degree of bond cleavage in the transition state is significantly higher for complex **3** than in **1** and **2**.

Returning to the motivation for this work, our results on the water-exchange mechanism of the porphyrins studied are in excellent agreement with the mechanistic interpretation offered by Ford and co-workers[21] for the complex-formation reactions of **1** and **3** with NO. Their reported activation volumes of $+8.3\pm1.5$ and $+13\pm1\ cm^3mol^{-1}$ for these reactions, respectively, are almost identical to those reported for the water-exchange reactions in the present study. Their conclusion that the observed $\Delta V^{\neq}$ for the "on" reaction with NO mainly represents $\Delta V^{\neq}(k_1)$ for reaction (1), is perfectly correct as shown by the data reported here. Thus the formation of **1** and **3** is not only controlled by the rate but also by the mechanism of the water-exchange process. Depending on the structural and electronic situation this process tends to occur according to an $I_d$ or D mechanism, the complex-formation reactions with nucleophiles such as NO follow the same mechanism.

The water-exchange rate and associated activation enthalpy of iron(III) porphyrins are significantly affected by the charge on the porphine and to a lesser degree by steric compression. The mechanism of the process, however, is controlled by steric factors and varies between a dissociative interchange and a limiting dissociative mechanism. Thus the lability of the axial-bound solvent molecules in these systems plays a key role in the mechanism and substitution behavior of porphyrin- and heme-based systems. High-pressure NMR spectroscopic techniques present a powerful tool to add to the mechanistic understanding of such processes, which could lead to a more profound understanding of the reactions and processes in biologically relevant macrocyclic systems such as metmyoglobin and cytochrome P-450.

*Experimental Section*

$Na_3[Fe^{III}(TPPS)(H_2O)_2]$ ($Na_3$-**1**) was synthesized as described elsewhere.[26] $[Fe^{III}(TMPyP)(H_2O)(OH)](pts)_4$ (**2**-$pts_4$), where pts = *p*-toluenesulfonate, and $Na_3[Fe^{III}(TMPS)(H_2O)_2]$ ($Na_3$-**3**) were purchased from Frontier Scientific Ltd. Fine Chemicals Utah, USA, and used without further purification. Ca. 20% enriched $^{17}O$-labeled water (D-Chem Ltd. Tel Aviv, Israel) was used for the $^{17}O$ NMR water-exchange measurements. $NaClO_4$ (Aldrich) was used to adjust the ionic strength to 0.5 M, and $HClO_4$ (**1** and **3**) and tosylic acid (**2**) were used to adjust the pH of the solution. No salt was added in the case of **2** to avoid precipitation. The porphyrin samples were prepared by combining weighted amounts of salt, perchloric or tosylic acid, and water. The resulting solution was transferred to the NMR tube. The pH was determined on identical samples prepared in ordinary water. The water exchange measurements were performed at pH 3 (for **1** and **3**) and pH 1.1 (for **2**), where only the monomeric aqua forms of the porphyrins are present in solution. The complex concentrations were $3.4\times10^{-2}$ M (**1**), $2.0\times10^{-2}$ M (**2**), and $3.0\times10^{-2}$ M (**3**).

