to the 26-kK value observed by Chien. The second transition $\psi_g \rightarrow (\text{core})(b_2)^1(a_1)^2(a_2)^1(a_1)^1$ gives 36.5 compared to the 37 kK measured. We know however that the $a_1$ and $a_2$ levels should be reversed, which involves the 7 kK which separates them.

We conclude that the "crystal field terms" play a significant role in a valid discussion of the electronic structure of $(C_5H_5)_2VCl_2$. Though the type II calculation predicts a ground state of incorrect symmetry, our previous discussion indicates that an energy shift of about 7 kK produces a MO picture which is in reasonable agreement with both the optical and epr data.

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# Electronic Spectra of the Negative Ions of Some Metal Phthalocyanines

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Reduction of metal phthalocyanines with sodium in tetrahydrofuran (or electrochemically at a mercury pool or platinum cathode) produces a series of negative ions, corresponding to the stepwise addition of electrons. The complexes with Zn(II), Ni(II), Fe(II), Mn(II), Mg(II), and $Al^{III}Cl$ form four distinct reduction stages, but for $Co^{II}Pc$ five reduction steps are found. The electronic absorption spectra are reported and used to discuss the electronic structures of the metal phthalocyanine negative ions. The spectroscopic observations indicate that all complexes, with the exception of $Co^{II}Pc$ and $Fe^{II}Pc$ give reduced species in which the additional electrons are confined essentially to the ring $e_g$ orbital. Reduction of $Co^{II}Pc$ and $Fe^{II}Pc$ and possibly also $Mn^{II}Pc$ appears to involve electron addition to both ligand ($e_g$) and metal orbitals.

## Introduction

Metal phthalocyanines and the closely related metal porphyrins may be reduced chemically[1,2] or electrochemically[3,4] to give a series of negative ions. This reduction corresponds to the successive addition of electrons to vacant or partially occupied orbitals of the metal complex. Which orbitals are used depends on the proximity of the vacant metal orbitals and the lowest unoccupied orbital $e_g$ of the phthalocyanine ligand system. For complexes with closed-shell central ions ($Mg^{2+}$, $Zn^{2+}$) electron addition is confined to the $\pi$ orbitals of the ligand system. It has been shown by both chemical[5] and polarographic[3,4,6] techniques that up to four electrons can be donated to these systems, and it is generally accepted that these negative ions result from the addition of electrons to the lowest vacant $e_g$ orbital of the ring. On the other hand, when the central ion is transitional, the metal d orbitals lie close to the highest filled $a_{1u}$ ring orbital and it is therefore possible that in some cases reduction of the central metal will take place.

Shablya and Terenin[7] first reported an anion of a metal phthalocyanine together with its electronic absorption spectrum by reducing magnesium phthalocyanine in tetrahydrofuran with sodium. A two-electron reduction of $Cu^{II}Pc$ (the abbreviation Pc for phthalocyanine will be used throughout this paper) using potassium in liquid ammonia has been observed and assigned to the species $Cu^{0}Pc$.[8] Taube has isolated higher reduction products of metal phthalocyanines as crystalline solids from solution by electron transfer from alkali metals and radical ions.[5] More recently the electronic absorption and electron spin resonance spectra of the mono- and dinegative ions of some metal phthalocyanine tetrasulfonates in dimethyl sulfoxide[9] and the electron spin resonance spectra of some transition metal phthalocyanines in tetrahydrofuran and hexamethylphosphoramide[10] have been reported. Polarographic measurements in dimethylformamide on the analogous metal porphyrins[3] have indicated that four reduction steps are possible which were assigned to the formation of mono-, di-, tri-, and tetranegative porphyrin ions, the latter having the $e_g$ orbital filled to its complement of four electrons.

Polarographic measurements on the metal phthalocyanines have yielded similar results,[6] and in general four reduction waves are observed with the exception of $Co^{II}Pc$, which exhibits five steps.

