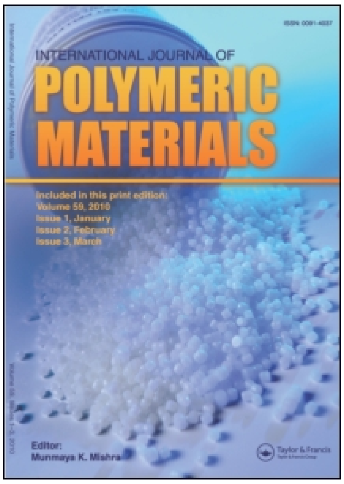

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers

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To cite this Article Aseeva, R. M. and Zaikov, G. E.(1993) 'Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers', International Journal of Polymeric Materials, 20: 1, 101 — 116

To link to this Article: DOI: 10.1080/00914039308048504

URL: http://dx.doi.org/10.1080/00914039308048504

Intern. J. Polymeric Mater., 1993, Vol. 20, pp. 101-116
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Printed in Malaysia

Metal Macrocyclic Complexes as Novel High Temperature Stabilizing Agents and Flame Retardants for Polymers

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Several macrocyclic complexes were identified that exhibit large heat stabilizing and flame retardant effects in polymers.

KEY WORDS Heat stabilizers, flame retardants, macrocyclic compounds.

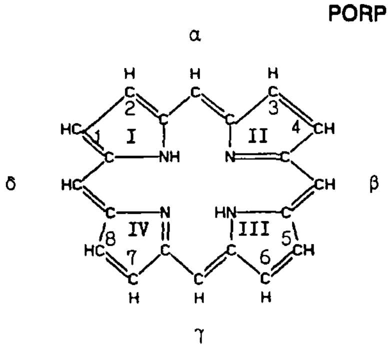
1. INTRODUCTION

A macrocyclic compound is usually defined as a compound with nine or more members (including all hetero atoms) in the cycle and with three or more donor atoms.

It is known that these compounds have the ability to function as macrocyclic ligands at coordination with different metal ions. Coordination chemistry of macrocyclic compounds has undergone intensive growth after sixty years. Since then a considerable number of the cyclic compounds containing ligating atoms of nitrogen, oxygen, sulphur, phosphorus and others have been synthesized. The most important classes of macrocyclic compounds are (I) porphyrins, (II) azaporphyrins, (III) their valent-saturated azamacrocyclic analogues, (IV) crown-ethers, (V) bi- or polycyclic cryptands and compounds with mixed structures (Figure 1a, b). The interest in macrocyclic compounds and their metal complexes is due first to the realization that they may serve as models for important natural products (chlorophyll, hemoglobin) and also as objects for modeling important life processes (photosynthesis, inversive oxygen fixation, and so forth).

Due to intensive investigation in the field of the synthesis of macrocyclic compounds and the development of a raw material base many compounds have become accessible for use in practice.[1-4] For analysis of the published data it may be concluded that metal macrocyclic compounds are mainly used as catalysts in different chemical, electrochemical and photochemical reactions. High catalytic activity was found for complexes of macrocyclic compounds with continuous systems of π-conjugated bonds.[3-5]

PORPHIN



I

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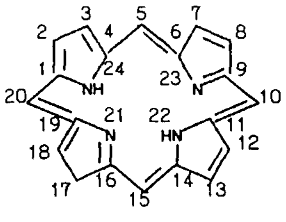

Ia

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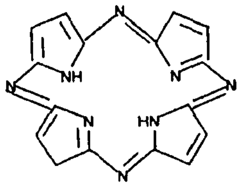


II

tetraazaporphin

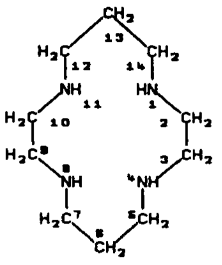
FIGURE 1a Some types of macrocyclic compounds.

Metal complexes of phthalocyanine and its substitute derivatives are used as commercial dyes. Phthalocyanine dyes are characterized by tone cleanliness, high light resistance and migrational stability. The problem of the use of metal macrocyclic complexes as high temperature stabilizing agents or flame retardants for polymers is of special interest to us. The work in this direction was begun seventy years ago and was temporarily interrupted for technical reasons.

In this report we give an account of the principles relative to the stabilizing capability of metal complexes of azaporphyrin macrocyclic compounds and their analogues. It was necessary to find the interrelation between a chemical structure and inhibition effectivity of macrocyclic compounds and their metal complexes.

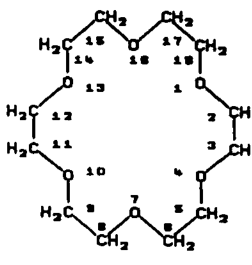
The next premises for the development of this investigation were taken into consideration. Azaporphyrin ligands and their metal complexes have a specific geometrical and electronic structure. Due to the presence of continuous systems of π-conjugated bonds macrocycle the compounds show both donor and acceptor properties. They may be able to accept or donate electrons with the formation of ion-radical particles. Thus these compounds may participate in redox reactions and in the reactions of radical type.

The considerable variation in the properties of metal macrocyclic complexes may be attained by changing the metal's nature and/or structure of the macrocyclic ligand. Superior thermal stability, nontoxicity, corrosive nonactivity and other functional features of these products were also taken into account.



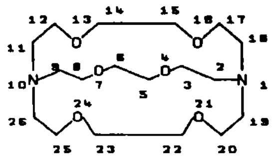
III

1,4,8,11-tetraazacyclotetradecane;-[14]-ane-N$_4$ by D. Busch and A. Melson



IV

1,4,10,13,16-hexaoxacyclooctadecane; [18]-ane-crown-6



4,7,13,21,24-hexaoxa-1,10 diaza-bicyclichexacosane; [2]-cryptand

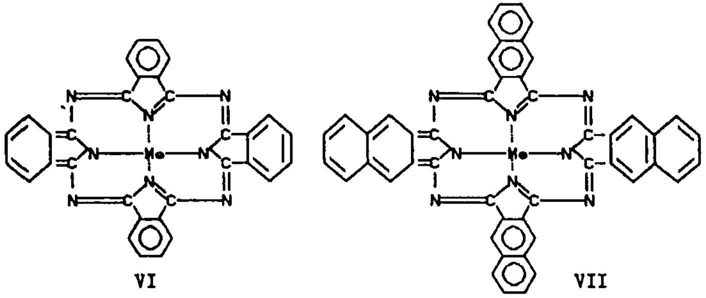
FIGURE 1b Some types of macrocyclic compounds.

