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<th>Journal:</th>
<th>Dalton Transactions</th>
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</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>DT-FRO-09-2017-003620</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Frontier</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>26-Sep-2017</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Büldt, Laura; University of Basel, Department of Chemistry Wenger, Oliver; University of Basel, Department of Chemistry</td>
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Luminescent complexes made from chelating isocyanide ligands and earth-abundant metals

Laura A. Büldt and Oliver S. Wenger*

In this invited frontier article, recently discovered d^6 and d^10 complexes with long-lived metal-to-ligand charge transfer (MLCT) excited states are highlighted. Chelating diisocyanide ligands give access to emissive Mo(0) and Cr(0) complexes with d^6 electron configuration exhibiting photophysical properties similar to those of Ru(II) polypyridines or cyclometalated Ir(III) complexes. With Ni(0), these ligands yield luminescent tetrahedral d^10 complexes similar to isoelectronic Cu(I) bis(diimine) compounds.

Introduction

Metal complexes with either 4d^6 or 5d^6 electron configuration and suitable ligands have long been known to exhibit favorable electronic structures that give rise to rich photophysics and photochemistry. The most prominent members of this family are arguably Ru(II) polypyridines (with Ru(2,2'-bipyridine)_3^2+ as a prototype) and cyclometalated Ir(III) complexes. Applications of such complexes include for example lighting devices, solar cells, photoredox catalysis, and sensors. The low-spin d^6 electron configuration as well as energetically low-lying empty ligand orbitals are crucially important for MLCT excited states with lifetimes on the order of ~100 ns and associated luminescence phenomena. There is a long-standing interest in replacing the precious metals Ru(II) and Ir(III) by more earth abundant elements, but this is not a straightforward endeavor. Fe(II) complexes, for example, typically exhibit very short-lived MLCT excited states (~130 fs – 37 ps), due to the presence of low-lying d-d excited states in the comparatively weak ligand field of the 3d^6 configuration.

Discussion

Building on a few papers published more than 40 years ago, and inspired by recent reports on W(0) complexes with monodentate isocyanide ligands, we synthesized and explored a new family of Cr(0) and Mo(0) complexes with chelating diisocyanide ligands. Isocyanide groups are needed to stabilize the low oxidation states of these metals, and a meta-terphenyl backbone was suitable for accessing a relatively rigid bidentate chelator. (With few exceptions, earlier studies of chelating diisocyanides had focused on more flexible and other types of ligand backbones). Homoleptic Cr(0) and Mo(0) tris(diisocyanide) complexes are readily obtained with our ligands, and they are luminescent in fluid solution at room temperature (Figure 1).
The Mo(0) complex emits $^3$MLCT luminescence with a band maximum ($\lambda_{\text{em}}$) at 596 nm and a lifetime ($\tau$) of 225 ns in de-aerated $n$-hexane at room temperature. For comparison, Ru(2,2'-bipyridine)$_3^{2+}$ emits at 618 nm with a lifetime of 950 ns in de-aerated CH$_2$CN. Like in the isoelectronic Ru(II) species, the first oxidation process of our Mo(0) complex is metal-based, but it occurs at much lower potential given the higher electronic density at Mo(0) compared to Ru(II). The oxidation potential in the long-lived $^3$MLCT excited state ($E_{\text{ox}}^{3}$) is -2.22 V vs. SCE, compared to -0.73 V vs. SCE for Ru(2,2'-bipyridine)$_3^{2+}$, and thus our complex is a considerably stronger excited-state reductant than Ir(2-phenylpyridine)$_3$ ($E_{\text{ox}}^{3}$ = -1.7 V vs. SCE), which is widely used for photoredox catalysis. We demonstrated that our Mo(0) complex is a competent photoredox catalyst for certain organic transformations that are inaccessible with $^3$MLCT excited Ir(2-phenylpyridine)$_3$. Since Fe(II) complexes are usually non-luminescent, the observation of photoluminescence from an isoelectronic 3d$^6$ state, due to lack of similarly strong reducing ability.$^{7,11b}$

