1,10-PHENANTHROLINE AND ITS COMPLEXES

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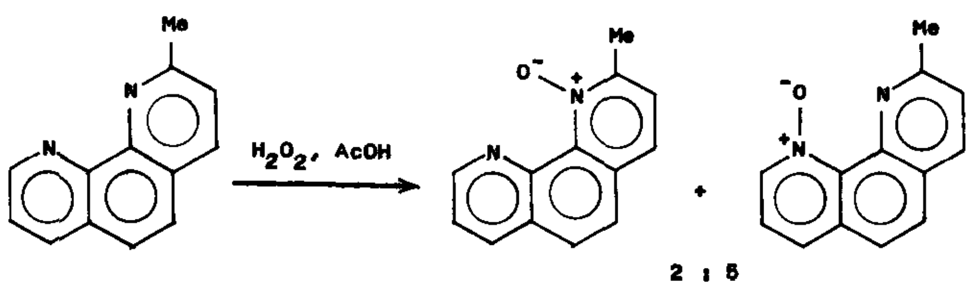
Abstract - The literature concerning 1,10-phenanthroline and its complexes has been reviewed with respect to their reactivity and properties.[x]

1,10-PHENANTHROLINE

Chemical reactivity

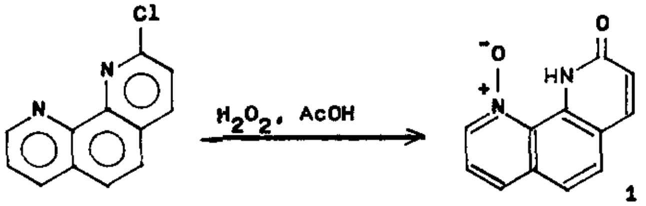
Among reactions of 1,10-phenanthroline (phen), at first its protonation ought to be mentioned. This process can be performed in NaCl aqueous solutions. Protonation constants have been determinated potentiometrically. Activity constants of phen and phenium ion are given [1]. Also the protonation of phen in $ClSO_3H$ is reported. In this totally anhydrous medium the protonation involves two protons.[2]

In the study of substituted phens, the oxidation of 2-methyl- and 2-chloro-phens was carried out.[3] 2-Methyl-phen reacts with H_2O_2 in AcOH to give 2:5 mixture of two mono-N-oxides:



x/ This paper is a continuation of a former one (Heterocycles 1979, 12, No.4,529) dealing with polyazaphenanthrenes.

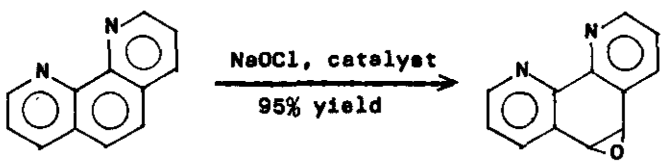
while 2-chloro-phen in a similar reaction yields a hydrolysis product (1)



1

The [1]H NMR spectral data of synthesized compounds are given.[3]

To investigate oxygen atom transfer reactions in enzyme systems, the direct oxidation of arenes and azaarenes was studied.[4] The epoxide (2) was prepared under mild conditions in high yield by treating phen with aqueous sodium hypochlorite in the presence of a phase transfer catalyst. In this novel epoxidation reaction none of the corresponding N-oxides could be detected.

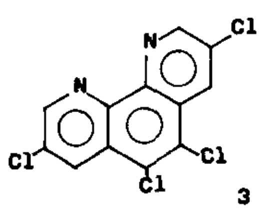


2

The mechanism of the above reaction is of interest, arene oxides being implicated as intermediates responsible for carcinogenicity and mutagenicity of polycyclic aromatic hydrocarbons.[4]

In spite of a resistancy of phen towards electrophiles, methods of its direct chlorination [5] and bromination [6] under mild conditions have been reported.

Chlorination performed with a mixture of thionyl and sulfuryl chloride, at 55-65°, resulted in (3) and (4):



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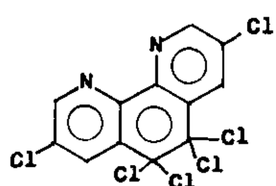

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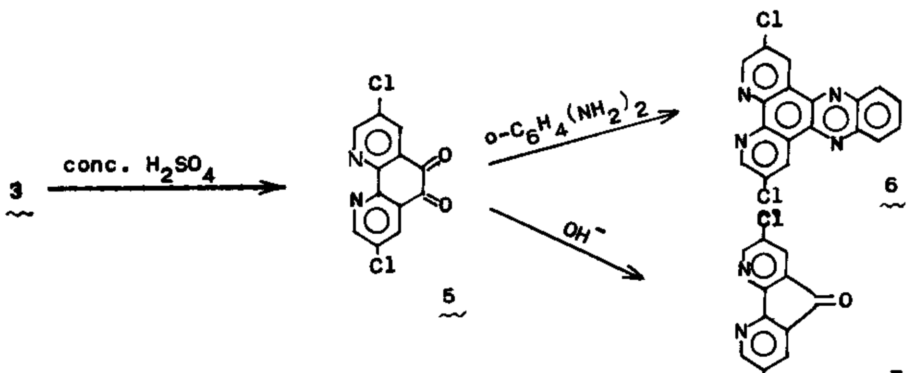
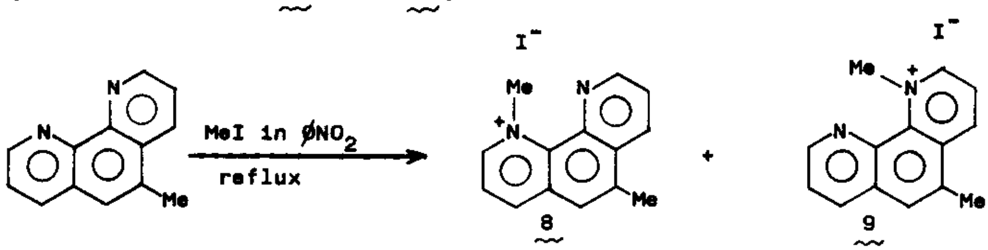
Treatment of (3) with conc. sulfuric acid yielded (5), which reacted with o-phenylenediamine to give (6), and with alkalies to give (7) via a benzilic acid type rearrangement.



The ^1H NMR and mass spectra are reported.

