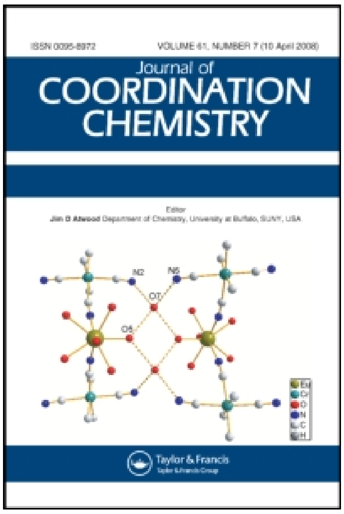

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE REACTIVITY OF ARENESELENINATO COMPLEXES. NEW ZINC(II) BENZENESELENINATO DERIVATIVES WITH 1,10-PHENANTHROLINE AS BIDENTATE NITROGEN DONOR LIGAND

Carlo Preti[a]; Giuseppe Tosi[a]; Paolo Zannini[a]
[a] Istituto di Chimica Generale ed Inorganica, University of Modena, Modena, Italy

To cite this Article Preti, Carlo , Tosi, Giuseppe and Zannini, Paolo(1980) 'THE REACTIVITY OF ARENESELENINATO COMPLEXES. NEW ZINC(II) BENZENESELENINATO DERIVATIVES WITH 1,10-PHENANTHROLINE AS BIDENTATE NITROGEN DONOR LIGAND', Journal of Coordination Chemistry, 10: 3, 143 — 147

To link to this Article: DOI: 10.1080/00958978008081008

URL: http://dx.doi.org/10.1080/00958978008081008

J. Coord. Chem., 1980, Vol. 10, pp. 143–147
0095-8972/80/1003-0143 $04.50/0

THE REACTIVITY OF ARENESELENINATO COMPLEXES. NEW ZINC(II) BENZENESELENINATO DERIVATIVES WITH 1,10-PHENANTHROLINE AS BIDENTATE NITROGEN DONOR LIGAND

CARLO PRETI, GIUSEPPE TOSI and PAOLO ZANNINI

Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy.

(*Received February 19, 1979; in final form September 16, 1979*)

Treatment of the O,O′-seleninatodiaquozinc(II) derivatives of the type $[Zn(H_2O)_2(X{-}C_6H_4SeO_2)_2]$ (X = H, p-Cl, m-Cl, p-Br, m-Br, p-Me, p-NO_2) with 1,10-phenanthroline produces 1 : 2 or 1 : 3 complexes, depending on the metal: o-phen stoichiometrical ratio. The 1 : 2 complexes were non-conducting and of the O-seleninato type, whereas the triscomplexes behaved as 1 : 2 electrolytes; the nitrogen donor ligand is always bidentate. The newly prepared complexes are characterized by far-I.R. and near-I.R. spectroscopy, as well as conductivity measurements. The possible stereochemistries of the complexes are discussed.

INTRODUCTION

The seleninate ion $RSeO_2^-$ is well known for its capability to coordinate to a metal ion as a unidentate ligand either through an oxygen atom, forming O-seleninato complexes, or through the selenium atom, producing Se-seleninato complexes. In the Se-seleninato complexes strong π interactions between the selenium atoms and the metal atoms exist. In addition the $RSeO_2^-$ group can behave as a bidentate ligand *via* both oxygen atoms in O,O′-seleninato complexes or through one oxygen and the selenium atom forming O,Se-seleninato derivatives. The frequencies $\nu_{asym.}(SeO)$ and $\nu_{sym.}(SeO)$ show whether the complex is of the O-seleninato or of the Se-seleninato type, and their difference indicates whether one or both the oxygen atoms are bonded to the central atom.

The areneseleninato ligand, furthermore, may act as a bidentate group either intra- or intermolecularly; the intramolecular arrangement should be, in any case, unlikely because of the excessive ring strain.

Bonding through one or two oxygen atoms, as well as *via* selenium or *via* oxygen and selenium has been reported in previous papers.[1-7] In the cobalt(II) and nickel(II) derivatives the areneseleninato group is O,O′-bonded in both the hydrated and anhydrous complexes,[1,7] whereas in the zinc(II), cadmium(II) and mercury(II) complexes the type of bonding appears to depend on the water content of the compounds.[4] The water containing complexes are always of the O,O′-seleninato type, whereas the anhydrous compounds are O,O′-seleninato for zinc(II), O-seleninato for cadmium(II) and Se-seleninato in the case of mercury(II).[4]

In connection with our continued interest in the coordination properties of the para- and meta-substituted benzeneseleninic acids, it became desirable to study the chemical reactivity and linkage isomers of the coordination compounds of such ligands.