2. EXPERIMENTAL

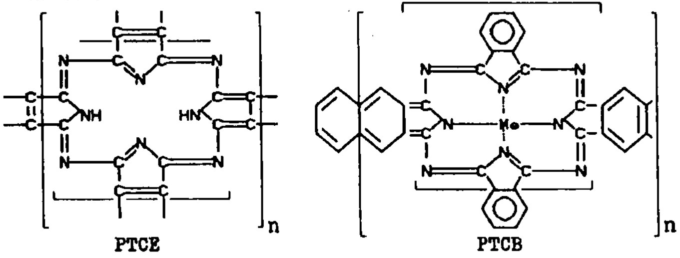
Figure 2 shows the types of macrocyclic compounds and their metal complexes used in this work. The first direction concerns metal complexes with monomeric phthalo- and naphthalocyanines. The products were obtained by a reaction between corresponding dinitriles and metal salts at a ratio of 4:1 in the presence of 18–20% mol urea in melt at 250–300°C for 5 hours. The compounds obtained were purified by toluene extraction and long heating at 200°C in vacuo of 10^{-4} mm Hg.

The second direction of the study concerns polymeric macrocyclic compounds based on tetracyaneethylene and tetracyanebenzene. Macrocyclic polymers were prepared by polymerization of monomeric tetranitriles from a gaseous state on the surface of silica filler. Silica filler of fumed Aerosil type is usually used for polyorganosiloxane elastomeric materials. The template synthesis of polymeric azaporphyrines was carried out in two sectional horizontal rotated reactors in vacuum at 270–300°C for 5–10 hours. Vapors of monomers from the first section went toward the second section of the reactor with silica filler. The weight ratio of monomer to filler varied from 2.5 to 7.5 per 100 weight part of filler. After modification the specific surface area of silica filler was almost invariable (S = 155–160 m^2/g). The free monomer on the surface was absent. The color reaction with

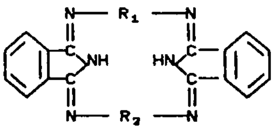
1. Phthalo- and naphthalocyanine complexes with Cu, CO, Ni, Fe, Zn, Ag, Hg.



2. Polymeric macrocyclic compounds with azaporphurine structure obtained on silica surface.



3. Metal complexes with macroazacyclic compounds of symmetrical and nonsymmetrical structure.



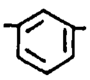
$R_1 = R_2$; $R_1 \neq R_2$

FIGURE 2 Metal complexes of macrocyclic compounds with azaporphyrine and analogous structures.

benzene was used for determination of free monomer. The fillers modified by macrocyclic polymers had a greyish or dark brown color, depending on polymer content. The concentration of paramagnetic centers was equal to 1.10^{17}–$8.5.10^{19}$ spin/g.

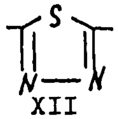
The third direction of the study concerns metal complexes with analogues of azaporphyrin macrocyclic compounds of symmetrical or nonsymmetrical structure.

The symmetrical macroazacyclic compounds were obtained by the procedure described for compounds with $R_1 = R_2$ in References 6, 7, and 8, respectively, for


X


XI

and


XII

The synthesis of these compounds was based on the reaction of phthalonitrile with

