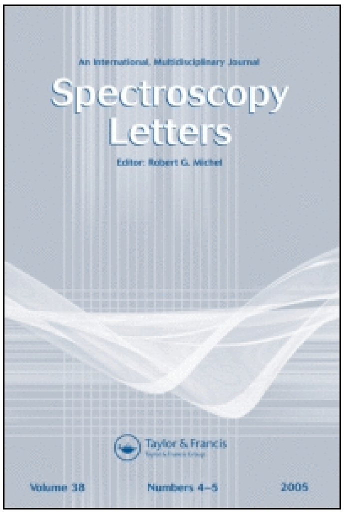

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectroscopic Investigations of Fine-Tuned Energy Differences in a Series of Substituted Rhenium and Technetium Complexes $[M(RPhCS_3)_2(RPhCS_2)]$ {M=Re, ^{99}Tc; R=H, F, Me, Et, OMe}

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To cite this Article Lepareur, Nicolas , Noiret, Nicolas and Jeftic, Jelena(2006) 'Spectroscopic Investigations of Fine-Tuned Energy Differences in a Series of Substituted Rhenium and Technetium Complexes $[M(RPhCS_3)_2(RPhCS_2)]$ {M=Re, ^{99}Tc; R=H, F, Me, Et, OMe}', Spectroscopy Letters, 39: 1, 45 — 61
To link to this Article: DOI: 10.1080/00387010500434305
URL: http://dx.doi.org/10.1080/00387010500434305

Spectroscopy Letters, 39: 45–61, 2006
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ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010500434305

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Spectroscopic Investigations of Fine-Tuned Energy Differences in a Series of Substituted Rhenium and Technetium Complexes $[M(RPhCS_3)_2(RPhCS_2)]$ {M = Re, ^{99}Tc; R = H, F, Me, Et, OMe}

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Abstract: A series of compounds of interest for nuclear medicine, $[M(RPhCS_3)_2(RPhCS_2)]$ (M = Re or ^{99}Tc, R = H, F, Me, Et, OMe), was investigated by spectroscopic analysis. We compared the relative increase in energy shift of the absorption bands of the same assignation. The highest energy is observed in case of meta- or ortho-substituted complexes compared with the lowest one in the case of para-substituted compounds, which we discuss in terms of steric influences. The energy shift, related to the ligand field strength, and further to the Lewis basicity gives us a spectrochemical series for variously substituted phenyl rings of the ligands, both in the rhenium and technetium series of complexes (→ shows the increasing ligand field).

For Re: 4-OMe → 4-Et → 4-Me → 3-OMe → 4-F → H → 2-OMe → 2-Et
For ^{99}Tc: 4-OMe → 4-Me → 4-Et → 3-OMe ≅ 4-F
≅ 3-F ≅ H → 2-OMe → 2-Et

Keywords: Dithiocarboxylate, rhenium, technetium, UV-Visible spectroscopy

Received 9 September 2005, Accepted 16 May 2005

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INTRODUCTION

We recently reported reduction-substitution reactions between high valent $[MOCl_4][NBu_4]$ or $[MNCl_4][NBu_4]$ complexes and aryldithiocarboxylate salts that lead to novel M(III) complexes with a S_6 mixed coordination sphere (M $=$ ^{99}Tc or Re).[1,2] The structure of these diamagnetic compounds $[M(PhCS_3)_2(PhCS_2)]$, containing two trithioperoxybenzoate ligands and one dithiobenzoate ligand, has been elucidated by NMR, FT-IR, mass spectrometry, elemental analysis, and X-ray diffraction analysis.

This paper presents a part of our work to extend their field of interest by, for instance, connecting the S_6 core to biomolecules or by modifying their hydrophilicity through functionalized ligands. Then, a series of complexes with various substituents on the phenyl ring has been synthesized. Our purpose was here to quantify the relation between substitution and stability of the complexes, both for technetium and rhenium complexes. This study provides a characterization of the series of rhenium and technetium complexes by UV-Visible optical absorption spectroscopy. This technique can provide useful information concerning the relationships between the ligands and the metal, and the determination of such a spectrochemical series with dithiobenzoates has already been described with nickel (II) [3] and hexacoordinated transition metals [Cr(III), Fe(III), Co(III)].[4] When coupled to other methods, such as cyclic voltammetry, it can be related to stability. For instance, a trend in stability for ^{99}Tc(III) complexes has been described by Konno et al. with various thiolato ligands.[5]

MATERIALS AND METHODS

Caution! ^{99}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in laboratories approved for low-level radioactivity using monitored hoods and gloveboxes. When handled in milligram amounts, ^{99}Tc does not present a serious health hazard because common laboratory glassware provides adequate shielding. *Bremsstrahlung* is not a significant problem due to the low energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation. All measurements on technetium complexes were performed at ICIS CNR Padua (Italy).

CH_2Cl_2 and petroleum ether were purified according to classical methods,[6] and MeOH was used as purchased (Aldrich, Saint Quentin Fallavier, France). $[ReOCl_4][NBu_4]$, $[^{99}TcOCl_4][NBu_4]$, dithiobenzoate sodium, and piperidinium salts were prepared according to literature methods.[7–9]

Analysis and Physical Measurements

All prepared compounds were characterized by ^{1}H and ^{13}C NMR recorded with a BRUKER ARX 400 at 400.13 and 100.62 MHz, respectively, in $CDCl_3$ for rhenium and BRUKER AC300 at 300.13 and 75.48 MHz respectively, in $CDCl_3$ for technetium (ICIS-CNR, Padua, Italy). Chemical shift values are referred to $CHCl_3$ (7.26 ppm ^{1}H NMR and 77.1 ppm ^{13}C NMR). IR spectra were obtained by a Nicolet 205 instrument in KBr pellets (4000–500 cm^{-1}). Carbon, hydrogen, and oxygen analyses were performed by I.C.S.N. (Gif sur Yvette, France) on a Carlo Erba elemental analyzer Model-1106. The UV-Vis spectra of rhenium and technetium complexes were measured on a Spectronic Unicam UV500 UV-Vis spectrometer equipped with Vision 32 software (ICIS-CNR, Padua, Italy). Spectra were recorded in the region from 190 nm to 780 nm ($\pm$2 nm). Dichloromethane serves as a solvent and for the baseline collection. The light source changeover from halogen to deuterium lamp occurs at 350 nm. The concentration range of solutions was typically 10^{-6} to 10^{-4} M. Absorption coefficients are of the order of magnitude between 10^{3} and 10^{5} $cm^{-1}M^{-1}$.