## Experimental Section

Electrochemical reduction in dimethylformamide–tetra-*n*-propylammonium perchlorate was effected in a three-electrode cell under an atmosphere of dry nitrogen using a controlled cathode potential. The absorption spectra were measured using a Beckman DK2 ratio recording spectrophotometer. Only the mono- and dinegative ions were sufficiently stable under these conditions to permit spectral measurements, the higher ions being oxidized by traces of atmospheric oxygen which unavoidably leaked into the cathode compartment.

The chemical reduction was carried out under high vacuum by slowly washing a solution of the metal phthalocyanine ($10^{-3}$ *M*) in tetrahydrofuran over a sodium film, prepared by thermal decomposition of sodium azide. The reduction was monitored by following the changes in the absorption spectra of the metal phthalocyanine after each washing. In this way it was possible by washing only small amounts at any one time to characterize

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the spectra for all the stages of reduction. When reduction was complete, the apparatus was opened to the air to effect oxidation of the reduced species. The reoxidized product remained as a supersaturated solution for a period long enough to allow the measurement of its absorption spectrum which showed that in all cases the neutral metal phthalocyanine was regenerated. Exact concentrations were calculated using extinction coefficients from the literature.[11,12]

**Materials.**—Manganese and zinc phthalocyanines were prepared according to the published methods.[13,14] The other phthalocyanines used were kindly donated by Imperial Chemical Industries (Dyestuffs Division, Manchester). All the metal phthalocyanines were purified by controlled-vacuum sublimation under nitrogen. The purification of the dimethylformamide and the preparation of the base electrolyte ($n$-Pr)$_4$NClO$_4$ have been described previously.[3] The tetrahydrofuran for the chemical reduction was purified as in ref 2.

## Results and Discussion

Four distinct reduction stages have been observed and their spectra characterized for each of the metal phthalocyanines examined, with the exception of Co$^{II}$Pc, where five stages were seen. This is in direct agreement with polarographic results obtained from solutions in dimethylformamide[6] and with Taube's observations.[5] A consideration of these two sets of data together with the results for the analogous metal porphyrins[3,4] indicates that these separate stages correspond to successive one-electron additions to the metal phthalocyanine complexes.

The electronic absorption spectra for the mononegative ions of Zn$^{II}$Pc, Mg$^{II}$Pc, and Al$^{III}$ClPc are all very similar and consist of a near-infrared band of moderate intensity between 900 and 970 m$\mu$, two very intense bands in the visible region between 560 and 650 m$\mu$, and a fairly strong band in the ultraviolet region at about 320 m$\mu$. For these complexes with closed-shell central ions the reduction process corresponds to addition of an electron to the lowest unfilled orbital of the phthalocyanine ring. Recently the magnetic circular dichroism spectra have been used in conjunction with SCF–MO $\pi$-type calculations to assign the electronic spectra of the negative ions of MgPc.[15] The low-energy absorption in MgPc$^-$ results from excitation from the e$_g$ level, and a fairly good overall agreement between the calculated and the observed spectrum was obtained. The above monoions therefore have an (e$_g$)$^1$ configuration and are paramagnetic.[16] The monoions of Cu$^{II}$Pc$^2$ and Ni$^{II}$Pc are extremely similar spectrally to MgPc$^-$ and there is therefore little doubt that these ions have an (e$_g$)$^1$ configuration and that the b$_{1g}$ (d$_{x^2-y^2}$) metal orbital is not being filled.

The spectra of the dinegative ions of these complexes are also very similar to each other and show very little absorption in the near-infrared region but an intense band in the visible region between 520 and 540 m$\mu$. The dinegative ions of metal phthalocyanines with diamagnetic central metal ions yielded no spin resonance signal[16] and Taube's susceptibility measurements,[5] nuclear magnetic resonance data,[17] and theoretical considerations[18] indicate a spin-paired (e$_g$)$^2$ diion, giving rise to a diamagnetic species. The monoions tend to be deep blue while the diions are purple. Typical spectra of mono- and dinegative metal phthalocyanine ions are shown in Figure 1.

