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MAGNETIC PROPERTIES OF OXIDATION PRODUCTS OF PHTHALOCYANINE COMPLEXES WITH METAL CHLORIDES WITH ELECTRON ACCEPTOR PROPERTIES

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Abstract—The effect of charge transfer complex formation on the oxidisability of various phthalocyanines complexes with Lewis acids has been investigated. Multistep electron transfer between phthalocyanine as electron donor and the molecules of electron acceptor was found to be possible, leading to the formation of mono- and polycation radicals with characteristic magnetic properties. The structure of the transition products has been established and an oxidation mechanism is suggested.

Phthalocyanines as porphyrin derivatives are interesting research objectives because of their structural analogies with some important, biologically active compounds. Their tendency to redox reactions is specially interesting because of the role these reactions in energy transformations proceeding in living organisms.

It has been found[1] that phthalocyanines create charge transfer complexes with anhydrous chlorides of metals having vacant p or d electron shell. MX_2^+ ions formed in anhydrous polar solvent as a result of chloride autodissociation exhibit pronounced electron acceptor properties. When interacting with the free electron pairs of external nitrogen atoms of the porphyrazine ring, they form charge transfer complexes of ionic nature stabilized by the corresponding anions (formed by chloride dissociation). In case of the complex with aluminium chloride, this reaction can be described by the formula:

$$MPc + 4Al_2Cl_6 \rightleftharpoons MPc(AlCl_2^+)_4 \ldots (AlCl_4^-)_4.$$

Since it was found that in contact with air the nitrobenzene solutions of the above complexes undergo spontaneous transformations, it was resolved on closely investigating their mechanism.

On account of its structure, the phthalocyanine molecule can act both as electron donor and electron acceptor, undergoing multistep redox reactions. According to Taube[2–3] and other authors,[4–7] the phthalocyanine molecule can undergo multi-step reduction, finally yielding tetraanions with well defined spectral characteristics. Depending on the central ion, the first reduction step takes place either on the metal atom or on the porphyrazine ring.

Oxidation processes may proceed analogously. According to some studies on electrochemical and chemical oxidation mono- and dications of phthalocyanines have been obtained.[8–13]

In the present studies we assumed that the formation, at the first stage, of a charge transfer complex between phthalocyanine and strong electron acceptor ought to lower the oxidation potential of phthalocyanine. We resolved to select appropriate conditions permitting four-step oxidation of the porphyrazine ring without its destruction. We studied the following phthalocyanines: free phthalocyanine H_2Pc, sodium phthalocyanine Na_2Pc, copper phthalocyanine CuPc, cobalt phthalocyanine CoPc, chloroaluminium phthalocyanine AlClPc, chloroiron phthalocyanine FeClPc, chlorogallium phthalocyanine GaClPc, chlorovanadium phthalocyanine VClPc, hydroxychromium phthalocyanine CrOHPc and vanadyl phthalocyanine VOPc as electron donors, and aluminium chloride $AlCl_3$, gallium chloride $GaCl_3$, ferric chloride $FeCl_3$ and stannic chloride $SnCl_4$ as electron acceptors. Experiments were performed in anhydrous nitrobenzene solutions, keeping the phthalocyanine concentration constant at 10^{-3} M/l, and chloride concentration varying from 1×10^{-3} to 220×10^{-3} M/l. Complexes obtained by mixing of components were green, and in the presence of atmospheric oxygen they turned violet. The violet form of the complex was metastable and could be reversed to the green form by bubbling through it dry, oxygen-free neutral gas (N_2 or Ar) for several hours. If the violet form of the complex was not liberated from oxygen, it underwent further spontaneous transformations, and was converted into the chemically stable yellow form. The yellow form could no longer be reversed into the violet and then the green form by bubbling neutral gas through it.

To determine the structure of the individual oxidation products we applied the UV vis, EPR and NMR methods.

Electronic spectra were recorded on a Beckman Acta VII spectrophotometer, and the EPR spectra—on a Brucker 418 BS spectrometer for band X. Magnetic susceptibility was determined by means of the NMR spectra taken on a Tesla spectrometer. In UV Vis and EPR, NMR studies anhydrous nitrobenzene was used as solvent. UV Vis and NMR spectra were studied at room temperature and EPR spectra at 144 K.

