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Asymmetric heterobimetallic mixed-valence complex *trans*-[(SO$_3$)Co(cyclam)(NCS)Ru(NH$_3$)$_4$(*N*CS)](BF$_4$): Synthesis and characterization

Maria Aparecida S. Silva [a], Tércio de F. Paulo [a], Solange de O. Pinheiro [a], Alzir A. Batista [b], Javier Ellena [c], Eduardo H.S. Sousa [a], Luiz G. de F. Lopes [a], Izaura C.N. Diógenes [a],*

[a] *Departmento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, Cx. Postal 6021, Campus do Pici, Fortaleza, Ceará, Brazil*
[b] *Departamento de Química, Universidade Federal de São Carlos, Cx. Postal 676, 13565-905 São Carlos, SP, Brazil*
[c] *Instituto de Física de São Carlos, USP, Cx. Postal 780, 13560-250 São Carlos, SP, Brazil*

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ABSTRACT

[(SO$_3$)Co(cyclam)(*N*CS)] and [(SO$_3$)Co(cyclam)-NCS-Ru(NH$_3$)$_4$(*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)(*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)-NCS-Ru(NH$_3$)$_4$-(*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)(*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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* Corresponding author. Tel.: +55 85 33669844; fax: +55 85 33669978.
E-mail addresses: izaura@dqoi.ufc.br, izauradiogenes@yahoo.com.br (I.C.N. Diógenes).

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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
ρ_{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