010**, *254*, 1570.

(8) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1966**, *88*, 3235. (b) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1964**, *86*, 2799.

(9) Cervilla, A.; Llopis, E.; Marco, D.; Pérez, F. *Inorg. Chem.* **2001**, *40*, 6525.

(10) Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2956.

(11) See ref 4 for the synthesis and Supporting Information for the sample preparation.

(12) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135.

(13) (a) Cervilla, A.; Llopis, E.; Marco, D.; Perez, F. *Inorg. Chem.* **2001**, *40*, 6525. (b) Isfort, C. S.; Pape, T.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2005**, 2607.

(14) See the Supporting Information for references on basis sets and functionals.