NEW ASPECTS OF THE CHEMISTRY OF TRANSITION METAL PHTHALOCYANINES

R. TAUBE

Sektion Verfahrenschemie, Technische Hochschule für Chemie 'Carl Schorlemmer', 42 Merseburg, Geusaer Strasse, GDR

Electron variability and complex formation of transition metal phthalocyanine are discussed. Under proper conditions the well-known metal(II) phthalocyanines [MPc] (M = Cr, Mn, Fe, Co, Ni, Cu, Zn) can take up four or, in two cases, five electrons. To elucidate the electronic structure of the isolated anionic complexes $Li_n[MPc].m$ THF a simple LCAO–MO model was derived which proved well suited to the interpretation of the chemical constitution of the various transition metal phthalocyanines. Properties like the oxidation potential, different multiplicities between isoelectronic species (e.g. manganese and iron phthalocyanines) and the Mössbauer spectra of iron phthalocyanines are explained. Further, preparation and properties of metal(III) phthalocyanines, complex formation of metal(II) phthalocyanines with pyridine and tetrahydrofuran and of iron(II) phthalocyanine with amines and various π-acid ligands, and the formation of σ-organyl transition metal phthalocyanines are treated.

INTRODUCTION

Nearly forty years ago Linstead published his first paper on the phthalocyanines[1], a new class of macrocyclic complex compounds. Together with his co-workers he synthesized the now well-known transition metal(II) phthalocyanines from manganese to zinc[2] whose detailed geometric structure (*Figure 1*) was elucidated by Robertson from single crystal x-ray investi-
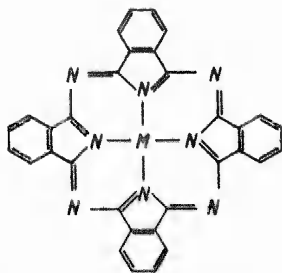
M = Mn, Fe, Co, Ni, Cu, Zn

Figure 1. Structure of transition metal phthalocyanines.

gations[3]. Owing to the planar porphyrin-like structure, the great stability, intense colour and their electric and catalytic properties the phthalocyanines have been the subject of growing interest[4, 5]. Today phthalocyanines have been prepared from nearly all metallic and semimetallic elements, but owing to their extreme low solubility the development of their chemistry is not easy.

ELECTRON VARIABILITY

Some years ago we found that metal phthalocyanines can be reduced in tetrahydrofuran with lithium and sodium, or with the adducts dilithium stilbene and sodium naphthalene, respectively, in accordance with the following scheme $[MPc] + n^- \rightarrow [MPc]^{n-}$

M:	Cr	Mn	Fe	Co	Ni	Cu	Zn	Li	Mg	Al
n_{max}:	4	5	4	5	4	4	4	3	4	4

to an extent of five steps[6-9].

The anionic complexes formed are quite soluble in polar organic solvents and are isolable as tetrahydrofuran solvated salts $Li_n[MPc].m$ THF in a pure crystalline state if oxygen and moisture are excluded perfectly. *Table 1* presents the chemical composition of the isolated metal phthalocyanines

$[Cr^{III}Pc\,Cl]$	$[Mn^{III}Pc\,Cl]$	$[Fe^{III}Pc\,Br]$	$[Co^{III}Pc\,J]$
$[Cr^{II}Pc]$	$[Mn^{II}Pc]$	$[Fe^{II}Pc]$	$[Co^{II}Pc]$
$\oplus$	$Li[Mn^{I}Pc]\cdot6T$	$Li[Fe^{I}Pc]\cdot4,5T$	$Li[Co^{I}Pc]\cdot4,5T$
$Li_2[Cr^{0}Pc]\cdot6T$	$Li_2[MnPc]\cdot6T$	$Li_2[Fe^{0}Pc]\cdot5,5T$	$Li_2[CoPc]\cdot6T$
$\oplus$	$Li_3[MnPc]\cdot9T$	$Li_3[FePc]\cdot8T$	$\odot$
$\oplus$	$Li_4[MnPc]\cdot10T$	$Li_4[FePc]\cdot9T$	$\odot$
—	$Li_5[MnPc]\cdot9T$	—	$\odot$
$[Ni^{II}Pc]$	$[Cu^{II}Pc]$	$[Zn^{II}Pc]$	$Li[Li^{I}Pc]\cdot4T$
$Li[NiPc]\cdot4,5T$	$Li[CuPc]\cdot4,5T$	$Li[ZnPc]\cdot5T$	$Li_2[LiPc]\cdot6T$
$Li_2[NiPc]\cdot6T$	$Li_2[CuPc]\cdot6T$	$Li_2[ZnPc]\cdot6T$	$Li_3[LiPc]\cdot8T$
$\oplus$	$\oplus$	$\oplus$	$Li_4[LiPc]\cdot12T$
$\oplus$	$\oplus$	$\oplus$	—

