hydrofuran[10] indicates that both resonance and polarization effects are larger in the former. This is certainly a consequence of the expected higher degree of solvation of ion pairs. It would be expected that in the same solvent with the same counterion, $(C_6H_5)_3Ge^-$ and $(C_6H_5)_3Si^-$ would display more comparable ^{13}C chemical shifts.

Relative Acidities. The above results are consistent with the postulate[9] that unlike the anions of phenyl-substituted arsines[7] the arylgermyl anions[8] have insufficient resonance stabilization to cause an increase in the acidities of their conjugate acids relative to GeH_4. Consequently phenyl substitution of germane results in a decreased acidity which has been attributed to the preferential solvation of the smaller anion $[GeH_3]^-$ relative to the substituted anion $[C_6H_5GeH_2]^-$.[8] Further reduction in acidity with increased phenyl substitution may also be attributed to this effect and also to the effect of steric crowding of the bulky phenyl groups.[8]

The group 5B hydrides, on the other hand, appear to show increased acidity upon phenyl substitution,[1,7] and this is consistent with the much larger degree of delocalization of the negative charge of the anions as evidenced by the ^{13}C chemical shifts of the ring carbon resonances.[1,21] It must be noted, however, that the acidities of phenyl- and diphenylphosphines have been recently remeasured[22] by using Me_2SO as solvent, and the relative order of their acid strengths was found to be reversed from that observed in the earlier work.[7] These recent measurements give a difference in acidity of 0.7 pKa unit.[22] In addition we estimate from the ^{31}P NMR spectrum of the equilibrium mixture, in THF solution, represented by

$$C_6H_5PHNa + PH_3 \rightleftarrows C_6H_5PH_2 + PH_2Na$$

that phenylphosphine is more acidic than phosphine by only 1 pKa unit. Issleib and Kümmel estimate this difference to be 4.5 pKa units. It would seem, therefore, that the difference between the germanes and the group 5B hydrides is not as great as was previously thought.

It may prove worthwhile to examine the relative acidities of the group 5B hydrides more closely so that values of comparable accuracy to those reported for the germanes[8] may be obtained. It will also be of interest to examine the acidities of group 6B phenyl hydrides such as C_6H_5SH relative to the parent dihydride for futher comparison. The ^{13}C NMR parameters of C_6H_5SNa[18] indicate that less resonance delocalization occurs in this salt than was observed for C_6H_5PHNa.[1]

Acknowledgment. The Natural Science and Engineering Research Council of Canada is thanked for financial support.

Registry No. $C_6H_5SiH_3$, 694-53-1; $(C_6H_5)_2SiH_2$, 775-12-2; $C_6H_5GeH_3$, 2875-92-5; $(C_6H_5)_2GeH_2$, 1675-58-7; $(C_6H_5)_3GeH$, 2816-43-5; $(C_6H_5)_4Ge$, 1048-05-1; $(p\text{-}CH_3C_6H_4)_3GeH$, 3351-47-1; $C_6H_5GeH_2Na$, 85649-52-1; $(C_6H_5)_2GeHNa$, 85649-53-2; $(C_6H_5)_3GeNa$, 34422-60-1; $(p\text{-}CH_3\text{-}C_6H_4)_3GeNa$, 85649-54-3; $(C_6H_5)_3As$, 603-32-7.

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Temperature-Dependent Single vs. Double Ionization in the Mass Spectra of Phthalocyanine and Its Metal(II) Complexes

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Abstract: Electron-ionizaton mass spectra of phthalocyanine and its complexes with Fe, Co, Ni, Cu, and Zn are given as functions of sublimation temperature between 600 and 670 K. Relative ion abundances are independent of residence time in the ion-source region, and no evidence for ion/neutral reaction is found. A novel effect is a decrease in relative abundances of the doubly charged molecular ions as gas temperatures are raised. This does not occur as ionizing energy is raised between 40 and 70 eV and is not a result of increased fragmentation. It is attributed to thermal enhancement of single ionization by vibrationally induced autoionization.