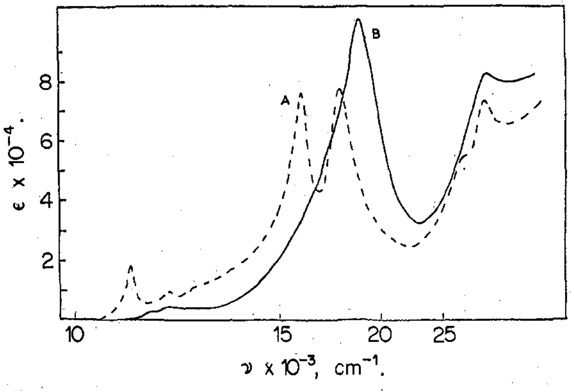

Figure 1.—Electronic absorption spectra of mono- and dinegative metal phthalocyanine ions: A, NiPc$^-$; B, NiPc$^{2-}$.

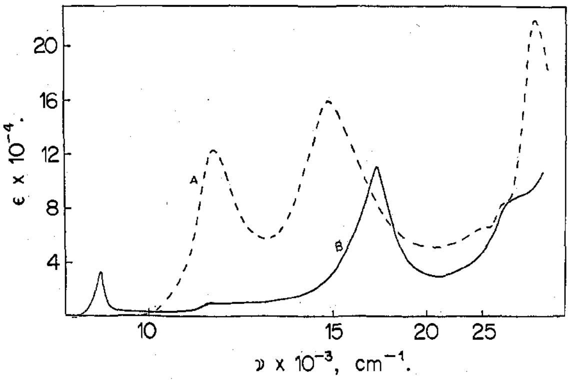

Figure 2.—Electronic absorption spectra of tri- and tetranegative metal phthalocyanine ions: A, NiPc$^{4-}$; B, NiPc$^{3-}$.

The trinegative ions of Zn(II), Mg(II), and Al$^{III}$ClPc all exhibit an absorption band in the near-infrared region around 1100 m$\mu$, as well as intense bands in the visible and ultraviolet region. The trinegative ions of the complexes containing central metal ions with closed shells were paramagnetic[16] as anticipated for an (e$_g$)$^3$ electronic configuration. Formation of the tetranegative ions results in a simplification of the overall spectrum. The near-infrared band disappears while intense absorption in the visible and ultraviolet region remains, Figure 2. No electron resonance spectrum was observed for the tetranegative ions of these complexes and it is reasonable to conclude that these ions are diamagnetic with an (e$_g$)$^4$ configuration. The theoretically calculated spectrum for this reduction stage fits extremely closely to the measured bands,[15] and on this basis, the e$_g$ level is filled with four electrons.

The spectra for all stages of reduction for NiPc resemble very closely those of MgPc and ZnPc and on this basis we believe that all reduction steps involve addition into the phthalocyanine ring e$_g$ orbital for NiPc. Although for a given stage of reduction the electronic spectra of the negative ions of the above metal phthalocyanines show certain similarities with

