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Ruthenium(II) Dichloride Complexes of Chiral, Tetradentate Aminosulfoxide Ligands: Stereoisomerism and Redox-Induced Linkage Isomerism

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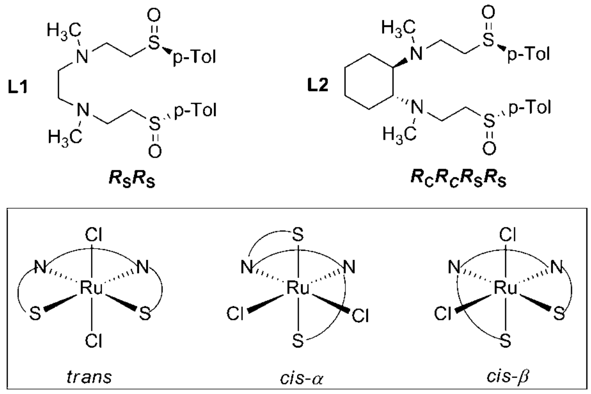
S *Supporting Information*

ABSTRACT: Ruthenium(II) dichloride complexes of two chiral tetradentate aminosulfoxide ligands, varying only in the N−N linker, were synthesized. With each ligand, two major isomers formed, and these were structurally assigned and characterized through a combination of NMR and UV−vis spectroscopies, X-ray crystallography, and density functional theory calculations. The *cis-β* geometric isomer was formed by each ligand, whereas the *trans* and *cis-α* geometric isomers were significant components for one ligand only. Cyclic voltammetry studies show that only the *cis-β* isomers undergo linkage isomerism upon oxidation to ruthenium(III), whereas the *trans* and *cis-α* isomers show simple reversible redox couples.

Examples of linkage isomerism of sulfoxide ligands [especially dimethyl sulfoxide (DMSO)], in which a sulfoxide ligand may coordinate through either its sulfur or oxygen donor atom, are prevalent in ruthenium sulfoxide complexes.[1,2] The sulfur-bound form is favored on ruthenium(II), $Ru^{2+}[S]$, and in certain complexes, linkage isomerism may be induced photochemically or upon oxidation of ruthenium(II) to ruthenium(III) (redox-induced linkage isomerism or RILI): In each case, a metastable oxygen-bound form results, $Ru^{n+}[O]$.[3−10] Manipulation of the coordination mode of the sulfoxide ligand by an external stimulus is of interest for applications as molecular switches. Complexes containing labile, monodentate sulfoxides are susceptible to substitution by solvents or other donors; however, certain complexes of chelating sulfoxides retain RILI and photoisomerism behavior.[11−15] Although these chelating sulfoxides contain sulfur stereocenters, only racemic ligands have been utilized to date. A complex containing a resolved chiral sulfoxide ligand could interconvert between two chiral linkage isomers and thus be of interest in chiroptical switching. We have investigated the synthesis of complexes of chiral, tetradentate aminosulfoxide ligands and report on the synthesis, structures, and electrochemistry of ruthenium(II) dichloride complexes of two such ligands (see Chart 1). Several complexes of the type $RuCl_2(N\text{-donor})_2(DMSO)_2$ are known to display RILI behavior although only by one of the possible metal complex geometric isomers in each case.[7,9,10] We demonstrate that, in our case, all three possible metal complex geometric isomers (shown in Chart 1) are synthetically accessible,[16] but only one displays the desired RILI behavior.[17]

Chart 1. Tetradentate Aminosulfoxide Ligands Synthesized Showing Absolute Configurations (top) and Possible Geometric Isomers of $Ru(L)Cl_2$ Complexes of Tetradentate Aminosulfoxide Ligands (bottom) and Complexes of Each Type Isolated



