Sulfur Reduction in Gasoline and Diesel Fuels by Extraction/Adsorption of Refractory Dibenzothiophenes

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ABSTRACT

Using the classical coordination compound, $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, we have prepared a metal complex with a 4,6-dimethyldibenzothiophene ligand. The compound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ also reacts with thiophene, benzothiophene and dibenzothiophene (DBT) at room temperature. We have found that $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ removes over 50% of the DBT in simulated petroleum feedstocks by a biphasic extraction process. The extraction phase is readily regenerated by air-oxidation thereby completing a cyclic process that removes DBT from petroleum feedstocks.

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EXECUTIVE SUMMARY

The removal of sulfur from gasoline and diesel fuels is an important aspect of this nation's effort to reduce pollution of the atmosphere by sulfur oxides. The current EPA-mandated 0.04% limit on sulfur in gasoline will be reduced to 0.0025% by 2006. This reduction will require the development of new technologies. Such reductions in sulfur content must focus on the unreactive dibenzothiophene (DBT) derivatives that contain alkyl groups near the sulfur; these compounds constitute the bulk of the remaining sulfur compounds in hydrotreated petroleum feedstocks.

The present investigation focuses on d^6 metal complexes that are capable of binding DBT and its derivatives. We have observed that $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ binds to DBT as well as its hindered 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) analog. It also reacts with thiophene and benzothiophene in acetone at 25° C. By employing a solution of dimethylformamide and water (70:30) containing $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, we have extracted 50% of the DBT present in a simulated petroleum feedstock. We have also demonstrated oxidative release of DBT from the resulting $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ complex. The oxidized ruthenium can be reduced back to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ for further use. A reactor design has been proposed to make use of this DBT extraction process.

INTRODUCTION

Sulfur removal from gasoline and diesel fuels is an important aspect of this nation's effort to reduce pollution of the atmosphere by sulfur oxides.¹ This reduction in sulfur has been largely accomplished by increasingly stringent restrictions on the sulfur content of these fuels. Currently, the sulfur content is limited to 0.04% by weight, but the EPA recently introduced a proposal aimed at reducing these levels gradually to 0.0025% by weight by 2006.² This ambitious agenda will require the development of new technologies in order to achieve such a reduction in sulfur content in a short period of time. Currently the extent of desulfurization and denitrogenation depends on the catalyst (Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃, and others) and the hydrotreating reaction conditions.³ The most easily desulfurized components are the thiols (RSH) and thioethers (RSR). Recent improvements have yielded catalysts that are also capable of desulfurizing the thiophenes, benzothiophenes and dibenzothiophenes (R = H) (below). It is the hindered dibenzothiophenes (R₂DBT) with alkyl groups in the 4- and 6- positions that are

Figure 1. Structures of thiophenes.

the slowest to undergo hydrodesulfurization.⁴ Moreover, it is these hindered dibenzothiophenes that must be desulfurized in order to reach lower sulfur levels in gasolines. It is the steric congestion of the 4,6-groups near the sulfur atom that reduces the activity of dibenzothiophenes in the hydrotreating process. The reaction on a catalytic surface requires the sulfur atom of a dibenzothiophene molecule to interact with the surface. This is nearly impossible due to the methyl groups at the 4,6-positions. Even in coordination compounds only one example of a η^1 -S bound 4,6-dimethyldibenzothiophene has been reported.⁹ Substantial efforts to create catalysts that are able to promote deep hydrodesulfurization of petroleum feedstocks, which requires the desulfurization of these hindered dibenzothiophenes at reasonable cost, have not been successful.

Considering the lack of success in developing more effective catalysts, we have developed a completely different approach to the removal of hindered dibenzothiophenes (R_2 DBT) from petroleum. This approach, elegant in its simplicity, involves the use of $Ru(NH_3)_5(H_2O)^{2+}$ to selectively bind and extract 4,6- R_2 DBT molecules from petroleum feedstocks. Then, the 4,6- R_2 DBT molecules can be removed from the $Ru(NH_3)_5(4,6-R_2DBT)^{2+}$ by air oxidation. Reduction of the resulting Ru^{3+} complex with H_2 gives back the extracting $Ru(NH_3)_5(H_2O)^{2+}$ complex.

EXPERIMENTAL

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether (Et_2O) was purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.⁵ All other chemicals were used without further purification as purchased from Aldrich. Filtrations were performed with celite on filter paper.