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TABLE I

ABSORPTION ENERGIES ($CM^{-1}$) AND OSCILLATOR STRENGTHS OF METAL PHTHALOCYANINE ANIONS[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | Magnesium Phthalocyanine | | | | |
| Monoion (blue) | 10,420 (0.013) | 11,630 | 12,530 | 15,670 (0.162) | 17,790 (0.242) | 23,810 (0.197) | 29,410 (0.835) |
| Diion (purple) | | 11,110 | 12,500 | 16,260 | | 19,230 (0.623) | 29,850 (0.693) |
| Triion (blue) | 8,970 (0.023) | | 12,120 (0.080) | 16,950 (0.517) | | | 29,500 (0.881) |
| Tetraion (blue-green) | | 11,910 (0.210) | | 16,130 (0.404) | | 24,270 (0.263) | 32,790 (0.581) |
| | | | Chloroaluminum Phthalocyanine | | | | |
| Monoion (blue) | 10,260 (0.033) | 11,110 | 12,200 | 13,810 | 16,180 (0.068) | 17,390 (0.116) | 30,400 (0.541) |
| Diion (purple) | | 11,110 | 12,500 | | | 19,310 (0.267) | 30,580 (0.494) |
| Triion (blue) | 9,620 (0.030) | | | 13,330 | 17,040 (0.195) | | 30,120 (0.418) |
| Tetraion (blue-green) | | | 12,350 (0.095) | 16,560 (0.158) | | 26,320 | 28,990 (0.393) |
| | | | Zinc Phthalocyanine | | | | |
| Monoion (blue) | 10,550 (0.070) | 11,770 | 12,740 | 15,720 (1.125) | 17,790 (1.375) | 24,270 | 30,960 (7.06) |
| Diion (purple) | | | 12,950 | | 19,160 (5.203) | 22,570 | 29,850 (6.30) |
| Triion (blue) | 9,090 (0.155) | | | | 17,540 (5.708) | | 29,410 (5.485) |
| Tetraion (blue-green) | | | 12,180 (2.038) | 16,130 (3.511) | | 25,970 | 32,890 (5.092) |
| | | | Nickel Phthalocyanine | | | | |
| Monoion (blue) | 10,930 (0.024) | 11,830 | 12,350 | 15,870 (0.449) | 17,610 (0.723) | 24,040 | 27,320<br>30,030 (1.516) |
| Diion (purple) | 10,990 | 11,360 | 11,770 | | 18,660 (1.661) | | 30,030 (1.985) |
| Triion (blue) | 9,220 (0.131) | 11,240 | | 16,950 (2.412) | | | 30,000 (5.0) |
| Tetraion (green) | | 11,360 (0.929) | 14,880 (1.885) | | 24,570 (0.980) | 27,430 | 32,150 (4.026) |
| | | | Cobalt Phthalocyanine | | | | |
| Monoion (green) | | | 14,410 (0.232) | 15,800 (0.080) | 21,410 (0.756) | 23,360 | 32,050 (3.018) |
| Diion (red) | 10,870 (0.050) | | 14,680 (0.177) | 16,000 (0.143) | 21,010 (1.379) | | 31,350 (2.345) |
| Triion (violet) | 8,480 (0.058) | 11,050 (0.079) | | | 19,610 (2.086) | | 30,670 (1.620) |
| Tetraion (blue) | 10,000 | 11,490 (0.095) | | | 17,480 (1.063) | 23,700 (0.515) | 31,550 |
| Pentaion (purple) | | 11,300 (0.060) | 14,490 (0.401) | | 18,520 (0.936) | | 28,010 |
| | | | Iron Phthalocyanine | | | | |
| Monoion (pink) | | 12,500 (0.017) | 15,040 (0.026) | 16,780 | 19,420 (0.245) | | 30,670 (0.748) |
| Diion (purple) | | | 13,510 (0.044) | 16,000 | 19,760 (0.633) | 25,320 | 29,410 (0.746) |
| Triion (violet) | | | | | 18,870 (0.885) | 26,810 | 29,590 (0.932) |
| Tetraion (green-blue) | 7,300 (0.025) | | 13,020 (0.333) | 16,640 (1.075) | 19,840 | 27,320 (1.287) | |
| | | | Manganese Phthalocyanine[b] | | | | |
| Monoion (purple) | 11,980 (0.78) | 13,510 (0.25) | 15,870 (1.02) | 17,240 (0.76) | 19,530 (3.0) | 28,250 (1.38) | 30,400 (1.38) |
| Diion (purple) | | | 14,120 (0.43) | | 19,160 (2.97) | | 30,210 (1.70) |
| Triion (blue) | 9,090 (0.49) | | | 17,670 (2.92) | | | 29,410 (1.59) |
| Tetraion (blue-green) | | 12,020 (2.47) | | 16,130 (2.70) | | 27,030 (1.34) | |