In recent papers[8-10] we reported the reactivity of complexes of the type $[M(H_2O)_2(XC_6H_4SeO_2)_2]$ (M = Co, Ni) toward 2,2′-bipyridyl (bpy), 1,10-phenanthroline (o-phen) and ethylenediamine (en). We obtained products in which the coordinated water is replaced by two moles of bipyridyl or phenanthroline, acting always as bidentate chelating agents. With bpy and o-phen the complexes with O-seleninato ligands had octahedral geometry. The more basic N-donor ligand, en, gave compounds containing three moles of ligand *per* metal ion. This ligand is monodentate in all the pentacoordinated, low-spin complexes of D_{3h} symmetry. The cobalt complexes contain O-bonded seleninato groups, whereas the pentacoordinated high-spin, distorted square-pyramidal nickel complexes have Se-seleninato-linked ligands.

In this paper we report the reactions of the $[Zn(H_2O)_2(XC_6H_4SeO_2)_2]$ complexes (X = H, p-Cl, m-Cl, p-Br, m-Br, p-Me, p-No_2) with 1,10-phenanthroline.

RESULTS AND DISCUSSION

The diaquobis(benzeneseleninato)zinc(II) complexes react with 1,10-phenanthroline according to equation (1)

$$[\mathrm{Zn(H_2O)_2(XC_6H_4SeO_2)_2}] + n\mathrm{L} \xrightarrow[\mathrm{EtOH}]{80^\circ\mathrm{C}} \mathrm{Zn(L)}_n\mathrm{(XC_6H_4SeO_2)_2} + 2\mathrm{H_2O} \quad (1)$$

$n = 2,3 \quad \mathrm{L} = $ o-phen

to give microcrystalline compounds, which are quite stable in air and soluble in common organic solvents. The metal complexes so prepared are listed in Table I, together with analytical data and some physical properties. The most important I.R. bands, in the 4000–100 cm^{-1} range, are given in Tables II and III.

The 1 : 2 derivatives are non-electrolytes in N,N'-dimethylformamide (DMF), whereas the 1 : 3 complexes behave as 1 : 2 electrolytes in the same solvent with Λ_M in the range 125–137 ohm^{-1} cm^2 mole^{-1}

Infrared Spectral Studies

The bands due to the substituent *X* in the benzeneseleninic acids and the out-of-plane ring bending vibrations appear in the complexes at the same wavenumbers as in the starting ligands.[11]

The infrared spectra of the 1 : 2 complexes, in the 870–600 cm^{-1} region, where ν(SeO) symmetric and antisymmetric and ν(SeC) usually lie, show selenium-oxygen stretching frequencies clearly indicative of O-seleninato coordination. The ν(SeO) mode is shifted toward higher wavenumbers and the $\nu_{\mathrm{asym.}}$(SeOM) is shifted to lower frequencies, as coordination removes the equivalence of the selenium-oxygen bonds; in these complexes the

