heptaamylose) back to the active isomer of $Co(NH_3)_4ATP$. By treatment with HIO_4, followed by aniline at pH 5, $Co(NH_3)_4ATP$ isomers are degraded to $Co(NH_3)_4H_2P_3O_{10}$ without loss of chirality. The CD of each enantiomer at 550 nm is the same in sign as that of the parent nucleotide, and x-ray analysis of a crystal of $Co(NH_3)_4H_2P_3O_{10}$ from the inactive isomer of $Co(NH_3)_4ATP$ (negative CD) shows that it corresponds to attachment of AMP in position b of the first diagram given above.[32] The active isomer (positive CD) corresponds to attachment of AMP in position a. The ^{31}P NMR spectra are in excellent agreement with the simulated ones in Figure 3, with (c) being the active and (d) the inactive isomer.

The diastereomers of $Co(NH_3)_4ADP$ separate cleanly on the cycloheptaamylose column, with the one whose α-phosphate is farthest downfield in Figure 2 coming off first and having a negative CD band at 540 nm. The second isomer (positive CD) probably corresponds in structure to attachment of adenosine in position a of the diagram. This work will be reported in detail at a later date.

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Registry No. $Co(NH_3)_4HATP$, 63915-26-4; $Co(NH_3)_4ADP$, 63937-09-7; $Co(NH_3)_5ADP$, 63937-08-6; $Co(NH_3)_5HP_2O_7$, 63915-25-3; $Co(NH_3)_4HP_2O_7$, 63915-24-2; $Co(en)_2HP_2O_7$, 63915-23-1; $Co(NH_3)_4H_2P_3O_{10}$, 63915-22-0; $Co(NH_3)_3H_2P_3O_{10}$, 63915-20-8; $[Co(NH_3)_5P_2O_7]^-$, 63915-21-9; $[Co(NH_3)_4P_2O_7]^-$, 63915-34-4; $[Co(en)_2P_2O_7]^-$, 63915-33-3; $[Co(NH_3)_4P_3O_{10}]^{2-}$, 63915-32-2; $[Co(NH_3)_3P_3O_{10}]^{2-}$, 63937-07-5; $[Co(NH_3)_5H_2PO_4]^{2+}$, 19169-72-3; $[Co(NH_3)_5H_3P_2O_7]^{2+}$, 63915-31-1; $[Co(NH_3)_4H_2P_2O_7]^+$, 63915-30-0; $[Co(NH_3)_4H_3P_3O_{10}]^+$, 63915-29-7; $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,PO_4)\text{-}Co(NH_3)_4]^{2+}$, 34420-25-2; $[Co(NH_3)_4HPO_4]^+$, 64023-30-9; $[Co(NH_3)_4ATP]^-$, 63915-28-6; $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$, 53861-32-8; $K[Co(NH_3)_2(NO_2)_4]$, 14285-97-3; $[Co(NH_3)_5CO_3]NO_3$, 15244-74-3; $[Co(NH_3)_4CO_3]NO_3$, 15040-52-5; *trans*-$[Co(en)_2Cl_2]Cl$, 14040-33-6; $[Co(NH_3)_3(H_2O)Cl_2]Cl$, 13820-77-4; H_4ATP, 3714-60-1; Co, 7440-48-4.

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(1) (a) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., 1976; see Abstracts, No. BIOL 121 and INOR 150. (b) To whom correspondence should be addressed at the Department of Chemistry, Wichita State University, Wichita, Kans. 67208.

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Study of the Reaction of Cobalt(II) and Nickel(II) Benzeneseleninato Complexes with Bidentate Nitrogen Donor Ligands

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The pseudooctahedral bis(benzeneseleninato-*O*)bis(2,2′-bipyridyl) and bis(benzeneseleninato-*O*)bis(1,10-phenanthroline) compounds of cobalt(II) and nickel(II) are obtained by reaction of the complexes $M(H_2O)_2(XPhSeO_2)_2$ (M = Co, Ni; X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-CH_3, *p*-NO_2) with 2,2′-bipyridyl and 1,10-phenanthroline according to eq 1. All the diaquo complexes react with 2 mol of 2,2′-bipyridyl or 1,10-phenanthroline in ethanol to form seleninato-*O* complexes. The newly prepared compounds are characterized on the basis of far-IR and near-IR spectroscopy and electronic spectra, as well as by magnetochemical investigations. A distorted octahedral geometry accounts for the room-temperature spectroscopic properties of these compounds. The nitrogen donor ligands behave always as bidentate. Our cobalt(II) and nickel(II) complexes show *Dq* values in keeping with the proposed structures and with literature data for CoN_4O_2 and NiN_4O_2 chromophores.