Table 1. Isolated metal phthalocyanines with different electron numbers (T = tetrahydrofuran).

with different total electron number. The dotted line marks the limit for lowering the oxidation number of the central atom. The lowest are 0 for chromium and iron, $+I$ for manganese and cobalt and $+II$ for nickel, copper and zinc. Further reduction leads to an occupation of the lowest anti-bonding π-orbitals of the phthalocyanine ligand as is the case, in general, for the main group metal phthalocyanines, too. Obviously the metal phthalocyanines show an unusually broad electron variability. Therefore and owing to their planar, highly symmetric, structure they are especially suited for investigations of electronic structure and bonding properties.

To understand the chemical constitution of the different metal phthalo-cyanines in an adequate manner we derived a simple LCAO–MO model from extended Hückel calculations[10]. The orbital basis we chose includes the 9 s-, p- and d-orbitals of the central atom, the 4 σ-hybrid orbitals from the inner nitrogen atoms and the 40 π-orbitals of the phthalocyanine. The resulting molecular orbitals are shown qualitatively in *Figure 2*.
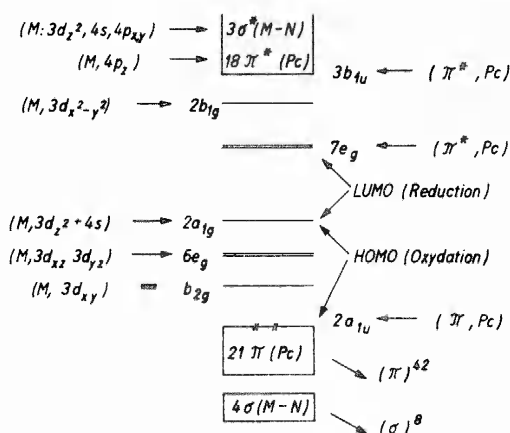

Figure 2. EHMO model for transition metal phthalocyanines.

There are four strong bonding σ-orbitals and 21 bonding and non-bonding π-orbitals arising mainly from the phthalocyanine. Especially important are the five so-called central atom orbitals b_{2g}, $6e_g$, $2a_{1g}$ and $2b_{1g}$ deriving themselves mainly from the corresponding $3d$-orbitals and the $4s$-orbital of the central atom, respectively. Their occupation determines the oxidation number of the central atom. Finally we had to note the lowest antibonding π-orbitals $7e_g$ and $3b_{1u}$ which are mainly or entirely phthalo-cyanine orbitals, respectively. Across the e_g-orbitals a d_π-p_π bonding inter-action between the central atom and the phthalocyanine can be realized transmitting each change in charge more or less over the whole complex.

In the usual way we can describe reduction by an occupation of the lowest unoccupied orbital and oxidation by elimination of an electron from the highest occupied orbital. *Figure 3* shows the calculated energies of the most important orbitals in this respect for MnPc to NiPc. Since the π-electron system is very extended, covering eight more electronegative nitrogen atoms, the relatively large electron acceptor capacity of the metal phthalocyanines becomes quite understandable. Further conclusions from our calculations are: (1) The stability of the central atom orbitals increases along the transition series. This is a consequence of the increasing nuclear charge at the central atom and means that in the same way the oxidation potential of the phthalocyanines must increase, too. This is the case indeed. In reasonable agreement with our calculated Hückel numbers Manassen[11] found the following oxidation potentials:

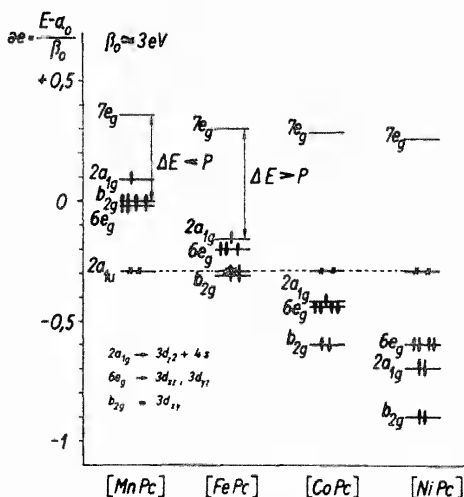| MnPc	FePc	CoPc	NiPc	CuPc	ZnPc
−0.11	+0.16	+0.77	+1.1	+1.0	+0.68

Figure 3. Calculated orbital energies for metal(II) phthalocyanines[10].

