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Asymmetric heterobimetallic mixed-valence complex trans-[(S'O IND.3')Co(cyclam)(NCS)Ru'(N'H IND.3') IND.4'(NCS)](B'F IND.4'): synthesis and characterization

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Asymmetric heterobimetallic mixed-valence complex *trans*-[$(SO_3)Co(cyclam)(NCS)Ru(NH_3)_4(\mathit{N}CS)](BF_4)$: Synthesis and characterization

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ABSTRACT

$[(SO_3)Co(cyclam)(\mathit{N}CS)]$ and $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(\mathit{N}CS)](BF_4)$ complexes were synthesized and characterized by means of X-ray diffraction, electrochemistry, elemental analysis, and spectroscopic techniques. Crystallographic and FTIR data indicated NCS^- ligand is coordinated to Co through the nitrogen atom in the monomer species. Electrochemistry and FTIR data of the material isolated after reductive electrolysis of $[(SO_3)Co(cyclam)(\mathit{N}CS)]$ hint that NCS^- and SO_3^{2-} are released thus forming $[Co(cyclam)(L)_2]^{2+}$, where L is solvent molecules. The formation of the heterobimetallic mixed-valence complex induced a thermodynamic stabilization of Co and Ru metal atoms in the oxidized and reduced states, respectively. According to the Robin and Day classification, a Class II system with a comproportionation constant of 5.78×10^6 is suggested for the mixed-valence complex based on the electrochemical and UV–Vis–NIR results.

1. Introduction

Throughout history, both ancient and modern, metals and metal compounds have been used in several applications ranging from dye pigments to medicine. A recent example in this sense is the use of coordination compounds as potential tools to treat drug-resistant *Mycobacterium tuberculosis* strains [1,2]. In the field of surface science, the attachment of a metal moiety to an organic monolayer, thus forming a coordination compound on surface [3–8], has been used to enhance the monolayer stability based on the π-back-bonding interaction, a brilliant approach firstly proposed by Taube [9]. Mixed-valence systems have been so far of academic interest due to the possibility of electronic communication between the metal centers [10–13]. Nowadays, with the growing interest on nano devices and supramolecular chemistry, mixed-valence compounds have been moved toward technological applications, for instance, in molecular magnetism and electronics [14–21]. Overall, these are examples that demonstrate the significant progress made in the field of Coordination Chemistry and how this theme is connected to almost all areas of Chemistry and other multidisciplinary fields such as Materials, Biology and Medicine.

Regarding the molecular electronics, polynuclear systems should be composed of monomers that present a linear conformation and are connected through bridging ligands such as conjugated molecules that allow electron delocalization. In addition, by considering metal centers that present π-back-bonding interaction, ancillary ligands constitute a relevant aspect since they should, preferably, not receive π electronic density from the metal atom. In this sense, the use of saturated macrocycles with nitrogen donor atoms may be a good choice, since they have no π-electron-withdrawing capability and also can provide an additional stabilization due to the ring formation during the coordination to the metal. In such case, all electronic density of the metals will be delocalized over the bridging ligands. To understand the electron transfer in such systems, one should detain the knowledge of the physical-chemistry properties of, at least, the smallest unit, usually a binuclear mixed-valence compound that contains donor and acceptor fragments.

This paper reports on the results obtained for the heterobimetallic mixed-valence complex $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4\text{-}(\mathit{N}CS)](BF_4)$, where cyclam = 1,4,8,11-tetraazacyclotetradecane and the cobalt and ruthenium metal centers are the acceptor and donor moieties, respectively. In addition, the results obtained for $[(SO_3)Co(cyclam)(\mathit{N}CS)]$ monomer upon reduction are discussed. For the sake of clarity, the donor atom of the thiocyanate ligand is italicised.

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2. Experimental

2.1. Chemicals

$C_{10}H_{24}N_4$ (1,4,8,11-tetraazacyclotetradecane – cyclam), Na_2SO_3, NH_4NCS, $CoCl_2{\cdot}6H_2O$, and $RuCl_3{\cdot}3H_2O$ were purchased from Aldrich and used as received. $K_2S_2O_8$, NH_4PF_6, $NaBF_4$ and n-Bu_4NPF_6 (TBA – 98%), from Aldrich, and CF_3COOH, from Acros Organics, were used without further purification. $(CH_3)_2NCOH$ (DMF) was distilled and stored in molecular sieves. Organic solvents and other reagents were all of reagent-grade quality and used as received. Aqueous solutions were prepared using Millipore ultrapure water of at least 18 MΩ cm resistance. A 0.1 mol L^{-1} aqueous solution (pH 3.4) of $NaCF_3COO$ (NaTFA) was used as electrolyte medium for the aqueous experiments while 0.1 mol L^{-1} TBA was employed in organic (DMF) medium. Electrolyte solutions were deoxygenated by bubbling argon for 30 min before the measurements.

Starting complexes *trans*-$[Co^{III}(cyclam)Cl_2]Cl$, *trans*-$[(SO_3)Co^{III}(cyclam)Cl]$, $[Ru^{III}(NH_3)_5Cl]Cl_2$, *trans*-$[(SO_2)Ru^{III}(NH_3)_4Cl]Cl_2$ and *trans*-$[(SO_4)Ru^{III}(NH_3)_4(NCS)]$ were synthesized according to literature procedures [22–27].

