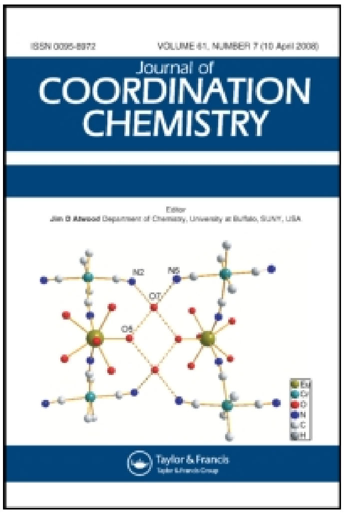

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Synthesis and Characterization of Lanthanide Complexes. Lanthanum(III), Cerium(III) and Europium(III) Derivatives with *Para*- and *Meta*-Substituted Benzeneseleninic Acids

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SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE COMPLEXES. LANTHANUM(III), CERIUM(III) AND EUROPIUM(III) DERIVATIVES WITH *PARA*- AND *META*-SUBSTITUTED BENZENESELENINIC ACIDS

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New complexes of lanthanum(III), cerium(III) and europium(III) with *para*- and *meta*-substituted benzeneseleninic acids of the type $XC_6H_4SeO_2H$ (X = H, *m*-Cl, *p*-Br, *p*-Me) are reported. The compounds $Ln(XC_6H_4SeO_2)_3$, $Ln(XC_6H_4SeO_2)_2Cl$, $Ln(XC_6H_4SeO_2)Cl_2$ and $Ln_2(XC_6H_4SeO_2)_3Cl_3$, where Ln denotes trivalent La, Ce, and Eu, have been studied using spectroscopic techniques (ir, far-ir and electronic spectra), magnetic susceptibility, thermogravimetric and conductivity measurements. The electronic spectra of the 1 : 3 derivatives have been analysed and spectral parameters are calculated and discussed for the europium complexes. The ir data point to a seleninato-*O,O'* coordination for all the complexes; in particular, the presence of three SeO bands with irreducible representation $A_2 + 2E$ in the ir spectra of the tris derivatives suggests an octahedral configuration with D_3 symmetry. All the halo derivatives are polymeric and octahedral in nature with bridging halide atoms. The magnetic moment values lie in the expected ranges and show very little deviation from Van Vleck values.

Keywords: Benzeneseleninic acids, lanthanides, complexes, synthesis

INTRODUCTION

The benzeneseleninato ion $RSeO_2^-$ is well known for its capability to coordinate a metal ion as a unidentate or bidentate ligand, in the latter case either inter- or intramolecularly, through the two oxygens as well as one oxygen and the selenium atom. Its behaviour has already been investigated in great detail and reported in previous papers. Infrared spectroscopy provides a convenient means to distinguish the different possibilities. Furthermore, the chemical reactivity and linkage isomers of several of these coordination compounds towards *N*-donor ligands have been described in other works. In addition, studies have described the ir spectra of *para*- and *meta*-substituted benzeneseleninic acids and their sodium salts, as well as their behaviour under electron impact, from which decomposition maps were proposed.[1]

This paper reports results concerning the preparation, properties and characterization of lanthanum(III), cerium(III), and europium(III) complexes with *para*- and *meta*-substituted benzeneseleninic acids, $XC_6H_4SeO_2H$ (X = H, *m*-Cl, *p*-Br, *p*-Me) in order to further our knowledge of this class of ligand and to gain information on *f*-block elements.

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TABLE I
Analytical data for the complexes.