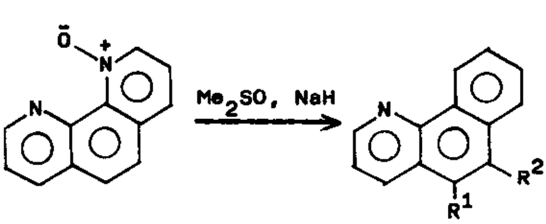
The direct bromination of phen was carried out with bromine in thionyl chloride to give as products 3-bromo-, 5-bromo-, 5,6-dibromo, 3,5,6-tribromo- and 3,5,6,8-tetrabromo-phens. The ^1H NMR spectra are reported.

In the quaternization reaction of 5-methyl-phen, there was obtained a mixture of two methiodides (8) and (9), in the 2:3 ratio.[7]



The ^1H NMR spectral data are presented.

In the reaction of phen-N-oxide with the carbanion of dimethyl sulfoxide, azaphenanthrenes were formed [8]:



$R^1 = R^2 = H$

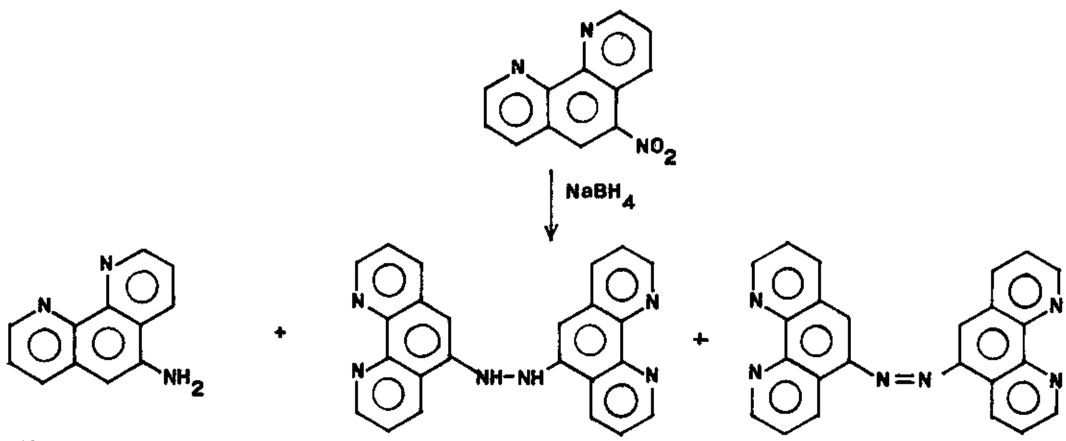
$R^1 = Me$, $R^2 = H$

$R^1 = H$, $R^2 = Me$

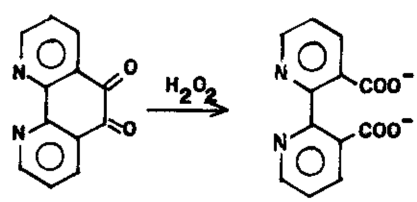
The reactivity of phens, free, and in the presence of some metal ions (Ru II, Fe II, Co II, Co III) has been compared; there was shown the alteration of reaction profile by metal ions.[9]

E.g., coupling of benzenediazonium ion occurs with $[Fe(phen)_3]^{3+}$, and not with the free phen. Nitration of $[Co(phen)_3]^{3+}$ was found to be about one hundred times faster than that of free ligand.[10] Nitration of $[Co(en)_2(phen)]^{3+}$ (en = ethylenediamine) occurs in a few seconds. During this reaction, the oxidation of phen to 5,6-dione also took place, especially in the presence of bromide ions.[11]

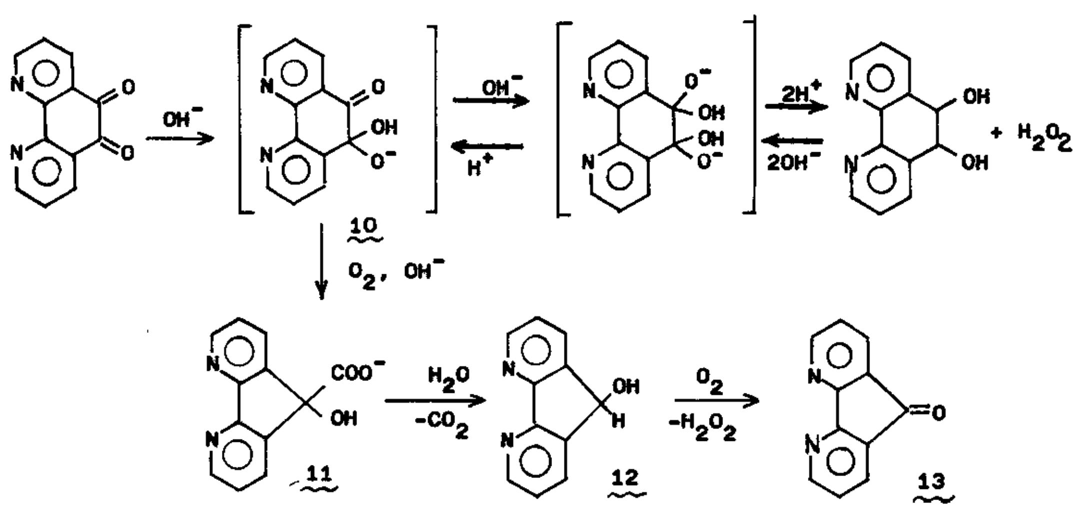
The reduction of 5-nitro-phen can be carried out with sodium borohydride:[9]



In the study of reactivity of phen-5,6-dione, it was oxidized by H_2O_2 to give 2,2'-dipyridyl-3,3'-dicarboxylic acid.



Other reactions of phen-5,6-dione are:

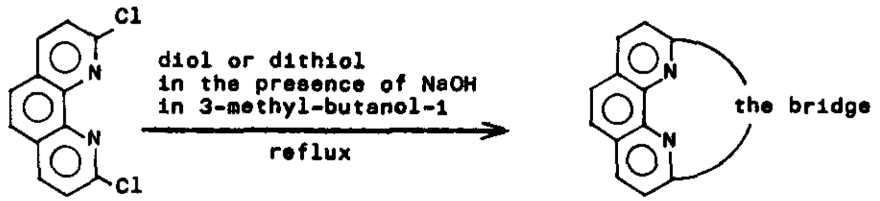


Conversion of phen-5,6-dione by OH^- ion to 4,5-diazafluoren-9-one (13) occurs via (10), (11) and (12), a route which is essentially the same as that known for phenanthrenequinone, i.e. a benzilic rearrangement, followed by decarboxylation and concurrent oxidation, all occuring in solution.