TABLE I
Analytical data and other physical properties

Compounds	Colour	Found (Calcd) %			Dec. range
		C	H	N	°C
$\mathrm{Zn(o\text{-}phen)_2(PhSeO_2)_2 \cdot 3H_2O}$	pink-white	50.7(50.5)	3.4(3.8)	6.6(6.5)	90– 95
$\mathrm{Zn(o\text{-}phen)_3(PhSeO_2)_2 \cdot 3H_2O}$	pale yellow	55.5(55.6)	4.2(3.9)	8.4(8.1)	75– 80
$\mathrm{Zn(o\text{-}phen)_2(p\text{-}ClC_6H_4SeO_2)_2 \cdot H_2O}$	orange	48.6(48.6)	3.1(2.9)	6.3(6.3)	95–100
$\mathrm{Zn(o\text{-}phen)_3(p\text{-}ClC_6H_4SeO_2)_2 \cdot 3H_2O}$	pink-white	52.1(52.2)	3.7(3.5)	7.4(7.6)	80– 85
$\mathrm{Zn(o\text{-}phen)_2(m\text{-}ClC_6H_4SeO_2)_2 \cdot 2H_2O}$	pale orange	47.9(47.7)	3.4(3.1)	6.1(6.2)	85– 90
$\mathrm{Zn(o\text{-}phen)_3(m\text{-}ClC_6H_4SeO_2)_2 \cdot 4H_2O}$	pale orange	50.9(51.3)	3.6(3.6)	7.1(7.5)	81– 86
$\mathrm{Zn(o\text{-}phen)_2(p\text{-}BrC_6H_4SeO_2)_2 \cdot 2H_2O}$	yellow	43.7(43.4)	2.9(2.8)	5.6(5.6)	100–105
$\mathrm{Zn(o\text{-}phen)_3(p\text{-}BrC_6H_4SeO_2)_2 \cdot 3H_2O}$	yellow	48.2(48.3)	3.1(3.2)	6.9(7.0)	88– 93
$\mathrm{Zn(o\text{-}phen)_2(m\text{-}BrC_6H_4SeO_2)_2 \cdot 2H_2O}$	orange	43.4(43.4)	2.6(2.8)	5.7(5.6)	98–103
$\mathrm{Zn(o\text{-}phen)_3(m\text{-}BrC_6H_4SeO_2)_2 \cdot 4H_2O}$	orange	47.4(47.6)	3.1(3.3)	6.7(6.9)	85– 90
$\mathrm{Zn(o\text{-}phen)_2(p\text{-}MeC_6H_4SeO_2)_2 \cdot 2H_2O}$	pale yellow	52.2(52.7)	3.8(4.0)	6.4(6.5)	87– 93
$\mathrm{Zn(o\text{-}phen)_3(p\text{-}MeC_6H_4SeO_2)_2 \cdot 4H_2O}$	orange	55.4(55.5)	4.1(4.3)	7.8(7.8)	75– 80
$\mathrm{Zn(o\text{-}phen)_3(p\text{-}NO_2C_6H_4SeO_2)_2 \cdot 3H_2O}$	yellow	51.2(51.2)	3.4(3.4)	9.7(9.9)	128–133

TABLE II
Most important I.R. bands of benzeneseleninato group (cm^{-1})

Substituent	H	p-Cl	m-Cl	p-Br	m-Br	p-Me	p-$\mathrm{NO_2}$
$\mathrm{XC_6H_4SeO_2Na}$							
ν(SeO) asym.	781	811	817	807	817	817	814
ν(SeO) sym.	768	796	795	786	798	792	789
ν(SeC)	666	–	652	708	645	700	681
$\mathrm{[Zn(o\text{-}phen)_2(XC_6H_4SeO_2)_2]}$							
ν(SeO)	866vs	865s	863s	862s	865s	861s	–
ν(SeOZn) asym.	752s	760s	750s	775s	780s	764s	–
ν(SeC)	668mw	–	649ms	703ms	640s[a]	705mw	–
$\mathrm{[Zn(o\text{-}phen)_3](XC_6H_4SeO_2)_2}$							
ν(SeO) asym.	783ms	815s	815s	810s	818m	815m	820sh
ν(SeO) sym.	770ms	793s	790s	785s	799ms	794s	795m
ν(SeC)	665mw	–	646m	702ms	639s[a]	700w	679m

[a] Overlapping a o-phen band which is markedly reinforced.

TABLE III
Most important far-infrared bands (cm^{-1})

Substituent	H	p-Cl	m-Cl	p-Br	m-Br	p-Me	p-NO_2
$XC_6H_4SeO_2Na$							
δ(OSeC)	384, 350	393, 360	379, 339	386, 348	379, 340	393, 363	385, 355
[Zn(o-phen)$_2$($XC_6H_4SeO_2$)$_2$]							
δ(OSeC)	387m, 347mw	395mw, 355m	371m, 317m	385mw, 345mw	380m, 350m	398mw, 372mw	–
ν(Zn-O)	434m	436m	437vs$^{a)}$	434m	432vs$^{a)}$	435m	–
ν(Zn-N)	204m, 178m	205ms, 180ms	197m, 172ms	201m, 175m	203m, 177m	201m, 174m	–
[Zn(o-phen)$_3$] ($XC_6H_4SeO_2$)$_2$							
δ(OSeC)	395m, 350w	395mw, 352m	380mw, 315m	380mw, 340w	380mw, 355w	390mw, 348m	395mw, 356ms
ν(Zn-N)	231mw, 202m, 171m	233m, 200ms, 176ms	228m, 200m, 175m	229m, 198m, 173m	230m, 200m, 172m	232m, 199m, 174m	228m, 199m, 175ms

[a]Overlapping a out-of-plane ring bending which is markedly reinforced.

frequency differences between these two vibrational modes are *ca.* 100 cm^{-1} (Table 2). The spectra of these complexes are similar to those of the anhydrous cadmium derivatives and of other cobalt(II) and nickel(II) complexes already reported to have O-seleninato bonding.[4,8]

The ν(SeO) sym. and asym. bands of the 1 : 3 complexes have a profile significantly different from that of the 1 : 2 derivatives, are typical of ionic areneseleninate moieties, and occur at the same wavenumbers as in the sodium benzeneseleninates (Table 2). These results are in accord with the conductivity data.

