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Synthesis of Rhodium(III), Iridium(III) and Osmium(III) Complexes with tris(2-Aminoethanethiolato)cobalt(III)

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Abstract

Polynuclear sulfur bridged complexes where the neutral complex tris(2-aminoethanethiolato)cobalt(III) acts as a tridentate ligand to rhodium(III), iridium(III) and osmium(III) have been prepared. These complexes have been characterized by electronic spectroscopy, vibrational spectroscopy and nuclear magnetic resonance spectroscopy. Along with the previously prepared complexes of iron(III), ruthenium(III) and cobalt(III), these complexes form two series of complexes with the group 8 and group 9 elements from all three transition series.

Introduction

Transition metal complexes of 2-aminoethanethiol are of considerable interest because of the similarity of this ligand to the naturally occurring amino acid cysteine and because of the known ability of divalent sulfur compounds to protect against ionizing radiation [1] and alkylating agents [2]. The ligand 2-aminoethanethiol has been shown to form both mononuclear and polynuclear complexes with various divalent and trivalent transition metal ions [3, 4]. The mononuclear complexes are known with many metal ions and several forms, including ML_2 and ML_3. Among the complexes of the ML_2 form, the complexes with palladium(II), cadmium and zinc are well known [4]. Of the mononuclear complexes of the ML_3 form, perhaps the most heavily studied is tris(2-aminoethanethiolato)cobalt(III) [5] which is also the starting material for many of the polynuclear complexes.

Polynuclear complexes are also known in several different formula types, including M_3L_4 and M_3L_6 for several metal ions. These complexes have been the subject of a number of studies, which have used various techniques, including X-ray crystallography [6], kinetic measurements [7] and various types of spectroscopy [8]. Of these complexes, the best known is hexakis-(μ(2-aminoethanethiolato-*N,S*:*S*)-tricobalt(III) which has been the subject of a number of studies [9–11].

The complexes of interest in this study are complexes of the form $M_2M'L_6$ where the neutral complex tris(2-aminoethanethiolato) cobalt(III) acts as a tridentate ligand toward various metal ions. Complexes of this type are known for various divalent metal ions; including lead(II) [9], cadmium [9], nickel(II) [5], copper(II) [10] and zinc [5], and trivalent metal ions including ruthenium(III) and iron(III) [11]. Many of these complexes have also been studied using various instrumental techniques.

In this study, we report the synthesis and characterization of the complexes hexakis(μ-(2-aminoethanethiolato-*N,S*:*S*))biscobalt(III) rhodium(III) perchlorate, hexakis(μ-(2-aminoethanethiolato-*N,S*:*S*))biscobalt(III) rhodium(III) perchlorate and hexakis(μ-(2-aminoethanethiolato-*N,S*:*S*))biscobalt(III) osmium(III) perchlorate. These complexes have been characterized using various instrumental methods, including electronic spectroscopy, vibrational spectroscopy and nuclear magnetic resonance spectroscopy. These complexes, along with the known complexes of tris(2-aminoethanethiolato)cobalt(III) with iron(III), ruthenium(III) and cobalt(III) represent two series of complexes with the trivalent metal ions of group 8 and group 9.

Experimental

Physical Methods

Electronic spectra were measured using a Perkin-Elmer Lambda 4b spectrophotometer in either aqueous or dimethylsulfoxide solution. Non-resolved peaks were analyzed using first and second derivatives of the measured spectrum. Infrared spectra between 4000 and 450 cm^{-1} were recorded as Nujol mulls between KBr windows and as KBr pellets using a Perkin-Elmer model 283 spectrophotometer. Far infrared (600–200 cm^{-1}) spectra were measured as cesium iodide pellets. Cesium iodide was dried at 200 °C under vacuum and stored in a desiccator prior to use. Proton NMR spectra were measured using a

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Varian model 360 L NMR spectrometer on D_2O or DMSO (d_6) solutions of the complex. Elemental analysis (C, H, N) was performed by Guelph Chemical Laboratories, Guelph, Ont., Canada.

Synthesis

Tris(2-aminoethanethiolato)cobalt(III) [CoL₃]

This complex was prepared by the method of Gorin *et al.* [12].