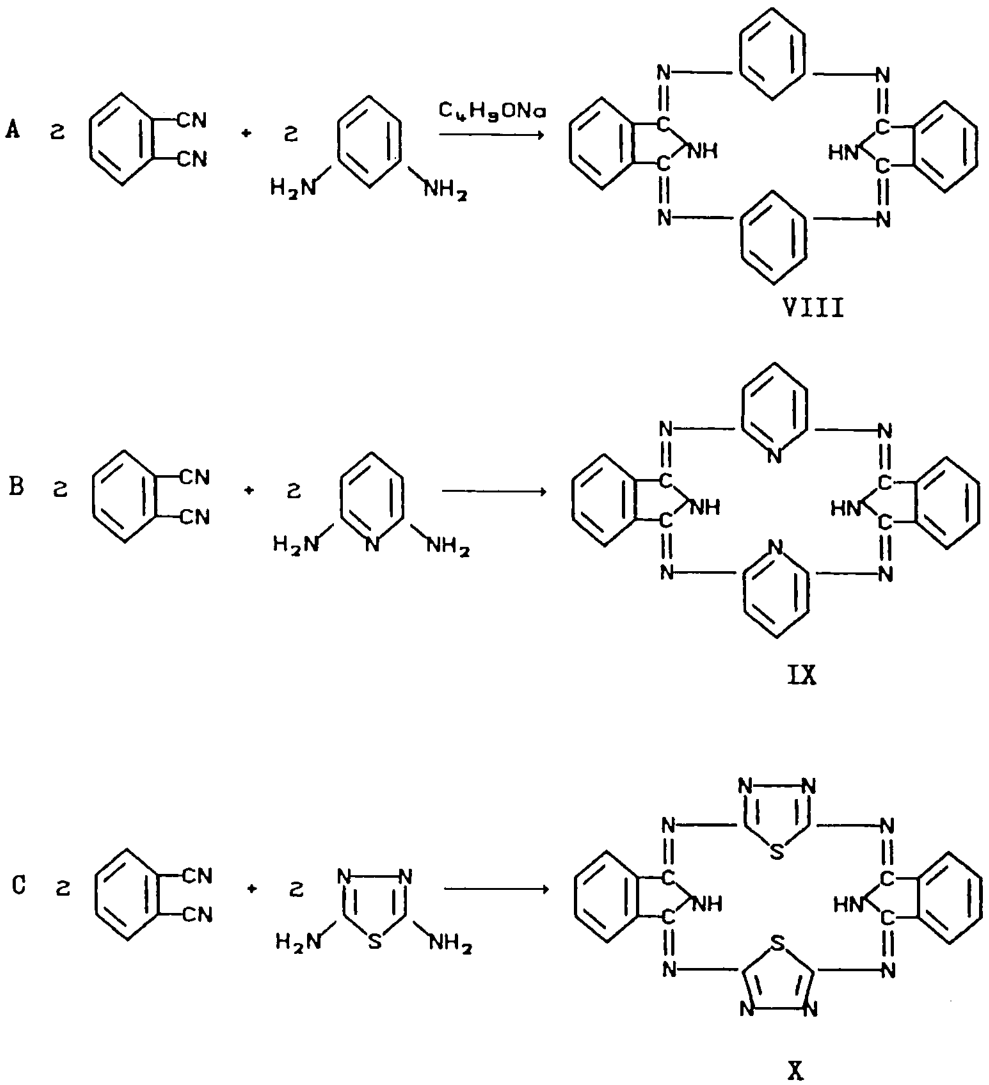
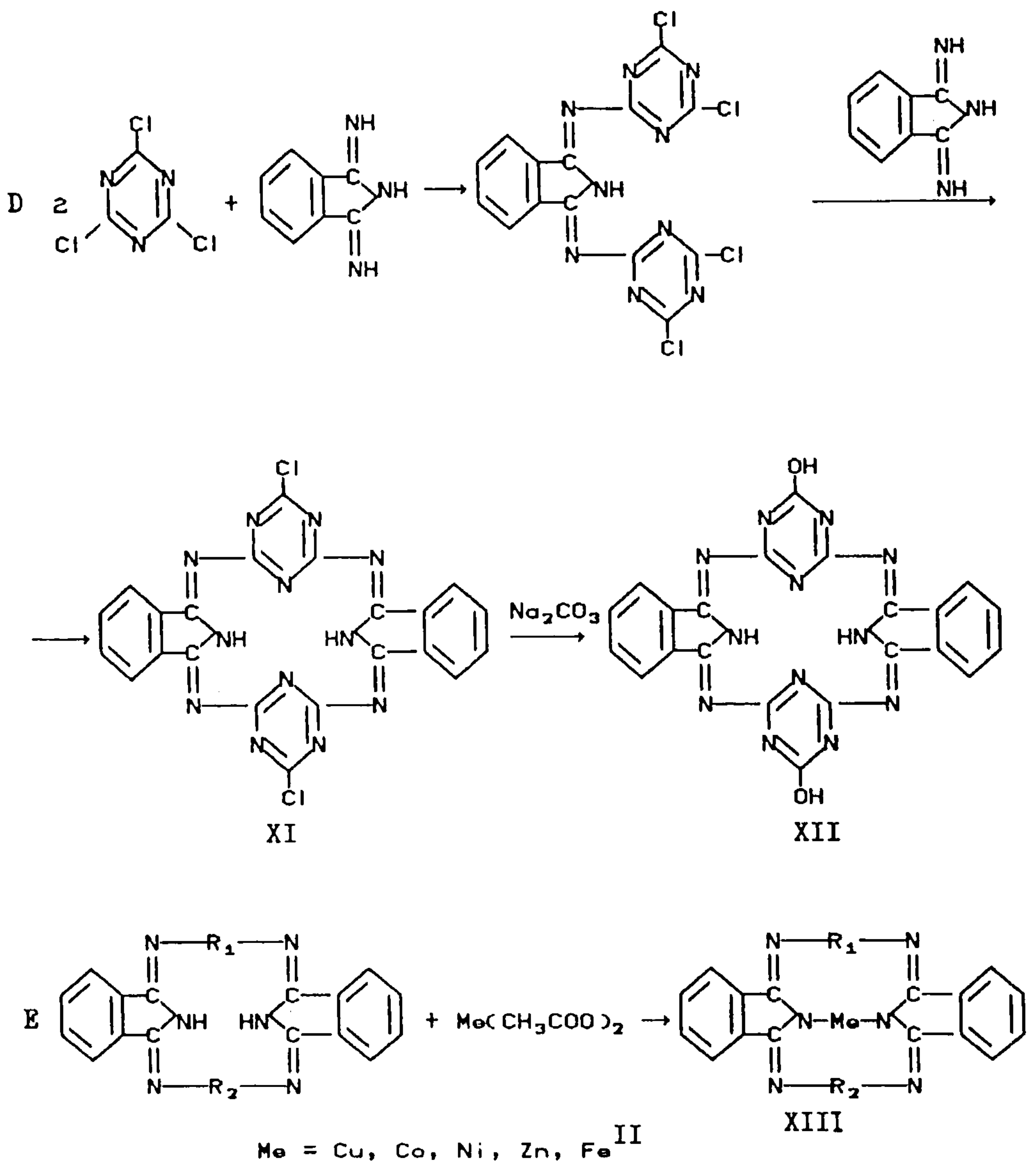


FIGURE 3a Synthesis of symmetrical macrocyclic compounds.

m-phenylenediamine or 2,6-diaminopyridine and 2,5-thiadiazol correspondingly (Figure 3a). The reaction was carried out in organic solvent in the presence of natrium alcoholate.

In the case of symmetrical macrocycles with triazene rings the stepwise condensation of diiminoisoindolenine with cyanuric chloride was realized (Figure 3b). Analogous reactions were used for synthesis of nonsymmetrical macrocyclic compounds (Figure 4).

Triisoindolbenzenemacrocycle, XIV (it is trivial name), was obtained by the reaction of phthalonitrile and *m*-phenylenediamine in a butanol solution in the presence of natrium butilate first at room temperature and then in refluxing solvent.



XI

XII

XIII

FIGURE 3b Synthesis of symmetrical macrocyclic compounds and their metal complexes.

Other macrocyclic compounds of type XV were synthesized by stepwise condensation of diiminoisoindolenine with cyanuric chloride and diaminoderivative (Figure 4b).