		found		calcd.	
Compounds	colour	C%	H%	C%	H%
$La(C_6H_5SeO_2)_3 \cdot 2H_2O$	white	29.49	2.39	29.25	2.59
$La(m\text{-}ClC_6H_4SeO_2)_3$	white	26.67	1.60	26.80	1.50
$La(p\text{-}BrC_6H_4SeO_2)_3$	white	23.03	1.26	23.00	1.29
$La(p\text{-}MeC_6H_4SeO_2)_3 \cdot H_2O$	white	32.26	3.14	32.29	3.22
$Ce(C_6H_5SeO_2)_3 \cdot 2H_2O$	pale yellow	29.36	2.51	29.20	2.57
$Ce(m\text{-}ClC_6H_4SeO_2)_3$	pale yellow	26.58	1.47	26.76	1.49
$Ce(p\text{-}BrC_6H_4SeO_2)_3$	pale yellow	23.07	1.23	22.97	1.28
$Ce(p\text{-}MeC_6H_4SeO_2)_3 \cdot H_2O$	pale yellow	33.04	2.81	32.00	3.03
$Eu(C_6H_5SeO_2)_3$	white	30.07	2.22	30.19	2.11
$Eu(m\text{-}ClC_6H_4SeO_2)_3$	white	26.20	1.50	26.38	1.47
$Eu(p\text{-}BrC_6H_4SeO_2)_3 \cdot H_2O$	white	22.21	1.20	22.27	1.45
$Eu(p\text{-}MeC_6H_4SeO_2)_3 \cdot 2H_2O$	white	31.43	2.84	31.76	3.17
$La(C_6H_5SeO_2)_2Cl \cdot H_2O$	white	25.09	2.35	25.35	2.13
$La(m\text{-}ClC_6H_4SeO_2)_2Cl$	white	23.46	1.48	23.27	1.30
$La(p\text{-}BrC_6H_4SeO_2)_2Cl$	white	19.96	1.06	20.35	1.14
$La(p\text{-}MeC_6H_4SeO_2)_2Cl \cdot 2H_2O$	white	27.02	2.70	27.36	2.95
$Ce(C_6H_5SeO_2)_2Cl \cdot H_2O$	yellow	25.30	2.15	25.30	2.12
$Ce(m\text{-}ClC_6H_4SeO_2)_2Cl$	pale yellow	23.27	1.32	23.22	1.30
$Ce(p\text{-}BrC_6H_4SeO_2)_2Cl$	pale yellow	20.74	1.12	20.31	1.13
$Ce(p\text{-}MeC_6H_4SeO_2)_2Cl$	pale yellow	29.06	2.81	29.00	2.43
$Eu(C_6H_5SeO_2)_2Cl \cdot H_2O$	ivory	24.92	2.11	24.82	2.08
$Eu(p\text{-}MeC_6H_4SeO_2)_2Cl \cdot H_2O$	pale yellow	27.32	2.86	27.58	2.65
$La_2(m\text{-}ClC_6H_4SeO_2)_3Cl_3$	white	20.47	1.17	20.56	1.15
$La_2(p\text{-}BrC_6H_4SeO_2)_3Cl_3$	white	18.39	1.11	18.24	1.02
$La_2(p\text{-}MeC_6H_4SeO_2)_3Cl_3$	white	25.68	2.31	25.47	2.13
$Ce_2(m\text{-}ClC_6H_4SeO_2)_3Cl_3 \cdot H_2O$	ivory	19.96	1.31	20.17	1.32
$Ce_2(p\text{-}BrC_6H_4SeO_2)_3Cl_3$	pale yellow	18.70	1.16	18.20	1.02
$La(m\text{-}ClC_6H_4SeO_2)Cl_2 \cdot H_2O$	white	16.16	1.18	16.00	1.34
$La(p\text{-}MeC_6H_4SeO_2)Cl_2 \cdot H_2O$	white	19.16	1.91	19.55	2.11
$Ce(C_6H_5SeO_2)Cl_2$	yellow	18.15	1.45	18.15	1.27
$Ce(m\text{-}ClC_6H_4SeO_2)Cl_2 \cdot 4H_2O$	ivory	14.25	1.79	14.25	2.39
$Ce(p\text{-}MeC_6H_4SeO_2)Cl_2 \cdot H_2O$	pale yellow	19.68	2.06	19.50	2.10

RESULTS AND DISCUSSION

The new compounds of general formula $Ln(XC_6H_4SeO_2)_3$, $Ln(XC_6H_4SeO_2)_2Cl$, $Ln(XC_6H_4SeO_2)Cl_2$ and $Ln_2(XC_6H_4SeO_2)_3Cl_3$, Ln = La(III), Ce(III), Eu(III), are obtained from $LaCl_3$, $CeCl_3$, and $EuCl_3$ and the corresponding sodium benzeneseleninate, according to the methods reported in the Experimental section. The complex formulae are reported in Table I together with their analytical data. They were characterized by conductivity measurements, room-temperature magnetic moment studies, electronic, ir and far-ir spectra, and thermal analyses (t.g. and d.t.g.). Major bands in the ir spectra are summarized in Tables II to V.