3-L1
1-L2

1-L1

2-L1
2-L2

The two single-enantiomer ligands, **L1** and **L2** in Chart 1, were synthesized by the conjugate addition of the corresponding secondary diamines to (*R*)-*p*-tolylvinyl sulfoxide.[18] The reaction of **L1** with $RuCl_2(PPh_3)_3$ in toluene at reflux precipitated two isomers of $RuCl_2(\mathbf{L1})$ (**1-L1** and **2-L1**) in a 4:5 ratio, as determined by ^1H NMR spectroscopy, separable by solubility differences in ethanol. The less-soluble, pink-orange isomer, **1-L1**, displayed a C_2-symmetric structure in solution, as evidenced by equivalent *p*-tolyl rings and *N*-methyl resonances in the ^1H NMR spectrum. The yellow isomer, **2-L1**, displayed two sets of peaks in both of these regions and is assigned as the *cis-β* isomer as discussed below. **1-L1** was identified as the *cis-α* isomer by single-crystal X-ray diffraction (Figure 1). It contains

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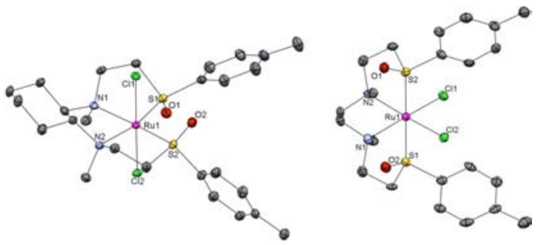

Figure 1. ORTEP plots of X-ray crystal structures of *trans*-**1**-**L2** (left) and *cis*-α-**1**-**L1** (right) with hydrogen atoms omitted for clarity.

a ruthenium stereocenter of Δ configuration, and both nitrogen stereocenters are of R configuration. **1**-**L1** is an unusual example of a ruthenium(II) complex containing *trans* sulfur-bound sulfoxide ligands. This arrangement is generally disfavored because of the substantial *trans* influence of sulfur-bound sulfoxides.[2,7,19]

The reaction of **L2** with $RuCl_2(PPh_3)_3$ in refluxing tetrahydrofuran precipitated two C_1-symmetric isomers of $RuCl_2$(**L2**) (**1**-**L2** and **2**-**L2**) in a 1:1 ratio, as determined by ^1H NMR spectroscopy, separable by solubility differences in acetonitrile. A single-crystal X-ray diffraction structure of the orange isomer, **1**-**L2**, identified it as the *trans* isomer (Figure 1). The nitrogen atoms adopt R,S configurations such that the *N*-methyl groups lie in a *cis*-like relationship, consistent with the lack of rotational symmetry observed by NMR. The second, yellow isomer, **2**-**L2**, is also assigned as the *cis*-β isomer.

Each geometric isomer gives rise to characteristic chemical shift patterns for the *p*-tolyl ring protons in the ^1H NMR spectra: Only the *cis*-β isomers, **2**-**L1** and **2**-**L2**, show resonances that are shielded relative to the free ligands. A third stereoisomer with the **L1** ligand, **3**-**L1**, was also isolated in small amounts from an alternate procedure (see the Supporting Information), is similar to that of **1**-**L2**, and so is also assigned as the *trans* isomer. By IR spectroscopy, the S−O stretching bands lie between 1060 and 1080 cm^{-1} and are shifted to slightly higher energies compared to the free ligands (1040−1050 cm^{-1}), as is consistently observed for metal complexes with sulfur-bound sulfoxides.[4]

To rationalize the stabilities of the various isomers, density functional theory (DFT) calculations were performed on isomers of a $RuCl_2$-L1′ complex in which the *p*-tolyl groups of **L1** are truncated to phenyl groups. Bond distances and angles for the *trans* and *cis*-α structures were in agreement with the X-ray structures of **1**-**L2** and **1**-**L1**, respectively. The lowest-energy *cis*-β structure was determined by a conformation search of the chelate rings. The *cis*-α isomer is the most stable of the three with the *trans* and *cis*-β isomers roughly equal in energy (ΔG = 7.9 and 9.3 kcal/mol, respectively). Common to these less-stable structures is the R,S conformation of the diamine, which suggests that the preference for the *trans* isomer with the **L2** ligand can be attributed to the steric constraints of the six-membered ring. The calculated lowest-energy *cis*-β stereoisomer (Λ-R_NS_N) is consistent with ^1H−^1H NOESY NMR data obtained for **2**-**L1** (see the Supporting Information, SI). For the **L1** ligand then, different relative nitrogen configurations appear to be necessary to adopt the *cis*-α (R,R) or *cis*-β (R,S) geometries.