[a] Oscillator strengths in parentheses; if none is given, its value is less than 0.005. [b] Optical densities in parentheses; all ions at the same concentration.

each other, nevertheless significant shifts in the peak positions are clearly apparent. The band positions of the tri- and tetranegative species also differ from those reported for the third and fourth stages of reduction of $H_2Pc$[2] and it is therefore concluded that metal replacement has not occurred. Copper is slowly replaced from its phthalocyanine by sodium and only the mono- and dinegative ion spectra have been characterized before complete replacement had occurred.[2] The absorption energies and oscillator strengths for all the ions of the series of metal phthalocyanines are given in Table I.

$Co^{II}Pc$ is unique and yields five distinct reduction stages. The mononegative ion is green whereas typical mononegative phthalocyanine ions ($Zn^{II}Pc$ and $Mg^{II}Pc$) are blue. The spectrum of $Co^{II}Pc^-$ differs from that of ZnPc in that there is no near-infrared absorption band. The main visible band for $CoPc^-$ lies about 30 mμ to longer wavelength than in the CoPc spectrum and fairly intense absorption at about 460 mμ appears. This spectrum is compared in Figure 3 with those of CoPc and ZnPc, which it closely resembles. A similar spectrum was observed for the tetrasulfonated cobalt phthalocyanine monoion in dimethyl sulfoxide.[9] Formation of the red dinegative ion $CoPc^{2-}$ yields the characteristic near-infrared band 920 mμ, typical of metal phthalocyanine mononegative ions, and its spectrum is compared with that of $ZnPc^-$ in Figure 4. One-electron reduction of CoPc is assigned to a species where the additional electron is essentially confined to an orbital located on the central cobalt. This is represented as $Co^IPc^-$. In view of the similarity of the spectrum of $ZnPc^-$ to that of the dinegative ion of CoPc, the second reduction stage is assigned to a ring orbital. The absorption band at 460 mμ for the mononegative ion $Co^IPc^-$ is assigned to metal → ligand charge transfer. Rollmann and Iwamoto were unable to characterize the optical spectrum for the dinegative species of cobalt phthalocyanine tetrasulfonate and on the basis of a very poorly resolved esr spectrum attributed the species of $Co^0Pc$ with the unpaired electron in the metal $b_{1g}$ orbital. Other esr measurements for the unsulfonated derivatives[16] have given a single narrow resonance consistent with the assignment of the dinegative ion as $Co^IPc^{2-}$ [$3d^8\ e_g{}^1$]. A similar interpretation has been suggested for the one-electron reduction of $Co^{II}Pc$ using borohydride ion[19] and of cobalt(II) porphyrins[4,20] producing the corresponding diamagnetic Co(I) complexes.

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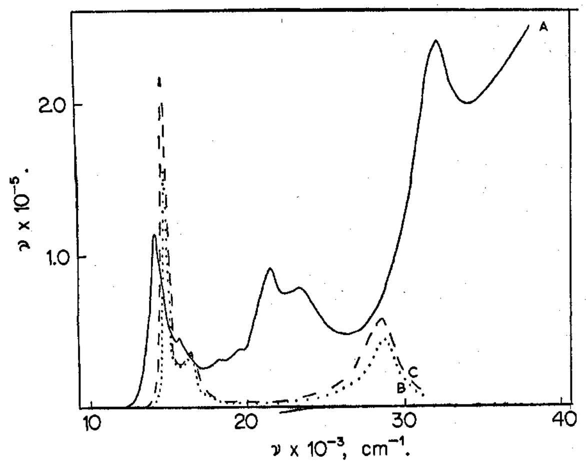

Figure 3.—Electronic absorption spectra: A, $Co^{I}Pc^{-}$; B, $Co^{II}Pc$; C, $Zn^{II}Pc$.