2.2. Synthesis of trans-$[(SO_3)Co^{III}(cyclam)(NCS)])\cdot 4H_2O$

About 20.55 mg (0.27 mmol) of NH_4SCN were added to an aqueous solution (3.0 mL of water) containing 100 mg (0.27 mmol) of *trans*-$[(SO_3)Co(cyclam)Cl]$. The solution was kept under stirring and argon flow for 4 h. The orange precipitate was filtered off, washed with cold acetone and dried under vacuum. Yield: 79%. *Anal.* Calc. for $[C_{11}H_{24}CoN_5O_3S_2]{\cdot}4H_2O$: C, 28.14; H, 6.87; N, 14.92; S, 13.66. Found: C, 27.58; H, 6.66; N, 14.64; S, 13.18%. Electronic spectrum in water [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 226 (1.86×10^4), 290 (1.42×10^4), and 481 (254.95). FTIR (ν_{SO}/cm^{-1}): 1090, 980, 624, 507. FTIR (ν_{CN}(NCS)/cm^{-1}): 2113. FTIR (ν_{CS}(NCS)/cm^{-1}): 760. FTIR (δ_{NCS}/cm^{-1}): 475.

2.3. Synthesis of trans-$[(SO_3)Co^{III}(cyclam)(NCS)Ru(NH_3)_4(NCS)]$-$(BF_4)\cdot 2H_2O$

83.96 mg (0.21 mmol) of *trans*-$[(SO_4)Ru^{III}(NH_3)_4(NCS)]$ were dissolved in 2.0 mL of water containing Zn/Hg and kept under stirring and argon flow for 30 min in order to be reduced originating the aqua-complex *trans*-$[(OH_2)Ru^{II}(NH_3)_4(NCS)]^+$. Then, through a flexible tubing, this mixture was carefully transferred to a previously deaerated aqueous solution (2.0 mL of water) containing *trans*-$[(SO_3)Co^{III}(cyclam)(NCS)]$ (100 mg, 0.21 mmol). After 12 h of argon flow and stirring, $NaBF_4$ was added and the precipitate was collected by filtration and dried under vacuum. Yield: 60%. *Anal.* Calc. for $[C_{12}H_{36}CoN_{10}O_3RuS_3](BF_4){\cdot}2H_2O$: C, 19.28; H, 5.39; N, 18.74; S, 12.87. Found: C, 19.42; H, 5.26; N, 18.37; S, 12.56%. Electronic spectrum in water [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 365 (9.1×10^2), 475 (7.5×10^2), 550 (7.1×10^2) and 725 (407.4). FTIR (ν_{SO}/cm^{-1}): 973, 621. FTIR (ν_{CN}(NCS)/cm^{-1}): 2112, 2067, 2004. FTIR (ν_{CS}(NCS)/cm^{-1}): 837, 740.

Recrystallization of $[(SO_3)Co(cyclam)(NCS)]$ from acetone/water solution yielded suitable orange crystals for the determination of X-ray structure. Attempts were made in order to isolate crystals of the binuclear complex, but these were unsuccessful. The isolated compounds were characterized assuming a high purity degree based on electrochemistry and elemental analysis. Table 1 presents the crystallographic data.

Table 1
Crystallographic data for $[(SO_3)Co(cyclam)(NCS)]$.

Formula weight for $CoS_2O_7N_5C_{11}H_{32}$	469.47 g mol^{-1}
T (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/a$
Cell dimensions	
a (Å)	13.6746(2)
b (Å)	8.9644(2)
c (Å)	16.2731(3)
β (°)	99.3050(10)
V (Å^3)	1968.58(6)
Z	4
$\rho_{calc.}$(g cm^{-3})	1.584
Absorption coefficient (mm^{-1})	1.127
F(0 0 0)	992
Crystal size (mm^3)	$0.059 \times 0.175 \times 0.236$
Method/θ range for data collection (°)	3.08–27.48
Index ranges	$-15 \leqslant h \leqslant 17$
	$-11 \leqslant k \leqslant 11$
	$-21 \leqslant l \leqslant 21$
Reflections collected	15864
Independent reflections/R_{int}	4484 [R_{int} = 0.0410]
Completeness to θ = 27.48°	99.3%
Absorption correction [28]	GAUSSIAN
Maximum and minimum transmission	0.935 and 0.779
Refinement method	full-matrix least-squares on F^2
Computing[a]	COLLECT [28], HKL DENZO and SCALEPACK [29] SHELXS-97 [30], SHELXL-97 [31]
Data/restraints/parameters	4484/0/281
Goodness-of-fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0411, wR_2 = 0.1067
R indices (all data)	R_1 = 0.0630, wR_2 = 0.1195
Largest difference in peak and hole (e Å^{-3})	0.375 and −0.498

[a] Data collection, data processing, structure solution and structure refinement respectively.