Since Fe(II) complexes are usually non-luminescent, the observation of photoluminescence from an isoelectronic 3d$^6$ complex, such as the Cr(0) tris(diisocyanide) complex in Figure 1, is remarkable.$^{11a}$ The current record $^3$MLCT lifetime for Fe(II) complexes is 37 ps on Al$_2$O$_3$ nanofilms,$^{13}$ whereas in Fe(2,2'-bipyridine)$_3$ the MLCT excited state relaxes to lower lying d-d states within ~130 fs.$^4$ Against these reference points, the 2.2 ns $^3$MLCT lifetime observed for our Cr(0) complex in de-aerated THF at room temperature compares very favorably and encourages further investigations of related 3d$^6$ complexes.$^{14}$ We demonstrated that the Cr(0) complex can be used as a sensitizer for triplet-triplet annihilation upconversion, but given the 2.2 ns $^3$MLCT lifetime comparatively high annihilator concentrations were of course required.$^{7,11a}$

Aside from the abovementioned 3d$^6$ species, 3d$^{10}$ complexes represent an important family of $^3$MLCT emitters. Key focus until now has been on Cu(I) complexes,$^{15}$ which show high homoleptic bis(diimines) and later on heteroleptic variants with diimine and diphosphine ligands.$^{16}$ Cu(dpp)$_2^{+}$ (dpp = 2,9-diphenyl-1,10-phenanthroline) is the prototype of this class of complexes, exhibiting an emission band maximum at 441 nm and a $^3$MLCT lifetime of 250 ns in de-aerated CH$_2$CN (Figure 2, left).$^{15}$ The phenyl-substituents in ortho-position to the ligating N atoms help impede planarization of the tetrahedral complex in the MLCT excited state,$^{17}$ thereby leading to higher luminescence quantum yields and longer $^3$MLCT lifetimes. We adapted this design strategy to disiocyanide ligands that can chelate to Ni(0), leading us to a ligand backbone comprised of five aryls and two isocyanide groups (Figure 2, right).$^{18}$ The resulting homoleptic Ni(0) complex emits at 511 nm, but only in frozen 2-methyl-THF solution at 77 K. Further improvements will be necessary to obtain Ni(0) isocyanide complexes that luminesce in fluid solution at room temperature, but this certainly is a very realistic goal.

Conclusions

In summary, chelating disiocyanide ligands provide access to photoactive metal complexes based on Cr(0), Mo(0), and Ni(0). The Cr(0) and Mo(0) systems seem particularly relevant because they are essentially analogues of Ru(2,2'-bipyridine)$_3^{2+}$ made from earth-abundant elements. The fact that the Cr(0) complex luminesces while isoelectronic Fe(II) complexes commonly relax nonradiatively would appear to be of fundamental importance, given the large number of prior studies on the photophysics of Fe(II) compounds. It remains to be seen what practical implications these new findings have, but the initial studies highlighted herein suggest that this new class of d$^5$ MLCT luminophores and photosensitizers has considerable potential.$^{19}$

There have been a series of highly interesting other recent developments in the area of photoactive metal complexes based on earth-abundant elements. This includes for example the synthesis and investigation of Zr(IV) and Fe(III) complexes exhibiting photoactive LMCT excited states,$^{20}$ the discovery of new Cr(III) polyphenyls and usage of such complexes in various photophysical and photochemical contexts,$^{21,22}$ or the successful use of Cu(I) complexes in a broad variety of photoredox-catalyzed reactions.$^{22}$ At the same time, work on photoactive Fe(II) complexes continues to get significant attention.$^{23}$ All these efforts and findings demonstrate that coordination chemistry, in combination with inorganic photophysics and photochemistry,$^{24}$ continues to make important contributions to chemistry at large.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Funding from the Swiss National Science Foundation through grant number 200021_156063/1 is gratefully acknowledged.

References


Cr(0), Mo(0), and Ni(0) complexes with diisocyanide ligands have recently been discovered as isoelectronic analogues of well-known Fe(II), Ru(II), and Cu(I) complexes.