Phthalocyanine and its complexes have become subjects of increased interest because of their utility as pigments, catalysts, semiconductors, and photoconductors and because of the similarity of their structure to that of the naturally occurring porphyrinic substances. These aspects of their importance have been recently reviewed.[1,2]

As mass spectrometric studies have come to include metal coordination complexes,[3,4] several such studies of phthalocyanine and its complexes have been reported.[5–9] Although disagreeing in certain aspects, these studies showed these compounds to have a very high thermal stability with little tendency of the molecular ions to undergo fragmentation. They showed also an unusually high abundance of doubly charged molecular ions, typically 20% of the total ionization at the routinely used ionizing energies. This is a manifestation of the stability of the aromatic macrocyclic

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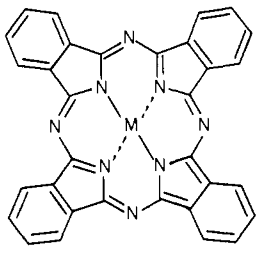
structure, involving four isoindole groups forming a sixteen-member ring with four bridging nitrogen atoms at the 1,3 carbons. With metal ions this macrocyclic dianion is usually a tetradentate ligand providing square-planar coordination.



MPc

The present work was undertaken to test the effects of various experimental conditions on the mass spectra of these compounds. Especially sought was evidence for ion/neutral reactions, as previously observed for other metal chelates[10,11] and which here might involve the abundant doubly charged ions. Also sought was evidence for a temperature dependence of the relative ion abundances, which for other molecules is rarely observed and usually assumed to be negligible. Such a thermal effect might be observable for these molecules, where temperature can be varied over an unusually wide range without decomposition of the original compound. Neither of these effects was noted for phthalocyanines by the earlier workers[5-9] although for ferrocene undergoing photoionization at 58.4 nm, substantial increases in the relative abundances of the fragment ions and of the doubly charged molecular ion were noted as the temperature was raised from 298 to 385 K.[12]

The compounds used in the present work are free phthalocyanine (tetrabenzoporphyrazine) and five metallophthalocyanines represented as MPc where Pc^{2-} is the base $(C_8H_4N_2)_4{}^{2-}$ and M is 2H, Fe, Co, Ni, Cu, or Zn.

Experimental Section

The compounds were obtained from Eastman Kodak Co. They were purified by heating to about 400 K under vacuum for several hours in the mass spectrometer's direct-probe inlet system immediately before introduction to the ion-source region. Following this treatment the mass spectra showed no significant impurities other than phthalonitrile (see Results).

Mass spectra were obtained with a CEC 21-491 double-focusing mass spectrometer. Unless otherwise noted, the ionizing energy was 70 eV, the ion-repeller potential was 2.2 V, and the ion-source temperature was 675 K to minimize condensation of the sample vapor. Nevertheless, frequent cleaning of the ion source was required. The mass range from approximately m/z 50 to 700 was scanned in about 8 s to obtain each spectrum although the upper limit was raised to m/z 1100 when searching for evidence of ion/neutral reactions.

Results

All relative peak intensities reported are for the predominant isotopic species for each chemically different ion. They are expressed as a percentage of the total and averaged for several spectra. Except where intensities are too low to do so, assignments of peaks are made by comparing observed and calculated patterns for isotopic multiplets and by comparison with previously reported spectra.

Although the previous studies[5-9] report significant but varying abundances of an ion at m/z 128 for each compound, it was suggested by Hill and Reed[9] and by Berkowitz[13] that this arises from depolymerization of the ligand to phthalonitrile $C_6H_4(CN)_2$ and is not chiefly a fragment from MPc. The present results support this explanation since the ion at m/z 128 tends to be most abundant when sample temperatures are too low to significantly sublime MPc but high enough that a phthalonitrile impurity should be detectable (approximately 550–600 K). Accordingly we do not consider this ion and other less abundant lower mass ions not containing a metal atom to be contributors to these MPc spectra. This improves the agreement among the present and the previously reported spectra.