NMR spectra were obtained on a modified 400 MHz Varian VXR-400 spectrometer using CD_3COCD_3 as internal lock and reference. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. UV-Vis spectra were obtained on a Hewlett Packard 8452A Diode Array Spectrophotometer with a deuterium lamp, using quartz cuvettes.

Synthesis of $[\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})][\text{PF}_6]_2$ (1**).** To a 50 mL flask containing 15 mL of acetone or dimethylformamide (DMF), freshly prepared $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ (50 mg, 0.102 mmol)⁶, 4,6-dimethyldibenzothiophene (4,6- Me_2DBT) (29 mg, 0.136 mmol), and palladium (10 wt. % on activated carbon) (10 mg) were added. The solution was cycled through three freeze/pump/thaw sequences to remove air from the system. The flask was warmed to room temperature and $\text{H}_2(\text{g})$ was bubbled through the solution for 15 min. The resulting yellow solution was allowed to stand under H_2 for 45 min. The product was precipitated with 35 mL of Et_2O , and the solution was filtered to remove excess 4,6- Me_2DBT . The product was dissolved by adding 10 mL of acetone, which had been cycled through three freeze/pump/thaw sequences and warmed to room temperature. Then, H_2 was bubbled through the solution for 5 min. The solution was then filtered (to remove

Pd/C) into another flask containing 35 mL of Et₂O, which gave the product as a precipitate. The Et₂O was removed by filtration and the product was dried under vacuum for 15 min to give an 86% yield. ¹H NMR (400 MHz, CD₃COCD₃): δ 8.37 (d, J_{H-H} = 12 Hz, 2 H, DBT-*H*), 8.05 (d, J_{H-H} = 12 Hz, 2 H, DBT-*H*), 7.68 (t, J_{H-H} = 12 Hz, 2 H, DBT-*H*), 2.62 (s, 6H, DBT-CH₃), 2.70 (s, br, 12 H, NH₃), 2.52 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ (quaternary C's unobservable) 127.50, 125.32, 119.82, 15.01 ppm.

Synthesis of [Ru(NH₃)₅(DBT)][PF₆]₂ (2). The same procedure as (1) was followed with the exception that DBT (25 mg, 0.136 mmol) was used in place of 4,6-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): δ 8.38 (d, 2H, J_{H-H} = 12 Hz, DBT-*H*), 8.05 (d, 2H, J_{H-H} = 12 Hz, DBT-*H*), 7.68 (t, 2H, J_{H-H} = 12 Hz, DBT-*H*), 7.54 (t, 2H, J_{H-H} = 12 Hz, DBT-*H*), 2.69 (s, br, 12 H, NH₃), 2.53 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 143.12, 138.62, 127.95, 125.10, 123.11, 121.95 ppm.

Synthesis of [Ru(NH₃)₅(BT)][PF₆]₂ (3). The same procedure as (1) was followed with the exception that BT (15 mg, 0.125 mmol) was used in place of 4,6-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): δ 8.1-7.4 (m, 4H, BT-*H*), 6.5 (d, 1H, J_{H-H} = 8 Hz, BT-*H*), 6.0 (d, 1H, J_{H-H} = 8 Hz, BT-*H*), 2.72 (s, br, 12 H, NH₃), 2.56 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 142.54, 139.52, 128.12, 127.72, 125.98, 124.68, 123.85, 122.56 ppm.

Synthesis of $[\text{Ru}(\text{NH}_3)_5(\text{T})][\text{PF}_6]_2$ (4**).** The same procedure as (**1**) was followed with the exception that T (15 μL , 0.188 mmol) was used in place of 4,6-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): δ 7.49(m, 2H, J_{H-H} = 8 Hz, T-*H*), 7.13 (m, 2H, J_{H-H} = 8 Hz, T-*H*), 2.71 (s, br, 12 H, NH₃), 2.48 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 127.08, 125.34 ppm.

Extraction of DBT from Simulated Petroleum Fuel. A mixture of toluene (45% by volume) and hexanes (55% by volume) was made to simulate the composition of a hydrotreated petroleum feedstock.^{4a} Into 10 mL of this liquid, DBT (17.6 mg, 0.095 mmol, 0.04% by weight) and triphenylmethane (15 mg, 0.061 mmol) (internal standard) were dissolved. The solution was cycled through 3 freeze/pump/thaw cycles and warmed to room temperature. Into a separate flask, 7 mL of DMF, 3 mL of H₂O, Pd (10 wt. % on activated carbon) (10 mg), and either a five-fold or ten-fold molar excess of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ was added (*five fold* = 234.78 mg, 0.477 mmol; *ten fold* = 469.54 mg, 0.954 mmol). The mixture was cycled through 3 freeze/pump/thaw cycles, warmed to room temperature, and H₂ (g) was bubbled through the solution for 10 min. A 0.4 mL aliquot of the DBT containing solution was taken for NMR analysis; the remainder of the DBT solution was added to the $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ mixture under argon. The mixture was sonicated and 0.4 mL aliquots of the organic phase were removed at 0.25, 0.5, 0.75, 1.0, 2.0, and 4.0 hrs. The organic solvents were removed by evaporation and the ratio of DBT (δ 8.33 ppm) to triphenylmethane (δ 5.63 ppm) was determined by integration of the ¹H NMR bands to establish the amount of DBT that was removed from the simulated fuel mixture.