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[1] A. P. Hong, D. W. Bahnemann, M. R. Hoffmann, *J. Phys. Chem.* **1987**, *91*, 6245.
[2] B. Meunier, *Chem. Rev.* **1992**, *92*, 1411.
[3] G. Behra, L. Sigg, *Nature* **1990**, *344*, 419.
[4] V. Lepentsiotis, R. van Eldik, *J. Chem. Soc. Dalton Trans.* **1998**, 999.
[5] V. Lepentsiotis, R. van Eldik, F. F. Prinsloo, J. J. Pienaar, *J. Chem. Soc. Dalton Trans.* **1999**, 2759.
[6] J. Lee, J. A. Hunt, J. T. Groves, *J. Am. Chem. Soc.* **1998**, *120*, 7493.
[7] H. B. Dunford, *Adv. Inorg. Chem.* **1982**, *4*, 41.
[8] Y. Watanabe, J. T. Groves, *The Enzymes*, *Vol. 20*, Academic Press, San Diego, CA, **1992**, p. 405.
[9] M. W. J. Cleeter, J. M. Cooper, V. M. Darley-Usmar, S. Moncada, A. H. V. Scapira, *FEBS Lett.* **1994**, *345*, 50.
[10] T. Noguchi, J. Honda, T. Nagamune, H. Sasabe, Y. Inoue, I. Endo, *FEBS Lett.* **1995**, *358*, 9.
[11] G. C. Brown, *Eur. J. Biochem.* **1995**, *232*, 188.
[12] D. K. Lavallee, *Coord. Chem. Rev.* **1985**, *61*, 55.
[13] M. Hoshino, L. Laverman, P. C. Ford, *Coord. Chem. Rev.* **1999**, *187*, 75.
[14] I. J. Ostrich, G. Liu, H. W. Dodgen, J. P. Hunt, *Inorg. Chem.* **1980**, *19*, 619.
[15] T. W. Swaddle, A. E. Merbach, *Inorg. Chem.* **1981**, *20*, 4212.
[16] a) A. Drljaca, C. D. Hubbard, R. van Eldik, T. Asano, M. V. Basilevsky, W. J. le Noble, *Chem. Rev.* **1988**, *98*, 2167; b) R. van Eldik, C. Dücker-Benfer, F. Thaler, *Adv. Inorg. Chem.* **2000**, *49*, 1.
[17] L. Helm, A. E. Merbach, *Coord. Chem. Rev.* **1999**, *187*, 151.
[18] S. Funahashi, M. Inamo, K. Ishihara, M. Tanaka, *Inorg. Chem.* **1982**, *21*, 447.
[19] J. G. Leipoldt, R. van Eldik, H. Kelm, *Inorg. Chem.* **1983**, *22*, 4146.
[20] G. J. Lamprecht, J. G. Leipoldt, T. W. Swaddle, *Inorg. Chim. Acta* **1987**, *129*, 21.
[21] L. E. Laverman, M. Hoshino, P. C. Ford, *J. Am. Chem. Soc.* **1997**, *119*, 12663.
[22] S.-H. Cheng, Y.-S. Chen, Y. O. Su, *J. Chin. Chem. Soc.* **1991**, *38*, 15.
[23] M. Ivanca, A. G. Lappin, W. R. Scheidt, *Inorg. Chem.* **1991**, *30*, 711.
[24] F. P. Rotzinger, *J. Am. Chem. Soc.* **1997**, *119*, 5230.
[25] M. Hartmann, T. Clark, R. van Eldik, *J. Phys. Chem. A* **1999**, *103*, 9899.
[26] E. B. Fleischer, J. M. Palmer, T. S. Srivastava, A. Chatterjee, *J. Am. Chem. Soc.* **1971**, *93*, 3162.

## Controlling the Lability of Square-Planar $Pt^{II}$ Complexes through Electronic Communication between π-Acceptor Ligands**

Deogratius Jaganyi, Andreas Hofmann, and Rudi van Eldik*

*Dedicated to Professor Ernst-G. Jäger on the occasion of his 65th birthday*

Studies on the substitution mechanism of low-spin $d^8$ square-planar complexes for many years centered around the σ *trans* influence or *trans* effect.[1] For $Pt^{II}$ complexes this has involved detailed systematic studies of different *trans* groups[2] using a range of different nucleophiles.[3] Mechanistic studies established that ligand-substitution reactions of $Pt^{II}$ complexes mainly occur by an associative process involving a trigonal-bipyramidal intermediate. In recent years, volumes of activation ($\Delta V^{\neq}$) obtained from high-pressure kinetic measurements, have been used in distinguishing mechanistic pathways of substitution reactions; negative values indicating

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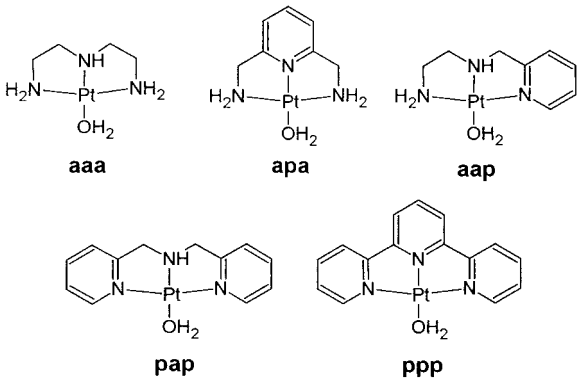
an associative-reaction route.[4] New experimental evidence has been published showing that the exchange of some sulfides or sulfoxides at $Pt^{II}$ complexes, such as *cis*-$[PtPh_2(Et_2S)_2]$, *cis*-$[PtPh_2(Me_2S)_2]$, and $[Pt(bph)(SR_2)_2]$ (R = Me and Et, bph = biphenyl), proceed under the influence of a σ *trans* influence and/or *trans* effect according to a dissociative mechanism in which a three-coordinate intermediate is formed.[5]