Metal complexes were obtained by the interaction of equimolecular quantities of macrocyclic ligand and corresponding metal chloride or acetate in boiling solvent.

After purification the macrocyclic compounds and their metal complexes were characterized by different methods. Elementary composition, infrared and electronic spectra, thermal stability at heating in isothermal and also dynamic conditions in the presence of or without air were determined.

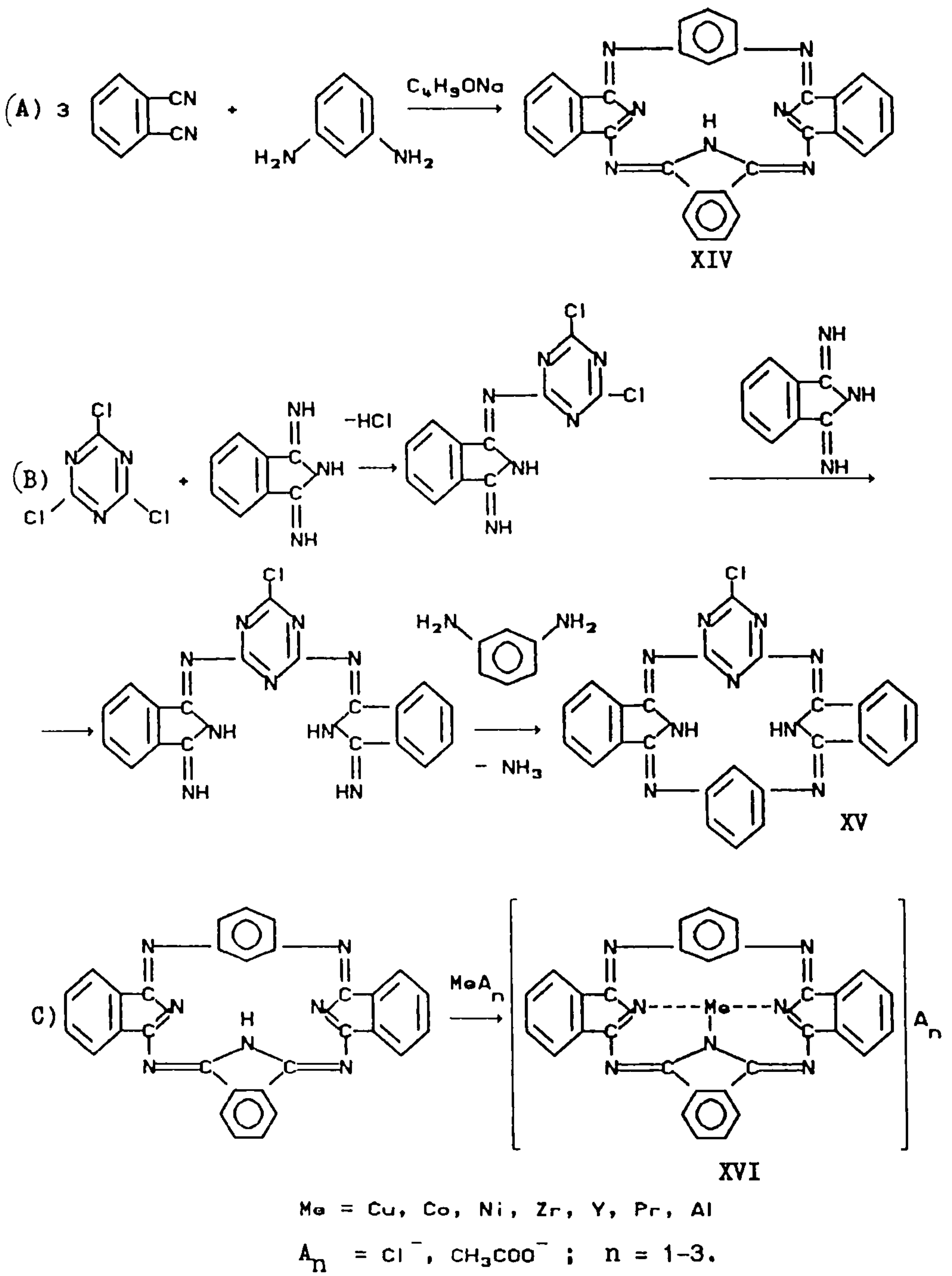


FIGURE 4 Synthesis of nonsymmetrical macrocyclic compounds and their metal complexes.

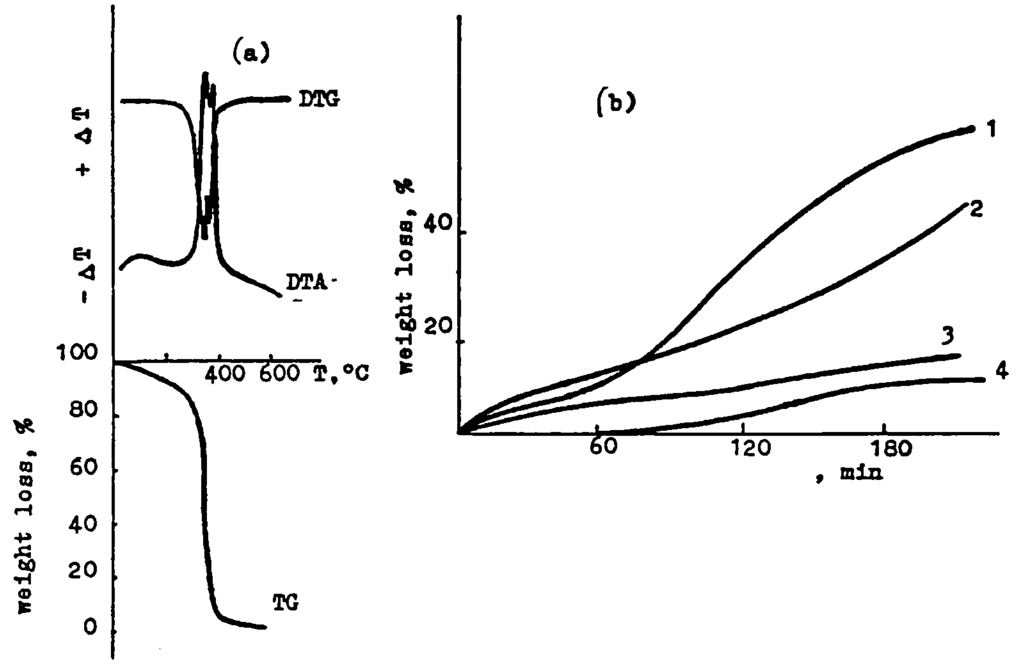


FIGURE 5 (a) TGA curves for CuPc at heating with 10 deg/min in air. (b) Isothermal TG curves (350°C) for (1) CuPc, (2) CoPc, (3), Pc, (4) ZnNPc in air. The order of the decrease in thermal stability of macrocyclic compounds and their Me complexes:

Pc > DCDBMc > TIBMc > DCDPyrMc > DIDCMc
VI VIII XIV IX XI
CuPc > CuDICBMC > CuDIDTMc > CuDIDCMc > CuTIBMc > CuDCDBMc
XV X XI XIV VIII
Me X: NiDIDTMc > ZnDIDTMG > CoDIDTMc > FeDIDTMc > CuDIDTMc
Me XIV: Ni > Co > Cu

Model reactions of cumene oxidation and methylphenyltriazene (MPT) decomposition were studied in order to ascertain the ability of metal complexes of macrocyclic compounds to take part in radical reactions. Cumene oxidation was carried out by molecular oxygen at 97–98°C in reactor shaken with a frequency of 500 times per minute. The content of metal complex was 8.3 g/l. Absorbed oxygen was measured by gaseous burette. Hydroperoxide content was determined by the iodometric method. Selectivity of oxidation was evaluated by the ratio of oxygen absorbed and oxygen reacted with formation of cumene hydroperoxide (Figure 5).

It is known that decomposition of methylphenyltriazene is a radical reaction accompanied by the formation of methane and nitrogen. The relative decrease of the CH_4/N_2 ratio in the presence of a macrocyclic compound was a measure of its ability to react with methyl radicals. MPT decomposition was carried out in cumene at 110°C for 80 min in inert atmosphere. The molar ratio of MPT:MeMc:cumene is equal to 1:2:70. The reaction at 200°C was carried out in tetradecamethylhexasiloxane with the molar ratio of MPT:MeMc:siloxane as 1:2:50 for 15 min. Macrocyclic compounds and their metal complexes were studied in detail as high temperature stabilizing agents for polyorganosyloxane (POS) systems. Different elastomers were used: polydimethylsiloxane of SKT and SKTN trademarks; polydimethylvinylsiloxane (SKTV); polydimethylmethylphenylsiloxane (SKTPV-803). POS compositions included 10–40 phr silica filler (Aerosil); vulcanizing agent (1–3 phr) and stabilizers (0.25–5 phr). The components were mixed at room temperature. POS composition was vulcanized in a press at 150°C and 70 kg/cm^2 for 20 min and then in thermostat at 200°C for 6 hours. The composite based on low molecular SKTN rubber was cured in special form at room temperature for 24 hours.

The following parameters were used for evaluation of the stabilizing action of metal macrocyclic complexes:

1. The change of the mechanical appearance of vulcanates after ageing in air at high temperature.
2. The influence of MeMc on thermal characteristics (weight loss, temperature of decomposition beginning with the displacement of exothermal peaks), ATV thermobalance (USSR) and MOM derivatograph (Hungary) were used for this purpose.
3. The change of solubility and equilibrium percentage of swelling of POS composition in toluene after ageing.

Flammability of POS samples with metal complexes of macrocyclic compounds was evaluated by the USSR standard method (OST 190094). Self-extinguish time of samples after removal of ignition source was determined. In this work the limiting oxygen index method was also used.

3. RESULTS AND DISCUSSION

Macrocycles with azporphyrin or analogous structures and their metal complexes studied in this work are highly thermally stable organic compounds. In vacuo ($>10^{-4}$ mm/Hg) they volatilize without decomposition at heating over 300–500°C.

TABLE I

The properties of metal triisoindolbenzene macrocyclic complexes

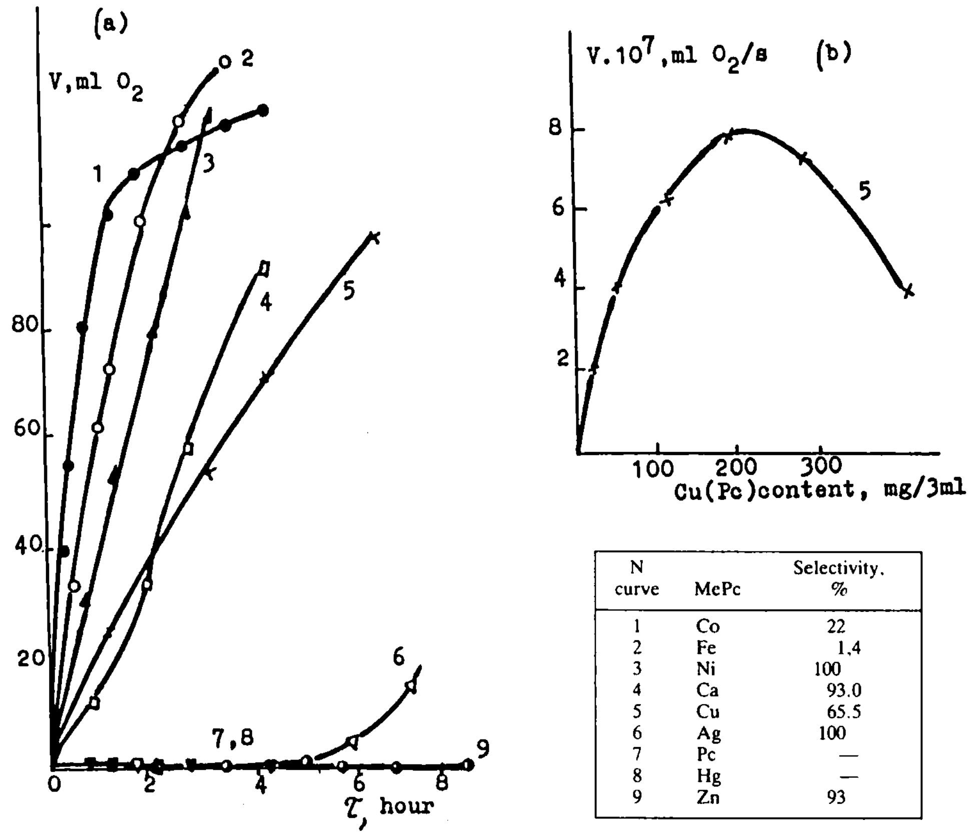
N Compound	T_d, °C	λ_{max}, nm
1. TIBMc	328–339	500.8 668.2 699.8
2. TIBMc Cu	>340	–
Co	345	–
Ni	360	–
Zr	375	602.4 669.9 700.3
Pd	257	635;665.5 700.9
Y	350	665.9;701.4
Al	280	626.5;696.4