Syntheses

The bis(trithioperoxybenzoate)(dithiobenzoate) rhenium and technetium (III) complexes were synthesized according to methods previously described.[1,2]

Bis(trithioperoxybenzoate)(dithiobenzoate)rhenium(III)

$[Re(PhCS_3)_2(PhCS_2)]$ 1A

Yield 50% (0.060 g). m.p. = 248°C. R_f (PE/CH_2Cl_2 7/3) = 0.62. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 7.29 (m, 5H, $H_{aromatic}$), 7.44 (t, $J = 8.0$ Hz, 4H, $H_{aromatic}$), 7.63 (dd, $J = 8.0$ and 2.5 Hz, 2H, $H_{aromatic}$), 7.96 (dd, $J = 8.5$ and 1.5 Hz, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 123.7, 126.4, 127.2, 130.8, 132.1, and 132.3 ($CH_{aromatic}$), 133.9 ($\underline{C}$-CS_3), 141.7 ($\underline{C}$-CS_2), 232.8 (CS_3), 237.6 (CS_2). IR (KBr disk) (cm^{-1}): 1482 (m), 1442 (s), 1332 (m), 1311 (w), 1263 (s), 1234 (w), 1179 (w), 1156 (w), 1096 (m), 1028 (m), 997 (s, $\nu_{C\text{-}S}$), 947 (w), 908 (w), 802 (m), 755 (s), 681 (w), 652 (w), 544(s, $\nu_{S\text{-}S}$), 454 (m), 399 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{21}H_{15}S_8Re$. Found: %C = 35.34, %H = 2.13, %S = 35.99; Calc. for $[Re(PhCS_3)_2(PhCS_2)]$: %C = 35.35, %H = 2.13, %S = 36.03.

$[Re(4\text{-}MePhCS_3)_2(4\text{-}MePhCS_2)]$ 2A

Yield 53% (0.068 g). m.p. = 168°C. R_f (PE/CH_2Cl_2 7/3) = 0.79. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 2.42 (s, 3H, CH_3), 2.59 (s, 6H, CH_3), 7.15 (d, $J = 8.4$ Hz, 2H, $H_{aromatic}$), 7.30 (d, $J = 8.4$ Hz, 4H, $H_{aromatic}$), 7.59 (d, $J = 8.1$ Hz, 2H, $H_{aromatic}$), 7.94 (d, $J = 8.1$ Hz, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): (${}_{C}$ 21.6 and 30.10 (OCH_3), 125.2, 128.6, 129.3, and 132.3 ($CH_{aromatic}$), 133.0 and 141.2 ($\underline{C}$-CH_3), 144.5 ($\underline{C}$-CS_3), 144.9 (C-CS_2), 234.2 (CS_3), 238.6 (CS_2). IR (KBr disk) (cm^{-1}): 1598 (s), 1501 (w), 1408 (w), 1309 (m), 1262 (s), 1220 (w), 1179 (s), 1096 (s), 1015 (s, $\nu_{C\text{-}S}$), 950 (m), 910 (w), 879 (w), 812 (s), 706 (w), 544 (m, $\nu_{S\text{-}S}$), 447 (m), 399 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{24}H_{21}S_8Re$. Found: %C = 38.83, %H = 2.76, %S = 34.05; Calc. for [Re(4-MePhCS_3)$_2$(4-MePhCS_2)]: %C = 38.33, %H = 2.81, %S = 34.10.

[Re(4-EtPhCS_3)$_2$(4-EtPhCS_2)] 3A

Yield 70% (0.095 g). m.p. = 164°C. R_f (PE/CH_2Cl_2 7/3) = 0.76. ^1H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 1.20 (t, $J = 7.6$ Hz, 3H, CH_3), 1.28 (t, $J = 7.6$ Hz, 6H, CH_3), 2.70 (q, $J = 7.4$ Hz, 2H, CH_2), 2.84 (q, $J = 7.6$ Hz, 4H, CH_2), 7.18 (d, $J = 8.4$ Hz, 2H, $H_{aromatic}$), 7.32 (d, $J = 8.4$ Hz, 4H, $H_{aromatic}$), 7.61 (d, $J = 8.4$ Hz, 2H, $H_{aromatic}$), 7.96 (d, $J = 8.1$ Hz, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 14.2 and 16.1 (CH_3), 28.9 and 29.2 (CH_2), 125.3, 127.4, 128.1, and 132.4 ($CH_{aromatic}$), 133.2, 141.4, 150.7, and 151.0 ($C_{aromatic}$), 234.2 (CS_3), 238.5 (CS_2). IR (KBr disk) (cm^{-1}): 1595 (s), 1449 (w), 1413 (w), 1273 (m), 1240 (s), 1179 (s), 1054 (m), 1008 (s, $\nu_{C\text{-}S}$), 964 (s), 905 (s), 832 (s), 768 (w), 593 (w), 561 (m, $\nu_{S\text{-}S}$), 465 (w), 438 (w), 408 (w), 385 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{27}H_{27}S_8Re$. Found: %C = 40.83, %H = 3.43, %S = 32.05; Calc. for [Re(4-EtPhCS_3)$_2$(4-EtPhCS_2)]: %C = 40.84, %H = 3.43, %S = 32.30.

[Re(2-EtPhCS_3)$_2$(2-EtPhCS_2)] 4A

Yield 62% (0.084 g). m.p. = 170°C. R_f (PE/CH_2Cl_2 7/3) = 0.70. ^1H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 1.19 (t, $J = 7.5$ Hz, 3H, CH_3), 1.24 (t, $J = 7.5$ Hz, 6H, CH_3), 2.77 (q, $J = 7.6$ Hz, 2H, CH_2), 3.00 (q, $J = 7.5$ Hz, 4H, CH_2), 7.19 (m, 2H, $H_{aromatic}$), 7.25 (m, 2H, $H_{aromatic}$), 7.36 (m, 4H, $H_{aromatic}$), 7.44 (m, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 16.2 (CH_3), 26.8 (CH_2), 125.4, 128.4, 129.7, 131.4, 125.7, 129.1, 130.9, and 131.8 ($CH_{aromatic}$), 134.0, 141.7, 143.9, and 145.5 ($C_{aromatic}$), 235.4 (CS_3), 243.9 (CS_2). IR (KBr disk) (cm^{-1}): 1476 (m), 1458 (m), 1441 (s), 1371 (w), 1259 (w), 1190 (w), 1160 (w), 1119 (w), 1057 (w), 1000 (s, $\nu_{C\text{-}S}$), 943 (m), 913 (w), 751 (s), 544 (s, $\nu_{S\text{-}S}$), 454 (m), 399 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{27}H_{27}S_8Re$. Found: %C = 40.81, %H = 3.43, %S = 31.95; Calc. for [Re(2-EtPhCS_3)$_2$(2-EtPhCS_2)]: %C = 40.84, %H = 3.43, %S = 32.30.