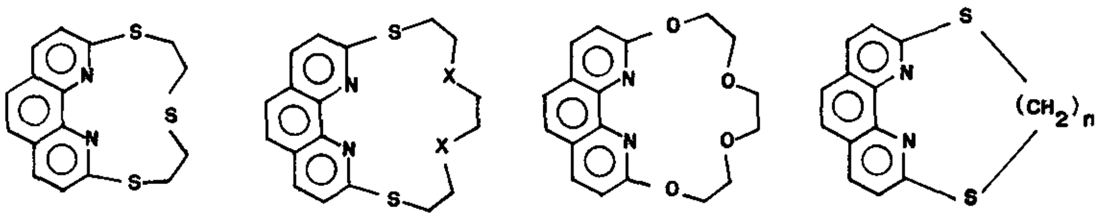
In the case of the heterocyclic (13), the decarboxylation is spontaneous.

Chemical reactivities of phen-5,6-dione and (13) were investigated in the presence and absence of metal ions. The results for the chemical interconversion of optically active phen complexes are presented and UV, CD and mass spectra discussed.[9]

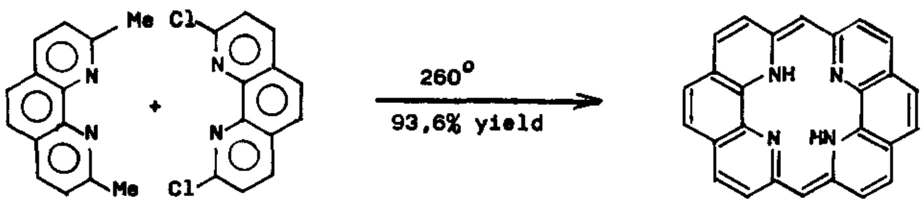
New cyclic ligands involving phen units bridged in the 2,9 positions have been synthesized.[12] The bridges involve chains of different lenghts and crown ether type oligo(ethyleneglycol)units. Ag^{+} and Hg^{2+} complexes have been isolated. The synthesis proceeds as follows:



For instance, the new cyclic ligands shown in the following chart were obtained:



Thermal dimerization of phen derivatives gives rise to macrocylic compounds, e.g.:



Similar condensations of 2,9-diamino-phen alone or as a mixture with 2,9-dichloro-phen have been performed. Above reactions were studied by differential thermal analysis.[13]

Properties

Crystal and molecular structures of phen and its hydrate were determined by the R map method and refined by least squares.[14] Mass spectra of phen derivatives are reported [9]. The IR [15] and far IR spectra of phen at liquid helium temperature [16] are described.

In the study of photoreduction of phen, the effects of solvent polarity on the fluorescence properties of phen indicate the close proximity of the (n,π^*) and (π,π^*) excited singlet states, the lowest triplet state being (π,π^*) in all solvents.[17]

There were investigated variations of quantum yields of fluorescence of the singly charged cation and neutral species derived from phen with pH.[18]
In the study of photo-Fries rearrangement, the SCF-SC (β^*)-LCI calculations of the absorption and fluorescence maxima of phen were performed.[19]

The effect of zinc ions on the luminescence, fluorescence and phosphorescence of phen was examined [20].

Investigations of NMR spectra of substituted phens included calculations of ,,long range'' effects, such as magnetic anisotropy and electric field effect of atoms and atom groups on ring protons. The results have been applied to determine the π electron densities.[21]

The electron spin density at the alkali nucleus in ion pairs with heteroaromatic radical ion was examined by measurement of ESR spectra of phen, reduced with Na in $MeOCH_2-CH_2OMe$.[22]
In the study of x-ray photoelectron spectroscopy (ESCA) of monoprotonated phen, the nitrogen 1s binding energy was measured.[23] The polarographic behaviour of phen is described [24].

Dissociation constants of phenium ion in different aqueous solutions were determined spectrophotometrically and pH-metrically, and the role of solvent has been discussed.[25]

Two empirical equations describing the variation of pK_a with temperature were compared for 2,9-dimethyl-phen.[26]

Acid dissociation constants of mono- and diprotonated polyalkyl phens were determined spectrophotometrically.[27] The close proximity (2,5 Å) of the two N atoms in the fused ring system favours addition of one proton, but discourages addition of second one, therefore in earlier research phen was considered as a monoacidic base.

Now there exist many evidences of diprotonated species of phen in strongly acidic media (e.g. [28,29]). The polyalkyl substituents enhance both protonation steps. For 2,9-dialkyl-phens, the mode of protonation is different than for other substituted phens. [27]

Dissociation constants for 5-nitro-phen in aq. MeOH and EtOH were determined spectrophotometrically. Solvent effects on the dissociation constants are discussed in the light of ion-solvent interactions.[30]

Phen can coagulate and reverse the charge of a AgBr sol. The mechanism of interactions is discussed.[31]

Biological activity

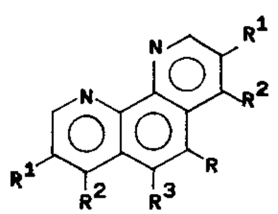
Antibacterial activity of phen compounds is reported [32], and the screening data for antitumor activity of 6-methyl-phen-N-methiodides are given [7]. There was studied the inhibition of photosynthetic electron transport by phen in Euglena gracilis [33], and by batho-phen* in isolated chloroplasts.[34]

The effect of prolongated action of phen as a photosynthetic inhibitor, affecting the connection between carotenoid content and chlorophyll in Euglena cells, has been described.[35] In the study of hydrogen metabolism by Rhodomicrobium vanielli, the inhibition of the photoassimilation by phen has been shown.[36]

Effects of batho-phen as an inhibitor of some enzyme activities in membranes from strains of Escherichia coli carrying mutations, were examined.[37] In the study of chemotherapeutic agents there were measured effects of combination of phen with nalidixic and piromidic acids on the growth of Escherichia coli. Phen was antagonistic to both acids.[38]

Investigations of properties of T 4D bacteriophage grown on Escheria coli B in synthetic media containing Zn^{2+}, Co^{2+} or Ni^{2+}, have shown, that the sensitivity of the nonradioactive phage particles to phen as the divalent metal cation chelating agent, varied greatly with the metal ions added to the growth medium.[39]

Hydrochlorides and methiodides of substituted phen,



R = H, Me, Cl, NO_2, ∅

R^1, R^2, R^3 = H or Me

and their chelates with transition metals were shown to have the lethal effects on dermatophytes and Candida albicans.[40]

Activation of D-glyceralaldehyde-3-phosphate dehydrogenase by phen is described [41]. The binding of two inhibitor molecules, phen and imidazole, to horse-liver alcohol dehydrogenase was studied by crystallographic methods.[42]