The complexes are powder-like or microcrystalline, stable in atmospheric conditions, and soluble in *N,N'*dimethylformamide (DMF), nitromethane and aceto-

TABLE II

Characteristic i.r. bands (cm^{-1}) for benzeneseleninato salts and lanthanide tris-derivatives.

Assignment	H	*m*-Cl	*p*-Br	*p*-Me
	Sodium salts			
$\nu(\mathrm{SeO})_{\mathrm{asym}}$	781	817	807	817
$\nu(\mathrm{SeO})_{\mathrm{sym}}$	768	795	786	792
$\nu(\mathrm{SeC})$	666	652	708	700
$\delta(\mathrm{OSeC})$	384, 350	379, 339	386, 348	393, 363
	Lanthanum derivatives			
$\nu(\mathrm{SeO})A_2$	760vs	790s	809s	800vs*
$\nu(\mathrm{SeO})E$	740vs	777s	795sh	760vs
$\nu(\mathrm{SeO})E$	690s	750s	751s	—
$\nu(\mathrm{SeC})$	665m	645m	701m	698m
$\delta(\mathrm{OSeC})$	394m, 340m	375m, 330m	380m, 340m	390m, 340m
$\nu(\mathrm{LaO})$	364s, 275m	395ms, 275mw	360m, 274m	355m, 275m
	Cerium derivatives			
$\nu(\mathrm{SeO})A_2$	760vs	789vs	810s	801vs*
$\nu(\mathrm{SeO})E$	745vs	772vs	795sh	759vs
$\nu(\mathrm{SeO})E$	689vs	749vs	752s	715m
$\nu(\mathrm{SeC})$	667m	648m	700m	698m
$\delta(\mathrm{OSeC})$	372m, 345m	355m, 328m	370m, 345m	392m, 345m
$\nu(\mathrm{CeO})$	356ms, 279m	360ms, 264m	360ms, 271m	360ms, 269m
	Europium derivatives			
$\nu(\mathrm{SeO})A_2$	762vs	790vs	806vs	800vs*
$\nu(\mathrm{SeO})E$	745vs	772vs	790ms	749vs
$\nu(\mathrm{SeO})E$	683vs	750vs	745vs	710m
$\nu(\mathrm{SeC})$	665m	644m	708m	695m
$\delta(\mathrm{OSeC})$	373m, 345m	375m, 325m	380m, 350m	390m, 360m
$\nu(\mathrm{EuO})$	360ms, 265m	368m, 271m	367m, 265m	360m, 262m

* Overlapping $\gamma(\mathrm{CH})$ of benzene.

nitrile. All these derivatives are non conducting in the above solvents, and the absence of ionic species is indicative of the covalent nature of the compounds.

Electronic Spectra

The cerium(III) complexes $\mathrm{Ce(XC_6H_4SeO_2)_3}$ exhibit in acetonitrile an intense absorption band at 29200 cm^{-1} and a group of bands at higher frequencies centred near 40000 cm^{-1}; these can be assigned to $4f \rightarrow 5d$ transitions. These bands are attributed to electron transitions from the ground state ${}^2F_{5/2}(4f^1)$ to the lowest ligand-field components originating from the ${}^2D_{3/2,\,5/2}(5d^1)$ levels. Such assignment is supported by the small values of the half-widths of these bands, ($\delta = 1000\ \mathrm{cm}^{-1}$), a feature which is considered to be characteristic of intershell transitions, in contrast to the larger half-widths of the electron-transfer transitions ($\delta = 2000$–$2500\ \mathrm{cm}^{-1}$).[2]

TABLE III
Characteristic i.r. bands (cm^{-1}) for lanthanum benzeneseleninato chloro derivatives.