[Re(4-MeOPhCS_3)$_2$(4-MeOPhCS_2)] 5A

Yield 54% (0.074 g). m.p. = 170°C. R_f (PE/CH_2Cl_2 7/3) = 0.25. ^1H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 3.83 (s, 3H, OCH_3), 3.92 (s, 6H,

OCH_3), 6.84 (d, $J = 8.9$ Hz, 2H, $H_{aromatic}$), 6.98 (d, $J = 8.9$ Hz, 4H, $H_{aromatic}$), 7.67 (d, $J = 9.2$ Hz, 2H, $H_{aromatic}$), 8.06 (d, $J = 6.7$ Hz, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 55.9 and 56.0 (OCH_3), 113.2, 113.9, 127.4, 128.9 ($CH_{aromatic}$), 134.2 ($\underline{C}$-CS_3), 137.6 ($\underline{C}$-CS_2), 164.5 and 165.0 ($\underline{C}$-OCH_3), 233.4 (CS_3), 237.1 (CS_2). IR (KBr disk) (cm^{-1}): 1592 (s), 1564 (w), 1501 (m), 1452 (w), 1305 (m), 1259 (s), 1169 (s), 1116 (w), 1027 (s, $\nu_{C\text{-}S}$), 992 (w), 948 (w), 912 (w), 883 (w), 827 (s), 805 (w), 733 (w), 631 (w), 593 (m, $\nu_{S\text{-}S}$), 545 (w), 398 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{24}H_{21}O_3S_8Re$. Found: %C = 36.03, %H = 2.64, %S = 31.96; Calc. for [Re(4-MeOPhCS$_3$)$_2$(4-MeOPhCS$_2$)]: %C = 36.03, %H = 2.65, %S = 32.06.

[Re(3-MeOPhCS$_3$)$_2$(3-MeOPhCS$_2$)] 6A

Yield 65% (0.089 g). m.p. = 178°C. R_f (PE/CH_2Cl_2 7/3) = 0.19. ^1H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 3.79 (s, 3H, OCH_3), 3.91 (s, 6H, OCH_3), 6.91 (m, 3H, $H_{aromatic}$), 7.20 (m, 1H, $H_{aromatic}$), 7.29 (m, 3H, $H_{aromatic}$), 7.41 (t, $J = 7.9$ Hz,1H, $H_{aromatic}$), 7.58 (m,4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 55.8 and 56.0 (OCH_3), 116.8, 119.9, 125.2, 129.5, ($CH_{aromatic}$), 136.4 ($\underline{C}$-CS_3), 144.4 ($\underline{C}$-CS_2), 159.0 and 159.4 ($\underline{C}$-OCH_3), 234.0 (CS_3), 238.6 (CS_2). IR (KBr disk) (cm^{-1}): 1593 (w), 1570 (s), 1476 (m), 1425 (m), 1321 (w), 1286 (m), 1261 (s), 1200 (w), 1162 (w), 1098 (s), 1050 (s), 1017 (s, $\nu_{C\text{-}S}$), 978 (w), 948 (w), 866 (m), 803 (s), 678 (s), 564 (m, $\nu_{S\text{-}S}$), 395 (m, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{24}H_{21}O_3S_8Re$. Found: %C = 36.11, %H = 2.63, %S = 31.71; Calc. for [Re(3-MeOPhCS$_3$)$_2$(3-MeOPhCS$_2$)]: %C = 36.03, %H = 2.65, %S = 32.06.

[Re(2-MeOPhCS$_3$)$_2$(2-MeOPhCS$_2$)] 7A

Yield 59% (0.080 g). m.p. = 180°C. R_f (PE/CH_2Cl_2 7/3) = 0.22. ^1H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 3.84 (s, 3H, OCH_3), 3.93 (s, 6H, OCH_3), 6.88 (d, $J = 8.4$ Hz, 1H, $H_{aromatic}$), 6.95 (t, $J = 7.1$ Hz, 1H, $H_{aromatic}$), 7.11 (m, 4H, $H_{aromatic}$), 7.22 (d, $J = 7.1$ Hz, 1H, $H_{aromatic}$), 7.35 (t, $J = 8.4$ Hz, 2H, $H_{aromatic}$), 7.79 (dd, $J = 8.1$ Hz and $J = 1.8$ Hz, 1H, $H_{aromatic}$), 7.91 (dd, $J = 7.6$ Hz and $J = 1.5$ Hz, 2H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): ν_C 55.8 and 56.4 (OCH_3), 111.2, 111.9, 119.7, 120.9, 126.1, 128.6 ($CH_{aromatic}$), 133.8 ($\underline{C}$-CS_3), 134.5 ($\underline{C}$-CS_2), 157.1 and 158.4 ($\underline{C}$-OCH_3), 229.4 (CS_3), 234.6 (CS_2). IR (KBr disk) (cm^{-1}): 1589 (m), 1568 (w), 1480 (s), 1458 (s), 1429 (m), 1284 (m), 1250 (s), 1164 (m), 1097 (s), 1047 (w), 1012 (s, $\nu_{C\text{-}S}$), 944 (w), 913 (w), 878 (w), 801 (s), 752 (s), 648 (w), 568 (w, ($_{S\text{-}S}$), 383 (w, $\nu_{Re\text{-}S}$). Elemental analysis: molecular formula $C_{24}H_{21}O_3S_8Re$. Found: %C = 36.10, %H = 2.59, %S = 32.00; Calc. for [Re(3-MeOPhCS$_3$)$_2$(3-MeOPhCS$_2$)]: %C = 36.03, %H = 2.65, %S = 32.06.

[Re(4-FPhCS$_3$)$_2$(4-FPhCS$_2$)] 8A

Yield 77% (0.100 g). m.p. = 120°C. R_f (PE/CH$_2$Cl$_2$ 7/3) = 0.67. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 7.00 (t, $J = 8.6$ Hz, 2H, H$_{\text{aromatic}}$), 7.15 (t, $J = 8.5$ Hz, 4H, H$_{\text{aromatic}}$), 7.64 (dd, $J = 5.3$ and 8.9 Hz, 2H, H$_{\text{aromatic}}$), 8.00 (dd, $J = 5.3$ and 8.9 Hz, 4H, H$_{\text{aromatic}}$). ^{13}C NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): δ_C 114.9 (d, $J = 22.2$ Hz, CH$_{\text{aromatic}}$), 115.5 (d, $J = 21.2$ Hz, CH$_{\text{aromatic}}$), 127.3 (d, $J = 9.1$ Hz, CH$_{\text{aromatic}}$), 131.3 ($\underline{\text{C}}$-CS$_3$), 131.4 ($\underline{\text{C}}$-CS$_2$), 134.0 (d, $J = 8.1$ Hz, CH$_{\text{aromatic}}$), 139.7, 142.0, 142.2, and 142.5 (C-F), 232.6 (CS$_3$), 244.4 (CS$_2$). IR (KBr disk) (cm^{-1}): 1591 (m), 1499 (s), 1407 (w), 1304 (w), 1280 (w), 1265 (w), 1237 (s), 1156 (m), 1008 (s, $\nu_{\text{C-S}}$), 1001 (s, $\nu_{\text{C-S}}$), 834 (m), 807 (w), 578 (w), 547 (w), 547 (s, $\nu_{\text{S-S}}$), 454 (m), 399 (m, $\nu_{\text{Re-S}}$). Elemental analysis: molecular formula C$_{21}$H$_{12}$F$_3$S$_8$Re. Found: %C = 33.12, %H = 1.63, %S = 30.70. Calc. for [Re(4-FPhCS$_3$)$_2$(4-FPhCS$_2$)] : %C = 33.00, %H = 1.60, %S = 33.60.