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* Batho-phen = 4,7-diphenyl-phen,
neocuproine = 2,9-dimethyl-phen,
bathocuproine = 2,9-dimethyl-4,7-diphenyl-phen

Inhibitor studies on particulate *sn*-glycerol-3-phosphate oxidase from Trypanosoma brucei showed that phen inhibited the dehydrogenase component.[43] Phen inhibits peroxidase in corn coleoptile sections.[44]

Phen hydrochloride is an antikininase agent; injected with bradykinin into the rat paw potentiates the bradykinin induced edema. Phen also potentiates the edema produced by carrageenin and celulose sulfate.[45]

The effect of phen on DNA binding, formation of a ternary DNA-nucleatide-enzyme complex, and pyrophosphate exchange by yeast RNA polymerase B was examined. There was found the relatively nonspecific inhibition of template and nucleotide binding by phen.[46]

The action of Armillaria mellea protease [47] and of rat kidney neutral peptidase [48] was inhibited by phen. Phen increased the activity of prolyl hydroxylase in 3T3 fibroblasts.[49]

In the kinetic studies of the removal of Zn^{2+} from bovine carbonic anhydrase, phen and 5-Me-phen were used as chelating agents.[50] Phen was found to stimulate the lipid peroxidation in rat liver microsomes due to its chelating properties.[51]

Investigations of the effect of phen on fluorescence spectra of submembrane particles of chloroplasts are described.[52] The effects of phen, as the metal chelating agent, on the cell progression of CCRF-CEM lymphoblasts were studied by flow microfluorometry.[53]

The binding of chick oviduct progosterone to nuclei was inhibited by phen. This fact is discussed in relation to the effects of phen on nucleic acid polymerases.[54] Phen was found to inhibit the light-induced oxygen uptake by chromatophores and subchromatophore-pigment complexes of Rhodospirillum rubrum.[55]

Applications

In oxidations, the molecular oxygen is activated by monovalent copper salts. A rearrangement of alcohols into aldehydes by the cuprous chloride-phen-oxygen system was studied. The alcohol RCH_2OH (R = ø, øCH=CH-) gave 83-6% RCHO, while, when instead of phen the pyridine was used, the yield decreased to 35-56%. [56]

The effect of phen as an additive in catalyzed liquid-phase oxidation of alkylaromatic hydrocarbons was examined. Action of phen involves formation of complexes with catalysts. [57] Phen inhibits the copper-catalyzed oxidation of ascorbic acid, this fact being due to the formed Cu(I) complex of phen.[58]

Drying properties of coatings and paints containing drying or semi-drying oils are improved by phen or 5-methyl-phen addition.[59] Polypropylene with an 0,5% addition of phen was blended at 90° to give a degradable, hot melt adhesive.[60] Utilization of phen as a vulcanization accelerator of vinylidene-fluoride-hexafluoropropene copolymers is described [61].

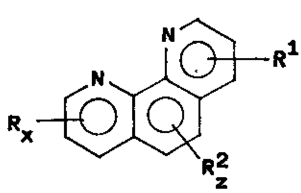
Phen can be applied as a stabilizer of aliphatic dienes, e.g. the dimerization of 1,3-butadiene and isoprene, containing $NaNO_2$ as polymerization inhibitor was strongly reduced by adding phen (1-50 ppm).[62] In study of effects of the nature of ligands in ion exchangers, the application of phen as a N-ligand is reported.[63] Phen makes the extraction of Zr and Hf from solutions by α-butyric acid in $CHCl_3$ more efficient.[64]

The effect of phen addition on electroreduction of metal complexes was investigated for copper electroplating in baths composed of CuCl, KSCN or CuCl, Na_2SO_3 [65], and for silver electroplating in baths composed of AgCl and $Na_2S_2O_3$, baths being cyanide free. [66]

Organic-electrolyte batteries with MnO_2 as the cathode active ingredient and organic electrolyte containing phen are described [67]. Phen improves the cathode efficiency.

Investigations of pressure sensitive copying materials composed of a substrate member coated with colour former and a transfer member coated with Fe compound and 4,7-R,R'-phen (R,R' = H, OH, ∅, pyridyl), are described.[68]

Substituted phens



R, R^1 = lower alkyl
R^2 = lower alkyl, ∅, NO_2, oxo, halogen
x, y, z = 0 - 2

are microbicides for industrial liquids, such as hydraulic fluids, metal cutting fluids, heating oils and others.[69]

1,10-PHENANTHROLINE COMPLEXES

Syntheses

The number of phen complexes is enormous, among those formed in the reaction of phen with metal halides, some will be mentioned.

Phen gives with $SnCl_4$ the complex $[SnCl_4 \cdot phen]$. With the excess of HCl, the $(phenH)_2SnCl_6$ is formed.[70] The syntheses of $(phenH)_2CeCl_4$ [71] and $[TlCl_3 \cdot phen]$ [72] are reported.

$SiHCl_3$ reacts with phen to form $[SiHCl_3 \cdot phen]$. In this process the side reaction resulting in 1,2,3,4-tetrahydro-phen occurs.[73] Complexes of the type

$[SiRR^1(phen)_2]I_2$

$R = R^1 = H, Cl, Me, \phi$

and $R = Me$, $R^1 = Cl$, OMe

were prepared in the reaction of phen with RR^1SiI_2. [74]

Phen-N-oxide reacts with SiX_4 to give the following complexes of halosilanes:[75]

$SiF_4 \cdot L$	$SiBr_4 \cdot 2L$	$(L = phen - N \rightarrow O)$
$SiCl_4 \cdot L$	$SiI_4 \cdot 2L$	
$SiCl_4 \cdot 2L$	$SiI_4 \cdot 3L$	

Phen forms with hexachloroplumbate $(phenH_2)PbCl_2$ [76], and with $K_2[ReCl_6]$ the complex $H_2[(phen)_2ReCl_6]$ results.[77]

Addition of phen to a conc. HBr solution of $H_2ReBr_5(NO)$ gives $(phen\ H_2)[ReBr_5(NO)]$, which on heating forms $[ReBr_3phen(NO)]$ [78].

Syntheses of 2,9-dimethyl-phen complexes of the type CuL_2Cl_2 and $CuLCl_2$ (L = 2,9-dimetyl-phen), are reported.[79]

Rhodium complexes, such as

$Rh[phen_3]^{3+}$

$Rh[phenX_4]^-$ X = Cl or Br

$Rh[phen(H_2O)X_3]$

$Rh[phen_2X_2]^+$

are described [80].