(2) In the same direction and for the same reason the energy difference ΔE between the four low-lying central atom orbitals b_{2g}, $6e_g$ and $2a_{1g}$ and the lowest antibonding π-orbitals $7e_g$ grows markedly. Therefore in chromium and manganese phthalocyanines the central atom orbitals can take up only 6 electrons [corresponding to the electron configuration $(6e_g)^4(b_{2g})^1(2a_{1g})^1$] while in iron, cobalt and nickel phthalocyanines these orbitals at first are filled up completely with 8 electrons before the $7e_g$-orbitals are occupied.

(3) As a consequence of the relatively short M–N distance in the transition metal phthalocyanines the fifth central atom orbital $2b_{1g}$ stemming mainly from the $d_{x^2-y^2}$ orbital is strongly antibonding and can not be occupied before copper.

(4) The order of the central atom orbitals $2a_{1g}$, $6e_g$ and b_{2g} changes from manganese to nickel phthalocyanine as a consequence of the different relative position between the d-orbital level of the central atom and the π-orbitals of the phthalocyanine system.

With these basic features in mind we can derive the electronic configuration for most transition metal phthalocyanines quite reasonably.

In *Figure 4* the electronic configurations and magnetic moments of isoelectronic manganese and iron phthalocyanines are given. There exist essential differences between isoelectronic species in both series. In the row of the manganese phthalocyanines the number of unpaired electrons drops down from four to two followed by an increase to five, while in the iron compounds unpaired electrons decrease to zero, increasing thereafter to two.

We believe that the striking differences in spin multiplicity between both series arise from the greater stability of the central atom orbitals and the change in position between the $6e_g$-orbitals and the b_{2g}-orbital going from manganese to iron phthalocyanine complexes. In our calculations the $6e_g$-orbitals and the b_{2g}-orbital in manganese phthalocyanine are nearly 'entartet'. Measurements of the magnetic anisotropy by Martin *et al.*[12]

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$[MnPc]^+$	$[MnPc]$	$[MnPc]^-$	$[MnPc]^{2-}$	$[MnPc]^{3-}$	$[MnPc]^{4-}$	$[MnPc]^{5-}$
4	3	2	3	4	5	4
4,90	4,33	2,80	4,13	4,92	5,96	5,77

$[FePc]^+$	$[FePc]$	$[FePc]^-$	$[FePc]^{2-}$	$[FePc]^{3-}$	$[FePc]^{4-}$
3	2	1	0	1	2
3,80	3,90	2,12	0,31	2,46	3,36

Figure 4. Electronic configuration, number of unpaired electrons and magnetic moments for isoelectronic manganese and iron phthalocyanines.

show that in manganese(II) phthalocyanine the b_{2g}-orbital is somewhat more stable than the $6e_g$-orbital. Therefore we suppose the change of order between the orbitals to take place at the transition from the manganese(II) to the manganese(I) complex.

This interpretation leads to perfect agreement between theory and magnetic moments in all other cases. The electronic configuration of the iron compounds could be established further by Mössbauer measurements made in conjunction with Fluck[13]; results are shown in *Figure 5.*

Despite a sixfold variation of electron number in the row of the iron phthalocyanines the change in isomeric shift is only relatively small. This gives direct experimental evidence of an extensive electron delocalization which can take place according to theory essentially through the $d_\pi - p_\pi$ interaction in the e_g-orbitals[10].

	$[FePc]^+$	$[FePc]$	$[FePc]^-$	$[FePc]^{2-}$	$[FePc]^{3-}$	$[FePc]^{4-}$
σ [mm/sec]	0,49	0,63	0,61	0,52	0,58	0,61
$\triangle E_Q$ [mm/sec]	3,95	2,58	3,24	1,86	1,77	1,65

Figure 5. Electronic configuration and Mössbauer parameters of iron phthalocyanines.

From our MO calculations we conclude that the electric field gradient in the iron phthalocyanines arises from a surplus of electronic charge in the xy-plane of the complex mainly as a result of the double occupied non-bonding $b_{2g}(d_{xy})$-orbital. The corresponding positive sign of the electric field gradient was established experimentally for iron(II) phthalocyanine by Dale *et al.*[14] and for the iron(0) complex through our own measurements of the Mössbauer spectra in an external magnetic field[15]. In full agreement with theory occupation of the e_g-orbitals causes an increase in the isomeric shift and a decrease in the quadrupole splitting. This arises from the corresponding increase of the d_{xz} and d_{yz} electron density reducing the s-electron density at the nucleus by shielding and partly compensating the positive electric field gradient. Owing to the very pronounced delocalization of the e_g-orbitals both effects are only small. The relatively strong changes in FePc may arise from mixing in excited configurations like $(b_{2g})^1(6e_g)^4(2a_{1g})^1$ to the ground state via spin–orbit coupling[14]. On the other hand with occupation of the $2a_{1g}$-orbital in the iron(0) complex the isomeric shift decreases and the quadrupole splitting drops very markedly. This must surely result from the $4s$ contribution to this orbital causing an increase of s-electron density at the iron nucleus and from the much larger compensating influence of the d_{z^2} orbital, the main component in the strongly localized $2a_{1g}$-orbital acting on the positive electric field gradient. So, the derived electron configurations of the iron phthalocyanines could be confirmed quite unequivocally.