Re(3-FPhCS$_3$)$_2$(3-FPhCS$_2$)] 9A

Yield 48% (0.063 g). m.p. = 125°C. R_f (PE/CH$_2$Cl$_2$ 7/3) = 0.70. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 7.07 (td, $J = 8.1$ and 2,6 Hz, 3H, H$_{\text{aromatic}}$), 7.36 (m, 2H, H$_{\text{aromatic}}$), 7.49 (m, 3H, H$_{\text{aromatic}}$), 7.80 (m, 4H, H$_{\text{aromatic}}$). ^{13}C NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): δ_C 115.3 122.0 and 124.4 (CH$_{\text{aromatic}}$), 131.2 and 137.3 ($\underline{\text{C}}$-CS$_2$), 161.9 and 164.4 ($\underline{\text{C}}$-F), 229.3 (CS$_3$), 242.3 (CS$_2$). IR (KBr disk) (cm^{-1}): 1581 (w), 1479 (m), 1433 (m), 1249 (s), 1158 (w), 1136 (w), 1026 (m, $\nu_{\text{C-S}}$), 1001 (w), 963 (s), 869 (m), 824 (w), 809 (m), 786 (s), 690 (m), 672 (s), 563 (w, $\nu_{\text{S-S}}$), 521 (w), 372 (w, $\nu_{\text{Re-S}}$). Elemental analysis: molecular formula C$_{21}$H$_{12}$F$_3$S$_8$Re. Found: %C = 33.01, %H = 1.58, %S = 30.57. Calc. for [Re(3-FPhCS$_3$)$_2$(3-FPhCS$_2$)] : %C = 33.00, %H = 1.60, %S = 33.60.

Bis(trithioperoxybenzoate)(dithiobenzoate)technetium(III)

[^{99}Tc(PhCS$_3$)$_2$(PhCS$_2$)] 1B

Yield 60% (0.077 g). R_f (PE/CH$_2$Cl$_2$ 7/3) = 0.62. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 7.29 (m, 3H, H$_{\text{aromatic}}$), 7.44 (m, 6H, H$_{\text{aromatic}}$), 7.85 (d, $J = 7.5$ Hz, 2H, H$_{\text{aromatic}}$), 8.04 (dd, $J = 7.5$ and 2.0 Hz, 4H, H$_{\text{aromatic}}$). ^{13}C NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): δ_C 124.3 128.1 128.7 129.4 131.6 and 132.6 (CH$_{\text{aromatic}}$), 137.8 and 141.9 (C$_{\text{aromatic}}$), 226.7 (CS$_3$), 226.1 (CS$_2$). IR (KBr disk) (cm^{-1}): 1733 (w), 1716 (w), 1699 (w), 1587 (m), 1335 (w), 1311 (w), 1262 (m), 1233 (w), 1117 (m), 1109 (w), 1077 (w), 998 (m, ($_{\text{C-S}}$), 942 (m, $\nu_{\text{S-S}}$), 906 (w), 838 (w), 759 (s), 723 (w), 682 (s), 663 (w), 651 (w), 615 (w), 566 (w), 447 (m, $\nu_{\text{Tc-S}}$).

[^{99}Tc(4-MePhCS$_3$)$_2$(4-MePhCS$_2$)] 2B

Yield 92% (0.100 g). R_f (PE/CH$_2$Cl$_2$ 7/3) = 0.79. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 2.33 (s, 3H, CH$_3$), 2.45 (s, 6H, CH$_3$), 7.11 (d, $J = 8.2$ Hz, 2H, H$_{\text{aromatic}}$), 7.25 (d, $J = 8.0$ Hz, 4H, H$_{\text{aromatic}}$), 7.78

(d, $J = 8.2$ Hz, 2H, H$_{\text{aromatic}}$), 7.97 (d, $J = 8.1$ Hz, 4H, H$_{\text{aromatic}}$). NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): $\delta_{\underline{C}}$ 22.0 (CH$_3$), 124.9, 129.3, 129.8, and 136.1 (CH$_{\text{aromatic}}$), 140.1 and 144.0 (C$_{\text{aromatic}}$), 227.1 (CS$_3$), 236.0 (CS$_2$). IR (KBr disk) (cm^{-1}): 1600 (s), 1563 (m), 1544 (m), 1450 (s), 1377 (s), 1309 (w), 1279 (w), 1264 (m), 1205 (w), 1176 (s), 1018 (m, $\nu_{\text{C-S}}$), 948 (w), 889 (m), 815 (s), 768 (m), 758 (w), 637 (w), 620 (w), 549 (w, $\nu_{\text{S-S}}$), 503 (w), 464 (m, $\nu_{\text{Tc-S}}$).

[^{99}Tc(4-EtPhCS$_3$)$_2$(4-EtPhCS$_2$)] 3B

Yield 92% (0.132 g). R$_f$ (PE/CH$_2$Cl$_2$ 7/3) = 0.76. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 1.19 (t, $J = 7.6$ Hz, 3H, CH$_3$), 1.27 (t, $J = 7.6$ Hz, 6H, CH$_3$), 2.63 (q, $J = 7.9$ Hz, 2H, CH$_2$), 2.73 (q, $J = 7.6$, 4H, CH$_2$), 7.14 (d, $J = 8.6$ Hz, 2H, H$_{\text{aromatic}}$), 7.27 (d, $J = 8.2$ Hz, 4H, H$_{\text{aromatic}}$), 7.80 (d, $J = 8.4$ Hz, 2H, H$_{\text{aromatic}}$), 7.99 (d, $J = 8.4$ Hz, 4H, H$_{\text{aromatic}}$). NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): δ_C 15.7 and 15.8 (CH$_3$), 29.3 and 29.4 (CH$_2$), 125.0, 128.1, 128.7, and 129.9 (CH$_{\text{aromatic}}$), 136.3 and 150.2 (C$_{\text{aromatic}}$), 227.2 (CS$_3$), 236.0 (CS$_2$). IR (KBr disk) (cm^{-1}): 1599 (s), 1461 (s), 1414 (w), 1376 (s), 1267 (s), 1232 (w), 1179 (s), 1130 (m), 1050 (w), 999 (s, $\nu_{\text{C-S}}$), 964 (w), 950 (w), 910 (w), 832 (s), 769 (w), 669 (m), 593 (w), 569 (w), 553 (w, $\nu_{\text{S-S}}$), 461 (m, ($_{\text{Tc-S}}$), 440 (w).