In UV−vis spectra, each complex shows several low-intensity bands between 300 and 550 nm (ε in the range 10−500 M^{-1} cm^{-1}), which we assign as d−d bands (*cis*-α-**1**-**L1**, 510 nm; *trans*-**1**-**L2**, 450 nm; *cis*-β-**2**-**L1** and -**2**-**L2**, below 400 nm). The largest ligand-field splitting in the *cis*-β complexes is in agreement with the reported UV−vis spectra for $RuCl_2(DMSO)_2L_2$ (L = imidazole and NH_3).[20] The intensities of electronic transitions determined by time-dependent DFT calculations are in good agreement with experimental UV−vis data. The *trans* and *cis*-β isomers show major transitions at shorter wavelengths (*trans*, 464 and 327 nm; *cis*-β: 430 and 337 nm). The *cis*-α structure has an additional transition at longer wavelengths (515, 391, and 341 nm). Each of these transitions is from a t_{2g}-type molecular orbital (MO) to a Ru−S antibonding MO heavily mixed with phenyl π^* character. The chiroptical properties of all complexes were also characterized by circular dichroism (CD) spectroscopy (see the SI for spectra).

To probe potential RILI behavior, cyclic voltammograms (CVs) were recorded in CH_2Cl_2 solution. **1**-**L1** and **1**-**L2** display couples at +0.21 and +0.41 V, respectively (vs Cp_2Fe^+/Cp_2Fe) that display reversibility similar to that of the internal Cp_2Fe standard at all scan rates measured. These are assigned to Ru^{3+}[S,S]/Ru^{2+}[S,S] couples; i.e., neither complex undergoes linkage isomerism upon oxidation on the cyclic voltammetry time scale. On the other hand, CVs of the *cis*-β complexes show more features and scan rate dependence. CVs of **2**-**L2** (see Figure 2) and **2**-**L1**, with an initial anodic scan direction, reveal waves corresponding to Ru^{3+}/Ru^{2+} couples with $i_{pc}/i_{pa} < 1$ ($E_{1/2}$ = 0.62 and 0.65 V vs Cp_2Fe^+/Cp_2Fe, respectively, at 50 mV/s). In each returning cathodic scan, an additional lower potential wave is also observed (cathodic shifts of 0.54 and 0.70 V, respectively, at 50 mV/s).[21] CVs recorded around the region of the second peak only are featureless in both cases, establishing that the second reduction is of a species formed after oxidation to Ru^{3+}. Multiple cycles do not reveal the corresponding anodic wave for the lower potential couple in the case of **2**-**L2**, although it is observed for **2**-**L1**. These data can be interpreted on the basis of an ECEC square scheme (see the inset to Figure 2), in which linkage isomerism follows oxidation to Ru^{3+} (Ru^{3+}[S,S] to Ru^{3+}[S,O]). The Ru^{3+}[S,O] species is then reduced at a lower potential than the Ru^{3+}[S,S] species. Rapid isomerism of Ru^{2+}[S,O] to Ru^{2+}[S,S] follows this reduction. Further evidence for a Ru^{3+}[S,O] isomer is given by the IR spectrum of the bulk oxidation product of **2**-**L2** with

