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Substituted benzeneseleninic acids as bidentate ligands. Synthesis and spectroscopic studies of manganese(II) and iron(II) complexes

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Abstract—The *para*- and *meta*-substituted seleninato anion, $XC_6H_4SeO_2^-$, forms complexes with manganese(II) and iron(II) of the type $[M(XC_6H_4SeO_2)_2(H_2O)_2]$, which have been shown to contain the bidentate ligand in seleninato-*O*, *O′* derivatives, the water molecules being coordinated to the metals. From the electronic absorption spectra and from the magnetic susceptibility data we have proposed for all the complexes a distorted octahedral D_{4h} symmetry. The structure of the anhydrous *para*- and *meta*-substituted benzeneseleninato complexes of manganese(II) and iron(II) have been investigated by means of electrical conductance measurements, spectral (electronic and i.r.) studies and magnetic susceptibility measurements. The anhydrous complexes are always of the seleninato-*O*, *O′* type with the ligands tetrahedrally coordinated to the central atom. The wavelengths of the principal absorption peaks have been accounted for quantitatively in terms of the crystal field theory for manganese(II) derivatives. The nephelauxetic parameters are all indicative of an appreciable metal–ligand covalency.

INTRODUCTION

Part of our interest in the study of the *para*- and *meta*-substituted benzeneseleninic acids centres on whether the seleninato ions $RSeO_2^-$ coordinate through selenium or oxygen in the metal complexes. The areneseleninato moiety is quite a peculiar ligand and its behaviour as monodentate or bidentate through the various potential donors (the two oxygen atoms and the selenium one) has already been investigated in great detail and reported in many previous papers [1–13]. Furthermore, the chemical reactivity and linkage isomers of several of these coordination compounds towards *N*-donor ligands have been observed in our studies [14–16].

In addition, in previous papers detailed studies have been described on the i.r. spectra of *para*- and *meta*-substituted benzeneseleninic acids and their sodium salts [17], as well as on their under-electron impact behaviour, from which decomposition maps were proposed [18, 19].

Our interest in this paper centres on whether the

Table 1. Analytical data and other physical properties

Compounds	Colour	Found % C	Found % H	Calcd. % C	Calcd. % H	μ B.M.
$Mn(C_6H_5SeO_2)_2$	ivory	33.2	2.3	33.4	2.3	5.92
$Mn(p\text{-}ClC_6H_4SeO_2)_2$	hazel brown	29.2	1.6	28.8	1.6	5.94
$Mn(m\text{-}ClC_6H_4SeO_2)_2$	light brown	28.5	1.7	28.8	1.6	5.89
$Mn(p\text{-}BrC_6H_4SeO_2)_2$	light brown	24.3	1.4	24.5	1.4	5.91
$Mn(m\text{-}BrC_6H_4SeO_2)_2$	pink-white	24.8	1.4	24.5	1.4	6.12
$Mn(p\text{-}MeC_6H_4SeO_2)_2$	ivory	37.0	3.0	36.6	3.1	6.14
$Fe(C_6H_5SeO_2)_2$	hazel brown	33.7	2.4	33.4	2.3	4.94
$Fe(p\text{-}ClC_6H_4SeO_2)_2$	brown	28.3	1.7	28.8	1.6	4.87
$Fe(m\text{-}ClC_6H_4SeO_2)_2$	brown	28.9	1.5	28.8	1.6	4.82
$Fe(p\text{-}BrC_6H_4SeO_2)_2$	pale brown	24.5	1.4	24.4	1.4	5.01
$Fe(m\text{-}BrC_6H_4SeO_2)_2$	pale brown	24.8	1.4	24.4	1.4	4.83
$Fe(p\text{-}MeC_6H_4SeO_2)_2$	brown	36.5	3.0	36.6	3.1	4.83

Table 2. Ligand field parameters and *Dq* independent bands (cm^{-1}) of manganese(II) derivatives