2.4. Apparatus

Absorption spectra in the ultraviolet and visible (UV–Vis) and in the UV–Vis and near infrared (UV–Vis–NIR) regions were taken, respectively, on a Hewlett–Packard 8453 diode array and on a Varian Cary 5000 spectrophotometers. Infrared vibrational spectra of the samples dispersed in KBr powder were acquired on a ABB Bomen FTLA 2000-102 spectrometer. Elemental analyses were done at the Microanalysis Laboratory at the Institute of Chemistry at São Paulo University on a Fison equipment, EA 1108 model. Cyclic voltammetric measurements were carried on a computer-controlled EC Epsilon Potentiostat (BAS – Bioanalytical Systems, Inc., West Lafayette, IN) by using an electrochemical glass cell of conventional design. Ag/AgCl reference electrodes were used in aqueous (3.5 mol L^{-1} KCl, BAS) and non-aqueous (Ag/AgCl wire immersed in a glass tube containing 0.1 mol L^{-1} TBA in DMF) medium. For the non-aqueous experiments, ferrocene ($Fc^{+/0}$, 0.355 V versus Ag/AgCl) was used as internal reference. To adjust the potentials to the Ag/gCl, the ferrocenium/ferrocene couple is assumed to lie at 0.72 V versus NHE in DMF [32]. Glassy carbon electrode (BAS, A = 0.0314 cm^2) and coiled platinum wires were used as working and auxiliary electrodes, respectively. For the electrolysis experiments, a compartmentalized cell was employed where the reference and the counter electrodes (Pt wire) were separately immersed in 0.1 mol L^{-1} NaTFA and isolated from the bulk solution by a glass frit. The working electrode was a platinum grid, which was cleaned by heating in a flame. UV–Vis spectra were simultaneously recorded by flow injection of the solution contained in the electrochemical cell into a UV quartz cell. Single crystals were used for data collection and cell parameter determination on an Enraf-Nonius Kappa-CCD diffractometer, using Mo Kα radiation (λ = 0.71073 Å). Data collection was made by using the COLLECT program [30]. Integration and scaling of the reflections were performed with the HKL DENZO-SCALEPACK system of programs [33]. Absorption corrections were carried out by using the GAUSSIAN method [32]. The structure was solved by direct methods with SHELXS-97

[31,33]. The models were refined by full-matrix least-squares on F^2 with SHELXL-97 [31,33].

3. Results and discussion

3.1. Precursor [(SO_3)Co(cyclam)(NCS)] complex

The simple [(SO_3)Co(cyclam)(*N*CS)] mononuclear complex only required recrystallization for purification. This process resulted in the formation of orange crystals suitable for determination of X-ray structure. Fig. 1 presents the ORTEP [35] view of *trans*-[(SO_3)Co(cyclam)(*N*CS)].

For the cyclam moiety, the C–C–N (112.28(2)°) average bond angle and the C–N (1.482(4) Å) and C–C (1.499(5) Å) average bond lengths are consistent with a *trans* configuration of nitrogen atoms of this ligand [36]. The S2–Co–N5 and Co–N5–C11 bond angles of 175.22(6)° and 178.3(2)°, respectively, are indicative of a linear conformation which is typically observed in complexes in which the NCS^- moiety is coordinated through the nitrogen atom [37–42]. This result is reinforced by the N5–C11 (1.149(3) Å) and C11–S1 (1.627(3) Å) bond lengths that are currently observed for complexes in which nitrogen is the donor atom of the NCS^- ligand [43–45]. The withdrawing effect of the $SO_3{}^{2-}$ ligand can be seen by comparing the Co–N(thiocyanate) bond lengths of two similar complexes, *trans* [(SO_3)Co(cyclam)(*N*CS)] (1.987(2) Å) and *trans*-[Co(cyclam)($NCS)_2$]NCS (1.883 Å) [43]. The observed difference is assigned to the *trans* influence induced by the $SO_3{}^{2-}$ ligand which decreases the Co–N(thiocyanate) bond strength thus increasing the respective bond length. This *trans* influence is well known and can be found elsewhere [27,46]. Additionally, for the $SO_3{}^{2-}$ group, the X-ray data indicate an approximate C_{3v} symmetry upon coordination to the metal through the sulfur atom. Similar result is observed for *trans*-[(OH_2)Co(Me_6[14]dieneN$_4$)(SO_3)] (Co–S(SO_3) = 2.2305 Å) [47].

The infrared spectrum of the *trans*-[(SO_3)Co(cyclam)(*N*CS)] complex presents the bands assigned [48,49] to a CH_2 rocking mode at 812 cm^{-1} and NH wagging modes of cyclam at 894 and 899 cm^{-1}. The bands observed at 507, 624, 980, and 1090 cm^{-1} are assigned to the vibrational modes of the $SO_3{}^{2-}$ ligand [50,51] and indicate the coordination through the sulfur atom as previously indicated by the X-ray discussion. The stretching vibrational mode of the CN bond, νCN, is observed at 2113 cm^{-1} which, in comparison to the NCS^- free ligand (2053 cm^{-1}), is indicative of a bond order increase. This is contrary to what would be expected based on the resonance structures proposed by Jones [52], where *N*-bonding favors a structure that results in a decrease of the CN bond order and vibrational frequency. However, the literature has shown that the νCN mode can exhibit more than one component due to distortions from regular octahedron symmetry which destroy the degeneracy of this band [53–55]. Therefore, for the *trans*-[(SO_3)Co(cyclam)(*N*CS)] complex, supported by the X-ray data, the band at 2113 cm^{-1} is assigned to the νCN mode of the *N*-bonded NCS^- moiety. The νCS and δNCS vibrational modes, which are observed at 760 and 475 cm^{-1}, respectively, reinforce this assignment.