[^{99}Tc(2-EtPhCS$_3$)$_2$(2-EtPhCS$_2$)] 4B

Yield 59% (0.055 g). R$_f$ (PE/CH$_2$Cl$_2$ 7/3) = 0.70. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 1.18 (t, $J = 5.8$ Hz, 3H, CH$_3$), 1.22 (t, $J = 7.6$ Hz, 6H, CH$_3$), 2.71 (q, $J = 7.5$ Hz, 4H, CH$_2$), 2.93 (q, $J = 7.4$ Hz, 2H, CH$_2$), 7.16 (m, 2H, H$_{\text{aromatic}}$), 7.31 (m, 3H, H$_{\text{aromatic}}$), 7.41 (m, 7H, H$_{\text{aromatic}}$). NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): ν_C 16.1 and 19.2 (CH$_3$), 26.5 and 29.7 (CH$_2$), 125.6, 127.6, 128.9, 129.3, 129.6, 129.7, 130.7, and 130.8 (CH$_{\text{aromatic}}$), 131.0, 136.6, 140.8, and 142.1 (C$_{\text{aromatic}}$), 229.1 (CS$_3$), 242.6 (CS$_2$). IR (KBr disk) (cm^{-1}): 1459 (s), 1376 (s), 1258 (m), 1224 (w), 1188 (w), 1160 (w), 1120 (m), 1073 (m), 999 (s, $\nu_{\text{C-S}}$), 945 (m), 910 (w), 881 (w), 864 (w), 754 (s), 670 (m), 648 (m), 577 (w), 551 (w, $\nu_{\text{S-S}}$), 491 (w), 465 (m, $\nu_{\text{Tc-S}}$).

[^{99}Tc(4-MeOPhCS$_3$)$_2$(4-MeOPhCS$_2$)] 5B

Yield 92% (0.140 g). R$_f$ (PE/CH$_2$Cl$_2$ 7/3) = 0.25. ^{1}H NMR (400.13 MHz, CDCl$_3$, SiMe$_4$): δ_H 3.82 (s, 3H, CH$_3$), 3.89 (s, 6H, CH$_3$), 6.80 (d, $J = 7.7$ Hz, 2H, H$_{\text{aromatic}}$), 6.93 (d, $J = 7.7$ Hz, 4H, H$_{\text{aromatic}}$), 7.87 (d, $J = 8.5$ Hz, 2H, H$_{\text{aromatic}}$), 8.08 (d, $J = 7.5$ Hz, 4H, H$_{\text{aromatic}}$). ^{13}C NMR (100.67 MHz, CDCl$_3$, SiMe$_4$): ($_C$ 56.1 (OCH$_3$), 113.8, 114.4, 127.1, 131.8 (CH$_{\text{aromatic}}$), 132.1 ($\underline{C}$-CS$_3$), 137.0 ($\underline{C}$-CS$_2$), 163.9 and 164.4 ($\underline{C}$-OCH$_3$), 226.2 (CS$_3$), 234.2 (CS$_2$). IR (KBr disk) (cm^{-1}): 1595 (s), 1560 (w), 1542 (w), 1506 (m), 1469 (s), 1377 (s), 1305 (m), 1264 (s), 1237 (w), 1168 (s), 1074 (m), 1029 (s, $\nu_{\text{C-S}}$), 949 (w), 829 (m), 739 (w), 668 (s), 594 (w, $\nu_{\text{S-S}}$), 549 (w), 456 (m, $\nu_{\text{Tc-S}}$).

[^{99}Tc(3-MeOPhCS$_3$)$_2$(3-MeOPhCS$_2$)] 6B

Yield 59% (0.060 g). R_f (PE/CH_2Cl_2 7/3) = 0.19. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): (${}_H$ 3.80 (s, 3H, CH_3), 3.90 (s, 6H, CH_3), 7.01 (m, 3H, $H_{aromatic}$), 7.24 (t, $J = 8.0$ Hz, 1H, $H_{aromatic}$), 7.36 (t, $J = 7.9$ Hz, 2H, $H_{aromatic}$), 7.40 (t, $J = 2.3$ Hz,,1H, $H_{aromatic}$), 7.49 (dq, $J = 7.6$ and 0.7 Hz, 1H, $H_{aromatic}$), 7.59–7.64 (m, 4H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 30.2 and 56.1 (OCH_3), 114.4, 119.4, 122.7, and 130.1 ($CH_{aromatic}$), 141.5 and 159.9 ($C_{aromatic}$), 227.1 (CS_3), 236.1 (CS_2). IR (KBr disk) (cm^{-1}): 1596 (s), 1572 (s), 1488 (m), 1478 (m), 1427 (m), 1377 (m), 1323 (m), 1286 (s), 1263 (s), 1195 (w), 1163 (w), 1053 (m), 1020 (m), 1003 (m, $\nu_{C\text{-}S}$), 978 (m), 947 (w), 870 (s), 806 (w), 786 (s), 681 (s), 568 (m), 465 (m, $\nu_{Tc\text{-}S}$).

[^{99}Tc(2-MeOPhCS$_3$)$_2$(2-MeOPhCS$_2$)] 7B

Yield 94% (0.066 g). R_f (PE/CH_2Cl_2 7/3) = 0.22. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 3.84 (s, 3H, CH_3), 3.92 (s, 6H, CH_3), 6.89 (t, $J = 7.8$ Hz, 2H, $H_{aromatic}$), 6.95 (t, $J = 8.0$ Hz, 2H, $H_{aromatic}$), 7.03 (t, $J = 7.8$ Hz, 1H, $H_{aromatic}$), 7.10 (t, $J = 7.3$ Hz, 1H, $H_{aromatic}$), 7.29 (t, $J = 7.3$ Hz, 2H, $H_{aromatic}$), 7.43 (t, $J = 7.4$ Hz, 1H, $H_{aromatic}$), 7.97 (dd, $J = 7.7$ and 1.5 Hz, 1H, $H_{aromatic}$), 8.01 (dd, $J = 5.3$ and 1.8 Hz, 2H, $H_{aromatic}$). ^{13}C NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 55.9 and 56.5 (OCH_3), 111.9, 112.6, 120.4, 121.4, 129.4, and 131.4, ($CH_{aromatic}$), 133.4 ($\underline{C}$-CS_3), 135.6 ($\underline{C}$-CS_2), 155.6 and 168.2 ($\underline{C}$-OCH_3), 222.3 (CS_3), 232.5 (CS_2). IR (KBr disk) (cm^{-1}): 1592 (m), 1569 (w), 1460 (s), 1376 (s), 1285 (m), 1246 (s), 1162 (m), 1110 (s), 1020 (s, $\nu_{C\text{-}S}$), 975 (w), 944 (w), 785 (w), 753 (s), 668 (m), 649 (w), 571 (w, (${}_{S\text{-}S}$), 467 (s, $\nu_{Tc\text{-}S}$).

[^{99}Tc(4-FPhCS$_3$)$_2$(4-FPhCS$_2$)] 8B

Yield 86% (0.080 g). R_f (PE/CH_2Cl_2 7/3) = 0.67. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 7.02 (dd, $J = 8.6$ Hz, 2H, $H_{aromatic}$), 7.16 (dd, $J = 6.5$ Hz, 4H, $H_{aromatic}$), 7.88 (dd, $J = 8.9$ and 5.3 Hz, 2H, $H_{aromatic}$), 8.09 (dd, $J = 6.9$ and 5.2 Hz, 4H, $H_{aromatic}$). NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 115.3, 115.9, 126.7, and 131.4 ($CH_{aromatic}$), 134.3 and 138.8 ($\underline{C}$-CS_2), 165.6 and 166.2 ($\underline{C}$-F), 225.3 (CS_3), 234.2 (CS_2). IR (KBr disk) (cm^{-1}): 1592 (s), 1499 (s), 1458 (s), 1407 (w), 1376 (m), 1261 (m), 1239 (s), 1156 (s), 1003 (s, $\nu_{C\text{-}S}$), 948 (w, $\nu_{as\ C\text{-}S}$), 908 (s), 835 (s), 807 (w), 588 (m), 546 (m, $\nu_{S\text{-}S}$), 472 (m, $\nu_{Tc\text{-}S}$).