Compounds	$^6A_1 \rightarrow {}^4E, {}^4A_1(^4G)$	$^6A_1 \rightarrow {}^4E(^4D)$	B	C	$\overline{10Dq}$	Z^*
$Mn(C_6H_5SeO_2)_2$	23950	27600	521	3748	6270	0.56
$Mn(p\text{-}ClC_6H_4SeO_2)_2$	25000	28985	569	3862	5680	0.70
$Mn(m\text{-}ClC_6H_4SeO_2)_2$	24570	28410	549	3816	5740	0.64
$Mn(p\text{-}BrC_6H_4SeO_2)_2$	25840	29670	547	4074	6000	0.64
$Mn(m\text{-}BrC_6H_4SeO_2)_2$	24750	28570	546	3858	6040	0.63
$Mn(p\text{-}MeC_6H_4SeO_2)_2$	24700	28570	553	3834	6310	0.66

seleninato group coordinates through the oxygen atoms or in a different way on passing from the bis(benzeneseleninato)diaquo manganese(II) and iron(II) complexes to the anhydrous bis(benzeneseleninato) metal(II) derivatives.

RESULTS AND DISCUSSION

The complexes $[M(XC_6H_4SeO_2)_2(H_2O)_2]$, (M = Mn, Fe; X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-Me) were prepared by reaction of $MnAc_2$ and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ with the corresponding *para-* and *meta-*substituted sodium benzeneseleninate in aqueous solution [10, 11]. The dehydrated derivatives were obtained by drying, for about 3–4 h at 170–180°C, the above compounds.

The obtained anhydrous complexes are reported in Table 1 together with their analytical data and room temperature magnetic moment values. The solid state electronic spectra and the ligand field parameters are shown in Tables 2–4, while the most important i.r. data for the ligands and their metal complexes in the 4000–50 cm^{-1} range are listed in Table 5.

The compounds are microcrystalline or powder-like, paramagnetic, stable in atmospheric conditions and soluble in the most common organic solvents. All these derivatives are non-conducting in *N*,*N*′-dimethylformamide (DMF) and the absence of ionic species indicates the covalent nature of the compounds.

Electronic spectra and magnetic measurements

Manganese(II) compounds. Having manganese(II) a d^5 configuration, the same type of energy-level diagram applies both for tetrahedral and octahedral environment of the metal. The energies of the ${}^6A_1 \rightarrow {}^4E({}^4D)$ and of the ${}^6A_1 \rightarrow {}^4E, {}^4A_1({}^4G)$ transitions are independent of Dq and depend only on B and C. As a consequence, once the assignment of the bands of the spectra has been made, the calculations of the values for B and C are easily performed using the expressions for the energies of the excited states relative to the ground state:

$${}^4E({}^4D) = 17B + 5C$$

$${}^4E, {}^4A_1({}^4G) = 10B + 5C$$

These values of B and C, reported in Table 2, were then used in solving the secular equation of TANABE and

Table 3. Electronic spectra of manganese(II) complexes: observed and calculated energies (cm^{-1})

Compounds	${}^6A_1 \rightarrow {}^4T_1({}^4G)$ Obs.	Calcd.	$\delta\nu$	$\delta\nu$ %	${}^6A_1 \rightarrow {}^4T_1({}^4P)$ Obs.	Calcd.	$\delta\nu$	$\delta\nu$ %	${}^6A_1 \rightarrow {}^4T_1({}^4F)$ Obs.	Calcd.	$\delta\nu$	$\delta\nu$ %
$Mn(C_6H_5SeO_2)_2$	19800	20239	+439	2.16	32570	32866	+296	0.90		38426		
$Mn(p\text{-}ClC_6H_4SeO_2)_2$	20500	21827	+1327	6.07	34250	33662	−588	1.74	39700	40079	+379	0.94
$Mn(m\text{-}ClC_6H_4SeO_2)_2$	20200	21334	+1134	5.31	33670	33232	−438	1.32	39000	39349	+349	0.89
$Mn(p\text{-}BrC_6H_4SeO_2)_2$	20400	22512	+2112	9.38	33600	35076	+1476	4.21		41150		
$Mn(m\text{-}BrC_6H_4SeO_2)_2$	20000	21282	+1282	6.02	33600	33667	+67	0.20	39370	39647	+277	0.70
$Mn(p\text{-}MeC_6H_4SeO_2)_2$	20000	20520	+520	2.53	34010	34042	+32	0.09	39700	39850	+150	0.38