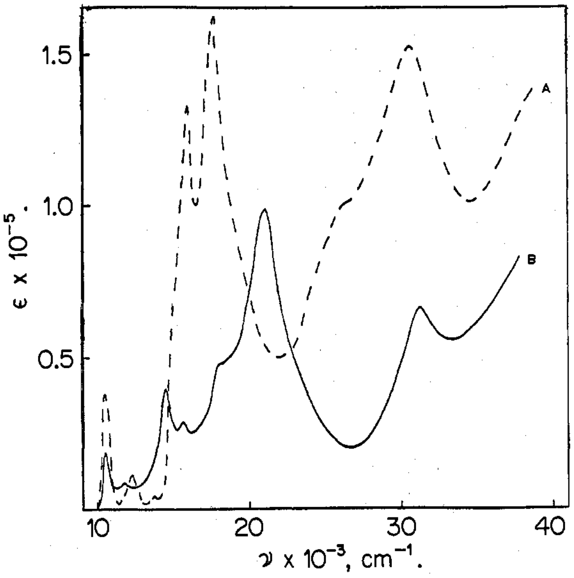

Figure 4.—Electronic absorption spectra: A, $Zn^{II}Pc^{-}$; B, $Co^{I}Pc^{2-}$.

The third reduction stage exhibits a band at 1180 mμ, which is characteristic of typical metal phthalocyanine trinegative ions, where all three electrons are assigned to the ring $e_g$ orbital. This suggests that in the trinegative ion of $Co^{II}Pc$ the central cobalt is in the 2+ oxidation state whereas the mono- and diions exist with the central cobalt in the 1+ oxidation state. Reduction potential data[6] appear to indicate also that the trinegative ion is not formed simply as a continuation of the addition of electrons to the ring orbital of a $Co^{I}Pc$ species. The disproportionation energy $^{3}\Delta^{4}E_{1/2}$ is only 0.28 eV, some 0.5 eV smaller than that anticipated if such a process were to occur.[8] On this basis it seems that the addition of electrons to the ring $e_g$ level raises the energy of the mainly d orbitals of the central metal to such an extent that a high-spin configuration becomes more stable. Both repulsion and exchange terms may well play a critical part in deciding which of the terms is lower in energy and until accurate SCF calculations are available for these large systems it would be presumptive to draw any further conclusions.

Although the tetranegative ion shows no near-infrared band of moderate intensity, the electron spin resonance data suggest that the unpaired electron is confined essentially to the phthalocyanine ring,[16] which implies that formation of the tetraion yields an ion where the central cobalt has reverted to the 1+ oxidation state. The spectrum of the fifth and final stage shows the general features of other tetraion spectra and this reduction stage is therefore attributed to the formation of $Co^{I}Pc^{5-}$ where the $e_g$ ring orbital has been filled to its complement of four electrons. We feel this configuration is more likely than a further donation of electrons into the cobalt $b_{1g}$ orbital since this orbital is of higher energy and repulsion terms will probably be lower for addition of electrons into the more diffuse phthalocyanine orbital as opposed to the more localized metal orbital.