Table I. Ions from Mass Spectra of Phthalocyanines MPc with Relative Intensities Showing Temperature Dependence between 600 and 670 K[a]

complex	ion	slope/K^{-1} [b]	N[c]
H_2Pc	H_2Pc^{2+}	−0.040 ± 0.017	17
	$(0.25Pc - 25)^{+}$[d]	−0.065 ± 0.029	17
FePc	$FePc^{2+}$	−0.052 ± 0.025	26
	$(0.5Pc + Fe)^{2+}$	−0.033 ± 0.016	26
	Fe^{+}	+0.055 ± 0.020	26
CoPc	$CoPc^{2+}$	−0.044 ± 0.019	32
NiPc	$NiPc^{2+}$	−0.057 ± 0.028	30
ZnPc	$ZnPc^{2+}$	−0.098 ± 0.039	30

[a] Ions for which the magnitude of the slope of relative intensity vs. temperature (linear least squares) is less than two standard deviations of the slope are not shown. Ionizing energy is 70 eV. [b] For relative intensity (total = 100) vs. temperature. Standard deviations are shown. [c] Number of spectral scans from which data are taken. [d] This ion at m/z 103 has been formulated as $(0.25Pc + 2H - HCN)^{+}$. See ref 7.

If ion/neutral reactions were occurring in the ion source, they should be enhanced by an increase in sample pressure or by a decrease in the ion-repeller potential V, which increases ion residence time. Since partial pressures of MPc cannot be varied separately from sample temperature, V is varied between 2 and 10 V. Evidence for ion/neutral reaction under these conditions cannot be adduced since no ions with masses above that of MPc^{+} are detected up to m/z ~1000, and the mass spectra do not vary significantly with V. A significant variation is considered to be one where the linear least-squares slope of the logarithm of the relative abundance of an ion vs. $V^{-1/2}$ is consistently greater than twice its standard deviation for about 17 to 30 spectra at the same temperature obtained on at least two different days. Significant variations in spectra with V have been observed with the present apparatus for systems where ion/neutral reactions are known to occur.[11,14]

A similar criterion is used to determine the significance of the temperature dependence of the mass spectra. The temperatures of the solid samples, and therefore the subliming vapor, are varied between 600 and 670 K. Slopes of relative ionic abundances vs. temperature are calculated. Significantly negative slopes are found for all MPc^{2+} except $CuPc^{2+}$. These and several other varying abundances are shown in Table I. All other ion abundances show temperature dependences too small to meet the criterion of significance.

The mass spectra of the present compounds are given for 623 K at 70 eV in Table II. These results are obtained by interpolation of the temperature-variation data already mentioned. Data from previous workers,[5-9] who assigned the base peak an intensity of 100, have been renormalized for comparison with the present results, using ions corresponding to those presently found. In those cases where previous reports omitted ions now being considered, the missing ions are assumed to have an intensity equal to that found in the present work for purposes of calculating intensities for the other ions that were reported. Thus one report[5] omits $(0.5Pc + Fe)^{2+}$ and $(0.5Pc + Co)^{2+}$ and another[8] omits $(0.5Pc + Fe)^{2+}$ and all the M^{+} ions.

Ions unique to H_2Pc, which are not shown in Table II, are $(0.25Pc + H)^{+}$ at m/z 129 and $(0.25Pc - 25)^{+}$ or $(0.25Pc + 2H - HCN)^{+}$ at m/z 103. The spectrum of H_2Pc reported by Lester[8] includes ions at m/z 128, 127, and 101, but the intensities reported for them are now reassigned to m/z 130, 129, and 103, respectively. This brings them into better agreement with the present results and those of Eley et al.[7] Thus the results for m/z 130 are shown in Table II. For m/z 129 the present relative intensity is

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Table II. Mass Spectra of Phthalocyanines MPc at 623 K and 70 eV[a]