Table 4. Electronic spectra or iron(II) complexes (cm^{-1})

Compounds	${}^5E \rightarrow {}^5T_2$
$Fe(C_6H_5SeO_2)_2$	5200
$Fe(p\text{-}ClC_6H_4SeO_2)_2$	5130
$Fe(m\text{-}ClC_6H_4SeO_2)_2$	5180
$Fe(p\text{-}BrC_6H_4SeO_2)_2$	5150
$Fe(m\text{-}BrC_6H_4SeO_2)_2$	5200
$Fe(p\text{-}MeC_6H_4SeO_2)_2$	5180

Table 5. Most important i.r. bands (cm^{-1})

	Substituent					
	H	*p*-Cl	*m*-Cl	*p*-Br	*m*-Br	*p*-Me
			Sodium salt			
ν(SeO) asym.	781	811	817	807	817	817
ν(SeO) sym.	768	796	795	786	798	792
ν(SeC)	666		652	708	645	700
δ(OSeC)	384, 350	393, 360	379, 339	386, 348	379, 340	393, 363
			Manganese(II) tetrahedral complexes			
ν(SeO) asym.	748 vs	808 vs	780 vs	796 vs	775 vs	800 vs
ν(SeO) sym.	727 vs	730 vs	730 vs	725 m	720 s	745 s
ν(SeC)	660 m	695 sh	648 m	708 s	641 m	698 m
δ(OSeC)	400 ms, 350 m	395 w, 358 m	385 m, 345 m	390 m, 345 m	380 mw, 335 m	385 m, 360 mw
ν(Mn–O)	421 m	431 m	440 m	425 m	433 ms	432 m
			Iron(II) tetrahedral complexes			
ν(SeO) asym.	745 vs	810 vs	775 vs	807 vs	780 vs	800 vs
ν(SeO) sym.	719 vs	725 vs	715 vs	720 vs	718 vs	720 vs
ν(SeC)	670 m		668 s	705 m	640 ms	700 sh
δ(OSeC)	415 m, 355 mw	390 w, 360 w	370 m, 342 m	400 w, 340 m	350 m, 325 m	400 w, 360 m
ν(Fe–O)	455 ms	450 m	458 vs	452 ms	455 ms	450 ms

SUGANO[20] to evaluate a single value of Dq. By standard treatment [21] we found the best value of C and consequently the best values of B and $10Dq$ that fitted the energy levels, and finally, by a least-squares method, the ligand field parameters. Good agreement between calculated and observed energies has been found for all the states, as shown in Table 3. The differences are of the order of 5.25 for the state $^4T_1$ (^4G), 1.41 for the state $^4T_1$(^4P) and 0.73% for the state $^4T_1$(^4F).

The $10Dq$ values show the order *p*-Me > H > *m*-Br > *p*-Br > *m*-Cl > *p*-Cl and are lower than those found in the previous paper regarding the analogous manganese(II) compounds of the type $[Mn(XC_6H_4SeO_2)_2(H_2O)_2]$ for which the sequence *p*-Me = *m*-Cl > *m*-Br > H > *p*-Br > *p*-Cl was obtained [11]. In both the series of complexes the $10Dq$ values of the *meta*-derivatives are higher than those of the *para*- ones.

The Z^* values lie in the 0.56–0.70 range, Table 2, considerably below the formal +2 oxidation state of the metal; furthermore, they are lower than those of the above reported analogous dihydrate derivatives, 0.88–1.03. This fact allows us to suggest a more pronounced covalency in the anhydrous complexes reported here. The nephelauxetic parameter β values in the 0.59–0.64 range (against the 0.70–0.74 range found for the octahedral hydrated derivatives) give further confirmation of a greater covalency in the metal–ligand bond for the anhydrous derivatives.