Introduction

Our interest in the coordination properties of the para- and meta-substituted benzeneseleninic acids as ligands was recently extended to the study of the chemical reactivity and linkage isomers of the coordination compounds of such ligands. Owing to the four possibilities for bonding the $RSeO_2^-$ ligand to coordination centers, the seleninato complexes are particularly suitable as model substances for the study of various isomerization phenomena.

The benzeneseleninato group can behave as a monodentate

Table I. Electronic Spectral Data and Ligand Field Parameters (cm^{-1})[a]

	ν_1	ν_2	ν_3	Dq	B'	β
$Co(bpy)_2(PhSeO_2)_2\cdot 3H_2O$	9 190	18 590	21 600	1085	938	0.97
$Co(bpy)_2(p\text{-}ClPhSeO_2)_2\cdot 2H_2O$	9 200	18 250	20 920	1041	862	0.89
$Co(bpy)_2(m\text{-}ClPhSeO_2)_2\cdot 3H_2O$	8 850	17 390	21 275	1007	910	0.94
$Co(bpy)_2(p\text{-}BrPhSeO_2)_2\cdot 4H_2O$	8 890	17 950	20 000	1005	818	0.84
$Co(bpy)_2(m\text{-}BrPhSeO_2)_2$	8 890	18 620	20 920	1010	883	0.91
$Co(bpy)_2(p\text{-}CH_3PhSeO_2)_2\cdot 4H_2O$	9 020	18 180	21 000	1033	886	0.92
$Co(bpy)_2(p\text{-}NO_2PhSeO_2)_2\cdot H_2O$	8 695	18 250	20 830	989	889	0.92
$Co(o\text{-}phen)_2(PhSeO_2)_2\cdot H_2O$	9 410	18 520	21 930	1067	919	0.95
$Co(o\text{-}phen)_2(p\text{-}ClPhSeO_2)_2\cdot 2H_2O$	9 010	18 870	21 230	1023	896	0.93
$Co(o\text{-}phen)_2(m\text{-}ClPhSeO_2)_2\cdot 6H_2O$	9 090	18 315	21 275	1033	895	0.93
$Co(o\text{-}phen)_2(p\text{-}BrPhSeO_2)_2\cdot 3H_2O$	9 050	18 520	21 370	1029	904	0.93
$Co(o\text{-}phen)_2(m\text{-}BrPhSeO_2)_2\cdot 3H_2O$	9 000	18 725	21 050	1022	885	0.91
$Co(o\text{-}phen)_2(p\text{-}CH_3PhSeO_2)_2\cdot 3H_2O$	9 430	19 050	21 690	1068	901	0.93
$Co(o\text{-}phen)_2(p\text{-}NO_2PhSeO_2)_2\cdot 3H_2O$	9 090	18 690	21 010	1031	876	0.91
$Ni(bpy)_2(PhSeO_2)_2\cdot 2H_2O$	10 360	17 545	26 595	1036	871	0.84
$Ni(bpy)_2(p\text{-}ClPhSeO_2)_2\cdot H_2O$	10 640	17 390	27 770	1064	883	0.85
$Ni(bpy)_2(m\text{-}ClPhSeO_2)_2$	11 110	18 180	27 930	1111	852	0.82
$Ni(bpy)_2(p\text{-}BrPhSeO_2)_2\cdot H_2O$	10 525	18 020	27 030	1052	898	0.86
$Ni(bpy)_2(m\text{-}BrPhSeO_2)_2$	10 525	16 665	26 315	1052	760	0.73
$Ni(bpy)_2(p\text{-}CH_3PhSeO_2)_2\cdot 2H_2O$	10 385	17 920	27 550	1038	954	0.92
$Ni(o\text{-}phen)_2(PhSeO_2)_2$	10 000	16 050	25 000	1000	737	0.71
$Ni(o\text{-}phen)_2(p\text{-}ClPhSeO_2)_2$	10 990	17 240	26 315	1099	706	0.68
$Ni(o\text{-}phen)_2(m\text{-}ClPhSeO_2)_2\cdot H_2O$	10 385	17 830	27 030	1038	914	0.88
$Ni(o\text{-}phen)_2(p\text{-}BrPhSeO_2)_2\cdot H_2O$	10 255	17 795	26 670	1026	913	0.88
$Ni(o\text{-}phen)_2(m\text{-}BrPhSeO_2)_2$	10 505	15 875	25 840	1050	680	0.65
$Ni(o\text{-}phen)_2(p\text{-}CH_3PhSeO_2)_2\cdot 4H_2O$	10 000	17 480	26 950	1000	962	0.92

[a] B is taken to be 967 and 1041 cm^{-1} for the Co^{2+} and Ni^{2+} free gaseous ions, respectively.

ligand in seleninato-*Se* or seleninato-*O* complexes; in the first case the metal ion is linked directly to the selenium with a strong π interaction between the metal and the selenium and in the second case by one oxygen atom. When the $RSeO_2^-$ group behaves as a bidentate ligand, coordination occurs through both oxygen atoms in seleninato-*O,O′* complexes or via oxygen and selenium in seleninato-*O,Se* complexes. Infrared spectroscopy provides a convenient means to distinguish between the different possibilities.