It has also been known for a long time that the rate of substitution of $Pt^{II}$ complexes is enhanced when groups having strong π-acceptor properties are attached to the metal center.[5, 6] The acceleration has been ascribed to the reduction of charge on the metal center by the employed ligand and results from back-donation of electrons from the filled d-orbitals of the $Pt^{II}$ center into the empty antibonding or nonbonding orbitals of the ligand.[7] Application of extended Hückel theory, molecular electrostatic potential, and ab initio calculations have been used to demonstrate the π-acceptor properties of specific ligands.[5] In addition, the π effect has been noted to be an important factor in the search for a possible mechanistic changeover in the substitution behavior of square-planar complexes. The displacement of thioethers by CO, which has π-acceptor capabilities, in systems such as *cis*-$[PtR_2S_2]$ (R = Me or Ph; S = $R_2S$ or $Me_2SO$),[5] prevents the substitution process from following a dissociative mechanism. Thus the presence or absence of π back-bonding is responsible for the mechanistic changeover in the case of thioether complexes of $Pt^{II}$.

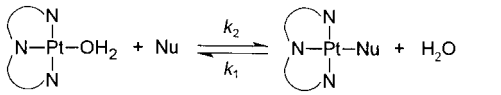
Despite its importance and influence in substitution reactions of $Pt^{II}$ complexes, there has been no systematic study carried out to investigate the π-acceptor (*cis* and *trans*) effect in more detail. In an effort to gain more insight into this property, a detailed study of its influence both in the *cis* and *trans* position has been undertaken using monoaqua $Pt^{II}$ complexes with tridentate N-donor ligands. The results clearly show that it is not so much the π-acceptor effect that controls the rate of the substitution process, but more importantly the communication between different π-acceptor ligands, an effect not recognized before.

Five complexes, $[Pt(diethylenetriamine)H_2O](CF_3SO_3)_2$ (**aaa**), $[Pt\{2,6\text{-bis(aminomethyl)pyridine}\}H_2O](CF_3SO_3)_2$ (**apa**), $[Pt\{N\text{-(pyridyl-2-methyl)-1,2-diaminoethane}\}H_2O](ClO_4)_2$ (**aap**), $[Pt\{bis(2\text{-pyridylmethyl})amine\}OH]ClO_4$ (**pap**), and $[Pt(terpyridine)H_2O](BF_4)_2$ (**ppp**) (Scheme 1) were synthesized. The aqua complexes were prepared by hydrolysis of the corresponding chloro complexes (see Experimental Section). These complexes allow a systematic study of the π-acceptor effect of the ligands in the *cis* and *trans* position on the ligand-substitution behavior of the complexes.




Scheme 1. Structures of the investigated $Pt^{II}$ complexes; the $CF_3SO_3$ and $ClO_4$ counterions are not shown.

The substitution of coordinated water [Eq. (1)] by three different nucleophiles (Nu), thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), and 1,1,3,3,-tetramethyl-2-thiourea




(1)

(TMTU), was investigated under pseudo first-order conditions using stopped-flow techniques. The reactions were carried out at a pH between 2 and 3 where the complexes exist in the aqua form, and the temperature was maintained at 25 °C.

The pseudo first-order rate constants, $k_{obs}$, calculated from the kinetic traces were plotted versus the concentrations of the entering nucleophiles. Straight lines were obtained with *y*-axis intercepts near to zero, indicating that Equation (2) can be used to represent $k_{obs}$ since $k_1$, which is from the reverse aquation reaction, is practically zero.

$$k_{obs} = k_1 + k_2[Nu] \approx k_2[Nu] \quad (2)$$

Concentration dependencies of $k_{obs}$ for DMTU as the entering ligand are shown in Figure 1 (note that this is a double *y*-axis plot in which the data for **ppp** are presented by the *y*-axis on the left). To accommodate the **aaa** data on the same scale, its true DMTU concentration had to be divided by ten. The second-order rate constants $k_2$ are in Table 1, along with the p$K_a$ values of the complexes. These values were determined spectrophotometrically and kinetically by recording the UV/Vis spectra and rate constants, respectively, over a wide pH range.

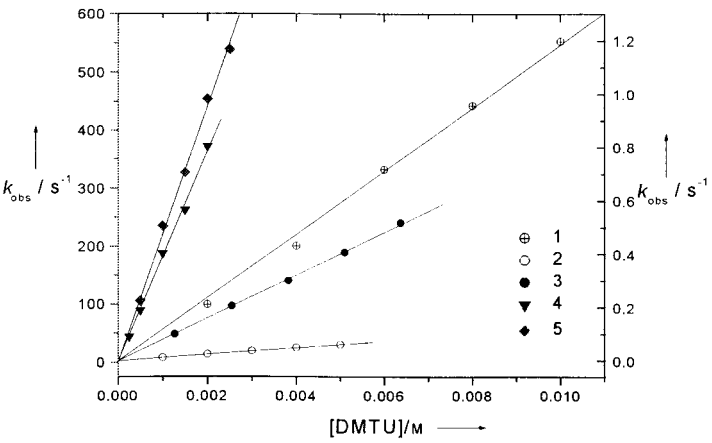



Figure 1. Dependence of observed rate constant $k_{obs}$ [$s^{-1}$] on the concentration of DMTU as the entering nucleophile at 25 °C in aqueous medium; $[NaClO_4]$ = 0.1M, pH 2–3. 1 = **aaa** (⊕), 2 = **apa** (○), 3 = **aap** (●), 4 = **pap** (▼), and 5 = **ppp** (◆). The concentration of DMTU used for **aaa** (⊕) has been divided by 10.