Assignment	H	*m*-Cl	*p*-Br	*p*-Me
		LaL_2Cl derivatives		
$\nu(SeO)_{asym}$	740vs	775ms	800vs*	795vs*
$\nu(SeO)_{sym}$	682vs	742ms	752ms	745ms
$\nu(SeC)$	665m	645m	704m	690m
$\delta(OSeC)$	382m, 344m	378m, 320m	378m, 325m	395m, 350m
$\nu(LaO)$	366ms	367ms	361ms	357m
$\nu(LaCl)$	197m$_b$	168s$_b$	189w$_b$	190m$_b$
		$La_2L_3Cl_3$ derivatives		
$\nu(SeO)_{asym}$		775s	809vs*	805vs*
$\nu(SeO)_{sym}$		747s	753vs	750m
$\nu(SeC)$		645m	700m	695m
$\delta(OSeC)$		376m, 330m	368m, 350m	400m, 368m
$\nu(LaO)$		360ms	358m	355m
$\nu(LaCl)$		172s$_b$	168m$_b$	189m$_b$
		$LaLCl_2$ derivatives		
$\nu(SeO)_{asym}$		770vs		789vs
$\nu(SeO)_{sym}$		741vs		754vs
$\nu(SeC)$		648m		690m
$\delta(OSeC)$		378m, 350m		398m, 351m
$\nu(LaO)$		365ms		359m
$\nu(LaCl)$		170ms$_b$		170ms$_b$

* Overlapping γ(CH) of benzene.

Indeed, a rough estimate of the nephelauxetic effect, $\beta(Ce^{III}, 5d)$, for 5*d* orbitals, may be calculated according to the formula:[3]

$$(1 - \beta)(Ce^{III}, 5d) = [h(XC_6H_4SeO_2H)][k(Ce^{III}, 5d)]$$

Use of values of $h(XC_6H_4SeO_2H)$ equal to 0.91, 0.89, 0.91 and 0.89 for X = H, *m*-Cl, *p*-Br and *p*-Me, respectively, calculated from our previous studies, $k(Ce^{III}, 5d) = 0.13$[4] and $E_{free\ ion}(Ce^{III}, 5d) = 51.200\,cm^{-1}$,[5] gives $\beta = 0.79$ and $E_{mean}(Ce^{III}, 5d) = [\beta(Ce^{III}, 5d)]\,[E_{free\ ion}(Ce^{III}, 5d)] = 40500$, in very good agreement with the position of the above reported bands. According to this spectral assignment the overall splitting of the 5*d* shell in this CeO_6 chromophore is 11300 cm^{-1}, a value which is to be compared with $\Delta(oct) = 8000–12000\,cm^{-1}$ for octahedral CeO_6 chromophores in a number of oxide lattices.[6]

For the europium(III) derivatives $Eu(XC_6H_4SeO_2)_3$, the ground multiplet of europium(III), $^7F_0$, is very deep and its levels do not overlap with those of the next multiplet, $^5D_0$. The $^7F_0 \rightarrow {}^5D_0$ transitions are located in the visible region. The excited levels of the ground multiplet, $^7F_1$, and $^7F_2$ are only 360 cm^{-1} and 1000 cm^{-1} above the ground level and are also populated at room temperature. Thus the number of possible transitions in the visible and ultraviolet regions of the absorption spectra of europium(III) is very high; however many of them are forbidden by selection rules. In the electronic spectra of the reported complexes the transition at 33760–30600 cm^{-1} may be assigned to the transitions $^7F_0 \rightarrow {}^5F_2$ and $^7F_1 \rightarrow {}^5F_4$, $^5I_4$ in overlap. The absorption bands at lower energy, 30100–29850 cm^{-1}, can be assigned to the $^7F_0 \rightarrow {}^5H_4$ transition superimposed upon the absorption arising from the $^7F_1 \rightarrow {}^5H_5$ transition.[7]

TABLE IV

Characteristic i.r. bands (cm^{-1}) for cerium benzeneseleninato chloro derivatives.

Assignment	H	*m*-Cl	*p*-Br	*p*-Me
		CeL_2Cl derivatives		
$\nu(SeO)_{asym}$	745vs	778ms	790vs	790vs*
$\nu(SeO)_{sym}$	689vs	745ms	730vs	730vs
$\nu(SeC)$	668m	644m	703m	692sh
$\delta(OSeC)$	370m, 341m	375m, 319m	379m, 320m	389m, 365m
$\nu(CeO)$	355m	365ms	362s	362m
$\nu(CeCl)$	168m$_b$	170m$_b$	170s$_b$	168m$_b$
		$Ce_2L_3Cl_3$ derivatives		
$\nu(SeO)_{asym}$			770vs	795vs
$\nu(SeO)_{sym}$			745vs	742m
$\nu(SeC)$			641m	699m
$\delta(OSeC)$			367m, 338m	405m, 371sh
$\nu(CeO)$			358ms	364m
$\nu(CeCl)$			170m$_b$	167m$_b$
		$CeLCl_2$ derivatives		
$\nu(SeO)_{asym}$	739vs	765vs		791vs*
$\nu(SeO)_{sym}$	685vs	739vs		745ms
$\nu(SeC)$	668m	651m		688m
$\delta(OSeC)$	385m, 352m	388m, 361m		395m, 355m
$\nu(CeO)$	364m	360ms		360ms
$\nu(CeCl)$	170m$_b$	168m$_b$		173m$_b$

* Overlapping γ(CH) of benzene.