Bonding through one oxygen or two oxygen atoms, as well as via selenium or via selenium and oxygen atoms has already been reported in previous papers.[1-7] Furthermore from a detailed IR study of zinc(II), cadmium(II), and mercury(II) complexes, we have found that the type of bonding is particularly dependent on the water content of the compounds.[4] The water-containing complexes are always seleninato-*O,O′*, while the anhydrous compounds are mainly selenihato-*O,O′* in the case of zinc, selenihato-*O* in the case of cadmium, and selenihato-*Se* in the case of mercury.[4] In the cobalt(II) and nickel(II) derivatives the areneseleninato group is O,O′-bonded in both the hydrated and anhydrous complexes.[1,7]

In this paper we report the reactivity of the complexes $M(H_2O)_2(XPhSeO_2)_2$ (M = Co, Ni; X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-CH_3, *p*-NO_2) with 2,2′-bipyridyl and 1,10-phenanthroline (hereafter abbreviated bpy and *o*-phen).

Results and Discussion

The diaquobis(seleninato)cobalt(II) and -nickel(II) complexes react, as reported in the Experimental Section, with the nitrogen donor ligands bpy and *o*-phen according to the equation

$$M(H_2O)_2(XPhSeO_2)_2 + 2L \xrightarrow[\text{EtOH}]{80\,^\circ\text{C}} M(L)_2(XPhSeO_2)_2 + 2H_2O \qquad (1)$$

M = Co, Ni; L = bpy, *o*-phen

to give microcrystalline compounds, stable in air, and slightly soluble in common organic solvents. Elemental analyses gave satisfactory results; all the complexes are paramagnetic, high spin, and nonelectrolytic in anhydrous ethyl alcohol (Λ_M lying in the range 5.8–10.2 $\Omega^{-1}\ cm^2\ mol^{-1}$; the Λ_M values even for 1:1 electrolytes should be 35–45 $\Omega^{-1}\ cm^2\ mol^{-1}$ in this solvent[8]).

Electronic Spectra and Magnetic Moments. Solid-state electronic spectra confirm an octahedral configuration of the central ion in the cobalt and nickel complexes (Table II). The d–d spectra of the cobalt derivatives show three bands, viz., at 8695–9430, 17 390–19 050, and 20 000–21 930 cm^{-1}, that can be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. In the nickel(II) derivatives three major bands, very weak in intensity, are present in the ranges 10 000–11 110, 15 875–18 180, and 25 000–27 930 cm^{-1}, assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively.

The transition energy ratios ν_2/ν_1 are in the ranges 1.96–2.10 and 1.51–1.74 in accordance with the literature data for octahedral cobalt(II) and nickel(II) derivatives.[9,10] From these data, $10Dq$, B', and β values were calculated and listed in Table I.

In this treatment we have applied the available methods,[11] which differ by the bands on which the fit is based, to obtain a numerical fit to the experimental data. The experimental absorption band energies observed in the spectra of the complexes were compared to the transition energies calculated on the basis of various numerical procedures and an interesting check on the accuracy of the method has been made.

By comparison of $\delta\nu\,\% = 100(\nu_{calcd} - \nu_{exptl})/\nu_{calcd}$ calculated by the different methods, we can conclude that the best results are achieved fitting ν_1 and ν_3 in the case of cobalt and fitting ν_1 and the sum of ν_2 and ν_3 in the case of nickel.

The superior performance of the method which does not involve the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition in its fitting is not surprising because of the difficulty of the accurate location of ν_2 in octahedral cobalt(II) complexes, owing to its low intensity.

A comparison of Dq and B' values for our cobalt complexes, using the values obtained from the best procedure, shows that in the spectrochemical series Dq decreases in the sequence *o*-phen > bpy with respect to the nitrogen donor ligands and in the order $PhSeO_2^-$ > *p*-$CH_3PhSeO_2^-$ > *p*-$ClPhSeO_2^-$ > *m*-$ClPhSeO_2^-$ > *p*-$BrPhSeO_2^-$ > *m*-$BrPhSeO_2^-$ > *p*-$NO_2PhSeO_2^-$ with respect to the areneseleninato moiety. The B' values are of the order of 90% of the free-ion value (967 cm^{-1}); the nephelauxetic parameter β shows an order *o*-phen