Finally in connection with the investigations on electron variability we are interested in the oxidation of transition metal phthalocyanines. As mentioned above the stability of the central atom orbitals increases across the transition series, causing growing oxidation potentials from manganese to nickel phthalocyanine. Some results of our preparative investigations on the oxidation of transition metal phthalocyanines are summarized in *Table 2*.

Manganese phthalocyanine can be oxidized in tetrahydrofuran by trityl chloride or oxygen, while iron and cobalt phthalocyanine do not react under the same conditions. Oxidation of the iron phthalocyanine with oxygen takes place only if a strong acid is present to increase the oxidation potential sufficiently:

$$2\,FePc + \tfrac{1}{2}O_2 + 2\,HX \rightarrow 2\,FePcX + H_2O$$

Besides the chloride we could prepare in this way with chloronaphthalene as solvent, we are also interested in p-toluenesulfonate, especially in view of the poor donor capacity of the p-toluenesulfonate anion. Remarkable properties of this compound mentioned already above are the extremely large quadrupole splitting reaching nearly $4\,mm\,s^{-1}$ and the magnetic moment corresponding to the spin only value for three unpaired electrons, both in full accord with the derived electron configuration $(b_{2g})^2(6e_g)^2(2a_{1g})^1$. The higher magnetic moments of the halides arise from a large temperature independent paramagnetism (for FePcCl we found $1600 \times 10^{-6}\,cm^3\,g^{-1}$) which might decrease on going to the heavier halogens. The cobalt(III) phthalocyanine iodide complexes, however, are diamagnetic certainly in consequence of the lower spin pairing energy for the configuration $(b_{2g})^2(6e_g)^4$. Their successful preparation needs a large excess of iodine while nickel phthalocyanine could not be oxidized at all.

M(II)Pc	oxidation ag.	M(III)Pc	colour	μ_{eff}(B.M.)	configuration
[MnPc]	$Ph_3C\,Cl\,/\,THF$	Mn Pc Cl	dark blue	4,90	$(b_{2g})^1(6e_g)^2(2a_{1g})^1$
	$O_2\,/\,THF$	$(MnPc)_2O \cdot 2THF$	red	2,99	
	$J_2\,/\,THF$	$Mn\,Pc\,J_3 \cdot 3,5\,THF$	dark green	4,82	
	$J_2\,/\,Cl-napht.$	Mn Pc J	green black	5,01	
[FePc]	$O_2\,/\,HX$	$Fe\,Pc\,O_3S\,C_6H_4\,CH_3$	olive black	3,80	$(b_{2g})^2(6e_g)^2(2a_{1g})^1$
	$(Cl-napht.)$	Fe Pc Cl	gray black	4,35	
	$Br_2\,/\,C_6H_6$	Fe Pc Br	brown black	4,13	
	$J_2\,/\,C_6H_6$	$Fe\,Pc\,J_2$	green black	4,10	
[CoPc]	$J_2\,/\,C_6H_6$	CoPc J	brown	1,08	$(b_{2g})^2(6e_g)^4$
	$J_2\,/\,Py$	$Co\,Pc\,J_3 \cdot 3\,Py$	violet	0,43	

Table 2. Oxidation of metal(II) to metal(III) phthalocyanines in organic solvents.

The electronic structure of iron(III) phthalocyanines could be established further by Mössbauer measurements (see *Table 3*). All compounds show nearly the same isomeric shift while the quadrupole splitting decreases in a regular way with increasing ligand field strength of the coordinated anion. The very tight bonding of the chloride ion also finds experimental confirmation in the kinetically inert character of the iron phthalocyanine chloride.

Compound	δ [mm/sec]	ΔE_Q [mm/sec]
$Fe\,Pc\,O_3SC_6H_4CH_3$	0,49	3,95
$Fe\,Pc\,J_2$	0,44	3,30
$Fe\,Pc\,Br$	0,37	3,16
$Fe\,Pc\,Cl$	0,46	2,75

Table 3. Mössbauer parameters of iron(III) phthalocyanines.

COMPLEX FORMATION

Besides electronic variability, complex formation is the other most important property determining the chemical constitution of transition metal phthalocyanines.