DISCUSSION OF RESULTS

Phthalocyanine complexes with chlorides of metals with electron acceptor properties, obtained in oxygen-free atmosphere, are green and exhibit a characteristic

EPR spectrum described in (1) and UV Vis spectrum. In the presence of atmospheric oxygen the following transformations take place: green form (I) → violet form (II) → yellow form (III). The observed change in colour is associated with marked changes of the EPR spectra of the complexes and in their electronic spectra.

Changes taking place in the complexes as a result of multi-step oxidation, reflected in the EPR spectrum, will be discussed in the instance of the complexes of copper phthalocyanine with $AlCl_3$ (Fig. 1) and cobalt phthalocyanine with $GaCl_3$ (Fig. 2). Figure 1(a) presents the EPR spectrum of the charge transfer complex formed by CuPc with $AlCl_3$ under anaerobic conditions; there appears the superhyperfine structure derived from the interactions of the spin of unpaired electron $3d^9$ of copper with four equivalent nuclei of the internal nitrogens atoms of the porphyrazine ring ($I_N = i$). Transition of the complex from the green (I) to the violet form (II) causes, as it is evident in Fig. 1(b), gradual disappearance of this structure. Upon further oxidation also the hyperfine structure disappears (Fig. 1(c)). The yellow form (III) of the complex is characterized by complete disappearance of the signal in the EPR spectrum (Fig. 1(d)).

Changes in the EPR spectrum of the CoPc complex with $GaCl_3$ as a function of oxidation are presented in Fig. 2. The curve (Fig. 2(a)) shows the hyperfine structure derived from the interaction of unpaired electron spin with cobalt nucleous; this structure is characteristic of the green, oxygen-free form of the complex. The first oxidation stage involves the appearance of the II-nd form characterized by broadening of the lines of the hyperfine structure and by the occurrence of the radical signal (Fig. 2(b)). Further oxidation causes disappearance of the EPR lines of the central ion and splitting of the radical signal (Figs. 2c, d, g). Upon transition to the III-rd form the EPR signal disappears.

Analogous relationships are observed for the complexes of all investigated phthalocyanines with central ions having paramagnetic properties. Only for CuPc complexes with the above-mentioned metal chlorides, in the violet form no radical line is observed. It is assumed that the lack of radical signal is caused by the facilitated interaction of free spin, occurring on the porphyrazine ring during oxidation, with unpaired electron of central ion, situated on orbital $3dx^2 - y^2$ in the ring plane. The oxygen-free green form of the complexes of free phthalocyanine and of phthalocyanines with diamagnetic central ions gives no signal in the EPR spectrum.

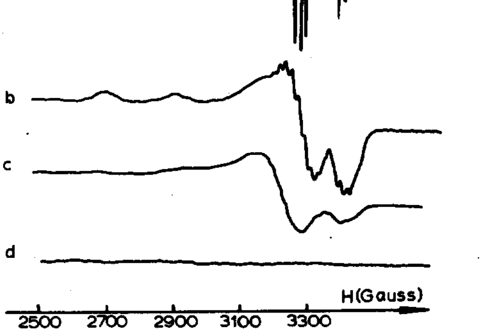


Fig. 1. Effect of oxygen on EPR spectrum of complex CuPc·$AlCl_3$ (1 : 220). [a]green form; [b,c]violet form; [d]yellow form.

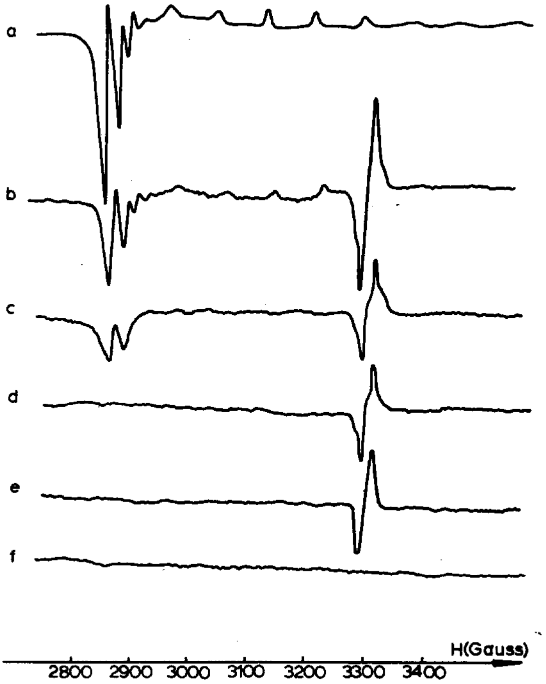


Fig. 2. Effect of oxygen on EPR spectrum of complex CoPc·$GaCl_3$ (1 : 220). [a]green form; [b,c,d,e]violet form; [f]yellow form.