Table II. Most Important Infrared Bands (cm^{-1})

	Substituent						
	H	*p*-Cl	*m*-Cl	*p*-Br	*m*-Br	*p*-CH_3	*p*-NO_2
Sodium Salt							
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
Co^{II}–bpy Derivatives							
ν(SeO)	810 vs	878 m	890 vs	870 m	885 m	850 m	860 m
ν(SeOCo) asym	698 vs	780 s	783 vs	775 vs	788 vs	745 s	780 vs
ν(SeC)	659 s[a]	710 m	640 ms	705 m	640 m	710 mw	690 m
ν(Co–O)	443 ms	440 s	451 s	440 ms	442 m	440 ms	465 m
ν(Co–N)	320 vs	325 ms, 296 m	318 vs	330 ms, 295 mw	310 m	341 m, 298 mw	335 m, 295 mw
Co^{II}–*o*-phen Derivatives							
ν(SeO)	860 vs	860 m	857 vs	860 vs	859 vs	860 vs	868 vs
ν(SeOCo) asym	750 m	790 vs	761 m	720 ms	760 ms	740 vs	750 ms
ν(SeC)	675 m		635 m	704 m	628 mw	710 sh	690 m
ν(Co–O)	440 m	441 m	447 ms	433 s	446 ms	440 ms	470 m
ν(Co–N)	340 sh, 295 m	345 m, 297 m	331 ms, 295 ms	331 s, 298 ms	330 m, 293 mw	340 ms, 300 ms	333 m, 294 mw
Ni^{II}–bpy Derivatives							
ν(SeO)	815 vs	825 s	890 m	840 m	890 m	850 m	
ν(SeONi) asym	698 s	737 s	785 vs	780 vs	784 vs	783 s	
ν(SeC)	660 ms	709 m	660 ms	705 mw	640 m	710 m	
ν(Ni–O)	450 ms	446 ms	445 ms	445 m	449 ms	447 m	
ν(Ni–N)	321 s, 297 m	340 ms, 295 m	320 ms, 295 m	330 m, 294 m	315 ms, 295 m	345 ms, 302 m	
Ni^{II}–*o*-phen Derivatives							
ν(SeO)	850 vs	860 vs	859 vs	862 vs	860 vs	865 vs	
ν(SeONi) asym	700 ms	790 vs	760 ms	740 m	790 vs	780 m	
ν(SeC)	650 m	710 m	670 mw	705 mw	630 mw	710 mw	
ν(Ni–O)	432 m	451 m	435 ms	453 m	433 ms	448 m	
ν(Ni–N)	340 m, 304 m	350 s, 303 ms	325 m, 305 ms	340 ms, 300 m	335 m, 306 ms	342 ms, 300 ms	

[a] Overlapping a band of bpy.

> bpy with respect to the nitrogen donor ligands, while the areneseleninato ions are in the order $PhSeO_2^- > m\text{-}ClPhSeO_2^- > p\text{-}CH_3PhSeO_2^- > p\text{-}NO_2PhSeO_2^- > p\text{-}ClPhSeO_2^- \simeq m\text{-}BrPhSeO_2^- > p\text{-}BrPhSeO_2^-$.

The same comparison for the nickel derivatives shows that *Dq* decreases in the order bpy > *o*-phen and $p\text{-}ClPhSeO_2^- > m\text{-}ClPhSeO_2^- > m\text{-}BrPhSeO_2^- > p\text{-}BrPhSeO_2^- > p\text{-}CH_3PhSeO_2^- > PhSeO_2^-$ for the two series of the ligands.

The *B'* values are of the order of 65–92% of the free-ion value (1041 cm^{-1}) suggesting a good covalency in the metal–ligand σ bond. The variation in the β_{35} parameter suggests the series bpy > *o*-phen and $p\text{-}CH_3PhSeO_2^- > p\text{-}BrPhSeO_2^- > m\text{-}ClPhSeO_2^- > PhSeO_2^- > p\text{-}ClPhSeO_2^- > m\text{-}BrPhSeO_2^-$. As regards the metals, they can be placed in the nephelauxetic series Co(II) > Ni(II).

Decreasing values of β are associated with a reduction in the effective positive charge of the cation and with an increasing tendency to be reduced to a lower oxidation state. For 3d metals the variation of Racah interelectronic repulsion parameter with the effective cationic charge Z^* and the number *q* of electrons in the partly filled d shell is expressed by the relation[12]

$$B' = 384 + 58q + 124(Z^* + 1) - 540/(Z^* + 1)$$

where *B'* is cm^{-1}.

The effective ionic charges for the cobalt(II) and nickel(II) complexes are in the ranges 1.77–1.20 and 1.60–0.52, respectively, below the formal +2 oxidation state of these metals.