The spectra for all stages of reduction for MnPc are extremely similar to the corresponding species of both MgPc and ZnPc with near-infrared absorption apparent at the mono- and triion stages and intense bands only in the visible and ultraviolet regions for the di- and tetraions. Although the low-energy band in the monoion does occur at a significantly higher energy than for the other monoions, it does seem likely that the reduction pattern for MnPc follows the same sequence as for typical metal phthalocyanines with all electrons assigned to the ring $e_g$ orbital. Taube inferred from his calculation that MnPc reduces initially to form $Mn^{I}Pc^{-}$ where the additional electron is associated with a manganese d orbital and that subsequent reduction occurs into the $e_g$ level of the ring system. His derived $n_{eff}$ of 4 for the triion does not appear consistent with this interpretation. The diion has three unpaired electrons which could indicate a configuration of either Mn(I) $b_{2g}^{2}e_g^{3}a_{1g}^{1}$, $e_g^{1}$(ring) or Mn(II) $b_{2g}^{2}e_g^{2}a_{1g}^{1}$, $e_g^{2}$(ring). On the other hand, the only configuration which would appear compatible with his susceptibilities for the triion is Mn(II) $b_{2g}^{2}e_g^{2}a_{1g}^{1}$, $e_g^{3}$(ring) where the manganese is in the 2+ oxidation state. The electronic spectrum of this stage does imply an $e_g^{3}$(ring) electronic configuration. If the first reduction does, however, correspond to addition to the manganese d orbital giving $Mn^{I}Pc^{-}$, then the manganese must revert to the 2+ oxidation state in either the diion or the triion, a situation similar to that proposed for the CoPc ions.

$Fe^{II}Pc$ (green) reduces to give a pink solution initially; further reduction yields a purple solution. Both of these species show a sharp band of moderate intensity in the near-infrared region, shifted somewhat to higher energy compared with other monoions. This band position is usually characteristic of single occupancy of the ring $e_g$ orbital. The third reduction stage shows no absorption in the near-infrared region but a strong band at 530 mμ closely resembling that of typical dinegative ions with an $e_g^{2}$(ring) electronic configuration. This third stage is therefore tentatively assigned to the species $Fe^{I}Pc^{3-}$ $b_{2g}^{2}e_g^{4}a_{1g}^{1}$, $e_g^{2}$(ring). The fourth and final stage shows the characteristic near-infrared band of a typical trinegative ion, although shifted some 200 mμ to a longer wavelength. It is not unreasonable to assume that this species is therefore $Fe^{I}Pc^{4-}$ with three electrons in the ring $e_g$ orbital. The fifth stage corresponding to $Fe^{I}Pc^{5-}$ is not seen (*cf.* CoPc). For the first two stages the assignment is more difficult. The spectra could suggest that both have an $e_g^1$(ring) configuration which leads to the assignment of Fe(II) $b_{2g}^2e_g^3a_{1g}^1$, $e_g^1$(ring) for the monoion and Fe(I) $b_{2g}^2e_g^4a_{1g}^1$, $e_g^1$(ring) for the diion. Taube's susceptibility results[1] indicate that both one- and two-electron reductions occur into the central metal ion. Preparations of the ions of FePc by reduction with sodium in tetrahydrofuran for electron spin resonance measurements[10] apparently produced only three stages, the colors of which are the same as in the later stages in the present work while no pink first stage was evident. Their first stage (purple) exhibited an esr spectrum of nine lines with a splitting of 2.4 G and for this reason was considered to be due to central metal reduction. We do not believe our pink stage to be due to an impurity for two reasons; first, the intensity of its spectrum is of the same order of magnitude as the later stages, and, second, there is no obvious reason that FePc should only reduce as a trinegative ion, if the first is discontinued, while the remainder of the metal phthalocyanine studies reduce to yield four steps, and five for CoPc. The nature of the reduced species for FePc must still remain in doubt although it seems probable that addition to the central metal ion does occur at some stage.

In conclusion it must be stressed that the authors are very much aware of the possibility that the reduction processes may well be assigned to other species when more data become available especially for the complexes with cobalt and iron, and possibly manganese; however, we do believe that the configurations suggested are the most consistent with the electron spin resonance and the electronic absorption data at the present time.