Recently the syntheses of carbonyl rhodium(I) complexes of phen and its derivatives: $[Rh(CO)_2L][RhX_2(CO)_2]$ (L = phen; 2,9-dimethyl-phen; 4,7-diphenyl-phen; X = Cl, Br), have been reported.[81]

Heterotrischelated (Rh III) complexes: $[Rh(bpy)_2L]^{3+}$ and $[Rh(bpy)L_2]^{3+}$ (b py = 2,2'-bipyridine ; L = phen, 2,6-dimethyl-phen) were synthesized and characterized by exponential luminescence decays.[82]

The reaction of mer$[RuCl_3(PMe_2\phi)_3]$ with 2,9-dimethyl-phen (L) gives $[RuCl_2L]Cl_2$; the complex was characterized by ^1H and ^{31}P NMR spectroscopy.[83] The syntheses of $[Pt(5\text{-}NO_2\text{-phen})]X_2$ [84] (X = Cl, ClO_4), and of $(phenH_2)UCl_6$ [85] are reported.

Among nitrate complexes of phen ought to be mentioned $(phenH)_2Ce(NO_3)_6\cdot 5H_2O$ [86] and $Mn(NO_3)_3\cdot$phen.[87]

Syntheses of complexes:

$Ru(phen)_3\cdot(CN)_2\cdot 6H_2O$

$Ru(5\text{-}NO_2\text{-phen})_3\cdot(CN)_2\cdot 2H_2O$

and $Fe(phen)_3(CN)_2\cdot H_2O$ have been reported.[88]

Synthesis of a 6-coordinated spin triplet (S = 1) ferrous complex, $Fe(phen)_2\cdot(NCBF_3)_2$ is described and its Moessbauer spectra are given.[89]

Complexes of the type

$Zn(SCN)_2L_2$ L = phen ; $5\text{-}NO_2$-phen

and $Zn(SCN)_2L'$ [90] L' = 2,9-diMe-phen

as well as $Ga(NCS)_3\cdot$2phen

$Ga(NCS)_3\cdot$1,5phen

and $Ga(NCS)_3\cdot$phen$\cdot$MeOH

were prepared and characterized by their IR spectra and thermal stability.[91]

There are known complexes of scandium thiocyanate, nitrate and chloride with phen:[92]

$ScX_3\cdot$2phen

and $(phenH)_3[Sc(NCS)_6]$ X = NCS^-, NO_3^-, Cl^-

To compounds of the ,,Reinecke salts'' type belong the complex anions $[Cr(NCS)_4phen]^-$, formed in the substitution reaction of $K_3[Cr(NCS)_6]$ with phen.[93] Ln chloride reacts with KSeCN and phen to give $Ln(phen)_3\cdot(NCSe)_3$ complexes.[94]

The syntheses of $Mn_2O_2(phen)_4\cdot(ClO_4)_4$ [95] and $Mn(232\text{-}N_5)(ClO_4)_2\cdot 2H_2O\cdot$phen$\cdot\frac{1}{2}$EtOH [96] were reported.

Reaction of phen in HF solution with UO_2F_2 gives $(phenH)[UO_2F_3]$ [97], and with Nb_2O_5, MoO_3 and $VO\cdot SO_4\cdot 3H_2O$ the complexes $(phenH)[NbOF_4]$ [98], $(phenH)[MoO_2F_3]\cdot 2H_2O$, [99] and $(phenH)[VOF_3(H_2O)]$, [100] respectively

The synthesis of phenium oxopentabromomolybdate(V), $(phenH_2)[MoOBr_5]$ was reported. By hydrolyzing the parent salt, $Mo_2O_3Br_4(phen)_2$ and $Mo_2O_4Br_2(phen)_2$ were isolated.[101] In the study of atranes, the synthesis of $(phenH^+)(NH_4^+)$-$\overline{N(CH_2COO)_3Mo}O_2(OH)_2^-$ has been reported.[102]

Oxodiperoxovanadate(V) complex of phen,

$M[VO(O_2)phen]\cdot nH_2O$ M = Na, K, NH_4

n = 2-5

was prepared from H_2O_2 solutions of VO_3^- in the presence of phen.[103] The synthesis of $(phenH)(HCrO_4)$ is described in [104].

Tripyrogallyl and tricatechyl germanates of phen were obtained by reacting pyrogallyl or pyrocatechyl esters of germanic acid with phen.[105]

The complex of phen with nitridoosmium $(phenH)[OsNX_4](H_2O)]$ X = Cl, Br is formed in the reaction of phen with $K[OsNX_4(H_2O)]$.[106]

The synthetic approach to the complex of phen with imido bis(sulfurylchloride), $phen\cdot HN(SO_2Cl)_2$, is described.[107]

The 1:1 complexes of phen and 5-methyl-phen with iodine are reported, and their association constants determined.[108] Syntheses of alkali metal complexes of phen and organic anions, [109] of the type

MA phen

MA $(phen)_2$ M = Na, K

M(A,HA)(phen) A = benzoate, 2-OH-benzoate

M(A, HA)$(phen)_2$, have been performed.

Studying stereochemistry of Co(III)complexes, compounds

$[CoA(phen)_2]ClO_4\cdot 2H_2O$ A = me-tart, D-malato

have been prepared and characterized by CD, IR and ^1H NMR spectra. [110]

The synthesis of ammonium complexes $NH_4\cdot A\cdot phen$.[111]

A = o-$C_6H_4(OH)_2$

2,4-dinitrophenol

2,4,6-trinitrophenol

and of $(phenH)^+[ReZ_3]^-$ [112] H_2Z = toluene-3,4-dithiol is reported.

Aryl mercury halides form with phen 1:1 adducts.[113] Diphenylmercury reacts with phen, 2,9-dimethyl-phen and 2,4,7,9-tetramethyl-phen (L) to give the $\phi_2Hg\cdot 2L$ adducts. [114] $(RC{\equiv}C)_2Hg$ when stirred with phen or 2,9-dimethyl-phen (L) in EtOH, yields a donor-acceptor complex $(RC{\equiv}C)_2HgL$ [115], R = Me, $ClCH_2$.

VCl_3 reacts with phen, 5-chloro-phen, 5-methyl-phen and 4,7-dimethyl-phen (L) in EtOH to give $VCl_3L{\cdot}EtOH$.[116] The synthesis of Cd phen$(CH_2SiMe_3)_2$ is reported[117].