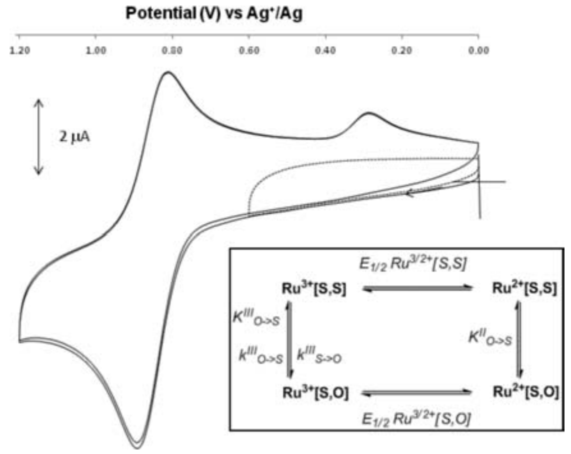

Figure 2. CV of **2**-**L2** with an initial cathodic scan direction (recorded in CH_2Cl_2, 50 mV/s, 0.1 M TBA·PF_6): solid line, 0−1.2 V; dashed line, 0−0.6 V vs Ag^+/Ag reference electrode. Inset: ECEC square scheme for RILI including parameter definitions.

$[NO]^+$, which displays a band at 924 cm^{-1} consistent with an oxygen-bound sulfoxide.[3] UV−vis spectroelectrochemical data were also obtained for the oxidized forms of **1-L1**, **1-L2**, and **2-L2**: The visible spectra are dominated by a moderately intense $Cl(p\pi) \rightarrow Ru(d\pi)$ LMCT transition in each case.

Various parameters were quantitatively determined for **2-L2** following earlier treatments of similar data: CVs with an initial anodic scan direction were recorded at a variety of scan rates (see the SI).[10] The equilibrium constant, $K^{III}_{O\rightarrow S}$, was calculated to be 1.33 ± 0.06, indicating marginally greater stability of Ru^{3+}[S,S] versus Ru^{3+}[S,O]. $K^{II}_{O\rightarrow S}$ was then determined to be 1.91×10^9; i.e., the Ru^{2+}[S,S] form is highly favored versus Ru^{2+}[S,O]. The rate constants $k^{III}_{O\rightarrow S}$ and $k^{III}_{S\rightarrow O}$ were also estimated as 2.8 and 2.1 s^{-1}, respectively. Compared to related DMSO complexes, the stability of the oxygen-bound form is decreased, but there is a slight increase in the isomerization kinetics (on Ru^{3+}).[9,10] Although difficulty in measuring accurate peak currents in CVs of **2-L1** precluded similar analysis, the forms of the CVs imply that both Ru^{3+}[S,O] and Ru^{2+}[S,O] have greater stability than that in **2-L2**.

In our ruthenium complexes, RILI occurs only with the *cis-β* isomers and within the strongest ligand-field environment, consistent with certain earlier reports.[7,10] Inspection of the DFT-calculated highest occupied molecular orbitals (HOMOs) of each isomer shows that all lie in the Cl−Ru−Cl plane (see Figure 3) and are predominantly of Ru(d)−Cl(π) antibonding character. Only in the *cis-β* isomer is the Ru−S bond also in this plane. We propose that depopulation of this HOMO upon oxidation leads to increased "hardness" in this plane, resulting in the tendency of this sulfoxide to isomerize in the *cis-β* isomer. Ongoing investigations will seek to further clarify the electronic origin of RILI in these complexes and other outstanding questions, including the relationship of the ligand structure to the metal complex geometric isomer distribution.

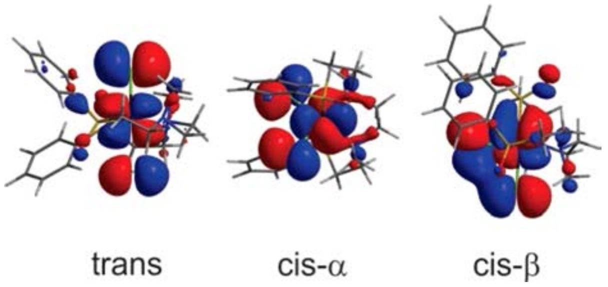

Figure 3. Calculated HOMOs of the three isomers.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, complete experimental details and characterization data for the synthesis of ligands and ruthenium complexes, UV−vis and CD spectral data, CV data and X-ray crystallographic data for solution and refinement, and table of selected bond lengths and angles, and details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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