Besides the intraligand absorption of the $SO_3{}^{2-}$ moiety at 226 nm, the electronic spectrum in the ultraviolet and visible regions of *trans*-[(SO_3)Co(cyclam)(*N*CS)] in water presents two absorptions at 290 and 481 nm. Because of the dependence of the former band on solvent, this absorption was assigned to a charge-transfer transition. By considering the data reported for Co^{3+} complexes [56] and *trans*-[(SO_3)Co(cyclam)(Cl)], this absorption is attributed to a ligand-to-metal charge transfer (LMCT) transition, $Co(d_{z2}) \leftarrow (\sigma)SO_3{}^{2-}$. The band of very low intensity at 481 nm, which presents no dependence on the solvent nature, is assigned to a d ← d transition of the metal atom although a LMCT contribution to NCS^- ligand cannot be ruled out [57].

It is well-known that the reduction of Co(III) to Co(II) in some complexes leads to the labilization of the axial ligands followed by

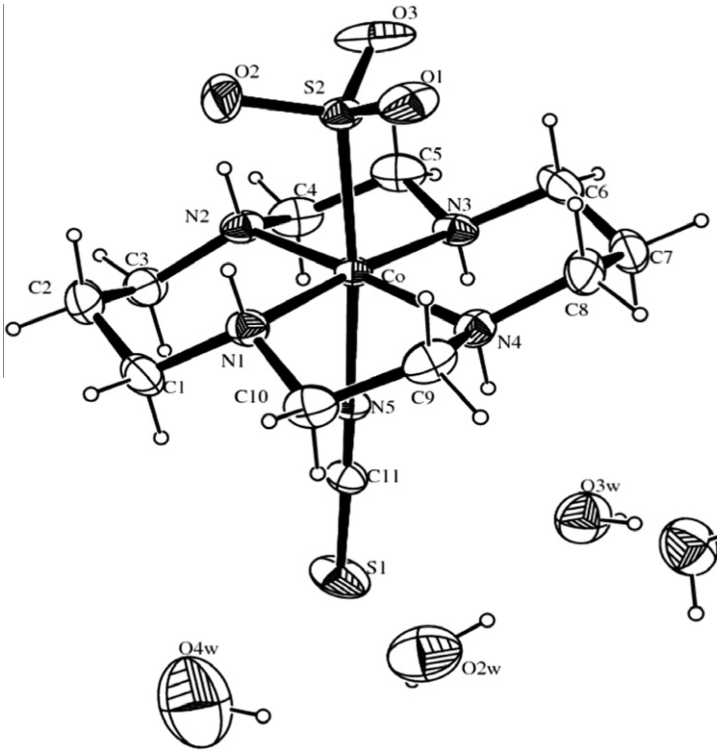


Fig. 1. ORTEP [34] view of *trans*-[(SO_3)Co(cyclam)(*N*CS)] showing the atoms labeling and 30% probability ellipsoids.