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# Mössbauer and Magnetic Susceptibility Studies of Uranium(III), Uranium(IV), Neptunium(III), and Neptunium(IV) Compounds with the Cyclopentadiene Ion[1]

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Mössbauer spectra of $NpCp_4$, $NpCp_3Cl$, and $NpCp_3 \cdot 3THF$ show isomer shifts indicative of covalent Np(IV)–Cp bonds (Cp = $C_5H_5^-$ ion) for $NpCp_4$ and $NpCp_3Cl$ and ionic Np(III)–Cp bonds for $NpCp_3 \cdot 3THF$. Quadrupole splitting of the Mössbauer spectrum of $Np^{4+}$ in $NpCp_4$ suggests a site of axial symmetry for the $Np^{4+}$ ion. The magnetic susceptibilities of $UCp_4$, $UCp_3Cl$, $UCp_3 \cdot THF$, $NpCp_3Cl$, and $NpCp_3 \cdot 3THF$ were measured from 2.5 to 25–100°K. Interpretation of magnetic susceptibilities in terms of crystalline field predictions indicates that $U^{4+}$ and $Np^{4+}$ in $UCp_3 \cdot THF$, $UCp_3Cl$, and $NpCp_3Cl$ are in sites of low symmetry; $U^{4+}$ in $UCp_4$ and $Np^{4+}$ in $NpCp_4$ are in sites with less than $T_d$ symmetry, but having a threefold axis; and the $Np^{3+}$ ion in $NpCp_3 \cdot 3THF$ is in a site descended from $O_h$ symmetry.

## Introduction

Several compounds of neptunium and uranium with the cyclopentadiene ion ($C_5H_5^-$ = Cp) have been prepared, and some of their properties investigated. Infrared spectra of $UCp_3Cl$,[2] $UCp_4$,[3] $UCp_3$,[4] $NpCp_3Cl$,[5] and $NpCp_4$[6] have been reported and analyzed in some detail.[7] Magnetic susceptibilities of $NpCp_4$ and $NpCp_3Cl$ have been measured at low temperatures;[8] the magnetic susceptibility of $UCp_3Cl$ has been measured from 313 to 77°K.[2]

This paper reports a new synthesis for the tetrahydrofuran (THF) adducts $UCp_3 \cdot THF$ and $NpCp_3 \cdot 3THF$, Mössbauer spectra for the neptunium cyclopentadiene compounds, and low-temperature magnetic susceptibility measurements for $UCp_3Cl$, $UCp_4$, $UCp_3 \cdot THF$, and $NpCp_3 \cdot 3THF$.

## Experimental Section

**Preparation of Compounds.** (a) **$UCp_4$ and $NpCp_4$.**—These compounds were prepared by stirring solid $UCl_4$ (or $NpCl_4$) with an excess of KCp in toluene for 3–5 days, following the procedure of Fischer and Hristidu.[3] The product was recovered by extracting the solids with toluene or by sublimation from the solids at 200–220° under a low pressure of *ca.* $4 \times 10^{-5}$ mm.

(b) **$UCp_3Cl$ and $NpCp_3Cl$.**—These compounds were prepared by the reaction of a 3:1 mole ratio of KCp to $UCl_4$ (or $NpCl_4$) in THF solution.[2] After stirring for 16 hr to complete the reaction, the solvent was removed by vacuum, and the product was recovered by vacuum sublimation at 180–200°.

(c) **$UCp_3 \cdot THF$ and $NpCp_3 \cdot 3THF$.**—These compounds were prepared by the reduction of $UCp_3Cl$ or $NpCp_3Cl$ by potassium metal with naphthalene as a catalyst, following the procedure of Watt and Drummond.[9] In a typical preparation, 0.51 g (1.09 mmol) of $NpCp_3Cl$ and 2.6 mg ($2 \times 10^{-2}$ mmol) of $C_{10}H_8$ were dissolved in 30 ml of THF, 43 mg (1.1 mmol) of potassium metal was added, and the solution was stirred at room temperature until the potassium dissolved (1–3 days). KCl was filtered from the solution, and the solvent was removed by vacuum. The product was warmed gently in a low pressure of 10–20 μ for 24

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