As shown in *Table 4* stable bispyridine complexes are formed only with chromium, manganese and iron phthalocyanine. Since in these cases the $2a_{1g}$-orbital can get free by spin pairing a strong bonding attraction is possible over the $3d_{z^2}$ and $4p_z$-orbitals on two ligands in the z-direction. In nickel and copper phthalocyanines on the other hand spin pairing can not be realized and from the doubly occupied $2a_{1g}$-orbital results a strong electronic repulsion preventing any further complex formation. This repulsion is of course considerably smaller in cobalt phthalocyanine with a single occupied $2a_{1g}$-orbital and in zinc phthalocyanine, the d-shell being strongly contracted. So, in these cases, a weak complex formation with one pyridine ligand takes place. Since tetrahydrofuran is a much weaker ligand than pyridine we could isolate definite THF complexes only with chromium manganese and iron phthalocyanines, generating these metal(II) phthalocyanines

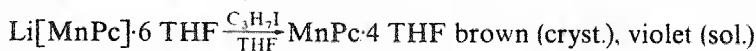| $M(II)Pc/Py$	Electron configuration		$\mu_{eff}(B.M)$	Author
$[CrPc]$	d^4	$(6e_g)^2(b_{2g})^1(2a_{1g})^1$	4,75	Ercolani
$[CrPc \cdot 2Py]$		$(6e_g)^3(b_{2g})^1$	3,15	Elvidge
$[MnPc]$	d^5	$(b_{2g})^2(6e_g)^2(2a_{1g})^1$	4,35	Calvin
$[MnPc \cdot 2Py]$		$(6e_g)^4(b_{2g})^1$	$S = \frac{1}{2}$	Phillips
$[FePc]$	d^6	$(b_{2g})^2(6e_g)^3(2a_{1g})^1$	3,90	Klemm
$[FePc \cdot 2Py]$		$(b_{2g})^2(6e_g)^4$	0	Klemm
$[CoPc]$	d^7	$(b_{2g})^2(6e_g)^4(2a_{1g})^1$	2,72	Figgis
$[CoPc \cdot Py]$		$(b_{2g})^2(6e_g)^4(2a_{1g})^1$	—	——
$[NiPc]$	d^8	$(b_{2g})^2(6e_g)^4(2a_{1g})^2$	0	Klemm
$[CuPc]$	d^9	$(b_{2g})^2(6e_g)^4(2a_{1g})^2(2b_{1g})^1$	1,73	Klemm
$[ZnPc]$	d^{10}	——	0	—
$[ZnPc \cdot 1Py]$		——	0	—

Table 4. Complex formation of transition metal(II) phthalocyanines with pyridine.

in tetrahydrofuran by appropriate chemical reactions at room temperature. The chromium complex was prepared by reduction of chromium phthalocyanine chloride with lithium benzophenone:
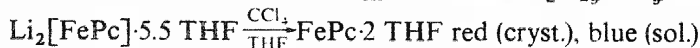
$$CrPcCl \xrightarrow[THF]{Libzph} CrPc \cdot 3\,THF \text{ brown (cryst.), blue (sol.)}$$
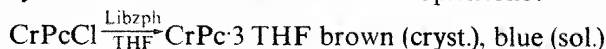
$$\mu_{eff} = 2.94 \text{ B.M. } [(6e_g)^3(b_{2g})^1] \text{ low spin!}$$

while the manganese and iron complexes could be obtained by oxidation of manganese(I) and iron(0) phthalocyanines with alkyl iodide or carbon tetrachloride, respectively:

$$Li[MnPc] \cdot 6\,THF \xrightarrow[THF]{C_3H_7I} MnPc \cdot 4\,THF \text{ brown (cryst.), violet (sol.)}$$

$$\mu_{eff} = 4.17 \text{ B.M. } [(b_{2g})^2(6e_g)^2(2a_{1g})^1] \text{ high spin!}$$

$$Li_2[FePc] \cdot 5.5\,THF \xrightarrow[THF]{CCl_4} FePc \cdot 2\,THF \text{ red (cryst.), blue (sol.)}$$

$$\mu_{eff} = 0.88 \text{ B.M. } [(b_{2g})^2(6e_g)^4] \text{ low spin!}$$

It is an interesting fact that the weak ligand tetrahydrofuran causes spin pairing in the case of chromium(II) and iron(II) phthalocyanines. Both complexes are therefore kinetically stabilized and can be recrystallized from hot tetrahydrofuran by extraction, while the manganese complex decomposes under these conditions.