Transition to the II-nd form is accompanied by the occurrence of radical signal which disappears after transition to form III. This is exemplified in Fig. 3. To elucidate whether the disappearance of signals in the EPR spectrum of the III-rd form is caused by transition of the complex into diamagnetic state or results from broadening of the lines because of spin–spin interaction, the magnetic susceptibility of the complexes and the effective magnetic moments of the individual forms of complexes were determined according to Evans.[14] According to these data, for the green form of the complexes of diamagnetic phthalocyanines the magnetic moment is zero, whereas in case of phthalocyanine complexes with paramagnetic central ion it is about 1.62 MB, this corresponding to the value for one unpaired electron. Transition to the violet form causes an increase in the magnetic moment to about 2 MB; for the yellow form of the complexes of all phthalocyanines studied this value is even higher, amounting to about 2.4 MB.

To ascertain that the increase in the magnetic susceptibility of the oxidized forms is not simply due to the physical effect of solvent saturation with molecular oxygen having its own paramagnetism a mixture of gaseous and ozone was bubbled through nitrobenzene until saturation. It was found that the magnetic susceptibility of this solution was much lower than that obtained for the yellow forms of the phthalocyanine complexes.

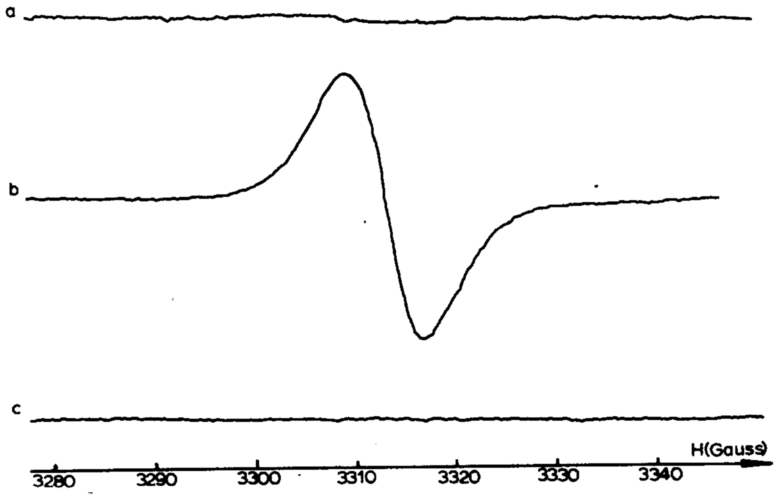


Fig. 3. Effect of oxygen on EPR spectrum of complex GaClPc·$SnCl_4$ (1 : 220). [a]green form; [b]violet form; [c]yellow form.

The fact that the III-rd form of the complex, characterized by disappearance of signal in the EPR spectrum, exhibits so high an effective magnetic moment for phthalocyanine complexes with both dia- and paramagnetic central ions indicates that there must occur unpaired spins on the porphyrazine ring. The observed disappearance of signal in the EPR spectrum is due to line broadening caused by the spin–spin interaction of unpaired spins occurring within one molecule.

Studies of the magnetic properties of the discussed complexes indicate that both the II-nd and III-rd forms are oxidized compounds. In order to establish their structure, the electronic spectra of the different forms were recorded. They will be discussed in the instance of $H_2Pc \cdot SnCl_4$ (Fig. 4) and CrOHPc·$SnCl_4$ complexes (Fig. 5). The green form of all investigated complexes, in addition to bands characteristic of the given phthalocyanine, additionally exhibits a new strong band in the long-wave range (about 720–760 nm), depending on the complex; this band is attributed to the charge transfer transition between phthalocyanine and acceptor chloride (curve a in Fig. 4 and b in Fig. 5).

Transition of the complex into the violet form is associated with the occurrence of three new bands in the near IR range with λ_{max} of 850 nm, 890 nm and 980 nm, as well as of new blue-shifted band with λ_{max} 550 nm for $H_2Pc \cdot SnCl_4$ (Fig. 4(b)) and CrOHPc·$SnCl_4$ (Fig. 5(c)) complexes.