Using the empirical relation $\Delta = [f(\text{ligand})] \cdot [g(\text{central ion})]$ and $(1 - \beta) = [h(\text{ligand})] \cdot [k(\text{central ion})]$ due to JORGENSEN [22], with f and h values of the $XC_6H_4SeO_2^-$ ligands equal to 0.91 and 1.63, 0.89 and 1.45, 0.89 and 1.56, 0.91 and 1.65, 0.89 and 1.48, 0.89 and 1.56 for X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br and *p*-Me respectively (calculated from our previous studies), we obtain for manganese(II) a g value of 6.70 kK and a k value of 0.25. These values seem to be reasonable and in accord with the above conclusions from $10Dq$ and B values even if it is difficult to estimate the inaccuracy introduced by the application of the above equations.

The effective magnetic moment values, 5.89–6.14 B.M., are in the range expected for five unpaired electrons, $S = 5/2$, and these μ_{eff} values are very close to the spin-only value [23].

Iron(II) compounds. Passing to the iron(II) derivatives, the crystal-field theory predicts that spin-free iron(II) complexes with six d electrons will form tetrahedral complexes in which the ground state has the electronic configuration $t_{2g}^3 e_g^3$. The solid state electronic spectra of our complexes exhibit a broad band in the near i.r. region in the 5130–5200 cm^{-1} range, Table 4, which is assignable to the transition $^5E \rightarrow {}^5T_2$, showing that the complexes have a tetrahedral symmetry, the position of the band maximum excluding other geometries [24]. By comparing the electronic spectra of these anhydrous complexes with those of the dihydrate derivatives, for which a distorted octahedral geometry has been proposed, we observe the disappearance of the absorption band, clearly split (probably due to a tetragonal distortion or Jahn–Teller effects) into two components in the 8000–9000 cm^{-1} range, which represents the transition to the ^5E_g state for octahedral iron(II) complexes [10].

Furthermore, the intensity of the d–d bands of the anhydrous iron(II) complexes is 40–50 times greater than the intensity of the ligand field bands of the dihydrate iron(II) ones, thus confirming the suggested tetrahedral arrangement of the ligands in the compounds reported here.

The magnetic susceptibility values at room temperature, 4.82–5.09 B.M., are in agreement with the fact that iron(II) has a $^5D_4$ ground state which, under the influence of the cubic field of a tetrahedral arrangement of ligands, splits into a lower doublet, ^5E, and an upper triplet, ${}^5T_2$, so that only a small orbital contribution to the magnetic moment above that of the spin-only value is predicted, in accordance with the μ values for the present complexes, reported above and quoted in Table 1 [23].

Infrared spectra

The assignments of the i.r. bands for the complexes were made on the basis of a detailed i.r. study of the *para*- and *meta*-substituted benzeneseleninic acids and their sodium salts [17], on the basis of the previous results with many other transition metals [1–16] and in particular by comparing the i.r. spectra of these anhydrous derivatives with those of the dihydrate ones of the previously reported $[M(XC_6H_4SeO_2)_2(H_2O)_2]$ type [10, 11]. The bands due to the substituent X and all the bands assigned to fundamentals of the benzene ring appear for the complexes at the same wavenumbers as for the starting ligands. The same behaviour is observed for the ν(SeC) stretching mode, Table 5.

No bands were observed in the 3430–3230 cm^{-1} range and at some 1650 cm^{-1} attributed to the $\nu(OH_2)$ antisymmetric and symmetric modes and δ(HOH) respectively; thus the presence of water in these complexes can be excluded. Moreover the bands observed in the hydrated derivatives in the ranges 985–935 cm^{-1} and 665–600 cm^{-1} (which were assigned to coordinated water) are absent [10, 11].

In all the manganese(II) and iron(II) complexes the bands due to the symmetric and antisymmetric stretching modes of the SeO_2 group undergo downward shifts, Table 5. This shift of $\nu(SeO_2)$ to longer wavelengths in comparison with the stretching values of the free ligands suggests that the benzeneseleninato ion is *O*, *O'*-bonded in these complexes, in accordance with the small frequency differences, of about 55 and 66 cm^{-1} for the manganese(II) and iron(II) derivatives respectively, between the symmetric and antisymmetric ν(SeO) modes [1, 4, 7, 9–13]. By comparing these frequency differences with those of the octahedral dihydrate derivatives we observe an increase in the values on passing from the octahedral to the tetrahedral complexes, these differences still being typical of an *O*, *O'*-coordination of the areneseleninato moiety.