The strong tendency of iron phthalocyanine to form stable bisamine complexes is already known. More recently Kenney demonstrated the usefulness of iron phthalocyanine as a resonance shift reagent in the n.m.r. spectroscopy of amines[16]. We have prepared some bisamine complexes of iron phthalocyanine and measured their Mössbauer spectra to study the bonding interaction with the different amines. The results are given in Table 5. From the nearly constant isomeric shift throughout the whole series of complexes we can conclude that the s-electron density at the iron nucleus remains also nearly constant independently of the bonding state of the coordinated nitrogen atom in the different amines. The quadrupole splitting on the other hand decreases slightly in the given order, indicating a

Complex	δ [mm/sec]	ΔE_Q [mm/sec]	stability
Fe Pc · 2 piperidine · 2THF	0,52	2,25	
Fe Pc · 2 diethylamine	0,51	2,22	low
Fe Pc · 6 aniline	0,53	2,11	
Fe Pc · 2 HOCH$_2$ CH$_2$ NH$_2$ · 2THF	0,53	2,01	
Fe Pc · 2 pyridine	0,52	1,99	high
Fe Pc · 2 n-C$_3$H$_7$NH$_2$	0,50	1,97	
Fe Pc · 2 n-C$_3$H$_7$NH$_2$ · 2THF	0,47	1,84	
Fe Pc · 2 imidzole · 3THF	0,52	1,73	high
Fe Pc · 2C$_6$H$_5$ CH$_2$ NH$_2$ 2THF	0,55	1,53	

Table 5. Mössbauer parameters of iron phthalocyanine amine complexes.

corresponding compensation of the positive electric field gradient in the xy-plane, which could arise from an increasing bonding interaction with decreasing steric requirements or increasing donor capacity of the amine, respectively.

To elucidate the coordinative properties of iron phthalocyanine more fully we tested its reactivity also against some π-acid ligands shown in *Table 6.* By simple addition reactions in benzene or THF, respectively, we could prepare for the first time the bis complexes of iron phthalocyanine with tributylphosphine, triethyl phosphite and p-toluene isonitrile and a carbon monoxide aniline complex, too. The corresponding group stretching frequencies indicate that the isonitrile coordinates essentially by σ-bonding while with carbon monoxide a remarkable contribution of π-backbonding is realized.

Nitric oxide complexes of transition metal phthalocyanines were first prepared by Ercolani in a solid state reaction[17]. As we found, manganese and iron phthalocyanines react with nitric oxide in tetrahydrofuran much more readily. The manganese compound crystallizing with two molecules of tetrahydrofuran is diamagnetic and can be considered therefore as an NO$^+$

Ligand	complex	ν_{x-y} [cm^{-1}]	μ_{eff} (B.M.)	electron config.
PR$_3$	Fe Pc · 2P(C$_4$H$_9$)$_3$	—	0,71	$(b_{2g})^2 (6e_g)^4$
P(OR)$_3$	Fe Pc · 2 P(OC$_2$H$_5$)$_3$	—	0,63	$(b_{2g})^2 (6e_g)^4$
R−NC	Fe Pc · 2CNC$_6$H$_4$ CH$_3$	2135 (2136)	0	$(b_{2g})^2 (6e_g)^4$
CO	Fe Pc · CO(C$_6$H$_5$ NH$_2$) · THF	2000 (2143) 1990	0	$(b_{2g})^2 (6e_g)^4$
NO	[Mn Pc (NO)] · 2THF	1750	0,87	$(6e_g)^4 (b_{2g})^2$ (NO$^+$)
	[Fe Pc (NO)]	1690	1,88	$(b_{2g})^2 (6e_g)^4 (\pi^*)^1$ (NO)
	Li [Fe Pc(NO)] · 4THF	1505	0,44	$(b_{2g})^2 (6e_g)^4 (\pi^*)^2$ (NO$^-$)

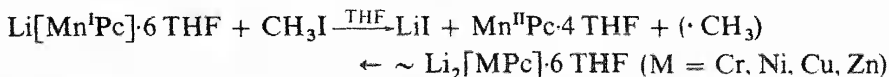*Table 6.* Transition metal phthalocyanine complexes with π-acid ligands.

complex of manganese(I). The solvent-free iron complex shows the magnetic, IR and ESR spectroscopic behaviour ($g = 2.038$; triplet; $a^N = 17\,G$)[18] of a typical nitroso compound. That means the existing unpaired electron must occupy an orbital corresponding mainly to the lowest antibonding π-orbital of the NO group. By reduction with one equivalent lithium benzophenone the lithium salt of an anionic nitrosyl iron phthalocyanine complex can be isolated which is diamagnetic. Therefore, the received electron must occupy the antibonding π-orbital of the NO group, and a nitrosylate complex with a coordinated NO^- ligand should be formed. Additional proof for this comes again from Mössbauer spectra[19]. Nearly identical Mössbauer parameters were found for the neutral and the anionic nitrosyl complex:

	$mm\,s^{-1}$	$E_Q\,mm\,s^{-1}$
FePc(NO)	0.43 ± 0.03	1.69 ± 0.06
Li[FePc(NO)]·4THF	0.40 ± 0.04	1.74 ± 0.08

This is in full accord with the supposed occupation of the antibonding π-orbital from the NO group, where iron atom orbital participation may be negligible. So all three main oxidation states of nitric oxide, NO^+, NO and NO^-, can be realized in coordination with transition metal phthalocyanines.