The same bands (three in the near IR range and one in the short-wave range) are observed for the complexes of both-free phthalocyanine and phthalocyanines with different central ions. It can be assumed that the new bands observed in the electronic spectrum of the phthalocyanine complexes with inorganic Lewis acids and their oxygen adducts are the result of intramolecular transitions in O_2 and transitions between oxygen molecules and the porphyrazine ring of phthalocyanine. This addition of molecular oxygen can be explained by the charge transfer interaction between O_2 as electron acceptor and the internal nitrogen atom of the porphyrazin ring, exhibiting the highest electron density.[22] Thus, the violet form generates by addition of molecular oxygen to the previously formed charge transfer phthalocyanine—Lewis acid complex. This interaction leads to the forma-

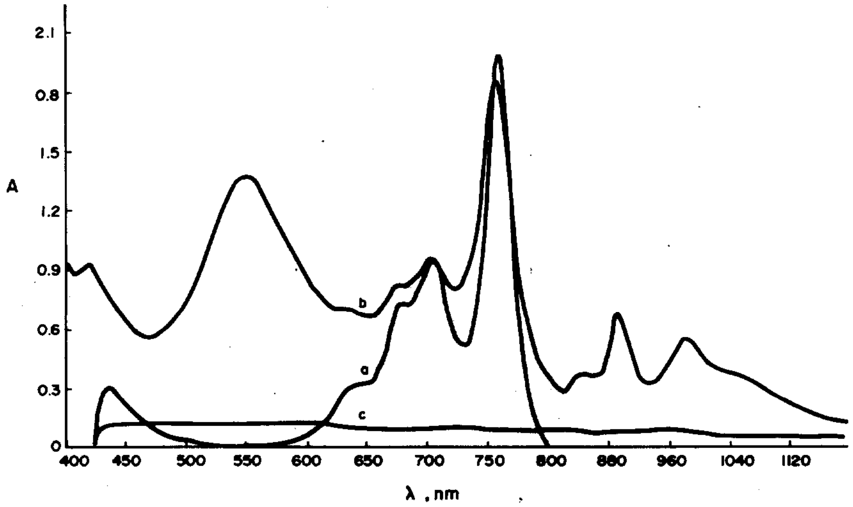


Fig. 4. Effect of oxygen on electronic spectrum of complex $H_2Pc \cdot SnCl_4$ (1 : 220). [a]green form; [b]violet form; [c]yellow form.

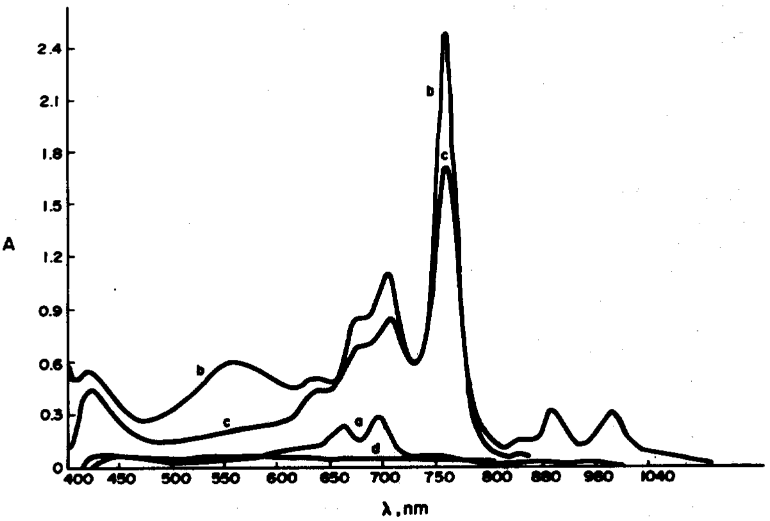
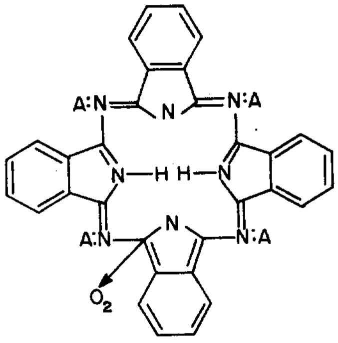