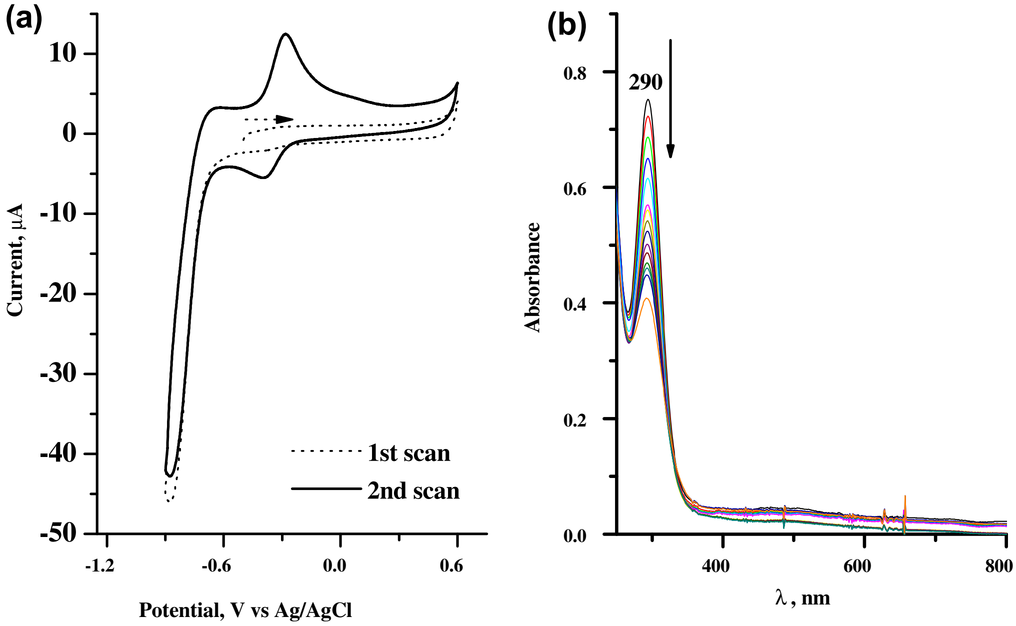


Fig. 2. (a) Cyclic voltammograms at 200 mV s^{-1} of the glassy carbon electrode in DMF containing 0.1 mol L^{-1} TBA and [(SO_3)Co(cyclam)(*N*CS)], (b) successive spectra of [(SO_3)Co(cyclam)(*N*CS)] in 0.1 mol L^{-1} NaTFA (pH 3.4) during electrolysis at −0.8 V versus Ag/AgCl.

$$\textit{trans}\text{-}[(SO_3)Co^{III}(cyclam)NCS] + e^- \rightleftharpoons \textit{trans}\text{-}[(SO_3)Co^{II}(cyclam)NCS]^- \qquad -0.80V$$

$$\textit{trans}\text{-}[(SO_3)Co^{II}(cyclam)NCS]^- \xrightleftharpoons{DMF} \textit{trans}\text{-}[Co^{II}(cyclam)(DMF)_2]^{2+} + SO_3^{2-} + NCS^-$$

$$\textit{trans}\text{-}[Co^{II}(cyclam)(DMF)_2]^{2+} \rightleftharpoons \textit{trans}\text{-}[Co^{III}(cyclam)(DMF)_2]^{3+} + e^- \qquad -0.28V$$

Scheme 1. Electrochemistry-chemistry-electrochemistry (ECE) mechanism suggested for [(SO_3)Co(cyclam)(*N*CS)] in DMF.

the substitution reaction of solvent molecules [58,59]. Therefore, from the electrochemistry of *trans*-[(SO_3)Co(cyclam)(*N*CS)] in DMF solution, illustrated in Fig. 2a, an electrochemistry-chemistry-electrochemistry (ECE) mechanism is suggested, which is summarized in Scheme 1.

According to Fig. 2a, the process centered at −0.28 V is dependent on the reduction of the cobalt center at −0.87 V for no process is observed at the first scan (dot line) in which the starting potential is −0.50 V (positive direction). Therefore, as suggested in Scheme 1, the wave observed at −0.87 V is assigned to the reduction of the metal center followed by a chemical reaction in which two solvent (DMF) molecules replace the axial ligands SO_3^{2-} and NCS^- forming [Co^{II}(cyclam)$(DMF)_2$]$^{2+}$. An irreversible reduction wave at −0.80 V was also observed for [Co(3-Cl-acacen)$(NH_3)_2$]Cl, where 3-Cl-acacen = bis(3-chloroacetylacetone)ethylenediimine, in acetonitrile being assigned to the reduction of Co^{III} to Co^{II} [59]. The proposed complex [Co^{II}(cyclam)$(DMF)_2$]$^{2+}$, in turn, experiences an electrochemical oxidation process at −0.28 V. This suggestion is reinforced by a decrease of the absorption at 290 nm (LMCT transition Co(d_{z2}) ← (σ)SO_3^{2-}) during the reductive electrolysis meaning that the metal center is being reduced (Fig. 2b). Similar behavior has been observed for the [(SO_3)Co^{III}(cyclam)Cl] starting complex. To reinforce this assignment, controlled potential electrolysis of [(SO_3)Co^{III}(cyclam)Cl] was carried out in aqueous medium and the product, upon isolation as a PF_6^- salt, was analyzed by FTIR and electrochemistry. The cyclic voltammogram of the isolated material in 0.1 mol L^{-1} NaTFA aqueous solution (pH 3.4) with glassy carbon working electrode presented two waves centered at −0.1 V versus Ag/AgCl. This value is in agreement with those reported for [Co(cyclam)$(H_2O)_2$]$^{3+}$ taking in account the pH of the electrolyte solution [22,60–63]. Fig. 3 presents the FTIR spectra of the material isolated before and after electrolysis at −0.80 V.

In the FTIR spectrum obtained after electrolysis, bands typically assigned to cyclam [48,49] are observed in the region from 3290 to 2850 cm^{-1} meaning that no demetalation (cobalt release) occurs upon Co reduction. In this spectrum, however, the bands associated with the SO_3^{2-} moiety (1020, 976, 614 and 495 cm^{-1}) are not observed. Also, the vibrational modes assigned [64,65] to the symmetric and asymmetric deformations of water (δ(HOH) and $\rho_r(H_2O)$) and to the symmetric stretching νCo–(OH_2) are observed, respectively, at 1678, 727 and 482 cm^{-1}. These observations corroborate with the suggestion of [Co^{II}(cyclam)$(H_2O)_2$]$^{2+}$ production upon reduction of [Co^{III}(cyclam)(SO_3)Cl] in aqueous medium. The bands at 846 and 559 cm^{-1} are assigned to the counter ion, PF_6^-.