Hexakis-(μ-(2-aminoethanethiolato-N,S:S)-tricobalt(III) bromide [Co₃L₆]Br₃

This complex was prepared by the method of Jicha and Busch [5]. The complex was converted to the perchlorate salt by recrystallization from aqueous sodium perchlorate.

Hexakis-(μ-(2-aminoethanethiolato-N,S:S))-biscobalt(III) iron(III) chloride [Fe(CoL₃)₂]Cl₃ and hexakis-(μ-(2-aminoethanethiolato-N,S:S))-biscobalt(III) ruthenium(III) chloride [Ru(CoL₃)₂](ClO₄)₃

These complexes were prepared by the method described by Blinn *et al.* [11]. These complexes were converted to the perchlorate salts upon recrystallization from a solution containing a large excess of sodium perchlorate. This complex was also prepared by the method described for $[Rh(CoL_3)_2](ClO_4)_3$.

Hexakis-(μ-2-aminoethanethiolato-N,S:S))-biscobalt(III) rhodium(III) perchlorate [Rh(CoL₃)₂](ClO₄)₃

This complex was prepared by placing 1.0 g of CoL_3 and 0.25 g of rhodium(III) chloride trihydrate in a soxhlet extraction thimble and extracting for 3 h with water. Sodium perchlorate was then added to the extraction flask and the flask cooled resulting in the crystallization of the desired complex. The product was recrystallized from an aqueous solution of sodium perchlorate. *Anal.* Calc. for $RhCo_2Cl_3S_6O_{12}C_{12}H_{36}N_6$: C, 14.77; H, 3.72; N, 8.61. Found: C, 14.80; H, 3.70; N, 8.56%.

Hexakis-(μ-(2-aminoethanethiolato-N,S:S))-biscobalt(III) iridium(III) perchlorate [Ir(CoL₃)₂](ClO₄)₃

This complex was prepared by the same method as $[Rh(CoL_3)_2](ClO_4)_3$ by substituting iridium(III) chloride trihydrate for rhodium(III) chloride trihydrate. *Anal.* Calc. for $IrCo_2Cl_3S_6O_{12}C_{12}H_{36}N_6$: C, 13.53; H, 3.41; N, 7.89. Found: C, 13.47; H, 3.39; N, 7.78%.

Hexakis-(μ-(2-aminoethanethiolato-N,S:S))-biscobalt(III) osmium(III) perchlorate [Os(CoL₃)₂](ClO₄)₃

This complex was prepared by the same method as $[Rh(CoL_3)_2](ClO_4)_3$ substituting osmium(III) chloride for rhodium(III) chloride trihydrate. *Anal.* Calc. for $OsCo_2Cl_3S_6O_{12}C_{12}H_{36}N_6$: C, 13.55; H, 3.41; N, 7.90. Found: C, 13.62; H, 3.43; N, 7.85%.

Results and Discussion

Synthesis

All of the complexes are dark brown crystalline or microcrystalline solids which are soluble in water and dimethylsulfoxide. The solids can be conveniently recrystallized from a concentrated aqueous solution of sodium perchlorate. After recrystallization, the complexes are similar in appearance to other known complexes of this type. The ruthenium complex prepared by the soxhlet extraction procedure has an identical electronic and vibrational spectrum to a sample prepared by previously published methods [11]. Yields of the desired complexes prepared by the extraction procedure are in the range of 50–70%. The solubility of the complexes in aqueous sodium perchlorate solution and the slow hydrolysis of these complexes to give $[Co_3L_6]^{3+}$ in aqueous solution tend to decrease the yields.

The preparative procedure using soxhlet extraction, described above, has advantages over previously used methods for the preparation of these complexes. Previous preparations rely upon a large excess of the hetero metal ion to minimize contamination by $[Co_3L_6]^{3+}$ formed from the hydrolysis of CoL_3 in aqueous solution [13]. Cost prohibits the use of large excesses of the metal ions used in this study so an alternative synthetic scheme was required. These metal ions form relatively inert complexes, suggesting a small excess of the metal ion could minimize contamination from $[Co_3L_6]^{3+}$. The controlled excess of the desired metal ion results from the dissolution of the metal chloride in the soxhlet extraction thimble. The extraction thimble also allows for the convenient removal of unreacted CoL_3 which is insoluble in water and often results in contamination of the products prepared by other methods [13]