RESULTS AND DISCUSSION

Syntheses and Structures of $[\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})][\text{PF}_6]_2$. As shown previously by Taube and co-workers,⁷ $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ coordinates thiophene to form the unstable $\text{Ru}(\text{NH}_3)_5(\text{T})^{2+}$ complex. We have found that BT, DBT, and most importantly 4,6-Me₂DBT react with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ under mild conditions in acetone to give the corresponding $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ complexes (Scheme 1).

As shown in Table 2, the chemical shifts of the ¹H and ¹³C NMR bands of the thiophene ligands are noticeably different in the $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ complexes than the free thiophenes. These NMR data clearly show that the thiophene ligands are η¹-S-coordinated in these complexes.⁸ The reactions of the thiophenes with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ are complete within 35 min, but the products are very air sensitive. For this reason, we add 10 mg of Pd/C (10% by weight) and bubble H₂ for 15 min through the solution in order to maintain the $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ products in the reduced Ru²⁺ form. Additional H₂ is added periodically when the solution begins to darken indicating the formation of the red $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ complex.

While many DBT metal complexes are known¹, $\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})^{2+}$ is among the first η¹-S coordinated 4,6-dimethyldibenzothiophene coordination complexes; due to its air sensitivity, satisfactory elemental analyses for this compound were not obtained. Jones and coworkers⁹ were the first to observe a 4,6-Me₂DBT complex, Cp^{*}Rh(PMe₃)(4,6-DMDBT), by ¹H NMR spectroscopy, but the compound was too unstable to isolate. Two other examples of 4,6-Me₂DBT complexes are known, *cis*

Scheme 1. Reactions of thiophene, benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$.

Table 1. Comparison of the Affinities of Ligands for $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ and $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$. Partially Adapted from Taube and Kuehn.⁷

	$\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$	$\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	Ratio	Ref
Pyridine	2.4×10^7	6×10^3	4×10^3	10
Imidazole	2.8×10^6	1.9×10^6	1.5	11
HS^-	1.5×10^6	2.4×10^{13}	6×10^{-8}	
$(\text{CH}_3)_2\text{S}$	$>10^5$	$>1.6 \times 10^{-2}$	$\sim 6 \times 10^6$	
NH_3	3.5×10^4	1.6×10^5	2×10^{-1}	
N_2	3.3×10^4	4×10^{-13}	8×10^{16}	12
2,8-Me ₂ DBT	3.6×10^3 (estimate)	-	-	16
H_2S	1.5×10^3	2.4×10^{-4}	6×10^6	
DBT	7.4×10^2 (estimate)	-	-	16
HO^-	6×10^2	6×10^{11}	1×10^{-9}	
Thiophene	~ 10	$\sim 2.5 \times 10^{-8}$	4×10^8	
H_2O	1	1	1	
Cl^-	0.4	1.1×10^2	4×10^{-1}	13

Table 2. ^1H and ^{13}C NMR Shifts (in ppm) of Thiophene (T), Benzothiophene (BT), Dibenzothiophene (DBT) and 4,6-Dimethyldibenzothiophene (4,6-Me₂DBT) Unbound and Bound in $\text{Ru}(\text{NH}_3)_5(\text{Thiophene})^{2+}$.