One frontier of modern coordination chemistry is the synthesis of σ-organyl transition metal compounds and in connection with our studies on the chemistry of transition metal phthalocyanines we also took up the question whether σ-organyl derivatives can be prepared.

We investigated the reaction of the anionic metal phthalocyanines with alkyl halides and found a remarkable connection between the electronic structure of the anionic metal phthalocyanine and the reaction route. In general, a reductive splitting of the carbon–halogen bond takes place and the metal(II) phthalocyanine is formed back as it is formulated here for manganese(I) phthalocyanine and methyl iodide:

$$Li[Mn^I Pc]·6\,THF + CH_3I \xrightarrow{THF} LiI + Mn^{II}Pc·4\,THF + (\cdot CH_3)$$
$$\leftarrow \sim Li_2[MPc]·6\,THF \quad (M = Cr, Ni, Cu, Zn)$$

With iron(0) and cobalt(I) phthalocyanine, however, owing to their strong nucleophilicity arising from the spin paired d^8-configuration and the low oxidation number of the central atoms, a nucleophilic substitution proceeds much more easily and stable σ-organyl complexes are formed[20]:

$$Li_2[Fe^0Pc]·5.5\,THF + CH_3I \xrightarrow{THF} Li[H_3CFePc]·6\,THF + LiI$$
$$Li[CoPc]·4.5\,THF + n\text{-}C_3H_7I \xrightarrow{THF} [n\text{-}C_3H_7CoPc]·3\,THF + LiI$$

Formulae and some properties of the isolated σ-organyl iron and cobalt phthalocyanines are given in *Table 7*. The constitution of each compound is fully established by elemental analyses, iodination in the absence of air and magnetic measurements. The iron complexes are sensitive to air and moisture. By heating the metal–carbon σ-bond is homolytically split and the corresponding reduced metal phthalocyanine is formed in each case. All compounds are diamagnetic in accord with a spin paired d^6-configuration

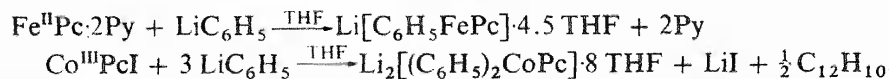| Complex	colour (cryst.)	μ_{eff} (B.M.)
Li $[H_3C - Fe\,Pc]\cdot 6\,THF$	blue green	0,29
Li $[Br(CH_2)_4 - Fe\,Pc]\cdot LiBr\cdot 8\,THF$	dark green	0,57
$Li_2[Pc\,Fe - (CH_2)_4 - Fe\,Pc]\cdot 10\,THF$	green	0
Li $[C_6H_5\,CH = CH - Fe\,Pc]\cdot 4\,THF$	green	1,04
Li $[C_6H_5 - Fe\,Pc]\cdot 4,5\,THF$	blue green	0,31
Li $[C_6H_5\,\underset{O}{C} - Fe\,Pc]\cdot 3\,THF$	red	0
$[n - C_3H_7\,Co\,Pc]\cdot 3\,THF$	red	0

Table 7. σ-Organyl metal phthalocyanines of iron and cobalt.

for the central atoms iron(II) and cobalt(III). Therewith the existence of vitamin B_{12}-like σ-organyl iron(II) chelates could be proved for the first time. Preparation of σ-organyl transition metal phthalocyanines by carbanion addition is possible, too, but the redox reaction must be avoided again.

With lithium methyl, lithium phenyl or the corresponding Grignard reagents the metal(II) phthalocyanines were reduced to their anionic complexes quite generally:

$$[MPc] + R^- \xrightarrow{\text{THF}} [MPc]^- + \tfrac{1}{2}R_2 \;(M = Cr \to Zn)$$
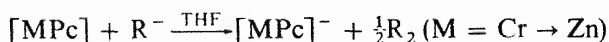
A coordinative addition could be realized, however, with the spin paired d^6-complexes bispyridineiron(II) phthalocyanine and cobalt(III) phthalocyanine iodide. With lithium phenyl, for example, the monophenyliron(II) and the bisphenylcobalt(II) complex were prepared in this way:

$$Fe^{II}Pc\cdot 2Py + LiC_6H_5 \xrightarrow{\text{THF}} Li[C_6H_5FePc]\cdot 4.5\,THF + 2Py$$
$$Co^{III}PcI + 3\,LiC_6H_5 \xrightarrow{\text{THF}} Li_2[(C_6H_5)_2CoPc]\cdot 8\,THF + LiI + \tfrac{1}{2}C_{12}H_{10}$$

No reduction takes place if lithium or sodium phenylacetylide is used as the carbanionic reagent. In this case complex formation is the general reaction mode. We suppose the high electron affinity of the phenylacetyl radical to be the deciding reason that no reduction occurs. Therefore, the rate of the redox reaction is only very slow and coordinative addition proceeds only if the metal phthalocyanine is capable of complex formation. The isolated phenylacetylide complexes are shown in *Table 8*.