Proton Magnetic Resonance

The proton nuclear magnetic resonance spectra for this series of complexes are very similar to the spectra observed for other complexes of this type. With the exception of $Fe(CoL_3)_2{}^{3+}$ the spectra all appear very similar (NMR data is given in Table I). The NMR spectrum of $Fe(CoL_3)_2{}^{3+}$ is substantially broader than the other spectra, consistent with a paramagnetic first row transition metal ion [14]. The NMR spectra are characterized by broad peaks assigned to the amine protons near 4.5 ppm. The chemical shift of the amine protons of the group 9 complexes increase as the size of the metal ion increases. For the group 8 complexes $[Ru(CoL_3)_2]^{3+}$ and $[Os(CoL_3)_2]^{3+}$ the same pattern is observed. The

TABLE I. Proton NMR Data for Polynuclear tris(2-Aminoethanethiolato)Cobalt(III) Complexes with Group 8 and 9 Metal Ions

Complex	N–H chemical shift (δ from TMS)[a]		C–H chemical shift (δ from TMS)	
Group 8				
$Fe(CoL_3)_2(ClO_4)_3$	5.3(2)		3.1(2)	2.1(2)
$Ru(CoL_3)_2(ClO_4)_3$	6.3(1)	5.5(1)	2.9(2)	2.2(2)
$Os(CoL_3)_2(ClO_4)_3$	4.7(1)	4.5(1)	2.8(2)	2.0(2)
Group 9				
$Co_3L_6(ClO_4)_3$	4.6(1)	4.3(1)	2.8(2)	2.0(2)
$Rh(CoL_3)_2(ClO_4)_3$	4.7(1)	4.3(1)	2.7(2)	1.9(2)
$Ir(CoL_3)_3(ClO_4)_3$	4.8(1)	4.4(1)	2.8(2)	1.7(2)

[a] All NMR spectra measured in DMSO solution. Chemical shifts are measured relative to TMS.

complex $[Fe(CoL_3)_2]^{3+}$ does not follow this pattern possibly due to the broadening due to the paramagnetism of the Fe^{3+} bridging metal atom [14].

The region between 3.3 and 1.2 ppm shows several broadened features due to the remainder of the ligand. The observed spectra are broad in part due to the coupling with the metal three ions [15] and, in the case of group 8 metal ions, the magnet associated with the bridging metal ion. The splitting of the amine resonances indicates that the chelate rings are rigid [16]. This observation is consistent with the fact that many of these complexes have been resolved into their optical isomers [17]. The observation that the NMR spectra of these complexes are all similar (particularly the complexes with the paramagnetic group 8 metals) indicates that the electronic structure of the hetero metal atom has at most a small effect on the electronic structure of the CoL_3 groups [8]. This observation is consistent with the observation by Brubaker and Douglas [8] that the electronic structure of these complexes can be treated as the sum of the trigonal CoL_3 electronic spectrum and the electronic spectrum of the hetero metal atom surrounded by six sulfur atoms.

Vibrational Spectroscopy

Vibrational spectra for all of the complexes in this study were measured in the solid state. While much of the spectrum appears the same, the spectra show small bridging ion dependent absorption bands in the regions 1620–1540, 1160–1020 and 1000–800 cm^{-1}. The energy differences between the various complexes are, however, small. An interpretation of these small differences in high energy vibrational modes will not be attempted.

The long wavelength region of the infrared spectrum has several absorption bands which show changes based on the bridging metal ion. The positions of these absorption bands are given in Table II.

TABLE II. Low Energy Vibrational Modes for Polynuclear Complexes with tris(2-Aminoethanethiolato)cobalt(III) and Group 8 and Group 9 Transition Metals

Complex	Infrared absorption bands (cm^{-1})						
CoL_3			280	356	400	493	512
Group 8							
$Fe(CoL_3)_2(ClO_4)_3$			260	355	392		510
$Ru(CoL_3)_2(ClO_4)_3$	210	231	242	366			517
$Os(CoL_3)_2(ClO_4)_3$	210	237	262	368			520
Group 9							
$Co(CoL_3)_2(ClO_4)_3$	228		251	369		452	523
$Rh(CoL_3)_2(ClO_4)_3$	211	236	260	360			511
$Ir(CoL_3)_2(ClO_4)_3$		245	260	362			517

The absorption bands at approximately 510 and 360 cm^{-1} appear in all of the complexes at about the same energy consistent with vibrational modes related to the Co–N stretching vibration [18]. The absorption band at 250–280 cm^{-1} also appears in all complexes although the energy is much more variable. This vibration has been assigned to a mode which is primarily Co–S stretching. This band, as expected, shifts to lower energy in the polynuclear complexes due to the sulfur acting as a bridging atom [19].