3.2. Binuclear [(SO_3)Co(cyclam)-NCS-Ru$(NH_3)_4$(NCS)](BF_4) complex

The binuclear complex *trans*-[(SO_3)Co(cyclam)-NCS-Ru$(NH_3)_4$(*N*CS)](BF_4) was obtained, as far as we know, for the first time in this work, by the reaction of equimolar quantities of the mononuclear complexes *trans*-[(SO_3)Co(cyclam)(*N*CS)] and *trans*-[(SO_4)Ru$(NH_3)_4$(*N*CS)] according to Scheme 2.

The bands assigned to the νNH of cyclam [48,49] and NH_3 groups [66] are observed in the region from 3320 to 3170 cm^{-1} of the FTIR spectrum of the mixed-valence complex. The bands associated to the SO_3^{2-} moiety [50,51] are observed at 973 and 621 cm^{-1}. According to the literature [55,67], in a binuclear species, the νCN mode of the NCS^- ligand of a monomer should appear as two absorptions due to a band splitting with the higher and

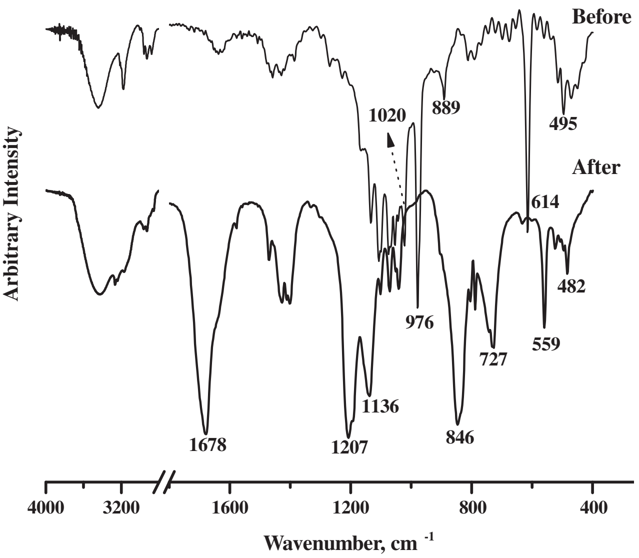


Fig. 3. IR spectra of the product isolated before and after electrolysis of $[(SO_3)Co^{III}(cyclam)Cl]$ at −0.8 V versus Ag/AgCl.

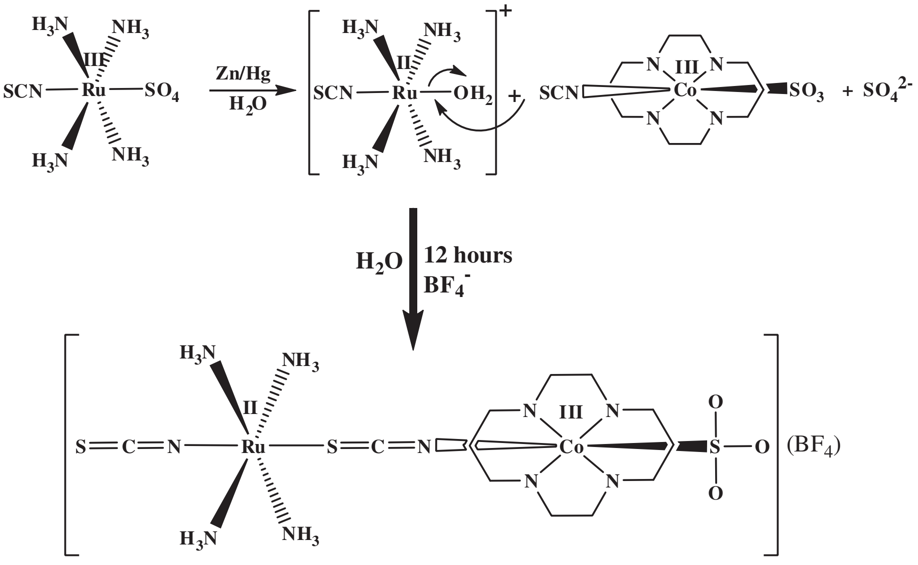
lower frequency values indicating the S- and N- coordination modes of the thiocyanate ligand, respectively. For the studied mixed-valence complex, there is, indeed, a splitting of the absorption observed at 2113 cm^{-1} in the spectrum of the cobalt monomer. However, a third band due to the NCS^- moiety of the $[Ru(NH_3)_4(NCS)_2]$ monomer (νCN at 2063 cm^{-1} [27]) is observed making the exact assignment difficult. Therefore, the bands observed at 2112, 2062 and 2004 cm^{-1} can be assigned to the νCN modes of the bridging and terminal NCS^- ligands. The νCS mode is observed at 740 cm^{-1} for the bridging NCS^- ligand and at 837 cm^{-1} for the terminal one.