[^{99}Tc(3-FPhCS$_3$)$_2$(3-FPhCS$_2$)] 9B

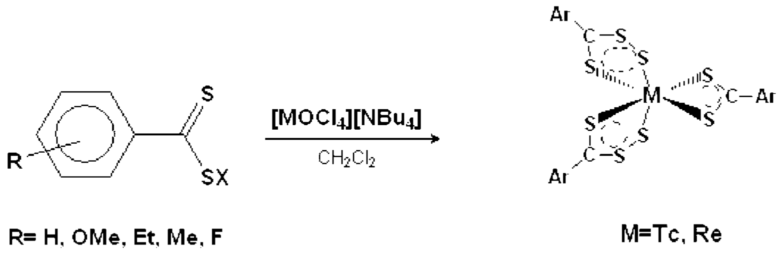
Yield 57% (0.035 g). R_f (PE/CH_2Cl_2 7/3) = 0.70. ^{1}H NMR (400.13 MHz, $CDCl_3$, $SiMe_4$): δ_H 7.11–7.22 (m, 3H, $H_{aromatic}$), 7.32 (qd, $J = 8.2$ and 2.5 Hz, 1H, $H_{aromatic}$), 7.44 (qd, $J = 8.2$ and 2.4 Hz, 2H, $H_{aromatic}$), 7.55 (dt, $J = 9.6$ and 2.3 Hz, 1H, $H_{aromatic}$), 7.65 (d, $J = 8.3$, 1H, $H_{aromatic}$), 7.81 (m, 4H, $H_{aromatic}$). NMR (100.67 MHz, $CDCl_3$, $SiMe_4$): δ_C 111.6, 116.7, 119.7, and 125.7 ($CH_{aromatic}$), 130.2 and 130.8 ($\underline{C}$-CS_2), 161.2 and 164.4 (C-F), 225.4, (CS_3), 234.8 (CS_2). IR (KBr disk) (cm^{-1}): 1578 (s), 1559 (w), 1544 (m), 1508 (m), 1465 (s), 1376 (s), 1340 (w), 1284 (w), 1148 (w), 1097 (s), 984 (m, $\nu_{C\text{-}S}$), 949 (m), 879 (s), 829 (m), 806 (m), 787 (m), 675 (s), 524 (w, $\nu_{S\text{-}S}$), 471 (s, $\nu_{Tc\text{-}S}$), 461 (s).

RESULTS AND DISCUSSION

Complexes were prepared according to previously reported methods (Scheme 1).[1,2] The UV-Vis spectra were then recorded for a series of rhenium and technetium complexes in dichloromethane solutions. The aim here was to evaluate the relative increase in the ligand field strength by observing the energy shift between equivalent absorption bands with the different ligands. This trend is further related to the Lewis basicity of the ligands by observing the absorption bands assigned as LMCT. In Fig. 1, a series of spectra is given for rhenium complexes $[Re(RPhCS_3)_2(RPhCS_2)]$ with para substituted ligands (H, Me, Et, OMe, F). In Fig. 2, for the −OMe substituent on the phenyl ring in ortho-, meta-, and para-position, we observe a different behavior for the para- substituted compound compared to ortho- or meta-substituted ones. The values of the absorption band maxima with corresponding absorbance values of the investigated complexes are given in Table 1. The assignment of the absorption bands has been established on the basis of the value of the absorption coefficient and the shape of the band.[10] Absorbance values are given as an indicative information to support the spectroscopical series. We do not list the values of the d-d band for Tc complexes because they appear as shoulders, which are difficult to point.

The spectral bands can be divided into three categories, as can be observed in Figs. 1 and 2, for instance.

(a) Absorptions occurring above 550 nm, and with absorption coefficients ε around $1000\,M^{-1}\cdot cm^{-1}$, are attributed to a d-d spectral transition, probably the spin-allowed $^3T_1 \rightarrow {}^3T_2$ transition, and is on the origin of



Scheme 1. Synthesis of $[M(RPhCS_3)_2(RPhCS_2)]$, M = Re, ^{99}Tc.

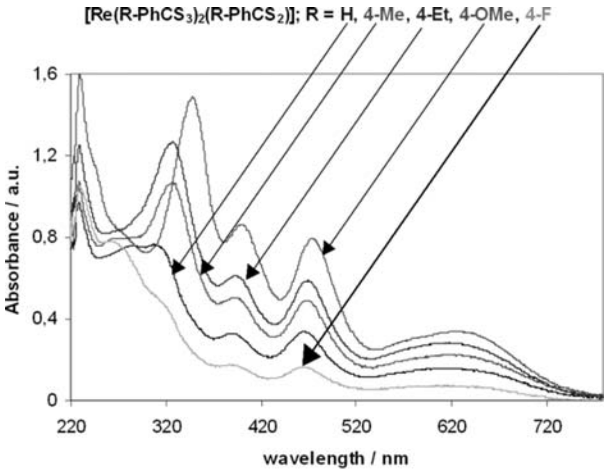


Figure 1. UV-Vis spectra of para-substituted Re complexes.

the green solutions of rhenium complexes ($\lambda \sim 610-620\,\text{nm}$). For technetium complexes, this band is blue-shifted, and has a maximum around 580–600 nm (occurring as a shoulder), which explains the dark-pink color of technetium complexes.

(b) Absorptions between 550 and 350 nm are assigned to charge transfer transitions, with typical absorption coefficients around $10^4\ \text{M}^{-1}\cdot\text{cm}^{-1}$. Rhenium and technetium complexes present two bands in this region, of

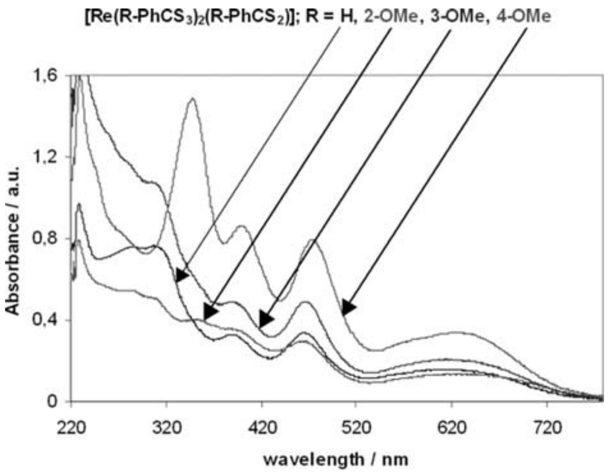


Figure 2. UV-Vis spectra of OMe Re complexes.