Similar to the pyridine complex formation explained above mono- and bis-phenylacetylide complexes could be prepared. The formation of a bisorganyl complex with iron(II) is certainly a consequence of the relatively

Complex	ox. nr.	μ_{eff}(B.M.)	ν_{cc}[cm^{-1}]
$Li[CrPc(Phac)_2]\cdot 5\,THF$	Cr (III)	3,73	2065/2075
$Li[MnPc(Phac)]\cdot 4,5\,THF$	Mn (II)	5,91!	—
$Li_2[FePc(Phac)_2]\cdot 7\,THF$	Fe (II)	0	2066/2076
$Li[FePc(Phac)Py]\cdot 4\,THF$	Fe (II)	0,53	2088
$Li_2[CoPc(Phac)_2]\cdot 8\,THF$	Co (II)	0,37	2096
$Li[CoPc(Phac)_2]\cdot 4\,THF$	Co (III)	0,32	2092/2103
$Na[ZnPc(Phac)]\cdot 5\,THF$	Zn (II)	0	2097

Table 8. Phenylacetylide complexes of transition metal phthalocyanines.

small *trans* effect of the phenylacetylide ion. Especially surprising is the high spin character of the manganese(II) complex. Probably the manganese atom has left the strong ligand field of the phthalocyanine in the plane and lies somewhat above the four nitrogen atoms. Being diamagnetic the cobalt(II) complex might possess a binuclear structure with a cobalt–cobalt bond. The change in the stretching frequency of the C—C triple bond with the central atom is only small. There is only a slight increase in the acceptor strength of the central atom and no indication of any π-bonding back-donation.

CONCLUSIONS

The investigations on electron variability and complex formation, especially the synthesis of σ-organyl compounds, represent an essential extension in the chemistry of transition metal phthalocyanines and contribute to the development of most fields in modern coordination chemistry. From the studies of ground state properties as a function of nuclear charge and electron number crucial conclusions on the electronic structure of transition metal phthalocyanines can be drawn. The derived LCAO–MO model permits of a comprehensive theoretical description and understanding of structure and reactivity for the various complexes. As the limiting factor for the synthesis of σ-organyl compounds the rate of the redox reaction between the metal phthalocyanine and the organyl halide or the organyl anion, respectively, was recognized. The achieved experimental and theoretical results furnish a valuable basis for other and further research work on chemical and physical properties of transition metal phthalocyanines and their derivatives.

REFERENCES

[1] R. P. Linstead, *J. Chem. Soc.* 1016 (1934).
[2] R. P. Linstead, *Ber. dtsch. chem. Ges.* **72**, 1. A, 93 (1939).
[3] J. M. Robertson and I. Woodward, *J. Chem. Soc.* 219 (1937).
[4] F. H. Moser and A. L. Thomas, *Phthalocyanine Compounds*, Reinhold,(New York, 1963).
[5] A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.* **7**, 28 (1965).
[6] R. Taube, *Chem. Zvesti*, **19**, 215 (1965).
[7] R. Taube and H. Arfert, *Z. Naturforsch.* **22b**, 219 (1967).
[8] R. Taube and H. Drevs, *Angew. Chem.* **79**, 313 (1967).
[9] R. Taube, H. Munke and J. Petersen, *Z. anorg. allg. Chem.* **390**, 257 (1972).
[10] R. Taube, *Z. Chem.* **6**, 8 (1966).
[11] J. Manassen and Amiram Bar-Ilan, *J. Catalysis*, **17**, 86 (1970).
[12] C. G. Barraclough, R. L. Martin and S. Mitra, *J. Chem. Phys.* **53**, 1638 (1970).
[13] R. Taube, H. Drevs, E. Fluck, P. Kuhn and K. F. Brauch, *Z. anorg. allg. Chem.* **364**, 297 (1969).
[14] B. W. Dale, R. J. P. Williams, P. R. Edwards and C. E. Johnson, *J. Chem. Phys.* **49**, 3445 (1968).
[15] H. Drevs, R. Taube, J. Jacob and E. Wieser, unpublished.
[16] J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.* **94**, 2132 (1972).
[17] C. Ercolani and C. Neri, *J. Chem. Soc.* 1715 (1967).
[18] R. Taube, H. Munke and W. Karthe, unpublished.
[19] R. Taube, H. Munke and H. Hobert, unpublished.
[20] R. Taube, H. Drevs and Tran Duc Hiep, *Z. Chem.* **9**, 115 (1969).