Analysis of the electronic spectra of octahedral cobalt(II) and nickel(II) complexes allows us to determine the mode of bonding of the ligands. By comparison of the *Dq* values, reported in the literature, for CoL_6 and NiL_6 groups[13] using the rule of average environment[14] to obtain an estimate of the octahedral ligand field splitting parameter, we can distinguish between MN_2O_4 and MN_4O_2 chromophores. The *Dq* values for CoO_6 chromophores are in the range 920–980 cm^{-1} while the values corresponding to CoN_6 chromophores are higher than 1000 cm^{-1}.[13-15] As for the octahedral complexes of nickel(II), the *Dq* values for NiO_6 and NiN_6 chromophores are in the ranges 850–930 and 1006–1150 cm^{-1}, respectively.[13-16]

Although our complexes show *Dq* values typical of MN_4O_2 chromophores, results of infrared and far-infrared spectral studies are needed before any conclusions can be drawn.

Using the empirical relation $10Dq = [f(\text{ligand})][g(\text{central ion})]$ due to Jorgensen[14] with $g(Ni^{2+}) = 8.9$, we obtain *f* values in the range 1.12–1.24. These values seem to be reasonable and in accord with the above conclusions from *Dq* values, although it is difficult to estimate the inaccuracy introduced by application of the above equation.

The μ_{eff} values of the cobalt derivatives, in the range 4.7–5.3, are indicative of six-coordinated high-spin cobalt(II), showing very high orbital contributions characteristic of octahedral geometry around cobalt(II). The magnetic moments of the nickel complexes (2.9–3.4 μ_B) are within the range commonly accepted for six-covalent octahedral nickel(II).

Infrared Spectra. Let us first note that the bands due to the substituent and the out-of-plane ring bending appear in the spectra of the complexes at the same wavenumbers as in the spectra of the free ligands.

These derivatives have selenium–oxygen stretching frequencies clearly indicative of a seleninato-*O* coordination, ν(SeO) is shifted toward higher wavenumbers, and ν_{asym}(SeOM) is shifted to lower frequencies as coordination removes the equivalence of the selenium–oxygen bonds; the frequency difference is ca. 100 cm^{-1}, Table II. The spectral patterns of these complexes are similar to those of anhydrous cadmium derivatives already reported to have seleninato-*O* bonding.[4]

The medium–strong absorption bands present in the ranges 3480–3460 cm^{-1}, ν(OH), and 1645–1620 cm^{-1}, δ(HOH), in all the water-containing complexes, clearly confirm the presence of water of crystallization. Since vibrational modes such as wagging, twisting, and rocking activated by coordination to the metal have not been found in the expected ranges,[4] it appears that coordinated water is not present.

The infrared spectra of the complexes show, in the ranges 1600–1400, 900–700, and 650–400 cm^{-1}, peaks giving evidence that the ligands bpy and *o*-phen are bound to the metal through the nitrogen. Qualitative interpretation of the spectra shows that the ligands are chelated to the metals.

New bands are observed at about 1600, 1490, and 1470 cm^{-1} in the bpy derivatives, clearly indicative of a chelating behavior of this ligand. These absorptions, involving the ring C–C and C–N vibrations of the 2,2′-bipyridyl, are observed at lower energies in the uncomplexed ligand.[17] Additional bands are observed in the complexes between 1310–1330 cm^{-1}, at 1160 cm^{-1}, and in the 1010–1030 cm^{-1} region. The absorption in the region near 1000 cm^{-1} is due to the pyridine breathing mode in the uncomplexed bpy; upon chelation this band undergoes a blue shift and intensifies. Sinha has made similar observations on related complexes.[18] Upon chelation splitting of the out-of-plane CH bending vibration at 751 cm^{-1} occurs in all the studied complexes.[18-20]

Slight blue shifts are noted for the vibrational modes at 657 and 622 cm^{-1}; in addition the 404-cm^{-1} band shifts to higher frequency. These shifts accompanied by the above reported behavior of bpy are typical of chelation of the ligand. 2,2′-Bipyridyl is free of absorptions in the region from 300 to 200 cm^{-1}.