Fig. 5. Effect of oxygen on electronic spectrum of complex CrOHPc·SnCl$_4$ (1 : 220). [a]CrOHPc in NB solution; [b]green form; [c]violet form; [d]yellow form.

tion of monocation radical exemplified by the following formula:



$A = MX_2^+ \ldots MX_4^-$

According to Fig. 2(g), the radical signal in the EPR spectrum being characteristic of the violet form of the complex, shows hyperfine structure. However, the components of the hyperfine structure fail to be sufficiently resolved to permitted calculation of the spin Hamiltonian parameters and consequently univocal determination of the spin centre. Raynor *et al.*[23] have reported a similar shape of the radical signal for phthalocyanine saturated with molecular oxygen.

Therefore, the processes taking place during the transition of the green form to the violet and then to the yellow form can be described by the following formula (for the complex of CuPc with AlCl$_3$):

$$\underset{\text{green forme}}{CuPc(AlCl_2^+)_4 \ldots (AlCl_4^-)_4} \xrightarrow{O_2} \underset{\text{violet forme}}{CuPc(AlCl_2^+)_4 \ldots (AlCl_4^-)_4 \cdot O_2} \xrightarrow{O_2} \underset{\text{yellow forme}}{[CuPc^{(\cdot+)4}(AlCl_2^+)_4 \ldots (AlCl_4^-)_4](O_2^{\cdot -})_3}$$

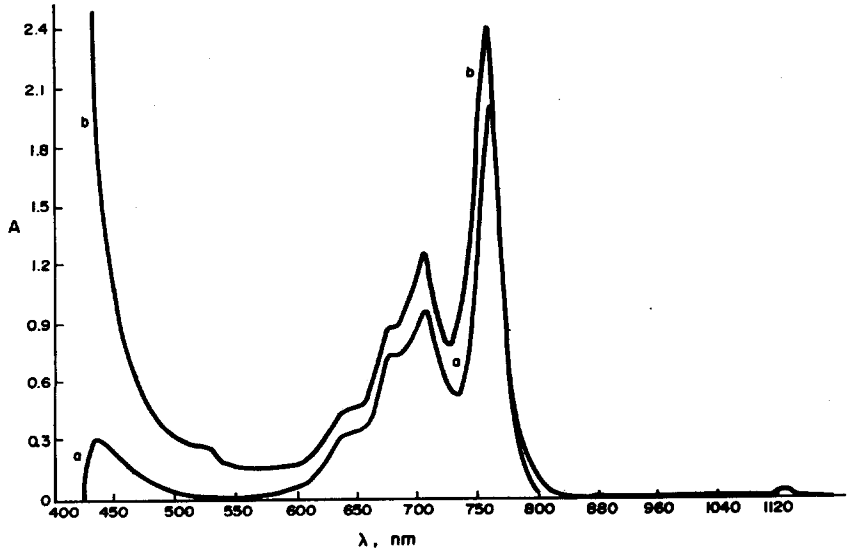


Fig. 6. H$_2$Pc·SnCl$_4$ (1 : 220). [a]green form; [b]yellow form reduced by hydroquinone.

The formation, in the first phase of oxidation, of a double charge transfer complex causes further lowering of redox potential of the whole system and facilitates high degree oxidation of the porphyrazine ring. In this case we obtain the yellow form of the complex which is chemically stable and undergoes no further spontaneous transformations.

In the electronic spectrum the yellow form is characterized by the disappearance of all absorption bands; both those derived from phthalocyanine and those originating upon the occurrence of the green and violet forms (Figs. 4(c) and Fig. 5(d)). The yellow form of the complex exhibits moreover, greatly increased electrolytic conductivity, as compared with the green and violet forms. This could indicate that the yellow form is higher ionized than the violet form.[21]