TABLE V

Characteristic i.r. bands (cm^{-1}) for europium benzeneseleninato chloro derivatives, EuL_2Cl.

Assignment	H	*p*-Me
$\nu(SeO)_{asym}$	750vs	775vs
$\nu(SeO)_{sym}$	682vs	710vs
$\nu(SeC)$	667m	688m
$\delta(OSeC)$	372m, 344m	381m, 350m
$\nu(EuO)$	350m	367m
$\nu(EuCl)$	173m$_b$	168m$_b$

The sharp, line-like internal $f \rightarrow f$ transitions originating within the $4f^n$ configuration of the lanthanide(III) ions are affected by the influence of the ligands on complexation. The nephelauxetic effect is usually of the order of a few per cent. The complexes reported show a negative shift in spectral bands when compared to those of the corresponding aquo ions due to the above reported nephelauxetic effect.[8,9] It has been generally agreed that the nature of the red shift may be conveniently used as a measure of metal–ligand covalent binding.[10–12] The nephelauxetic parameter β, where β is the average value of the ratio ν_{comp}/ν_{aquo}, taking into account as many transitions as possible, is in the range 0.92–0.93 for the europium(III) derivatives. From the β values, the δ parameter of covalency to express the covalency of metal–ligand bond, $\delta = 100(1 - \beta)/\beta$, and the bonding parameter $b^{1/2}$ have been evaluated,[9,14] where $b^{1/2} = (1 - \beta)^{1/2}/2$.

The δ values lie in the range 7.53 to 8.69 and the $b^{1/2}$ values vary from 0.14 to 0.13. The values of β, which are less than unity, and the positive values of δ and $b^{1/2}$ support covalent bonding between metal and ligand.

Magnetic Measurements

The magnetic moments of most of the lanthanide ions can be calculated by the use of the equation $\mu_{eff} = g[J(J + 1)]^{1/2}$. Unlike the *d* electrons of the transition metal ions, the *f* electrons of the lanthanide ions are almost unaffected by chemical environment and the energy levels are the same as in the free ion, due to the very effective shielding by the overlying $5s^2$ and $5p^6$ shells. For most of the lanthanide ions the ground state is separated by many hundreds of cm^{-1} from the next higher lying state.

Under these conditions the magnetic properties can be taken as those of the ground state alone, making the lanthanide ion in the compound act in the same way as the free ion, as far as the *f* electrons are concerned. However, the above equation fails to account for the magnetic behaviour of the Eu(III) ion (f^6), for which experimentally determined magnetic moments vary considerably with temperature. For this ion the first, and even the second and third, excited J states are sufficiently close in energy to the ground state to be appreciably populated at room temperature. Since these excited states have higher J values than the ground state, the actual magnetic moments are higher than those calculated by the use of the above equation with the value of J for the ground state. The lanthanum(III) complexes are diamagnetic, while μ values (room temperature) are in the ranges 2.00–2.21 B.M. and 2.71–3.05 B.M. for the cerium(III) and europium(III) derivatives, respectively.

Infrared Spectra

Assignments of i.r. bands were made on the basis of a detailed i.r. study of *para-* and *meta*-substituted benzeneseleninic acids and their sodium salts[15] and previous results concerning other transition metals.[1] The vibrational modes attributed to the substituent and fundamentals of benzene ring in the complexes appear at the same wavenumbers as in the free ligands; the same behaviour is observed for the ν(SeC) mode.

In the tris derivatives, $Ln(XC_6H_4SeO_2)_3$, three selenium–oxygen bands with irreducible representation $A_2 + 2E$ are present, Table II, as previously observed for analogous metal(III) complexes. This indicates that the complexes have an octahedral configuration with D_3 symmetry. Taking into account the fact that the mono- and disubstituted benzene ring behaves differently (1000–650 cm^{-1}) in benzeneseleninic acid compared with *para*- and *meta*-substituted derivatives,[15–17] we observed in some cases overlapping of γ(C–H) with split ν(SeO) modes. In all halo derivatives, the symmetric and antisymmetric stretching modes of SeO_2 are shifted towards lower wavenumbers, Tables III–V. This shift suggests that the benzeneseleninato ion is *O,O'*-bonded, in accordance with the small frequency difference between modes, as previously observed for similar complexes.