In the far-i.r. region, Table 5, we can assign the sym. and asym. δ(OSeC) in the 415–325 cm^{-1} range as observed for the previously reported *d*- and *p*-block metal derivatives. In addition, new bands are present in the ranges 440–421 and 458–450 cm^{-1} for the manganese(II) and iron(II) complexes respectively; these vibrational modes, absent in the spectra of the starting materials, but present in the spectra of the corresponding dihydrated octahedral complexes can be assigned to metal–oxygen stretching modes.

CONCLUSIONS

During the conversion of the hydrated into the anhydrous metal derivatives, the split-off of the coordinated water is accompanied by a change of the stereochemistry passing from a tetragonally distorted octahedral symmetry to pseudotetrahedral geometries. The mode of coordination of the seleninato ion remains unchanged in the anhydrous complexes as in the dihydrated ones; in fact, the resulting derivatives are always of the *O*, *O'*-seleninato type.

The ν(M–O) vibrational modes lie in these derivatives at higher wavenumbers than in the hydrated complexes and this is in accordance with the fact that in a change in the stereochemistry, accompanied by a decrease in the coordination number, there is an increase in the metal–ligand stretching vibration.

The spectroscopic splitting parameter Δ_t for a tetrahedral chromophore is equal to four ninths of the corresponding parameter Δ_o for an octahedral chromophore. Experimentally, for our complexes the ratio Δ_t/Δ_o is in the 0.81–0.89 range and this value agrees with the fact that the above quoted factor of 4/9 is valid only if the metal–ligand distance R_t in the tetrahedral complexes is the same as the corresponding distance R_o in the octahedral derivatives. We can conclude that R_t in the anhydrous complexes is much less than R_o in the dihydrated ones.

Using the crystal field theory and accepting the validity of the crystal field R^{-5} law, bearing in mind that it is followed only by a limited number of systems over a limited range of internuclear distances, the relation between Δ_t and Δ_o can be expressed by [25–28]

$$\Delta_t/\Delta_o = 4/9\,(R_o/R_t)^5.$$

Using the above reported Δ_t/Δ_o calculated ratios for our complexes, we have obtained values for R_o/R_t in the 1.13–1.15 range.

EXPERIMENTAL

Starting materials

Benzeneseleninic acid, its *para*- and *meta*-substituted derivatives and the corresponding sodium salts were prepared and purified according to described methods to which small modifications have been introduced in order to improve the yields [1, 29–31].

Preparation of the complexes

The bis(seleninato)diaquometal(II) complexes have been obtained by adding dropwise a solution of $MnAc_2 \cdot 4H_2O$ or of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in water to an aqueous solution of the areneseleninato sodium salt in the 1:2 metal:ligand molar ratio, under vigorous stirring at room temperature for 5–10 h in the case of manganese(II) and for about 30 min in the case of iron(II). The resulting precipitate was filtered, washed with water, acetone or ethanol and diethyl ether and dried over P_4O_{10}.

The anhydrous derivatives were obtained by drying the hydrated complexes for a period of 3–4 h at about 180°C.

Infrared spectra

The i.r. spectra have been recorded in the 4000–50 cm^{-1} range with a Perkin–Elmer 180 spectrophotometer of the Instruments Centre of Modena University. The spectra in the 4000–400 cm^{-1} range were measured for KBr discs or Nujol mulls. Far-i.r. spectra were measured for Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

Electronic spectra

The electronic spectra have been recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 4000–45000 cm^{-1} range. Samples were prepared by grinding the complexes in Nujol suspension on a filter paper as supported by the method of VENANZI *et al.* [32].

Magnetic susceptibility measurements

These measurements were carried out by Gouy's method. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal's constants.

Conductivity measurements

These measurements were carried out with a WTW LBR type conductivity bridge for freshly prepared 10^{-3} M solutions in N, N'-dimethylformamide at 25 ± 0.1°C.

Elemental analyses

Carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyzer.

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