As for the *o*-phen derivatives, the 1499-cm^{-1} band appears to shift to higher wavenumbers, at about 1520 cm^{-1}; the same behavior is observed for the strong band at 1415 cm^{-1}. A new absorption also occurs on chelation at about 1150 cm^{-1} in all the complexes. The weak absorption band at 1131 cm^{-1} is reinforced and shifted toward lower energies; in addition a medium or medium–strong band appears at some 876 cm^{-1} in the complexes, whereas only a shoulder is present in the ligand itself. This behavior is typical of complexes containing the ligand *o*-phen acting as a chelating group.[21]

The weak band at 620 cm^{-1} appears to be shifted toward higher frequency and intensifies upon chelation; it appears, in fact, as a medium–strong band in the 635–651-cm^{-1} region. The 404-cm^{-1} band in the uncomplexed ligand also appears to shift to higher frequency and intensifies upon chelation. Some weak bands are found in the region 500–590 cm^{-1}.[22]

In the far-infrared region many bands are present; we can assign the deforming symmetric and antisymmetric δ(OSeC) in the range 410–338 cm^{-1}, in good accord with the previously reported studies. In all the complexes a medium–strong or strong band is present in the range 470–432 cm^{-1} and can be assigned to the ν(Co–O) and ν(Ni–O) stretching mode, Table II; this assignment is in keeping with the observations on the previously reported complexes $\mathrm{M(H_2O)_2(XPhSeO_2)_2}$ (M = Co, Ni).[1]

New bands are present in the 345–293-cm^{-1} region and in the range 350–294 cm^{-1} in the cobalt and nickel derivatives, respectively, absent in the spectra of starting materials used in this study, and they can be assigned to metal–ligand vibrations involving the nitrogen atoms of the ligands,[23] Table II.

The cobalt(II) and nickel(II) complexes of the type $\mathrm{M(H_2O)_2(XPhSeO_2)_2}$ react with bpy and *o*-phen giving products in which the coordinated water is substituted by the nitrogen donor ligands. These ligands are always bidentate chelating agents in all the complexes. During the substitution reaction in which the water is replaced by the nitrogen donor ligands, the $\mathrm{RSeO_2^-}$ group undergoes a reorientation passing from bidentate seleninato-*O,O′* to monodentate seleninato-*O*.

The infrared results as regards the metal–ligand assignments, the chelating behavior of bpy and *o*-phen, and the fact that the benzeneseleninato ion resulted monodentate are confirmed by the results of the electronic spectra.

Our cobalt and nickel complexes show *Dq* values that are, using the rule of average environment, typical of $\mathrm{MN_4O_2}$ chromophores. The spectroscopic splitting parameter Δ_t for a tetrahedral chromophore is equal to four-ninths of the corresponding parameter Δ_o for the octahedral chromophore.

If we compare the spectroscopic splitting parameter Δ_t for the tetrahedral anhydrous derivatives[7] of the type $\mathrm{Co(XPhSeO_2)_2}$ with the Δ_o for the present complexes, the ratio Δ_t/Δ_o is in the ranges 0.47–0.53 and 0.46–0.52 for the cobalt bpy and *o*-phen derivatives, respectively. This behavior agrees with the fact that the above quoted factor of $^4/_9$ is valid only if the metal–ligand distance R_t in tetrahedral complexes is the same as the corresponding distance R_o in octahedral derivatives; we can conclude that R_t in the anhydrous complexes is less than R_o in the reported ones.

Available structural data suggest that the ratio R_o/R_t lies usually in the range 1.08–1.10; 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[24-27]

$$\Delta_t/\Delta_o = {}^4/_9 (R_o/R_t)^5$$

Using the above reported ratios Δ_t/Δ_o calculated for our complexes, we have obtained values for R_o/R_t in the ranges 1.01–1.04 and 1.00–1.03 for the Co–bpy and –*o*-phen complexes, respectively.

A comparison of the effective positive charges Z^* for bpy and *o*-phen derivatives for octahedral diaquo and tetrahedral areneseleninato derivatives[7] shows for the cobalt complexes an increase of the Z^* values on passing from the diaquo derivatives to the bpy and *o*-phen complexes, with the exception of the *p*-$\mathrm{CH_3}$ and *p*-$\mathrm{NO_2}$ derivatives. The values of the tetrahedral complexes are always consistently lower than those of the other complexes.

Experimental Section

Preparation of the Ligands. Benzeneseleninic acid, its meta- and para-substituted derivatives, and the corresponding sodium salts were prepared and purified according to previously reported methods.[1]

Preparation of the Complexes. The diaquobis(seleninato)metal(II) derivatives were obtained by reaction of metal halide with sodium arylseleninate in water or ethanol at temperatures between 25 and 60 °C in the stoichiometric ratio 1:2 metal:ligand. The compounds which precipitated immediately or after rotary evaporation were filtered, washed with water, ethanol, and diethyl ether, and dried over $\mathrm{P_4O_{10}}$. The complexes of bpy and *o*-phen were obtained by adding an ethanolic solution of the ligand to a suspension of cobalt or nickel diaquo(aryl)seleninate with a metal:ligand molar ratio 1:2. The solution was refluxed and vigorously stirred for about 15 min. Upon addition of the nitrogen donor ligand the solution becomes clear and the color changes to orange-yellow in the case of cobalt and to pale green in the case of nickel derivatives. The solution at the end of the reaction was filtered in order to remove the unreacted starting complexes and reduced to small volume under vacuum. After addition of diethyl ether the compounds were obtained in good yield as crystalline products which were filtered, washed with diethyl ether, and dried over $\mathrm{P_4O_{10}}$.