The assignments of the I.R. bands for 1 : 2 and 1 : 3 derivatives were made on the basis of previous results with other transition metals[1-10] and on the basis of a detailed infrared study of the para- and metasubstituted benzeneseleninic acids and their sodium salts.[11]

The medium-strong absorption bands present in all the complexes in the ranges 3470–3450 cm^{-1}, ν(OH), and 1650–1625 cm^{-1}, δ(HOH), clearly confirm the presence of water of crystallization. Since vibrational modes such as wagging, twisting and rocking activated by coordination to the metal and present in the di-aquo starting complexes have not been found in the expected ranges,[4] it appears that coordinated water is now not present.

The I.R. spectra of the o-phen complexes contain peaks in the ranges 1550–1400 cm^{-1}, 1150–800 cm^{-1} and 750–400 cm^{-1}, giving evidence that the ligand is bound to the zinc through the nitrogen. Qualitative interpretation of the spectra show that the ligand is chelated to the metal both in the 1 : 2 and 1 : 3 complexes.

The band present at 1499 cm^{-1} in the free ligand shifts to *ca.* 1515 cm^{-1} in the complexes; the same behaviour is observed for the strong band at 1415 cm^{-1}. A new absorption occurs in all the complexes in the 1143–1135 cm^{-1} range, characteristic of a chelating behaviour of the ligand. Furthermore the weak absorption bands at 1131 cm^{-1} became more intense and shifted to lower energies, 1104–1098 cm^{-1}; in addition a strong or very strong band appears between 851–844 cm^{-1} in the complexes, whereas only a shoulder at 876 cm^{-1} was present in the free ligand, thus confirming that o-phen acts as a chelating group in these derivatives.[12]

The weak band at 620 cm^{-1} appears shifted to higher energies and intensified upon chelation; it is present in fact as medium-strong band near 640 cm^{-1}. The band occurring at 404 cm^{-1} in the uncomplexed ligand shifted to *ca.* 420 cm^{-1} and intensified on chelation. Some weak bands are present in the 590–500 cm^{-1} region.[13]

Far-infrared Spectra

The far-infrared spectra of the 1 : 2 and 1 : 3 derivatives confirm that the metal ions are present in the complexes in different environments.

In the 400–100 cm^{-1} region many bands are present, but their assignment is made difficult by the molecular complexity; in fact besides the stretching vibrations ν(M-L), L= benzeneseleninate ions and o-phen, we should find in this region δ(OMO), δ(NMN), δ(OMN) and the out-of-plane bending (π), normal modes of vibration of molecules having approximatively D_{4h} (1 : 2 complexes) and D_3 (1 : 3 derivatives) symmetry, respectively. We can assign the symmetric and anti-symmetric δ(OSeC) in the range 398–315 cm^{-1}, Table III, in good accord with the previously reported studies.

In all the 1 : 2 complexes a band is present approximately at 435 cm^{-1}; this vibrational mode, absent in the spectra of the free ligands and in those of the 1 : 3 derivatives, may be associated with ν(Zn-O) mode. This assignment is in agreement with observations on previously reported complexes $[Zn(H_2O)_2(XC_6H_4SeO_2)_2]$.[4]

New bands (two in the 1 : 2 complexes in the range 172–205 cm^{-1}, and three in the 1 : 3 derivatives between 171 and 233 cm^{-1}) are present in the far-infrared region, but absent in the spectra of the starting materials used in this study. They can be assigned to metal-ligand vibrations involving the nitrogen atoms of the o-phen ligand (Table III). The presence of three ν(Zn-N) stretching modes (A_2 + 2E) in the derivatives containing the complex ion $[Zn(o\text{-}phen)_3]^{2+}$ is in accord with the fact that this ion has D_3 symmetry; furthermore these assignments are fully confirmed by comparison with literature data obtained by isotopic studies with ^{64}Zn-^{68}Zn substitution.[14]

We can conclude that during the substitution reaction in which the water is replaced by the N-donor ligand, the $RSeO_2^-$ group undergoes a reorientation passing from bidentate O,O′-seleninato to monodentate O-seleninato in the 1 : 2 complexes and passing to the ionic form in the 1 : 3 derivatives, to which should be given the ionic formulation $[Zn(o\text{-}phen)_3](XC_6H_4SeO_2)_2$.