The compounds are hardly soluble in polar solvents. Metal macrocyclic complexes have intensive colors. Electronic spectra show a number of strong absorption bands in the visible and ultraviolet regions. Phthalo-and naphthalocyanines are the most stable due to the fact that the molecules are planar and the delocalization of π-electrons in the macrocycle's plane leads to the increase in the compound's aromatic character. The distortion of the macrocycle's structure from planar is accompanied by a short-wave shift of bonds in electronic spectra. This situation is found for nonsymmetrical macrocycles, for example, TIBMC. Coordination with metals also has an affect on the intensity and location of absorption bands in the 200–800 nm region of the spectrum. Table I shows the influence of the metal's nature on properties of complexes with TIBMC. In comparison with the original macrocycle, a long-wave shift is observed as result of the strengthening of the $\text{Me} \xrightarrow{\pi} \text{N}$ bond or extracoordination effect. Thermooxidative stability of macrocyclic complexes also depends on the metal's nature.

It is interesting to note that nonmetal phthalocyanine is more stable than its copper and cobalt complexes. As shown in Figure 5 autocatalysis of degradation is observed for these compounds. The order of decrease in thermooxidative stability of macrocycles and their copper (II) complexes is quite different (Figure 5). However, in the case of triisoindolbenzene and diisoindoldithiadiazol macrocycle complexes the change in the order of thermal stability was similar for the following metals: Ni > Co > Cu. Thus stability of the compounds depends on the character of the system of π-conjugated bonds in macrocyclic and steric factors.

It was interesting to study the activity of macrocyclic compounds in radical reaction of cumene oxidation. Figure 6 shows the influence of phthalocyanine complexes on oxygen uptake by cumene. Complexes of Zn, Hg, Ag are inactive as catalysts. The rate of oxygen uptake by cumene in the presence of phthalocyanine complexes with transitional metals decreases in the following order: Co > Fe > Ni > Cu. High selectivity is observed for the phthalocyanine complexes with Ni and Cu. Catalytic activity of CuPc in cumene oxidation depends on compound content. As shown in Figure 6b, the oxidation rate decreases with an increase in CuPc content. This is possible due to the dual function of the compound, that is, its ability to initiate and inhibit radical reaction. It is interesting to note that the inhibition function correlates with the low thermooxidative stability of CuPc. Nonsymmetrical CuTIBMc is inactive as a catalyst for cumene oxidation. The compound reacts with the methyl radicals formed at decomposition of methylphenyltriazene. As shown in Table II TIBMc can also react with methyl radicals. However the Cu complex is more active than the original macrocycle. Reaction of the methyl radicals with CuTIBMc is observed at high temperature.

Hydrocarbon autooxidation at ambient pressure to yield hydroperoxide is promoted by solid MeMc at 80–110°C. The kinetic scheme of hydrocarbon oxidation involves initiation, propagation, branching of kinetic chains, and breaking of active radicals. Metal macrocycle complexes are involved in at least three steps in the chain radical oxidation process. Figure 7 shows the kinetic scheme of hydrocarbon oxidation in the presence of metal macrocyclic complexes. In reaction (2) of Figure 7 the oxygen molecule is bound and activated presumably by electron transfer to it from MeMc. MeMc acts as an electron donor. Activated intermediates react with



N curve	MePc	Selectivity, %
1	Co	22
2	Fe	1.4
3	Ni	100
4	Ca	93.0
5	Cu	65.5
6	Ag	100
7	Pc	—
8	Hg	—
9	Zn	93

FIGURE 6 (a) The influence of the nature of phthalocyanine metal complexes on catalytic activity, and (b) selectivity of cumene oxidation reaction.

TABLE II

The reaction of the Cu macrocyclic complex with methyl radicals

	110°C, 80 min		200°C, 15 min	
Compound	CH_4/N_2	R_{accept}, %	Ch_4/N_2	R_{accept}, %
No additive	0.55	-	0.43	-
Triisoindolbenzene-macrocycle, XIX (TIBMc)	0.52	5.4	0.43	-
Cu complex of TIBMc	0.36	34.5	0.35	18.6

hydrocarbon molecules and form free radicals, which initiates oxidation. It is believed that at high temperatures metal complexes decompose hydroperoxide by reaction (6). The Pc complexes with copper(II), Zn(II), and Ag do not catalyze the decomposition of the peroxide. They are characterized by high selectivity of the action. Metal macrocyclic compounds can react with free radicals as in reaction (8), the reaction of inversional inhibition. The cycle of catalytic inhibition is described by reactions (9) and (10) of the scheme in Figure 7. According to this scheme the transfer of hydrogen atoms from radicals accepted to MeMc takes

The Initiation

1. $RH + O_2 \longrightarrow [R^\bullet + HO_2^\bullet] \longrightarrow \delta R$

$$\left[\begin{array}{l} \text{2a. } MeMc + O_2 \rightleftharpoons MeMc^+ \ldots O_2^- \\ \text{2b. } MeMc^+ \ldots O_2^- + RH \longrightarrow MeMc + R^\bullet + HO_2^\bullet \end{array}\right.$$