Table 1. Band position and absorption of complexes [$M(RPhCS_3)_2(RPhCS_2)$], M = Rw, ^{99}Tc

	Rhenium		Technetium	
Ligand	Band maximum position λ/nm [$\pm$2 nm] (E/cm^{-1})	Absorption (a.u.) [ε/cm$^{-1}\cdot$M^{-1}]	Band maximum position λ/nm [$\pm$2 nm] (E/cm^{-1})	Absorption (a.u.) [ε/cm$^{-1}\cdot$M^{-1}]
H	A_{1A} 618 (16181)	0.315 [2.2 × 10^3]		
	B_{1A} 465 (21505)	0.674 [4.6 × 10^3]	B_{1B} 517 (19342)	0.404 [1.3 × 10^4]
	C_{1A} 389 (25707)	0.652 [4.5 × 10^3]	C_{1B} 400 (25000)	0.454 [1.5 × 10^4]
	D_{1A} 308 (32468)	1.530 [1.1 × 10^4]	D_{1B} 312 (32051)	1.235 [4.7 × 10^4]
4-Me	A_{2A} 618 (16181)	0.243 [3.5 × 10^3]		
	B_{2A} 468 (21368)	0.548 [7.6 × 10^3]	B_{2B} 524 (19084)	0.532 [5.6 × 10^3]
	C_{2A} 395 (25316)	0.556 [7.9 × 10^3]	C_{2B} 411 (24331)	0.569 [6.0 × 10^3]
	D_{2A} 326 (30675)	1.175 [1.7 × 10^4]	D_{2B} 328 (30488)	1.488 [1.6 × 10^4]
4-Et	A_{3A} 616 (16234)	0.283 [3.0 × 10^3]		
	B_{3A} 469 (21322)	0.588 [6.2 × 10^3]	B_{3B} 524 (19084)	0.276 [3.0 × 10^4]
	C_{3A} 394 (25381)	0.613 [6.4 × 10^3]	C_{3B} 408 (24510)	0.314 [3.4 × 10^4]
	D_{3A} 327 (30581)	1.268 [1.3 × 10^4]	D_{3B} 327 (30581)	0.829 [9.4 × 10^4]
2-Et	A_{4A} 578 (17301)	0.253 [5.2 × 10^3]		
	B_{4A} 446 (22421)	0.499 [1.0 × 10^4]	B_{4B} 509 (19646)	0.224 [5.0 × 10^3]
	C_{4A} 371 (26954)	0.692 [1.4 × 10^4]	C_{4B} 388 (25773)	0.301 [6.6 × 10^3]
4-OMe	A_{5A} 623 (16051)	0.340 [7.8 × 10^3]		
	B_{5A} 474 (21097)	0.795 [1.8 × 10^4]	B_{5B} 528 (18939)	0.484 [2.6 × 10^4]
	C_{5A} 398 (25126)	0.863 [2.0 × 10^4]		
	D_{5A} 348 (28736)	1.489 [3.4 × 10^4]	D_{5B} 350 (28571)	1.530 [8.3 × 10^4]
3-OMe	A_{6A} 612 (16340)	1.544 [4.4 × 10^3]		
	B_{6A} 465 (21505)	0.829 [1.1 × 10^4]	B_{6B} 520 (19231)	0.489 [2.3 × 10^4]
	C_{6A} 388 (25773)	0.845 [1.1 × 10^4]	C_{6B} 410 (24390)	0.522 [2.5 × 10^4]
	D_{6A} 313 (31949)	1.544 [2.0 × 10^4]	D_{6B} 315 (31746)	1.088 [5.3 × 10^4]
2-OMe	A_{7A} 629 (15898)	0.531 [6.9 × 10^3]		
	B_{7A} 465 (21505)	1.153 [1.5 × 10^4]	B_{7B} 517 (19342)	0.200 [4.7 × 10^2]
	C_{7A} 390 (25641)	1.373 [1.9 × 10^4]	C_{7B} 413 (24213)	0.252 [6.0 × 10^2]
	D_{7A} 351 (28490)	1.564 [2.1 × 10^4]	D_{7B} 307 (32573)	0.481 [1.1 × 10^3]
4-F	A_{8A} 609 (16420)	0.227 [7.6 × 10^2]		
	B_{8A} 465 (21505)	0.490 [1.6 × 10^3]	B_{8B} 519 (19268)	0.702 [1.4 × 10^4]
	C_{8A} 387 (25840)	0.514 [1.7 × 10^3]	C_{8B} 408 (24510)	0.748 [1.5 × 10^4]
			D_{8B} 316 (31647)	1.928 [4.0 × 10^4]
3-F			B_{9B} 519 (19268)	0.331 [8.8 × 10^3]
			C_{9B} 409 (24450)	0.338 [8.9 × 10^3]
			D_{9B} 309 (32362)	0.810 [2.2 × 10^4]

similar band width (around 80 nm), respectively, at 470 and 390 nm for rhenium and 520 and 400 nm for technetium. Knowing the valence band electronic valence structure of sulfur, which is rich in electrons compared to the one of rhenium (III), we attribute this charge-transfer band to the ligand to metal charge transfer (LMCT). This assignment is further confirmed by the shift toward longer wavelengths with the increasing electron-donating ability of the ligand. These two bands are used to determine the subtle differences in energy between the complexes and to establish a spectrochemical series of ligands in order of their increasing Lewis basicity.

(c) High-intensity ($\varepsilon > 10^4$ $M^{-1}\cdot cm^{-1}$) absorptions in the UV region ($\lambda < 350$ nm) are attributed to internal ligand π-π^* transitions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ligands. This is supported by the comparison with the free ligand spectra in aqueous solutions (data not shown) that have absorption band maxima at energy around 340 nm. The other absorption band observed on the ligand spectra, and attributed to n-π^* transitions localized on the C=S group ($\sim$ 480 nm, $\varepsilon \sim 10^2$),[7,11] is not observable on the complexes spectra, covered by the very intense charge-transfer transitions. As well, the probable absorption bands originating from the spin-allowed d-d transitions in this wavelength region are covered by higher intensity LMCT or π-π^* transitions and therefore cannot be observed. This is very common with dithiobenzoate and perthiocarboxylate complexes.[4,12,13] Due to the relatively low resolution of these bands, they are not specifically considered in further analysis.

Compared to other 1,1-dithiolates (dithiophosphates, dithiocarbamates, xanthates), dithiocarboxylates are located on the upper end of the spectrochemical series of chelating sulfur anions.[14,15] Compared with other donor atoms, the spectrochemical series is the following: $Cl^- < F^- <$ urea $< RCSS^- < H_2O < ox^{2-} < NR_3$. In the current study, we compared the effect of the substitution on the aromatic ring on the increase of the ligand field strength, which is further related to the Lewis basicity of the ligand. The spectrochemical series obtained by comparing the band maxima of charge transfer absorption bands between 350 and 550 nm is the following for rhenium complexes (Fig. 3), where arrows ($\rightarrow$) mean that the ligand field is increasing (4-OMe substituent has a weaker ligand field than 2-Et):

Low energy High energy
4-OMe → 4-Et → 4-Me → 3-OMe → 4-F → H → 2-OMe → 2-Et
High Lewis acidity High Lewis basicity

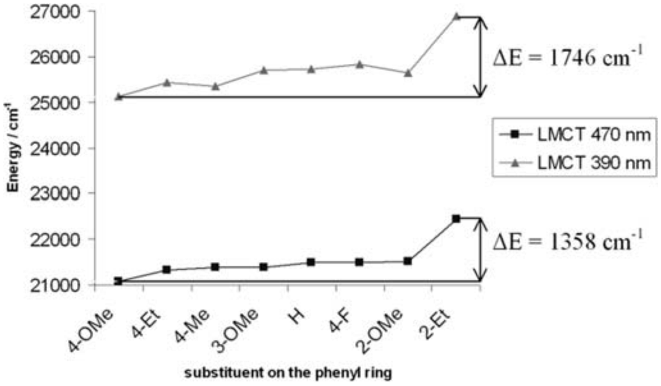


Figure 3. Energy shift for the series of phenyl-substituted rhenium complexes.