Several other low energy vibrations are also present in these complexes. These modes may be due to vibrations around the bridging metal atom. Although the symmetric stretching vibrations around this bridging metal atom are expected to be extremely weak due to the nearly octahedral geometry [6] of the coordination sphere, some of the other vibrational modes are expected to be infrared active [18].

Electronic Spectroscopy

The visible regions of the electronic spectrum of the complexes prepared in this study are all dominated by transitions at the CoL_3 ligands. The absorption maxima and molar extinction coefficients for the three complexes prepared in this study and several known compounds are shown in Table III. This observation is consistent with the electronic spectra of other complexes in this series. The visible absorption bands (due to the CoL_3 ligand) do show small changes in energy with changes in the bridging metal ion.

The lowest energy visible absorption band can be assigned to the $^1A_{1g} > {}^1T_{2g}$ transition of the cobalt(III) ion in an octahedral symmetry. The second absorption band, at a higher energy is assigned to the $^1A_{1g} > {}^1T_{1g}$ transition of the cobalt(III) ion [8]. The splitting of these transitions due to the trigonal nature of the ligand field has been previously observed to be small, and not resolvable by visible absorption spectroscopy. These transitions, while

TABLE III. Electronic Spectral Data for Complexes of Group 8 and Group 9 Transition Metal Ions with tris(2-Aminoethanethiolato)Cobalt(III)

Complex	${}^1A_{1g}$–${}^1T_{2g}$ $^{a, b}$	${}^1A_{1g}$–${}^1T_{1g}$	Ultraviolet transitions
Group 8			
$Fe(CoL_3)_2(ClO_4)_3$	580(sh)	436(6400)	342(20000) 251(27000)
$Ru(CoL_3)_2(ClO_4)_3$	560(sh)	435(7900)	348(18700) 271(25200)
$Os(CoL_3)_2(ClO_4)_3$	570(sh)	439(8300)	348(24000) 276(28000)
Group 9			
$Co(CoL_3)_2(ClO_4)_3$	540(sh)	438(4600)	350(21000) 276(28000)
$Rh(CoL_3)_2(ClO_4)_3$	560(sh)	432(6400)	346(14000) 274(22000)
$Ir(CoL_3)_2(ClO_4)_3$	570(sh)	433(8900)	349(22000) 279(28000)

^{a}Numbers in parentheses are the molar absorptivities for the complexes. ^{b}Electronic transitions assigned based upon octahedral symmetry.

assigned to ligand field transitions of the cobalt ion, are unusually intense due in part to charge transfer involving the sulfur bridges. The energy of the visible absorption bands has been shown to depend upon the Alred electronegativity of the bridging metal ion, however this dependence is only small [9].

The ultraviolet absorption bands observed for this series of complexes are much more intense than the visible absorption bands. These transitions have been ascribed to a complex charge transfer transition involving the terminal cobalt(III) ions, the sulfur bridges and the central metal ion [8]. The energies and molar extinction coefficients for these absorption bands are also included in Table II. The ultraviolet bands, which do have a dependence on the bridging metal ion, still appear to be strongly dependent upon the cobalt. The general appearance of the electronic spectra suggests that the transitions of the cobalt complex, which act as a ligand, are much more intense than any transitions involving the bridging metal ion.

Conclusions

In this study, we have demonstrated the utility of a synthetic scheme which allows for the preparation of polynuclear complexes with heavier transition elements. These complexes have been characterized using spectroscopic methods. The spectroscopic studies are consistent with an earlier study [8] in which the electronic spectra were found to be dominated by transitions from the CoL_3 ligand with small perturbations from the bridging metal ion. The low energy vibrational spectroscopic studies and NMR spectroscopic studies indicate small perturbations in the structure of the CoL_3 ligands due to the size and electronegativity properties of the bridging metal ion, in much the same manner as was observed in previous studies [9].

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