In the study of dimethyl compounds of Pt, there were obtained complexes of the type $PtMe_2X(HgX)L$ L = 2,9-dimethyl-4,7-diphenyl-phen

X = Cl, Br, I, OAc

from $PtMe_2L$ and HgX_2 [118]; and the reaction of $PtMe_2L$ with GeR_nX_{4-n} resulted in $PtMe_2X(GeR_nX_{3-n})L$.[119] X = Cl, R = Me, n = 1,2,3

X = Cl, R = ϕ , n = 2,3

X = Br, R = Me, ϕ, n = 3

To carbonyl complexes of phen belong $K[Cr_2H(CO)_{10}(phen)_3]$ and $Bu_4N[Cr_2H(CO)_{10}phen]$. These compounds are formed in reactions of phen as a N-donor bidentate ligand and $M[Cr_2H(CO)_{10}]$ [120]. M = K, Bu_4N

Phen forms salts with complex anions $[Cr(NCS)_4(N\text{-benzylaniline})_2]^-$ and $[Cr(NCS)_4(N\text{-dimethylaniline})_2]^-$.[121]

Chemical rectivity

Phen complexes with Li, Na and K exchange their hydrogen with gaseous D. The ESR spectra are discussed.[122] The effect of ligand substitution on the kinetics of aquation of complexes FeL_3 L = phen; 5-chloro-phen; 5-nitro-phen; 4,7-dimethyl-phen

is described in [123].

In the kinetic studies of acid hydrolysis of oxalatobis(phen)chromium(III)ions, $[Cr(C_2O_4)(phen)_2]^+$, the activation parameters were measured. Enthalpies of activation are the same as those reported for the racemisation of the same complexes.[124]

The kinetics of CN^- substitution for phen derivatives in complexes: biscyanobis(5-chloro-phen)iron(II) and tetracarbonyl(5-nitro-phen)molybdenum (O) have been determined and found to be consistent with 2-stage mechanism with the CN^- ion first attaching to a 2- or 9-position intramolecularly to the metal ion. A rapid second step substitutes CN^- for the second phen N atom[125].

In the spectroscopic study of the reaction of $[Ru(5\text{-}NO_2\text{-phen})_3]^{3+}$ with MeO^- and EtO^- ions, there was shown the addition of alcoxide ion to the

2-position of each heterocyclic ligand. [126]

$Fe_2(phen)_4OCl_4$ reacts with oxalic acid to give $(phenH)_3[Fe(C_2O_4)_3]\cdot 5H_2O$. [127] The oxidation of the $[FeL_3]^{3+}$ ion (L = 4,7-dihydroxy-phen) by air or $K_3Fe(CN)_6$ gave the Fe(III) compound; the vis spectra of complexes are presented. [128]

Reactions of $PtMe_2L$ L = phen
2,9-dimethyl-4,7-diphenyl-phen

with SnR_4Cl_{4-n}, $Pb\phi_2Cl_2$ and $Pb\phi_3Cl$, in which R = Me, ϕ; n = 0-3, proceed via an oxidative addition involving the Sn-Cl or Pb-Cl bond to give $PtMe_2ClL(SnR_nCl_{3-n})$ and $PtMe_2ClL(Pb\phi_mCl_{3-m})$ [129] m = 1,2

$W(CO)_4phen$ reacts with $[NO][PF_6]$, and $Mo(CO)_4phen$ with NO^+ in Me_2CO to yield mer-$[W(CO)_3phen(NO)][PF_6]$ and fac-$[Mo(CO)_3phen(NO)]^+$, resp. [130]

$(PhenH)_2[ReCl_5(NO)]$ thermally decomposes at 220° to give $[ReCl_3phen(NO)]$. [131] Thermal decomposition of $(phenH_2)(CoCl_4)$, $(phen\,H_2)(ZnCl_4)$ and $(phen\,H_2)(MnCl_5)$ [132] as well as of $phen\cdot Hg(CN)_2$ [133] and of $(phen\,H)_2(UO_2Cl_4)$ [134] was also studied.

Photoreduction of mono L Cu(II) cation (L = 2,9-dimethyl-phen) observed during the irradiation of this compound produces the corresponding Cu(I) complex: [135] $CuLX_2 \rightarrow CuLX$ (X = Cl, Br)

The intermediate radicals were detected by ESR spectroscopy, using a spin trap technique, in the photoreduction of diphenylacetato LCu(II) [136] (L = 2,9 -dimethyl-phen).

Properties

Numerous publications are dealing with the determination of crystal structure of phen salts and complexes. In most cases the determination is based on the x-ray diffraction, refined by least squares procedures to a final conventional R index.

Crystal structures of phen hydrochloride and hydrobromide, dinitrate, sulfate, perchlorate, diperchlorate [137] and perrhenate [138] were determined as well as crystal structures of complexes:

$Cu(gg)L\cdot 5H_2O$ [139] gg = glycyl glycine
L = 2,9-dimethyl-phen

$[Cu(H_2O)(phen)_2]BF_4$ [140]

$\{Cu[CS(NH_2)_2phen\}$ I·phen [141]

$(phenH_2)(MnCl_5)$ [142]

$[M(phen)_2(OH_2)_4][ClO_4]_2 \cdot 2phen$ [143] M = Sr, Ba

$[Zn(CN)_2 \cdot (2,9\text{-diMe-phen})]$ [144]

$(phen)_2Hg(NO_3)_2$ [145]

(phen)·(TCNQ) [146] TCNQ = 7,7,8,8-tetracyanoquinodimethane

In the study of photophysical behaviour of complexes

cis-$IrL_2Cl_2^+$ L = 2,9-dimethyl-phen

their absorption and emission spectra are reported. [147]

The oxidation state and coordination number of metal ions in some halogen phen complexes of Mn(III), Co(II), Cr(III), Zn(II), Cd(II) and Fe(III) were determined by examining metal-halogen stretching frequencies in IR spectra. [148]

IR spectra of (phen H)$[Ga(NCS)_4phen]$, [149] and far IR spectra of $(phenH)_2[MX_4] \cdot HX$ [150] M = Zn, Cd

X = Cl, Br, I

as well as of (phenH)$(FeX_4) \cdot HX$ and $FephenCl_3$ [151], have been reported.

IR spectra of phen-N-oxide salts with HCl, HBr, HI, $HClO_4$ and HBF_4, and of their deuterated analogues have been recorded. The type of hydrogen bond in these compounds, as well as the changes in spectra of protonated species are discussed. [152]

Study of vis spectroscopy allowed to examine the ability of p-, d- and f-elements to form complexes with hydroxy derivatives of triarylmethane in the presence of phen.[153]

Electronic spectra of $(phenH)_3(MoX_9)$ X=Cl,Br are given [154]. Luminescence of $(phenH)^+(IrCl_4)^-$ [155] and chemiluminescence occuring during interaction of cobalt phen complexes with H_2O_2 [156] have been studied.