The i.r. data as regards ν(OH) and δ(HOH) for all water-containing complexes clearly confirm the presence of lattice water and exclude the presence of coordinated water. These results agree well with the observations made on the thermogravimetric studies.

In the far i.r., Tables II–V, it is possible to assign the symmetric and antisymmetric deformations of δ(OSeC) in the 394–319 cm^{-1} range. In addition, in the spectra of all complexes, new bands, absent in the spectra of the starting materials, are present between 370 and 260 cm^{-1} in the case of the tris derivatives and around 360 cm^{-1} in the case of the halo complexes; these can be assigned to metal–oxygen stretches involving the SeO_2 group.[18,19] The medium or medium-strong bands present in the 197–167 cm^{-1} range for the chloro derivatives can be attributed to metal–halide vibrational modes. These are not present in the spectra of the starting materials and in those of the 1 : 3 derivatives reported here, are at frequencies too low to be attributed to terminal halide atoms; this is clearly indicative of the presence of bridging chloride atoms.[20] We thus propose polymeric structures for the halo derivatives, with the areneseleninato anions acting as *O,O'*-bidentates, either inter- or intramolecularly, and with all the halide atoms bridging metal ions to form octahedral geometries.

Thermogravimetric Studies

Results exclude the presence of coordinated water in the complexes, and unambiguously confirm the presence of lattice water. The t.g. curves of the 1 : 3 derivatives are characterized by a multistage process in the 35–1000°C range. The observed and calculated weight losses in the 45–140°C range agree with a loss of 1, 2, or 4 moles of water, depending on the water content of the complex, Table I. Following decomposition is quite complicated and most likely involves breakdown of ligands. The complexes lose all ligand molecules by 600°C to leave Ln_2O_3.

For the chloro derivatives, decomposition starts with loss of water in the 50–135°C range; second and third steps are characterized by successive loss of ligands over 140–600°C, then loss of halide giving the corresponding metal trioxides.

EXPERIMENTAL

Starting Materials

Benzeneseleninic acid, its *para*- and *meta*-substituted derivatives, and the corresponding sodium salts were prepared and purified according to previously described methods with small modifications introduced in order to improve yields.[1,21] Hydrated lanthanum(III), cerium(III) and europium(III) chlorides were obtained from Fluka (high purity).

Preparation of Complexes

The metal complexes were prepared by adding to an aqueous methanolic solution of the metal halide a methanolic solution of the ligands in 1 : 3, 1 : 2, 1 : 1.5 or 1 : 1 metal : ligand molar ratios; the solution was vigorously stirred at room temperature for about 30 minutes under nitrogen. The complexes, which precipitated spontaneously, were filtered off and washed with methanol and diethyl ether and dried over P_4O_{10}. Repeated syntheses (elemental analyses) gave reproducible results.

Measurements

I.r. spectra were recorded in the region 4000–50 cm^{-1} with a Bruker 113v FT-IR spectrophotometer. The spectra were measured in KBr in the 4000–400 cm^{-1} range and in polyethylene in the 400–50 cm^{-1} range. Atmospheric water was removed by flushing with dry nitrogen. Electronic spectra were recorded with a Shimadzu MPS-50L spectrophotometer in the solid state, the method of Venanzi and coworkers being used.[22] Solution spectra were recorded with a Varian Cary 2300 spectrophotometer using freshly prepared 10^{-2} M acetonitrile solutions. Susceptibility measurements were carried out at room temperature by the Gouy method and corrected for diamagnetism by use of Pascal's constants. The standard was Hg[$Co(SCN)_4$]. Thermogravimetric studies (t.g. and d.t.g) were performed in air on a Mettler TG50 thermobalance equipped with a Mettler TC10TA processor. A scan rate of 10°C min^{-1} was used. Conductivities were measured with a WTW LBR conductivity bridge using freshly prepared 10^{-3} M solutions in *N,N'*-dimethylformamide or acetonitrile at 25°C. Carbon and hydrogen analyses were performed using a Carlo Erba 1106 elemental analyser.

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