The cyclic voltammogram of the binuclear complex presents two redox waves centered at 0.13 and −0.27 V versus Ag/AgCl in 0.1 mol L^{-1} NaTFA aqueous solution. The fact that the former process was observed in the first scan when the potential was scanned from +0.80 to −0.80 V versus Ag/AgCl suggests that the waves centered at 0.13 and −0.27 V can be assigned, respectively, to the $Ru^{II} \rightarrow Ru^{III}$ and $Co^{III} \rightarrow Co^{II}$ redox processes. Surprisingly, the redox processes of both the monomers, $[Co^{II}(cyclam)(H_2O)_2]^{2+}$ and $[Ru(NH_3)_4(NCS)_2]$, are observed at the same potential value, −0.10 V versus Ag/AgCl. The potential shift indicates a thermodynamic stabilization of the oxidized and reduced states of the cobalt and ruthenium metal centers, respectively, after the formation of the binuclear complex. At this point, a comment must be addressed: if $[(NCS)Ru(NH_3)_4(NCS)]$ is considered as monomer instead of $[Ru(NH_3)_4(NCS)_2]$, a more positive potential than −0.10 V would be expected based on the thermodynamic stabilization effect of the reduced state of transition metal atoms provided by sulfur atoms upon coordination [68–70]. Attempts were made in order to isolate $[(NCS)Ru(NH_3)_4(NCS)]$ but these were unsuccessful and only the *N*-bonded isomer, $[Ru(NH_3)_4(NCS)_2]$, was formed. By the way, this possibility reinforces the assignment of the more positive potential (0.13 V versus Ag/AgCl) to the $Ru^{III/II}$ redox couple.

The fact that the separation of the potential waves for the binuclear complex ($\Delta E_{1/2} = 0.40$ V) is higher than that observed between the monomers $[Co^{II}(cyclam)(H_2O)_2]^{2+}$ and $[Ru(NH_3)_4(NCS)_2]$ ($\Delta E_{1/2} = 0.0$ V), is an indication that such behavior is not only due to a different environment on the metal units but also to electronic interaction suffered by the second metal center. This conclusion indicates that there is electronic communication in the molecule through the bridging ligand. In addition, the value of the comproportionation constant, which was calculated [71] based on the $\Delta E_{1/2}$ value as 5.78×10^6, indicates a Class II system according to Robin and Day classification [72]. A similar value of 1.2×10^6 was observed for a cuboidal compound of molybdenum in which NCS^- is the bridging ligand [73].

Addition of oxidant and reductant species has been explored aiming to study the intervalence transition in mixed-valence compounds [10–13,74–77]. Persulphate and ascorbic acid were used in this work as oxidant and reductant species, respectively, and the effect of their addition to an aqueous solution of $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(NCS)]^+$ is illustrated in Fig. 4.

Spectrum (b) shows the absorption bands of $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(NCS)]^+$ without the addition of a redox agent. In comparison to the monomers, the UV–Vis–NIR spectrum of the binuclear complex presents new transitions in addition to those of the separated compounds suggesting a Class II system as anticipated by electrochemistry results. The absorption at 365 nm is assigned [55,56] to the LMCT transitions $Co(d\pi) \leftarrow (\pi)NCS^-$ and $Co(d_{z2}) \leftarrow (\sigma)SO_3^{2-}$. In comparison to the precursor cobalt complex, the bathochromic shift of this transition is suggested to be due to the coordination of $[Ru(NH_3)_4(NCS)]^+$ moiety which changes



Scheme 2. Schematic representation of the synthetic procedure of the heterobimetallic mixed-valence complex *trans*-$[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(NCS)](BF_4)$.

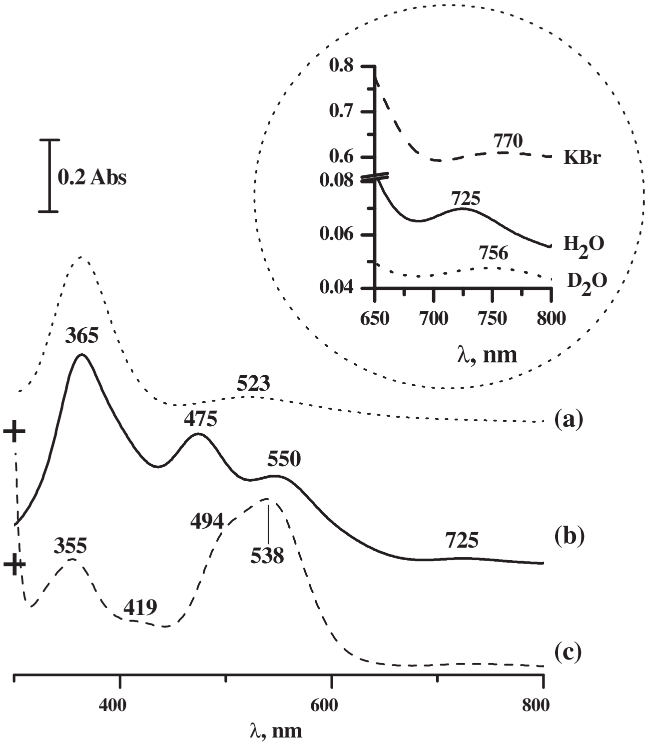


Fig. 4. UV–Vis–NIR spectra of $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(\mathit{N}CS)]^+$ in water (b) and after the addition of persulphate (a) and (c) ascorbic acid. Inset presents the spectra obtained in D_2O, KBr and water showing the region from 650 to 800 nm. **+** → zero absorbance for spectra (a) and (b).