Recently the mechanism of quenching of the emission of $[RuL_3]^{2+}$ complex (L = phen; 5-chloro-phen; 4,7-dimethyl-phen) by europium(II) [157], as well as the application of the continuous variation method to the Ni(II) complex of phen [158], have been described.

Relation between magnetic and structural properties of complexes $NiLX_2$

L = 2,9-dimethyl-phen ; 2,9-dimethyl-4,7-diphenyl-phen

X = Cl, Br, I

was investigated; structure of complexes was determined by x-ray diffraction.[159]

^1H NMR and IR spectra were used to determine structure of complexes $PdL(CN)_2$ and $PdLX_2$ [160] L = 2,9-dimethyl-phen

X = Cl, Br, I

^{14}N NQR spectra of Pd(II) complexes of phen are reported. The ^{14}N NQR data can be utilized to order the monodentate X ligands in phen PdX_2 or bidentate ligand Y in phen PdY in terms of electron donation toward Pd(II). The obtained order is $CN^- = I^- > SCN^- = NO_2^- > Br^- > Cl^- > NO_3^- \sim$ phen, position of phen at the end of the series being rather anomalous.[161]

ESR spectra of CuL_2Br_2 (L = 2,9-dimethyl-phen) are described[162]. Optical activity of $[Ru(5\text{-}NH_2\text{-phen})_3]^{2+}$ is discussed, and its CD, IR and electronic spectra are presented.[9]

As an example of application of MICE (magnetically induced circular polarization of emission) to metal complexes, the analysis of MICE of $Ru(4,7\text{-di}\phi\text{phen})_3Cl_2$, dispersed in a polymethacrylate matrix, is reported.[163]

The calculation of energy profiles and of electronic structure of phen-TCNQ complex has been performed by HMO method. Calculations of intermolecular overlaps involving the lowest vacant MO of TCNQ and one or more highest occupied orbitals of each of donors have been correlated with the donor-TCNQ geometrical configurations.[164]

In the study of complex $[Co(phen)_2(C_2O_4)]^+$, electronic structure of phen ligand was calculated by NDDO method. The lone-pair densities are a suitable measure for a σ-donor capability of the ligand.[165]

Structure of phen complexes with p- and f-elements and pyrocatechol violet was studied by UV-vis spectroscopy and by HMO calculations.[166]

Moessbauer parameters were determined for $[FeL_3]X_2$ L = phen, phen-N→O

X = ClO_4, I, NO_3

and the results interpreted by a model based on the MO picture of the cation.[167]

The variable-temperature ^{57}Fe Moessbauer spectra of $[Fe(2\text{-MeO-phen})_3](ClO_4)_2\cdot H_2O$[168] and $[Fe(2\text{-Me-phen})_3][BF_4]_2$[169] were studied.

Moessbauer emission spectra of ^{57}Co labeled $Co(phen)_2(NCS)_2$ and of ^{57}Co doped $Fe(phen)_2(NCS)_2$ were determined and compared with the absorption spectrum of $Fe(phen)_2(NCS)_2$.[170]

In paper electrophoretic study of ion-pair formation, the electrophoretic behaviour of $[CoL_3]^{3+}$ L = phen ; 4,7-dimethyl-phen; 5,6-dimethyl-phen in the presence of halide, NCS^-, NO_2^- and NO_3^- ions was examined.[171]

In investigation of hydrophobic and charge-dipole interactions, salting effects of metal chelate electrolytes: $Fe(phen)_3Br_2$, $Co(phen)_3Br_2$ and $Co(phen)_3Br_3$ on the solubilities of nitrobenzene and toluene have been studied.[172]

Electrochromic display devices were prepared by using solutions of $[CoL_3]^{2+}$ [173] (L = phen derivatives)

Polarographic catalytic currents in solutions of Ni and Co complexes with phen are described [174].

Spectral sensitization of single-crystal n-type TiO_2 electrodes by ruthenium(II) complexes RuL_3Cl_2 L = 5-chloro-phen; 4,7-dimethyl-phen has been studied as a function of pH of solution. Implication of results for a solar energy conversion system is discussed. [175]

Stability constants of phen complexes of Cu(II), Zn(II), Mg(II) and Ca(II) with adenine [176] or adenosine-5'-triphosphate [177] were determined by potentiometric titration. Also the stability constants of CuZphen (Z = bis[carboxymethyl]-dithiocarbamate) are reported.[178]

There were calculated formation enthalpies for the iodine complexes of phen and 5-methyl-phen [179], as well as the rate constants and activation parameters for formation of complexes of Ni(II) ion with phen, 5-chloro-phen, 5-methyl-phen and 5,6-dimethyl-phen,[180] and of those of $Ni(H_2O)_6^+$ or $NiNTA(H_2O)_6^-$ (NTA = nitrilotriacetate) with phen, 4,7-dihydroxy-phen and phen-2-carboxylate.[181]

For the manganese complexes of phen, $[Mn\ phen]^{2+}$, $[Mn(phen)_2]^{2+}$ and $[Mn(phen)_3]^{2+}$, there were calculated formation constants and catalytic coefficients in a hydrogen peroxide decomposition reaction.[182]

The enthalpy data for formation of adducts of phen with R_3SiCl, $RSiCl_3$ and $SiCl_4$,[183] (R = Me, ∅) or with $\emptyset_2Sn(CO_2Me)_2$, $Bu_2Sn(CO_2Me)_2$, [184] as well as with Cu(II) complexes of fluorinated β-diketones [185], are reported.

Investigations of the kinetics for the reaction of $\emptyset_3SbW(CO)_5$ with phen, resulting in $[Wphen(CO)_4]$, are described.[186]

Biological activity

Complexes M^{2+}-phen-α-amino acid (M = Ni, Zn, Cd) were found to be of interest in relation to biological systems.[187] In the reseach of antineoplastic agents, the transition metal complexes of phen have been studied with regard to their antitumor activity.[188]

Hydrolysis of acetyl phosphate, catalyzed by Cu^{2+}, Co^{2+}, Ni^{2+} or Zn^{2+} was examined by addition of phen. Mechanism of catalysis is discussed in relation to metal-enzyme bonding.[189]

Phen complexes of Co(II) were studied in relation to respiratory metalloproteins.[190] There were investigated the kinetics of oxidation of horse heart ferrocytochrome c and Pseudomonas aeruginosa ferrocytochrome c_{551}, by $[CoL_3]^{3+}$ ions [191] (L = phen; 5-chloro-phen; 5,6-dimethyl-phen; 4,7-dimethyl-phen).