Ligand	^1H NMR Unbound	^1H NMR Bound	^{13}C NMR Unbound	^{13}C NMR Bound
T	7.47, 7.15	7.49, 7.13	127.12, 125.39	127.08, 125.34
BT	7.97, 7.88, 7.64, 7.43, 7.36	8.1-7.4 (m), 6.5, 6.0	140.08, 139.91, 126.81, 124.46, 124.39, 124.16, 123.82, 122.62	142.54, 139.52, 128.12, 127.72, 125.98, 124.68, 123.85, 122.56
DBT	8.33, 7.98, 7.51 (m)	8.38, 8.05, 7.68, 7.54	139.38, 136.82, 127.23, 124.82, 123.05, 122.01	143.12, 138.62, 127.95, 125.10, 123.11, 121.95
4,6-Me ₂ DBT	8.12, 7.43, 7.35, 2.59	8.37, 8.05, 7.68, 2.62	139.12, 136.28, 127.30, 125.31, 119.71, 19.82	127.50, 125.32, 119.82, 15.01

$-(\text{PEt}_3)_2\text{Pt}(4,6\text{-Me}_2\text{DBT})]^{14}$ and $[(\text{dippe})\text{Pt}(4,6\text{-Me}_2\text{DBT})]^{15}$; neither are $\eta^1\text{-S}$ -coordinated but the result of Pt insertion into a C-S bond.

The affinity of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ for different ligands is summarized in Table 1. In hydrotreated petroleum feedstocks DBT and R₂DBT are the main components that must be removed. Table 1 shows that thiophene binds favorably to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. However, DBT binds even more strongly based on equilibrium studies of thiophene displacement from other Ru complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PPh}_3)(\text{Thiophene})^+$.¹⁶ When comparing the binding strengths of thiophenes, DBT and 2,8-dimethyldibenzothiophene bind 74.1 and 358 times *more* strongly than thiophene.¹⁷ As shown in Table 1, 2,8-Me₂DBT with methyl groups in the non-hindering 2,8-positions binds five times more strongly to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ than DBT due to the enhanced σ -donating ability of the

methyl groups. This result suggests that the placement of the methyl groups in the 4,6-positions in 4,6-Me₂DBT sterically inhibits its binding in metal complexes.

By slightly changing the NH₃ ligands in Ru(NH₃)₅(H₂O)²⁺, the reactivity of the system is changed greatly. We have found that *trans*- [Ru(pyridine)(NH₃)₄(H₂O)²⁺]¹⁸ and *mer*-[Ru(bipy)(NH₃)₃(H₂O)²⁺]¹⁹ both do not react with thiophene or dibenzothiophene, despite the fact that molecular models show no obvious steric interactions. This reactivity is counter-intuitive, since removal of electron density from the Ru by the pyridine ligand should enhance the ability of Ru to bind σ-donating thiophenes.

Table 3. UV-Vis Spectra of Ru(NH₃)₅(H₂O)²⁺ and Related Complexes in Acetone Solvent.

Compound	λ_{max}
DBT	330 nm
Ru(NH ₃) ₅ (H ₂ O) ²⁺	358 (br), 420 (sh) nm
Ru(NH ₃) ₅ (DBT) ²⁺	328, 358 (br), 420 (sh) nm
Ru(NH ₃) ₅ (H ₂ O) ²⁺ oxidized 25 min to Ru(NH ₃) ₅ (H ₂ O) ³⁺	380 (br), 535 (br) nm
Ru(NH ₃) ₅ (H ₂ O) ³⁺ reduced to Ru(NH ₃) ₅ (H ₂ O) ²⁺	348 (br), 420 (sh) nm

Oxidation of [Ru(NH₃)₅(Thiophenes)][PF₆]₂. The Ru-thiophene bond in the Ru(NH₃)₅(Thiophene)²⁺ complexes appears to be quite weak. This weak interaction is reflected in the nearly identical UV-Vis spectra (Table 3) of Ru(NH₃)₅(H₂O)²⁺ and Ru(NH₃)₅(DBT)²⁺.

The $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ complexes are very air sensitive with respect to oxidation. When an acetone solution of $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ is exposed to air, the $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$ complexes are oxidized within 20 minutes to $\text{Ru}(\text{NH}_3)_5(\text{solvent})^{3+}$. The fact that Ru^{3+} has essentially no affinity for thiophenes means that upon oxidation, any thiophene coordinated to Ru^{3+} is released into solution forming $\text{Ru}(\text{NH}_3)_5(\text{solvent})^{3+}$. This means that if $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ is used to extract thiophenes from petroleum fuels by forming $\text{Ru}(\text{NH}_3)_5(\text{Thiophenes})^{2+}$, the thiophene may be released from the Ru^{2+} complex by air-oxidation to Ru^{3+} .

Scheme 2. Cyclic oxidation of Ru^{II} releasing DBT and reduction of Ru^{III} by H_2 on Pd/C.