	M					
ion	2H[b]	Fe	Co	Ni	Cu	Zn
MPc^+	45.6 (514) (48.7,[e] 49.0[f])	53.5 (568) (58.2,[c] 55.8,[e] 46.5[f])	54.7 (571) (64.4,[c] 62.0[e])	59.4 (570) (63.0[e])	66.3 (575) (61.5,[d] 60.1,[e] 54.8,[f] 55.6[g])	53.0 (576) (54.9,[e] 53.7[f])
MPc^{2+}	5.7 (257) (8.4,[e] 9.8[f])	12.9 (284) (16.9,[c] 17.2,[e] 17.2[f])	18.0 (285.5) (18.1,[c] 14.6[e])	17.7 (285) (25.4[e])	13.9 (287.5) (15.5,[d] 18.9,[e] 25.8,[f] 16.4[g])	19.7 (288) (18.1,[e] 20.4[f])
$(0.25Pc + M)^+$	14.0 (130) (12.0,[e] 13.2[f])	10.5 (184) (4.7,[c] 5.6,[e] 12.5[f])	9.9 (187) (5.8,[c] 7.1[e])	13.3 (186) (4.7[e])	10.7 (191) (12.1,[d] 7.0,[e] 9.9,[f] 12.9[g])	7.3 (192) (4.2,[e] 7.5[f])
$(0.5Pc + M)^{2+}$		13.2 (156) (13.2[e])	9.6 (157.5) (7.6[e])			7.5 (160) (7.4,[e] 5.9[f])
M^+		10.0 (56) (7.0,[c] 8.3[e])	7.8 (59) (3.9,[c] 8.7[e])	9.6 (58) (6.9[e])	9.2 (63) (10.9,[d] 14.0,[e] 15.2[g])	12.6 (64) (15.4[e])

[a] On the first line for each ion is the peak intensity for the principal isotopic species relative to a total of 100 followed in parentheses by *m/z*. On the second line in parentheses are relative intensities calculated from previously reported data. [b] Other ions unique to H_2Pc are mentioned in the text. A spectrum given in ref 6 for H_2Pc is apparently for phthalonitrile since no peaks above *m/z* 128 are shown. [c] Reference 5 at 523–563 K (70 eV). [d] Reference 6 at 653 K (75 eV). [e] Reference 7 up to 573 K (70 eV). [f] Reference 8 at unspecified temperature (70 eV). See text regarding reassignment of some peaks in H_2Pc spectrum. [g] Reference 9 at unspecified temperature and ionizing energy.

Table III. Ions from Mass Spectrum of ZnPc with Relative Intensities Showing Dependence on Ionizing Energy between 50 and 70 eV[a]

ion[b]	slope/eV^{-1} [c]
$ZnPc^+$	−0.42 ± 0.10
$ZnPc^{2+}$	−0.12 ± 0.03
$(0.5Pc + Zn)^{2+}$	+0.21 ± 0.10
Zn^+	+0.35 ± 0.13

[a] Temperature is about 645 K. [b] The fragment $(0.25Pc + Zn)^+$ does not vary significantly. [c] Linear least-squares slope of relative intensity (total = 100) vs. ionizing energy. Standard deviations are shown. Data are from 20 spectra in the specified energy range.

17.4 comparing with 15.2[7] and 12.3,[8] while for *m/z* 103 the present result is 17.3 comparing with 15.7 as calculated from both previous reports.[7,8]

Since the abundance of $ZnPc^{2+}$ shows the strongest temperature dependence of all ions investigated here (Table I), the relative intensity of $ZnPc^{2+}$ is measured also as a function of ionizing energy to see whether this effect is related to that of varying thermal energy. At a temperature of 645 K the relative intensity of the $ZnPc^{2+}$ peak increases, as expected, as the ionizing energy is raised from near the appearance energy to about 50 eV, but then it decreases from a maximum of 17.4 at 50 eV to 15.0 at 70 eV. This and the corresponding effects for other ions from ZnPc are shown in Table III. Although these data do not provide reliable appearance energies, it is noted that $(0.5Pc + Zn)^{2+}$ has the greatest appearance energy of all the ions from ZnPc as might be expected for a doubly charged fragment.

Discussion

Considering the differences typically encountered among mass spectra obtained by different workers using different instruments under the different conditions noted, the present and the previous spectra[5-9] compare rather well as seen in Table II if the interference from phthalonitrile is removed (see above).

The temperature dependence of the spectra (Table I) has not been previously recognized. Belousov et al. reported the spectrum of CuPc at five temperatures from 523 to 653 K and noted that the relative intensities (base peak = 100) changed "only insignificantly".[6] It is now seen that by considering intensities relative to the total, the results of these workers give a slightly negative temperature dependence for $CuPc^{2+}$ especially if only their higher temperature results are used. In the present case a temperature dependence for $CuPc^{2+}$ could not be established reliably because of uncertainties in the data, but a possible negative effect (slope = −0.036 ± 0.066 K^{-1} as defined in Table I) is indicated here, too. Of all the MPc complexes studied here, CuPc gives the smallest thermal effect, and this, fortuitously, is the only one for which Belousov et al. gave results. Eley et al. reported mass spectra for all the present complexes, and, although no supporting data were shown, they stated that relative intensities were independent of crucible temperature up to 573 K.[7] This temperature is below the range in which thermal effects are now seen.