The yellow form is chemically stable in air. However, it readily undergoes reduction, e.g. in the reaction with a phthalocyanine molecule, giving the violet form which then can be reduced to the green form with a potassium iodide solution in nitrobenzene. To determine the degree of oxidation of the porphyrazine ring, we titrated the yellow form of the $\mathrm{CuPc \cdot SnCl_4}$ complex with a solution of phthalocyanine alone, and then with potassium iodide. The results can be described by the following formula:

$$\begin{array}{l}
\mathrm{CuPc^{\cdot +4} + CuPc \rightleftharpoons CuPc^{\cdot +3} + CuPc^{\cdot +1}} \\
\mathrm{CuPc^{\cdot +3} + CuPc \rightleftharpoons CuPc^{\cdot +2} + CuPc^{\cdot +1}} \\
\mathrm{CuPc^{\cdot +2} + CuPc \rightleftharpoons CuPc^{\cdot +1} + CuPc^{\cdot +1}} \\
\hline
\mathrm{CuPc^{\cdot +4} + 3CuPc \rightleftharpoons 4CuPc^{\cdot +1}} \\
\mathrm{CuPc^{\cdot +1} + J^{-} \rightleftharpoons CuPc + J^{0}.}
\end{array}$$

The tetracation can also be reduced with hydroquinone, this yielding directly the initial green form of the complex (Fig. 6). This indicates that the porphyrazine ring was not destroyed on oxidation.

In the four investigated series of phthalocyanine complexes with different acceptor chlorides, the oxidation rate depended on the concentration and kind of chloride, as $\mathrm{FeCl_3 > SnCl_4 > GaCl_3 \geq AlCl_3}$. Summing up, our observations indicate that preliminary binding of phthalocyanines into charge transfer complexes with appropriate electron acceptors causes lowering of the oxidation potential of phthalocyanines. In consequence, the porphyrazine ring can without destruction be oxidized to tetracation. The tetracation can be reversibly reduced in the reaction with a nonoxidized molecule; this can be of importance when intense oxidation in living organism is required.

REFERENCES

[1] E. Białkowska and A. Graczyk, *OMR* **11**, 167 (1978).
[2] R. Taube, *Z. Chem.* **6**, 8 (1966).
[3] R. Taube, *Pure Appl. Chem.* **38**, 427 (1974).
[4] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.* **85**, 818 (1963).
[5] D. W. Clack and J. R. Jandle, *Inorg. Chem.* **11**(8), 1738 (1972).
[6] J. W. Dodd and N. S. Hush, *J. Chem. Soc.* 4607 (1964).
[7] V. E. Kolmogorov, *Opt. Spectr.* **17**, 155 (1964).
[8] A. Wolberg and J. Manassen, *J. Am. Chem. Soc.* **92**, 10 (1970).
[9] J. Fajer, D. C. Borg, A. Forman, D. Dolfin and R. H. Felton, *J. Am. Chem. Soc.* **92**, 3451 (1970).
[10] J. H. Fuhrhop, K. M. Kadish and D. G. Davis, *J. Am. Chem. Soc.* **95**, 5140 (1973).
[11] C. J. Pedersen, *J. Org. Chem.* **22**, 127 (1957).
[12] C. W. Wilfson, O. L. Kalia, O. L. Lebiediev and E. A. Lukeniec, *Zhur. Org. Chim.* **12**, 123 (1970).
[13] G. W. R. Canham, J. Myers and A. B. P. Lever, *Chem. Comm.* **15**, 483 (1973).
[14] D. F. Evans, *J. Chem. Soc.* 2003 (1959).
[15] J. Bargon, H. Fischer and U. Johnson, *Z Naturforsch.* **22a**, 1551 (1967).
[16] H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.* **89**, 5518 (1967).
[17] H. R. Ward, R. G. Lowler and Th. A. Marzilli, *Tetrahedron Letters* 521 (1970).
[18] NMR Basic Principles and Progress, *Grundlagen und Fortschritte*, Vol. 8. Chemically Induced Dynamic Nuclear and Electron Polarisations CIDNP and CIDEP (Edited by P. Diehl, E. Fluck and R. Kosfeld), Springer Verlag, Berlin Heidelberg, New York (1974).
[19] A. Gracyk and A. Konarzewski, private communication.
[20] A. Graczyk, E. Białkowska and J. Sobczyńska, *Proc. III Int. Symp. Specific Interactions between Molecules or Ions*, Vol. 1, p. 159 (1976).
[21] A. Graczyk, K. Wieczffiński, 3*rd IUPAC Conf. Physical Organic Chemistry*, p. 80. La Grande Motte-France, September 1976.
[22] S. C. Mathur and J. Singh, *Int. J. Quant. Chem.* **6**, 57 (1972).
[23] J. B. Raynor, M. Robson and A. S. M. Torens-Burton, *J. Chem. Soc. Dalton* 2360 (1977).