Physical Measurements. The electronic spectra of the solid compounds were recorded with a Shimadzu MPS-50L spectrophotometer. Samples were prepared by grinding the complexes on a filter paper as support. The infrared spectra of KBr pellets were recorded with a Perkin-Elmer 457 (4000–400 cm^{-1}) and far-infrared spectra of Nujol mulls with a Perkin-Elmer 225 (450–200 cm^{-1}) spectrophotometer. Atmospheric water was removed from the spectrophotometer housing with a stream of dry nitrogen. The room-temperature magnetic moments were measured with the Gouy method using $\mathrm{HgCo(NCS)_4}$ or $\mathrm{Ni(en)_3S_2O_3}$ as calibrants and correcting for diamagnetism with the appropriate Pascal's constants. The conductivities of the complexes in 10^{-3}M solution in anhydrous ethyl alcohol were measured with a WTW (Wissenschaftlich Technische Werkstatten) LBR conductivity bridge at 25 °C. Carbon, nitrogen, and hydrogen were determined using a Perkin-Elmer 240 elemental analyzer.

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Registry No. $Co(bpy)_2(PhSeO_2)_2$, 63714-24-9; $Co(bpy)_2(p\text{-}ClPhSeO_2)_2$, 63714-25-0; $Co(bpy)_2(m\text{-}ClPhSeO_2)_2$, 63714-26-1; $Co(bpy)_2(p\text{-}BrPhSeO_2)_2$, 63714-27-2; $Co(bpy)_2(m\text{-}BrPhSeO_2)_2$, 63714-28-3; $Co(bpy)_2(p\text{-}CH_3PhSeO_2)_2$, 63743-87-3; $Co(bpy)_2(p\text{-}NO_2PhSeO_2)_2$, 63743-88-4; $Co(o\text{-}phen)_2(PhSeO_2)_2$, 63714-29-4; $Co(o\text{-}phen)_2(p\text{-}ClPhSeO_2)_2$, 63714-30-7; $Co(o\text{-}phen)_2(m\text{-}ClPhSeO_2)_2$, 63714-31-8; $Co(o\text{-}phen)_2(p\text{-}BrPhSeO_2)_2$; 63714-32-9; $Co(o\text{-}phen)_2(m\text{-}BrPhSeO_2)_2$, 63714-33-0; $Co(o\text{-}phen)_2(p\text{-}CH_3PhSeO_2)_2$, 63714-34-1; $Co(o\text{-}phen)_2(p\text{-}NO_2PhSeO_2)_2$, 63714-35-2; $Ni(bpy)_2(PhSeO_2)_2$, 63743-89-5; $Ni(bpy)_2(p\text{-}ClPhSeO_2)_2$, 63714-13-6; $Ni(bpy)_2(m\text{-}ClPhSeO_2)_2$, 63714-14-7; $Ni(bpy)_2(p\text{-}BrPhSeO_2)_2$, 63714-15-8; $Ni(bpy)_2(m\text{-}BrPhSeO_2)_2$, 63714-16-9; $Ni(bpy)_2(p\text{-}CH_3PhSeO_2)_2$, 63714-17-0; $Ni(o\text{-}phen)_2(PhSeO_2)_2$, 63714-18-1; $Ni(o\text{-}phen)_2(p\text{-}ClPhSeO_2)_2$, 63714-19-2; $Ni(o\text{-}phen)_2(m\text{-}ClPhSeO_2)_2$, 63714-20-5; $Ni(o\text{-}phen)_2(p\text{-}BrPhSeO_2)_2$, 63714-21-6; $Ni(o\text{-}phen)_2(m\text{-}BrPhSeO_2)_2$, 63714-22-7; $Ni(o\text{-}phen)_2(p\text{-}CH_3PhSeO_2)_2$, 63714-23-8; $Co(H_2O)_2(PhSeO_2)_2$, 55060-50-9; $Co(H_2O)_2(p\text{-}ClPhSeO_2)_2$, 55060-51-0; $Co(H_2O)_2(m\text{-}ClPhSeO_2)_2$, 55060-52-1; $Co(H_2O)_2(p\text{-}BrPhSeO_2)_2$, 55060-53-2; $Co(H_2O)_2(m\text{-}BrPhSeO_2)_2$, 55060-54-3; $Co(H_2O)_2(p\text{-}CH_3PhSeO_2)_2$, 55060-55-4; $Co(H_2O)_2(p\text{-}NO_2PhSeO_2)_2$, 55060-56-5; $Co(PhSeO_2)_2$, 63743-85-1; $Co(p\text{-}ClPhSeO_2)_2$, 63714-01-2; $Co(m\text{-}ClPhSeO_2)_2$, 63714-02-3; $Co(p\text{-}BrPhSeO_2)_2$, 63714-03-4; $Co(m\text{-}BrPhSeO_2)_2$, 63714-04-5; $Co(p\text{-}CH_3PhSeO_2)_2$, 63714-05-6; $Co(p\text{-}NO_2PhSeO_2)_2$, 63714-06-7; $Ni(H_2O)_2(PhSeO_2)_2$, 55060-72-5; $Ni(H_2O)_2(p\text{-}ClPhSeO_2)_2$, 55060-73-6; $Ni(H_2O)_2(m\text{-}ClPhSeO_2)_2$, 55060-74-7; $Ni(H_2O)_2(p\text{-}BrPhSeO_2)_2$, 55060-75-8; $Ni(H_2O)_2(m\text{-}BrPhSeO_2)_2$, 55060-76-9; $Ni(PhSeO_2)_2$, 63714-07-8; $Ni(p\text{-}ClPhSeO_2)_2$, 63714-08-9; $Ni(m\text{-}ClPhSeO_2)_2$, 63714-09-0; $Ni(p\text{-}BrPhSeO_2)_2$, 63714-10-3.