Although ion/neutral reactions were found with the present apparatus in the cases of ferrocene[14] and metal β-diketonates,[10,11] failure to detect any here is attributed to the lower volatility of MPc. Sublimation data for CoPc[15] and CuPc[15,16] indicate a vapor pressure of the order 10^{-3} torr at 670 K, the highest temperature used here. It is estimated that for a reaction between MPc^{2+} and MPc, for example, the rate constant would have to be at least 4×10^{-9} cm^3 molecule^{-1} s^{-1} for the reaction to be detected as a significant decrease in abundance of MPc^{2+} for the present conditions. This value is nearly equal to the upper limit for the rate constant predicted by simple polarization theory[17] using the polarizability of CuPc quoted by Lever,[18] so the lack of evidence for such reactions under the present conditions is consistent with theory.

Since collision of MPc^{2+} with neutral molecules does not explain the decrease in relative abundance of MPc^{2+} as temperature increases, how is this thermal effect to be interpreted? Higher temperature must favor formation of MPc^+ realtive to MPc^{2+}, or it must favor subsequent fragmentation of MPc^{2+} relative to that of MPc^+.

The latter possibility is not supported by the results. Eley et al.[7] concluded that the doubly charged molecular ion MPc^{2+} yields only doubly charged fragments to the extent that it fragments at all. A precedent for such independent, parallel fragmentation pathways for singly and doubly charged ions has been established for metal carbonyl complexes.[19] If higher temperatures favored fragmentation of MPc^{2+} to form other doubly charged ions, the relative abundances of the latter should increase with temperature. It is found that such fragment ions have negligible abundance for H_2Pc, NiPc, and CuPc as already noted, or they are independent of temperature as for $(0.5Pc + Co)^{2+}$ and $(0.5Pc + Zn)^{2+}$, or they decrease with temperature as for $(0.5Pc + Fe)^{2+}$ as shown in Table I, so although such fragmentation seems to occur, it does not explain the observed thermal effects. The possibility that MPc^{2+} fragments to give two singly charged ions

$$MPc^{2+} \rightarrow A^+ + B^+$$

is ruled out since pairs of A^+ and B^+ ions with the required composition are not observed in the spectra. Thus if A^+ were either of the observed fragments $(0.25Pc + M)^+$ or M^+, then B^+ would be $0.75Pc^+$ at *m/z* 384 or Pc^+ at *m/z* 512, respectively. These latter ions as well as $0.5Pc^+$ at *m/z* 256 were sought but not detected. Neither were they reported by any of the previous workers.[5-9] An alternate process, a concerted double cleavage

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$$MPc^{2+} \rightarrow A^+ + C^+ + D$$

seems even less likely than the previous reaction although it is not ruled out experimentally if C^+ is hidden by the phthalonitrile impurity at $m/z \leq 128$. Such a process would have a much higher appearance energy than the preceding single cleavage. If two ions were produced, they should adequately dissipate any excess energy without the need for the extra neutral fragment. If C^+ with $m/z \leq 128$ were formed in such a process, it would be unusual also in that the neutral D would have to be at least as large as 0.5Pc, whereas fragmentation occurs typically with the charge residing on the larger fragment. Formation of two ions and two or more neutral fragments would be at still a greater energetic disadvantage.

Consider the remaining explanation for the thermal effect, that the initial ionization process yields increased MPc^+ relative to MPc^{2+} at higher temperatures. Since the relative abundances of MPc^+ and MPc^{2+} do not vary with ion-repeller potential, it is inferred, in agreement with Lester,[8] that single and double ionization are each induced by a single electron.