The Propagation

3. $R^\bullet + O_2 \longrightarrow RO_2^\bullet$

4a. $RO_2^\bullet + RH \longrightarrow ROOH + R^\bullet$ 4b. $RO^\bullet + RH \longrightarrow ROH + R^\bullet$

The Branching

5. $ROOH + RH \longrightarrow \delta RO_2^\bullet$

$$\left[\begin{array}{l} \text{6a. } MeMc + ROOH \longrightarrow MeMc^+ + RO^\bullet + HO^- \\ \text{6b. } MeMc^+ + ROOH \longrightarrow MeMc + RO_2^\bullet + H^+ \end{array}\right.$$

The Chain Breaking

$$\left.\begin{array}{l} \text{7a. } R^\bullet + R^\bullet \longrightarrow \\ \text{7b. } RO_2^\bullet + R \longrightarrow \\ \text{7c. } RO_2^\bullet + RO_2^\bullet \longrightarrow \end{array}\right\} \text{nonactive products}$$

8. $R + MeMc \rightleftharpoons RMeMc$

9. $RMeMc \longrightarrow HMeMc + R(=)$

10. $HMeMc + R \longrightarrow RH + MeMc$

FIGURE 7 Kinetic scheme of hydrocarbon oxidation in the presence of metal macrocyclic complexes.

place. The hydride of the macrocyclic complex reacts with free radicals and is reduced. In hydride transfer the macrocyclic ligand is an acceptor. The effect of catalytic inhibition by the hydride transfer mechanism was shown in the polymerization reaction of (meth)acrylates.[3]

The metal macrocyclic compounds were used by us as stabilizing agents for POS systems. Cu complexes of phthalo- and naphthalocyanine retard the polyorganosiloxane decomposition at ageing in air atmosphere at 250–350°C. However, stabilizing activity is low. Polymeric azaporphyrines obtained on silica filler surface are more effective. Figure 8 illustrates the influence of Aerosil modified by PTCE or PTCB on weight losses of polydimethylsiloxane composition at air ageing at 350°C for 3.5 hours. For comparison the composition with standard Fe_2O_3 stabilization is shown. It is seen that polymeric macrocyclic compounds obtained on filler surface are more effective than the standard stabilizing agent. Compositions maintain a high percentage of equilibrium swelling of elastomer in solvent. For analogue of azaporphyrin macrocyclic complexes the stabilizing activity depends on both the structure of the macrocycle and the nature of the metal. The breaking of the azaporphyrin structure and the distortion of the symmetry of macrocyclic

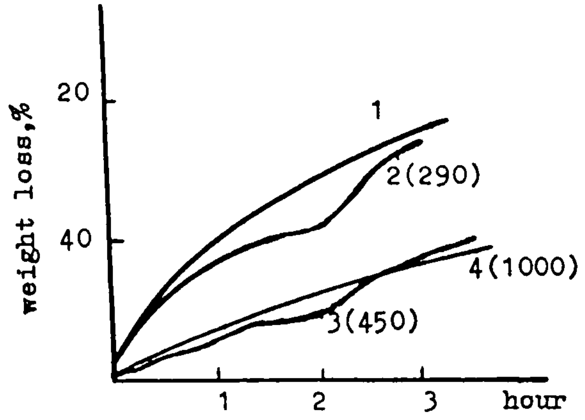


FIGURE 8 The influence of Aerosil modified on siloxane rubber decomposition at 350°C in air: (1) with filler nonmodified; (2) silica + Fe_2O_3 (3 phr); (3) filler modified PTCE; (4) filler modified PTCB. Brackets indicate the percent of equilibrium swelling of rubber in toluene after 3.5 hours of ageing at 350°C in air. Filler content is 35 phr.

TABLE III

The influence of CuMc content on the change of polydimethylvinylsiloxane vulcanate properties after ageing in air (330°C, 2 days)

	Content additive, phr				
Properties	0.1	0.25	0.5	1.0	5.0
Tensile strength, kg/cm^2	33/–	38/42	44/42	38/42	43/–
Elongation, %	110/–	195/60	215/180	130/110	110/–

Numerator, CuTIBMc; denominator, CuDICBMc.

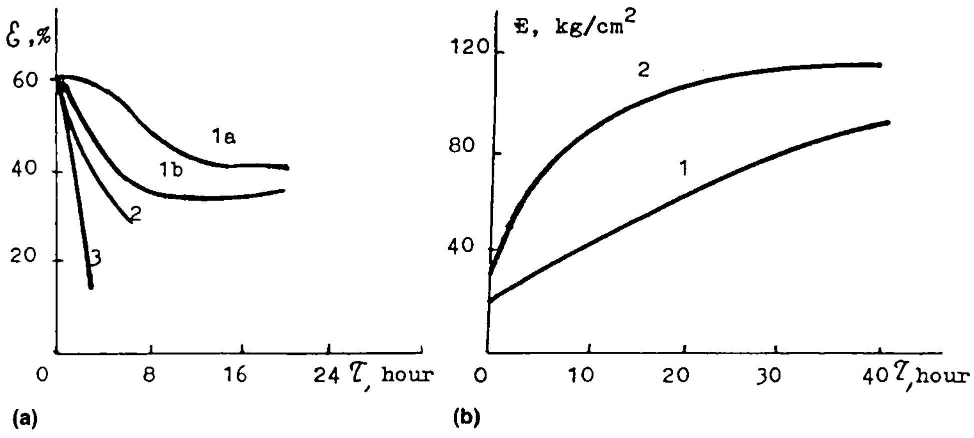


FIGURE 9 (a) The change of elasticity and (b) elastic modules of siloxane resins at ageing in air (300°C): (1) CuTIBMc (0.5 phr); (2) with 5 phr Fe_2O_3; (3) without additive; (1a) in argon; (1b) in air.