The action of phen transition metal complexes on the rat isolated diaphragm muscle-phrenic nerve preparation is reported [192]. Phen and its Zn complex have been found to yield skeletal defect in mice.[193]

Investigations of the effect of phen Fe(III) complex on the kinetics of iron accumulation and excretion in mussel Mytilus edulis (L) are described.[194] Phen complex of Cu(I) was found to be a potent reversible inhibitor of Escherichia coli DNA polymerase.[195]
Also there was studied the use of nonradiative phen complex of Ru in a digest marker system for the measurement of nutritial flow at the proximal duodenum of calves.[196]

Applications

Complexes of the type [Rh(phen)(1,5-hexadiene)]X (X = PF_6^- , $B\phi_4^-$) were found to be good catalysts for hydrogenation of ketones.[197] Catalytic activity of Cu, Mn and Co phen complexes was studied, e.g. in the oxidation of arsenic trioxide solutions,[198] or in the oxidation of tiron by H_2O_2. [199]

Phen salts with H_2CrO_4 are wet or atmospheric corrosion inhibitors of steel, brass and copper.[200]

An important application of phen complexes is their use in analytical chemistry. Numerous analytical methods for metal determination with use of phen involve a formation of coloured complex, its extraction to the organic solvent, and the spectrophotometric study of the extract.

For instance, Cd(II) was detected in zinc by selective extraction with dithizone in $CHCl_3$ in the presence of phen, followed by the spectrophotometric analysis of the extract.[201]

Thenoyltrifluoroacetone (HTTA) and phen reacted with Eu^{3+} and Sm^{3+} to form complexes Eu $(TTA)_3$phen and $Sm(TTA)_3$phen, which were extracted with benzene, and their fluorescence spectra were measured.[202] In an analogous manner, using thiothenoyltrifluoroacetone, Ag in lead metals [203], or Cd in tin metals [204] can be determined.

There was reported the extraction of Cu from aq. tartaric acid by solutions *of* $PrCO_2H$ *and* $EtCHBrCO_2H$, *containing phen.*[205] Eu can be determined by extraction of its complex with 1-naphthoic acid and phen, followed by luminescence spectroscopy of the extract.[206]

Au^{3+} was determined spectrophotometrically by reduction with Co^{2+} in the presence of phen.[207] Chromatography on phen tungstosilicate impregnated paper can be used to resolve mixtures of Ca^{2+}, Ag^{+}, Au^{3+}, Pt^{4+} and Pd^{2+}.[208]

Besides phen, also batho-phen, neocuproine and bathocuproine are useful analytic agents. For instance, there is described a number of ions (Pb, HgII, Bi, Cd, SnII, Ni, CoII, MnII, Ca, Sr, Ba, Mg, Zr and others), precipitated by batho-phen, and number of ions (Ag, HgI and II, CuI and II, Cd, FeII) giving coloured soluble complexes. The pD values are presented.[209]

A simple method for rapid colorimetric determination of Cu with a polyvinyl chloride film, impregnated with bathocuproine is described[210]. U can be indirectly determined spectrophotometrically by reducing U(VI), oxidizing by excess of Cu(II) and complexing the produced Cu(I) with neocuproine.[211]

By the formation of $CuL_2(ReO_4)_2$ L = 2,9-dimethyl-phen from $[CuL_2]^{2+}$ and ReO_4^-, the determination of rhenium can be accomplished.[212] Batho-phen is used for determination of iron[213] or for identification of submicro quantities of iodide ions.[214]

4,7-Bis[p-phenylazo)-anilino]-phen was found to be a sensitive reagent for the determination of Fe[215]; Ag reacts with phen and 2,4-dinitropyrocatechol to form a complex, used for the Ag determination[216], V can be analyzed by its complexes with phen and pyrocatechol violet.[217]

Co, Ni, Cd and Zn complexes of phen form with eosine, erythrosine, Bengal Pink, fluorescein and Bromophenol Blue complexes, extracted by $CHCl_3$. Metals are determined spectrophotometrically.[218]

Also investigations of the phen complexes of Zn, Cd and Hg with Bromophenol *Blue or Bromocresol Green*,[219] *as well as phen complexes of Zn and Cd with* Eriochrome Black T or Eriochrome Red B[220], have been performed.

Pd[221] and Sc[222] can be determined by forming complexes with phen and eosine. The fluorometric determination of Cd by its complex with thioxime was extended by using the cooperative effect of phen.[223]

Cu can be determined spectrophotometrically by complexation with phen and phloxine.[224] In the formation of the complex of Ag^{+}, phen and Bromopyrogallol Red, there was observed the inhibitory effect of $S^{=}$ ions; this fact can be applied for the spectrophotometric determination of trace amounts of sulfide ion.[225]

Adding Fe^{3+} to solutions containing phenothiazine, the formed Fe^{2+} is complexed with phen, and phenothiazine is determined spectrophotometrically.[226] Phen was found to accelerate the rate of colour change of Xylenol Orange (XO) indicator in Cu(II) - EDTA titrations (EDTA = ethylenediaminetetraacetic acid) due to the formation of the $(Cu\,phen)_2XO$ complex.[227]

Phen can be used as a precipitant of $[GaCl_4]^-$, forming $(phenH)GaCl_4$.[228] Phen complexes of Fe(II) were studied as pH-markers for gel isoelectric focussing.[229] The use of insoluble complex $Cd(phen)_2I_2$ to determine Cd by conductometric titration was reported.[230]. Ce(IV) can be determined in solution of its salts by application of a cobalt electrode to coulometric titration in the presence of phen.[231]

Te is separated from Se from Molten Salt Reactor fuel fission products by precipitation with phen [232]; the analysis of low levels of peroxides in PVC is made by formation of coloured phen complex with Fe(III).[233]

Ionic detergents in water can be determined by complexation of an anionic detergent, e.g. Na dioctylsulfosuccinate with Cu and phen, followed by spectroscopic analysis.[234] The determination of silicic acid content in detergents with the use of $H_4SiMo_{12}O_{40}(phen)_4.nH_2O$ complex, is described [235].

Serum iron concentration can be determined using batho-phen sulfonate in a formate system, without prior protein precipitation.[236] Reducing sugars, such as galactose, glucose, mannose, are detected by the measurement of colour formed with neocuproine hydrochloride-$CuSO_4$ treatment of sugars separated on a column of anion exchanger.[237]

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