The reorientation of the $RSeO_2^-$ group is dependent on the number of moles of the bidentate entering ligand. In fact when two moles of o-phen are reacting, the zinc(II) ion maintains its coordination number as in the starting complexes with the areneseleninato moiety acting as monodentate only in O-seleninato complexes. In presence of a third mole of the N-donor ligand the metal achieves its favoured coordination number six with the ligands acting as bidentate chelating and the $RSeO_2^-$ groups becoming ionic, and moving out of the primary coordination sphere.

EXPERIMENTAL

Preparation of the Ligands

Benzeneseleninic acid, its meta- and parasubstituted derivatives and the corresponding sodium salts were prepared and purified according to previously reported methods.[1] The 1,10-phenanthroline ligand (high purity grade), supplied by Riedel-De Haën AG, was used without further purification.

Preparation of the Complexes

The diaquobis(benzeneseleninato)zinc(II) derivatives were obtained by reaction between the metal chloride with sodium areneseleninate in H_2O or EtOH according to the previously reported method.[4]

The o-phen complexes were obtained by adding 0.50 or 0.75 mmoles of the ligand dissolved in 10 ml of EtOH to a suspension in 10 ml. of EtOH of 0.25 mmoles of the diaquobis(areneseleninato)zinc(II) (metal : ligand molar ratio 1 : 2 and 1 : 3 respectively). Upon adding the nitrogen donor ligand the solution became clear. The reaction mixture was refluxed and vigorously stirred for about 3 hrs., filtered in order to remove the unreacted starting complexes and reduced to a small volume (10 ml) under vacuum. The products (yield 70–80%) were filtered, washed with diethyl ether or acetone and dried over P_4O_{10}.

Infrared Measurements

The I.R. spectra were recorded in the 4000–100 cm^{-1} range with a Perkin-Elmer 180 spectrophotometer employing KBr discs. The 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.

Conductivity Measurements

These were carried out with a WTW LBR conductivity bridge for 10^{-3} M solutions in DMF.

Analyses

Carbon, nitrogen and hydrogen were determined using a Perkin-Elmer 240 elemental analyzer.

ACKNOWLEDGMENTS

We thank Mr. G. Pistoni for elemental analyses and the National Research Council (C.N.R.) of Italy for financial support.

REFERENCES

1. C. Preti, G. Tosi, D. De Filippo and G. Verani, *J. Inorg. Nucl. Chem.*, 36, 2203 (1974).
2. C. Preti, G. Tosi, D. De Filippo and G. Verani, *Inorg. Nucl. Chem. Lett.*, 10, 541 (1974).
3. E. Bertelli, C. Preti and G. Tosi, *J. Inorg. Nucl. Chem.*, 37, 1421 (1975).
4. C. Preti and G. Tosi, *Spectrochim. Acta*, 31A, 1139 (1975).
5. C. Preti and G. Tosi, *Z. Anorg. allg. Chem.*, 432, 259 (1977).
6. C. Preti and G. Tosi, *Transition Met. Chem.*, 2, 1 (1977).
7. C. Preti, G. Razzoli and G. Tosi, *Spectrochim. Acta*, 34A, 269 (1978).
8. C. Preti and G. Tosi, *Inorg. Chem.*, 16, 2805 (1977).
9. C. Preti, G. Tosi and P. Zannini, *Transition Met. Chem.*, 2, 232 (1977).
10. C. Preti, G. Tosi and P. Zannini, *Transition Met. Chem.*, 4, 123 (1979).
11. D. De Filippo, F. Momicchioli, C. Preti, A. Rastelli and G. Verani, *J. Chem. Soc.* (B), 1065 (1971).
12. J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, 4, 1382 (1965).
13. J. R. Ferraro, L. J. Basile and D. L. Kovacic, *Inorg. Chem.*, 5, 391 (1966).
14. B. Hutchinson, J. Takemoto and K. Nakamoto, *J. Am. Chem. Soc.*, 92, 3335 (1970).