For the investigated series of the technetium complexes, the trend is similar (Fig. 4):

Low energy High energy
4-OMe → 4-Me → 4-Et → 3-OMe ≅ 4-F ≅ 3
-F ≅ H → 2-OMe → 2-Et
High Lewis acidity High Lewis basicity

We observe that the complexes with the lowest energy of the electronic transition are the para-complexes, while the meta- or ortho-substituted complexes are placed on the high-energy end of the series. For different para-substituents, the chain length of the substituent is inversely proportional to the energy increase. Another feature observed is that methoxy ligands (4-OMe and 2-OMe) lie lower in energy than their alkyl analogues. The

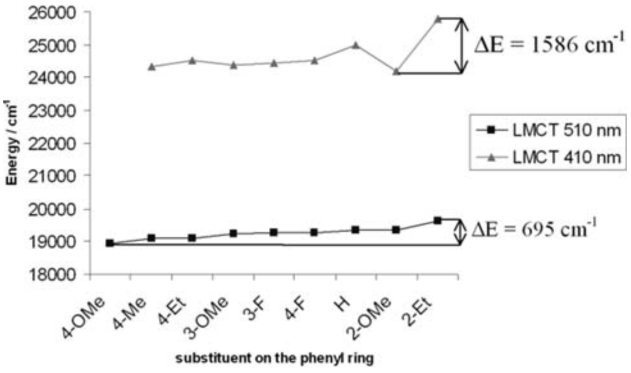


Figure 4. Energy shift for the series of phenyl-substituted technetium complexes.

behavior of the fluorine-substituted ring, either in para or in meta position, is more or less similar to that of the nonsubstituted phenyl ring, which is explained by low steric hindrance of the fluorine atom.

To quantitatively discuss the differences in energy, for the first LMCT band (470 and 510 nm), there is a difference of around 1358 and 695 cm^{-1} between the complexes at the two ends of the series (4-OMe and 2-Et), for Re and ^{99}Tc, respectively (Figs. 3 and 4). For the second LMCT (390 and 410 nm), the differences between the two ends of the series are 1746 and 1586 cm^{-1} for Re and ^{99}Tc, respectively (Figs. 3 and 4). Technetium seems to be less sensitive to the substituent variations, as the observed range of values is smaller than with rhenium.

For ortho substitutions, the transitions are the most elevated in energy compared with the other substituents in both cases (rhenium and technetium). However, in this case, two contributions must be considered: the electronic and the steric ones. Indeed, the structure of the compound from the unsubstituted ligand is distorted trigonal bipyramidal (twist angles between the upper and the lower triangular faces of 8.9° and 17.1° for Re and ^{99}Tc, respectively) and, in first approximation, it can be considered as quasi-octahedral.[16] Indeed, in the literature, $[MS_6]$ chromophores of transition metals are described to behave practically as octahedral,[14] even if some exceptions exist, such as $[M(tdt)_3]$ (M = Re, ^{99}Tc; tdt = toluene-3,4-dithiolate) and $[Re(S_2C_2Ph_2)_3]$, which are perfectly trigonal prismatic.[17] But, depending on the position of the substituent, the relative dihedral angle between the phenyl ring and the CS_2 or CS_3 groups could be different than 0° due to hindrance interactions: in the ortho-position especially, this could imply that the aromatic ring and the CS_2 (or CS_3) group can be not in the same plane, due to rotation of the CS group relating to the aromatic ring. This steric effect at the ortho position has also been observed, for instance by ^{13}C-NMR, for various aromatic carbonyl compounds or acetophenones.[18] Substituent effects on chemical shifts due to mono ortho substitutions are difficult to evaluate because they are a combination of inductive, mesomeric, and, depending on the hindrance of the substituent, steric effects. But, these steric interactions with neighboring groups can force a substituent group out of the π-electron plane, reducing its electronic influence.

Comparison of the ^{13}C chemical shift of C=S showed again that substitution has low effect on the values, as shown in Table 2. Moreover, complexation led to a high shielding of the δ, both for ^{99}Tc and Re complexes (about 20 ppm for CS_2). The main effect is observed on perthiocarbonyl carbon (CS_3), both for rhenium and technetium complexes, where a $\Delta\delta$ of about 5 ppm shielding is observed. This could imply differences of thermodynamic and/or kinetic stabilities between the two metals.

Comparing rhenium and technetium spectra, the same patterns are observed, with the absorption bands for technetium shifted toward higher wavelengths, which is consistent with other Re and ^{99}Tc complexes

Table 2. ^{13}C chemical shifts of C═S

	Free ligand (D_2O)	Rhenium ($CDCl_3$)		Technetium ($CDCl_3$)	
		CS_3	CS_2	CS_3	CS_2
H	258.6	232.8	237.6	226.0	236.7
4-Me	257.4	234.2	238.6	227.1	236.0
4-Et	257.2	234.2	238.5		
2-Et	256.9	235.4	243.9	229.1	242.6
4-OMe	254.9	233.4	237.1	226.2	233.4
3-OMe	257.6	234.0	238.6	227.1	236.1
2-OMe	259.4	229.4	234.6	222.3	232.5
4-F	260.0	232.6	244.4	225.3	234.8

described in the literature.[19–22] This effect can be understood on the basis that technetium is a stronger oxidant than rhenium.[20,23]

CONCLUSIONS

A series of 17 complexes of rhenium and technetium, $[M(R\text{-}PhCS_3)_2(R\text{-}PhCS_2)]$, $\{M = Re, {}^{99}Tc; R = H, F, Me, Et, OMe\}$, has been synthesized in order to investigate the fine-tuned differences in their optical properties. We used absorption spectroscopy in order to measure the relative increase of the ligand field strength in the series of complexes and to relate it to their Lewis basicity or acidity. The two scales, with rhenium and technetium, are very similar. Substitutions on the phenyl group have low influences on spectroscopic properties of the complexes (UV-Vis and NMR), except for ortho-substituted ones compared with the $PhCS_2$ derivative.

ACKNOWLEDGMENTS

We thank F. Tisato, F. Mévellec, A. Hauser, and J. J. McGarvey for useful discussions. We gratefully acknowledge the financial support from the Region of Brittany and Rennes Métropole.

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