$$MPc + e^- \rightarrow MPc^+ + 2e^-$$

$$MPc + e^- \rightarrow MPc^{2+} + 3e^-$$

The influence of temperature is understood if we assume that autoionization makes a significant contribution to production of MPc^+, i.e., that this ion is formed from a superexcited vibronic state of neutral MPc which undergoes an internal conversion of vibrational energy into electronic energy resulting in an electronic state corresponding to $MPc^+ + e^-$. The importance of such vibrationally induced autoionization has been shown in simpler molecular systems[20] and is expected to be especially significant for large systems undergoing excitation by ~70-eV electrons[21] as in the present work. Considering the low vibrational frequencies for analogous molecules[22] the increasing temperature will result in significantly increased initial populations of vibrationally excited MPc. In the electronic excitation process (Franck–Condon) this vibrational energy seems to be largely maintained, enhancing the subsequent autoionization and producing the observed increase in abundance of MPc^+ relative to that of MPc^{2+}. Thermal energy is effective since the electronic excitation per se need not result in substantial vibrational excitation in the new electronic state when the electronic states have similar nuclear potential surfaces. Such surfaces seem to be common in the MPc systems according to photoelectron spectra,[13] laser-induced fluorescence spectra,[22] and electronic absorption spectra.[23] For MPc^{2+} such a process must be less important if it occurs at all.

The temperature dependence of the relative abundances of the doubly charged molecular ions here might seem to contradict the positive effect reported in the photoionization mass spectrum of ferrocene.[12] The increase in relative abundance of $Fe(C_5H_5)_2{}^{2+}$ from ferrocene as temperature was raised from 298 to 358 K accompanied increased relative abundances of the singly charged fragments and is consistent with the effectiveness of thermal energy in ion decomposition at low ionizing energies.[24] The photons used in the ferrocene study[12] corresponded to 21.2 eV, which is not much higher than the appearance energies of these ions and where a thermal shift in the ionization efficiency curve should give a significantly increased ion abundance. This is not the case in the present work, where the MPc complexes are ionized at 70 eV and where the ratio of partial cross sections for double and single ionization are not so sensitive to ionizing energy. As Table III shows for the example of ZnPc, both molecular ions, $ZnPc^+$ and $ZnPc^{2+}$, decrease in relative abundance as ionizing energy increases from 50 to 70 eV, but this is balanced by growth of their respective fragments so the probability of single vs. double ionization in this range of ionizing energy is nearly constant. Considering both doubly charged species, $ZnPc^{2+}$ and $(0.5Pc + Zn)^{2+}$, the sum of their relative abundances rises as ionizing energy is increased to about 40 eV, but it remains constant at (24.6 ± 1.4)% between 40 and 70 eV. Of course the other 75.4% of total ionization also remains constant for the three singly charged species above 40 eV. These results show that increasing the energy of the ionizing electrons, when this energy is well beyond the threshold for double ionization, does not have the effect as does increasing the temperature of the molecules. This further supports the mechanism of vibrationally induced autoionization in the formation of MPc^+.

Conclusions

The mass spectra of the MPc complexes compare well in most cases with those previously reported. They show no dependence on ion-repeller potential and no evidence of ion/neutral reactions occurring in the ion source of the mass spectrometer. Nevertheless it is supposed that such reactions might occur to a significant extent with greater available reaction time or greater reactant concentrations.

The dominant thermal effect noted in every case except possibly for M = Cu is the decrease in the relative abundance of MPc^{2+} as sample temperature is increased. Although temperature factors in mass spectrometry have been recognized, the previous explanations of their origins[25] do not seem to apply in the present case. The effect is attributed here to a variation in the probability of formation of MPc^+ vs. that of MPc^{2+}. We hypothesize that vibrationally induced autoionization, the importance of which must increase with temperature, makes a significant contribution to the formation of MPc^+.

A thermal effect such as this may not have been noted previously for other molecular systems because few of them have the favorable properties of the phthalocyanines, namely, gaseous molecules large enough and stable enough to undergo thermal vibrational excitation without decomposing, to show exceptionally high abundances of doubly charged molecular ions, and to show simple mass spectra with little ionic fragmentation. Other large aromatic systems should be investigated to test the generality of this effect, and, to test the generality of this explanation, theoretical and experimental studies of autoionization need to be extended from the smaller molecules[26] to the larger ones.

Registry No. H_2Pc, 574-93-6; FePc, 132-16-1; CoPc, 3317-67-7; NiPc, 14055-02-8; CuPc, 147-14-8; ZnPc, 14320-04-8.

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