Extraction of DBT from Simulated Fuel by $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$. The traditional method of removing sulfur from feedstocks by hydrotreating over Co-Mo/ Al_2O_3 and Ni-Mo/ Al_2O_3 catalysts is a mature field and unlikely to achieve the necessary low-sulfur fuels required by the EPA.² A new approach is needed to reach these very low levels of sulfur. We believe that such an approach must meet the following criteria: 1) it must be able to reduce or remove DBT and 4,6-Me₂DBT, 2) it must be economically viable, 3)

and it must be heterogeneous in nature. These criteria are addressed by our process in the following ways: 1) we have shown that DBT and 4,6-Me₂DBT coordinate to Ru(NH₃)₅(H₂O)²⁺, 2) the oxidation process is economically viable because Ru(NH₃)₅(H₂O)²⁺ is recycled after each step, and only H₂ and O₂ are consumed, and 3) this process is heterogeneous, because the DBT and the 4,6-Me₂DBT molecules are extracted from the hydrocarbon fuel phase into an aqueous phase.

Here, we offer a process (Scheme 2) based on the above studies of Ru(NH₃)₅(H₂O)²⁺ extraction of DBT from hydrotreated petroleum feedstocks. The process uses two phases, one hydrophilic (70% DMF, 30% H₂O) and the other hydrophobic (the fuel feedstock that has already been hydrotreated). In chamber **A** (Scheme 2), DBT is extracted from the feedstock phase into the hydrophilic phase that contains Ru(NH₃)₅(H₂O)²⁺, Pd/C, and bubbling H₂. It is the complexation of the DBT as Ru(NH₃)₅(DBT)²⁺ that causes the DBT to move into the DMF/H₂O phase. This DMF/H₂O phase containing Ru(NH₃)₅(DBT)²⁺ is drained into a second chamber **B** where the Ru(NH₃)₅(DBT)²⁺ is oxidized with O₂(air) to give Ru(NH₃)₅(H₂O)³⁺ and free DBT. The DBT, preferring a hydrophobic solvent, transfers into a hydrocarbon phase (which could be incinerated as waste). Finally the Ru(NH₃)₅(H₂O)³⁺ is cycled back to the main chamber **A** where it is reduced by H₂/Pd/C back to the active Ru(NH₃)₅(H₂O)²⁺, which can extract more DBT from the fuel.

In order to demonstrate the feasibility of the DBT extraction in chamber **A**, we performed the following series of extraction studies. First a simulated feedstock of 45% toluene and 55% hexane containing 0.04% DBT was extracted with 70% DMF and 30%

Scheme 2. Separator design for the removal of DBT from low-sulfur feedstocks.

H₂O containing Pd/C under bubbling H₂. The top line in Scheme 3 shows that this extraction decreases the DBT level slightly to 0.035%. However, when a five-fold molar excess (5x, with respect to DBT) of Ru(NH₃)₅(H₂O)²⁺ is added to the DMF/H₂O phase, 32.5% of the DBT is removed from the feedstock leaving the feedstock with only 0.027% sulfur. When the amount of Ru(NH₃)₅(H₂O)²⁺ is increased to a ten-fold molar excess (bottom line in Scheme 3), the DBT content of the feedstock phase is reduced to 0.020%, which means that 50% of the DBT in the feedstock is removed.

These DBT extractions reach equilibrium within one hour at room temperature. Equilibrium constants calculated for the two extractions give an average value of $K_{eq} = 0.0108$ (Scheme 4).

Scheme 3. Extraction of DBT from Simulated Petroleum Fuel by [Ru(NH₃)₅(H₂O)][PF₆]₂ in a 70:30 DMF: H₂O Mixture.

$$K_{5\text{-Fold Excess}} = 0.111 (\pm 0.004)$$

$$K_{10\text{-Fold Excess}} = 0.105 (\pm 0.008)$$

$$K_{\text{Average}} = 0.108$$

Scheme 4. Equilibrium values for extraction process.

CONCLUSIONS

Reducing further the sulfur content in hydrotreated petroleum feedstocks is a challenging goal. Our results reported herein make a significant contribution towards that end. We have prepared and characterized the metal complex $\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})^{2+}$. On the basis of the demonstrated ability of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ to bind DBT, we have developed a process for the removal of DBT from simulated feedstocks. These initial studies show that at least 50% of the DBT in fuel feedstocks can be removed by using this system. Moreover, the DBT can be removed from the extracted form, $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$, and $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ can be regenerated for re-use in the extractions. Each step of this process has been demonstrated in laboratory experiments. Future studies will focus on extractions of a broader range of organosulfur compounds in petroleum feedstocks.

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