Supplementary Material Available: Tables containing analytical data and other physical properties, substituent absorption and out-of-plane ring bending frequencies of the benzeneseleninato ligands, most important infrared bands of 2,2′-bipyridyl and 1,10-phenanthroline derivatives (1700–200 cm^{-1}), and a comparison of the effective positive charges Z^* (5 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Ligand Dissociation of Cobalt(II)–Polyamine Complexes in Aqueous Solution

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The kinetics of dissociation of Co(II)–polyamine (en, ethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine), which were formed by the reaction of hydrated electrons e_{aq}^- with the corresponding Co(III) complexes, have been investigated by conductometric pulse radiolysis in weakly acid aqueous solutions. The dissociation (detachment) rate constants for all ligands examined increase with increasing hydrogen ion concentration and attain a limiting value: $[Co(en)_3]^{2+}$, 1.5×10^4 s^{-1}; $[Co(en)_2(OH_2)_2]^{2+}$, 1.4×10^3 s^{-1}; $[Co(en)(OH_2)_4]^{2+}$, 1.7×10^2 s^{-1}; $[Co(dien)_2]^{2+}$, 1.8×10^4 s^{-1}; $[Co(dien)(OH_2)_3]^{2+}$, 8.7×10^2 s^{-1}; $[Co(trien)(OH_2)_2]^{2+}$, 2.1×10^3 s^{-1}. The dissociation of these multidentates proceeds by a proton-catalyzed mechanism in which the first N–Co(II) bond rupture is the rate-determining step. A proton adds to this released amino group and accelerates further dissociation of the rest of the donor groups. The enhancement ratios of rate constants with increasing number of N donors in Co(II)–ammine complexes are larger for dissociation (~7 for the first two NH_3) than for formation (~2).

I. Introduction

The kinetics of the stepwise "unwrapping" (peeling off) of multidentate amino ligands from nickel(II)[1-5] and chromium(III)[6-9] have been well investigated in aqueous solution. However, few kinetic data exist on the dissociation of labile chelate complexes containing cobalt(II) as the central atom.

In our preceding paper[10] the dissociation rate constants of some ammine- and polyaminecobalt(II) complexes formed by the reduction with hydrated electrons, e_{aq}^-, were determined. In the case of Co(II)–ammine complexes such as $[Co(NH_3)_6]^{2+}$, $[Co(NH_3)_5Cl]^+$, etc., the first three ligands are detached very rapidly ($k > 7 \times 10^5$ s^{-1}) whereas the last three ligands $[Co(NH_3)_3(OH_2)_3]^{2+}$ are detached successively with rate constants of 6.4×10^4, 8.6×10^3, and 1.1×10^3 s^{-1}. The rate constants are independent of pH in the pH range 3–4.5. On the other hand, Co(II)–polyamine complexes such as ethylenediamine and triethylenetetramine dissociate more slowly and the dissociation rates depend on pH. Further we present the data for the dissociation of $Co(dien)_2^{2+}$ (dien = diethylenetriamine) and discuss the dissociation kinetics and mechanisms in more detail.

II. Experimental Section

$[Co(en)_3]Br_3$,[11] $[Co(dien)_2](ClO_4)_3$,[12] and *cis*-$[Co(trien)Cl_2]Cl$[13] were prepared according to the literature and $[Co(en)_3]Br_3$ was