the energy of d_{z2} orbital of Co^{3+} thus making it closer in energy to the σ orbitals of SO_3^{2-} ligand. The absorptions at 475 and 550 nm are associated to metal-to-ligand charge transfer (MLCT) transitions of ruthenium to thiocyanate, $\pi^*(NCS^-) \leftarrow d\pi(Ru^{II})$, since they disappear after oxidation (spectrum (c)). Also, this MLCT transition is observed at 490 nm in the UV–Vis spectrum of $[Ru(NH_3)_4(\mathit{N}CS)_2]$ in water. Because of the dependence of the absorption at 725 nm on the solvent nature (see Fig. 4 inset) and on the oxidation state of the metal centers, this band is assigned to an intervalence transition. From the Gaussian fit of this band in D_2O ($\lambda_{max.}$ = 756 nm), the experimental value of the band width at half height ($\Delta\nu_{1/2}$) was determined as $7166\ \mathrm{cm}^{-1}$ being higher than the calculated value of $4797\ \mathrm{cm}^{-1}$.[1] This result not only indicates a Class II system, but also allows the application of the Hush theory [77] for the determination of the electronic coupling parameter between the metal centers ($H_{MM} = 599\ \mathrm{cm}^{-1}$). This parameter, in turn, is important for understanding how efficiently the bridging ligand mediates the charge transitions between the metal centers. In fact, for the mixed-valence complex $[Cl(bpy)_2RuNCSRu(bpy)_2Cl]^{2+}$, where bpy = 2,2′-bipyridine is a non-innocent ligand, a H_{MM} of $453\ \mathrm{cm}^{-1}$ was observed indicating a relatively lower electronic communication-between the metal centers [78].

Upon oxidation of Ru^{2+} to Ru^{3+} (spectrum (a), addition of 0.5 equivalent of persulphate) or the reduction of Co^{3+} to Co^{2+} (spectrum (c), ascorbic acid addition), a strong decrease in intensity or even the disappearance of the band at 725 nm is observed. The band of low intensity observed at 523 nm in the spectrum (a) is assigned to a d–d transition of Ru^{3+} metal atom based on similar result observed for $[Ru(NH_3)_4(\mathit{N}CS)_2]^+$. The reduction of the oxidized solution leads to the same original spectrum (b) indicating the reversibility of the system upon oxidation. On the other hand, after reduction of Co^{3+} to Co^{2+} (spectrum (c)), no reversibility is observed. In fact, it is well known that some complexes of Co^{3+} release the ligands upon reduction [58,59] as previously commented. The spectrum of the reduced solution presents the bands typically assigned to the d–d transitions of Co^{2+} ion at 355 and 419 nm [57]. The band at 538 nm and the shoulder at 494 nm can be assigned to the MLCT transitions $NCS(p\pi^*) \leftarrow (d\pi)Ru^{2+}$ of $[(NC\mathit{S})Ru(NH_3)_4(\mathit{N}CS)]$ species in solution. While somewhat speculative on our part, a reasonable assignment is that, upon reduction, $[Co(cyclam)(H_2O)_2]^{2+}$ and $[(NC\mathit{S})Ru(NH_3)_4(\mathit{N}CS)]$ are produced.

4. Conclusions

The results all together indicate the isolation of $[(SO_3)Co(cyclam)(\mathit{N}CS)]$ and $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(\mathit{N}CS)](BF_4)$. For the $[(SO_3)Co(cyclam)Cl]$ starting complex, the release of SO_3^{2-} and Cl^- ligands was observed after the reduction of the metal center reinforcing the results acquired for the $[(SO_3)Co(cyclam)(\mathit{N}CS)]$ monomer. Electrochemistry and FTIR measurements acquired for the product isolated after reductive electrolysis indicated that $[Co(cyclam)(L)_2]^{2+}$ is formed after reduction, where L is solvent molecules. Upon coordination of $[(SO_3)Co(cyclam)(\mathit{N}CS)]$ to the $[Ru(NH_3)_4(\mathit{N}CS)]^{2+}$ metal center with the formation of the heterobimetallic mixed-valence complex, a thermodynamic stabilization of Co and Ru metal atoms in the oxidized and reduced states, respectively, was observed. According to the electrochemical results, there is electronic communication between the metal centers with a comproportionation constant of 5.78×10^6, which indicates a Class II system according to the Robin and Day classification. The UV–Vis–NIR spectrum of $[(SO_3)Co(cyclam)\text{-}NCS\text{-}Ru(NH_3)_4(\mathit{N}CS)]$ presented new transitions in addition to those of the separate compounds reinforcing this conclusion.

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Appendix A. Supplementary data

CCDC 803920 contains the supplementary crystallographic data for $[(SO_3)Co(cyclam)(\mathit{N}CS)]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[1] The calculated value was determined by using the following equation: $\Delta\nu_{1/2} = [2310(\nu_{max} - \Delta G)]^{1/2}$ where ν_{max} is the maximum of the intervalence band and ΔG is the driving force of the reaction, which was obtained from the difference between the redox potentials.

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