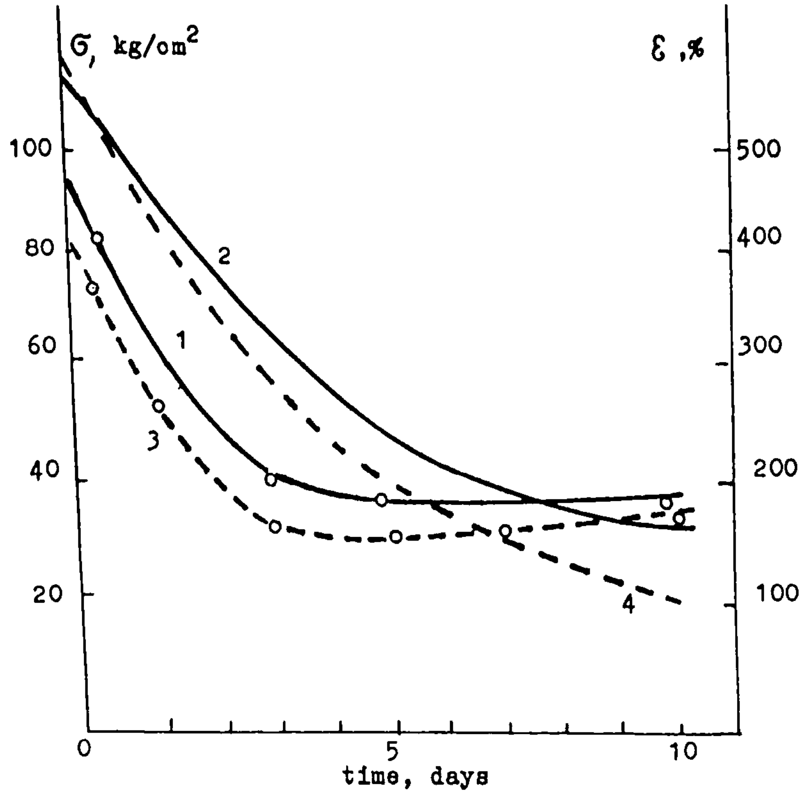


FIGURE 10 (1, 2) The change of tensile strength and (3, 4) elongation of polydimethylvinylsiloxane vulcanates at ageing in air at 300°C: (1, 2) with 0.5 phr CuTIBMc; (3, 4) with 5 phr Fe_2O_3.

TABLE IV

The influence of the nature of metal in a complex with the triiosindolbenzene macrocycle on the self-extinguishing time of polydimethylsiloxane nonfilled films
(s = 0.4 mm)

Additive content, phr	Self-extinguishing time, s[a]					
	Without Me	Cu	Pd	Al	Y	Zr
1	50	10	46	40	38	30

[a]By standard: OST-190094.

molecules are accompanied by an increase in their stabilizing activity. High activity is observed for copper macrocyclic complexes. The influence of ligand structure can be considered for Cu complexes. The following order is found:

CuDICBMc ≥ CuTIBMc > CuDIDTMc > CuDIDBMc > CuDIDCMc

Thus complexes of nonsymmetrical macrocycles show more stabilizing activity than symmetrical ones.

The effectivity of complexes of triisoindolbenzenemacrocycle decreases in the following order: Cu > Ni > Co. The same order is observed in the change of effectivity for metal complexes of diisoindoldithiazolmacrocycle at SKTV ageing: Cu > Ni > Zn > Co > Fe. The regularities observed apparently are not accidental. It is interesting to note that the content of macrocyclic compounds in POS composition has an influence on the stabilizing effect. Table III shows the influence of CuMc content on physico-mechanical properties of SKTV vulcanates after ageing in air at 330°C for 2 days. Here the numerator is CuTIBMc; the denominator is CuDICBMc. Vulcanates without stabilizing agents or with 5 phr of Fe_2O_3 were completely destroyed during that time. There is a certain optimum concentration of CuMc complexes over which the stabilizing effect worsens. The limits of this optimum are from 0.25 to 0.5 phr. Figures 9 and 10 illustrate the influence of CuTIBMc taken in optimum amount on the change of the physico-mechanical properties of polydimethylvinylsiloxane vulcanates in the course of ageing in air at 300°C. The corresponding curves of vulcanates without additives or with 5 phr Fe_2O_3 are given for comparison.

It is seen from Figure 9 that the elasticity of SKTV compositions decreases more slowly during ageing in inert atmosphere than in air. A dramatic fall in elasticity value is observed for compositions without stabilizing agents. Redoxiol as a standard stabilizer is less effective than the copper macrocyclic complex. Elastic modules, tensile strength and elongation values for polydimethylvinylsiloxane vulcanates with CuMc are changed more slowly than for those with Fe_2O_3 (Figures 9, 10).

The stabilizing effect of metal macrocyclic complexes is observed for all types of polyorganosiloxanes used. The high temperature stabilizers proposed are able to give a twofold increase in the exploitation resource of polyorganosiloxane vulcanizates at ageing in air and a 20–30 time increase under limited air access conditions. It was determined that the copper complex of triisoindolbenzenemacrocycle is an effective stabilizer for phenoloformaldehyde foams and also polyamides. The study of metal complexes of macrocycles as flame retardants for POS and PF foam was carried out.

Table IV shows the influence of the metal's nature in the coordination sphere for the triisoindolbenzene macrocycle on the self-extinguishing time of SKT nonfilled films. It is interesting to note that the original macrocycle also decreases the self-extinguishing time of the POS sample. Additives in the amount of 1 phr permit us to increase the limited oxygen index of SKT films on 5 units as compared to the original composition. At the present time the influence of CuTiBMc on thermostability and flammability of polyethylene is being studied. It has established the possibility of an increase of LOI in PE composites.

CONCLUSION

Some properties of metal complexes of macrocyclic compounds with azophrphyrin and analogous structures have been studied. The thermal stability of these compounds decreases when distortion is observed from the planarity of the macrocycle or the continuous system of the π-conjugation in the ligand is reached. Metal complexes of macrocycles are able to react with free radicals. The compounds can catalyze or inhibit the oxidation reaction. It is shown that the copper complex of the triisoindolbenzene macrocycle is a very effective high temperature stabilizer for polyorganosiloxane systems. The compounds may be used as flame retardants.

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