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Table 1. Second-order rate constants and p$K_a$ values determined kinetically and from UV/Vis measurements, respectively; ionic strength 0.1 mol dm$^{-3}$ ($NaClO_4$), $T = 25\,^{\circ}C$.

| Nucleophile | $k_2$ [M$^{-1}$ s$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **aaa** | **apa** | **aap** | **pap** | **ppp** |
| TU | $29.1 \pm 0.4$[a] | $101.1 \pm 0.7$ | $110 \pm 1$ | $393 \pm 2$ | $163\,400 \pm 2230$ |
| DMTU | $11.9 \pm 0.2$ | $41.2 \pm 0.3$ | $80.4 \pm 0.5$ | $393 \pm 5$ | $216\,970 \pm 2980$ |
| TMTU | $3.2 \pm 0.02$ | $12.3 \pm 0.1$ | $29.3 \pm 0.2$ | $182 \pm 2$ | $152\,900 \pm 2700$ |
| | p$K_a$ | | | | |
| kinetic | $6.35 \pm 0.03$ | $5.96 \pm 0.05$ | $5.60 \pm 0.06$ | $5.30 \pm 0.03$ | $4.42 \pm 0.05$ |
| thermodynamic | $6.26 \pm 0.10$[a] | $6.04 \pm 0.08$ | $5.71 \pm 0.03$ | $5.53 \pm 0.07$ | $4.62 \pm 0.04$ |

[a] Data are in good agreement with the data in ref. [12].

It is reasonable to assume that the σ *trans* effect is the same for pyridine and amine ligands.[8] It is also known that the electronic influence of the *cis* ligands is usually small.[1, 7] Thus, it can be concluded that the observed kinetic effects are mainly because of π-acceptor effects. The data clearly demonstrate that by introducing the pyridine unit with π-acceptor properties to the **aaa** complex, the rate of substitution of coordinated water increases significantly by at least a factor of four in going from **aaa** to **apa**, the effect for the other ligands being much larger.

The *cis* effect is more dominant than the *trans* effect. The values of $k_2$ for the reactions with TU are only 10% larger, but in the case of DMTU and TMTU, $k_2$ doubles from **apa** (the *trans* complex) to **aap** (the *cis* complex). These observations on the π *cis* effect are contrary to what is generally known. The σ *cis* effect has generally been accepted to be always smaller than its *trans* counterpart.[1, 7]

The structures of the selected complexes are such that the π effect of the different pyridine ligands should be additive or at least increase with the number of pyridine ligands. In going from **aap** to **pap**, it is reasonable to expect an increase in $k_2$ similar to that observed in going from **aaa** to **aap**, that is, a doubling of the π *cis* effect. This is indeed approximately the case. Furthermore, in going from **aaa** to **ppp**, $k_2$ is expected to increase in a similar way as the combined effect of **apa** and **pap** compared to **aaa**. However, the observed increase in $k_2$, a factor of between $5.6 \times 10^3$ and $4.8 \times 10^4$ in going from **aaa** to **ppp** is much larger than predicted on the basis of the combined effects observed for **apa** and **pap**, (between 47 and 219) for the different entering nucleophiles. This means that the very large labilization effect observed for the **ppp** complex cannot simply arise from the combination of the π-acceptor effects of the three pyridine groups. In fact, the conjugated nature of the chelate must be responsible for this significant increase in lability, that is, electronic communication within the chelate controls the overall observed π-acceptor effect.

The nucleophiles selected have different degrees of steric hindrance and nucleophilicity. The results in Table 1 show that substitution of coordinated water depends on the steric nature of the nucleophiles. The most sterically hindered nucleophile TMTU reacts significantly slower than the less hindered TU in going from **aaa** to **apa**. The trend in the results as one moves from **aaa** to **ppp** is that the effect of steric hindrance on the rate of the substitution process diminishes, and disappears totally in the case of the **ppp** complex. This can be accounted for by the increase in electrophilicity of the $Pt^{II}$ center in the series of complexes reaching a maximum for **ppp**. In the latter case, the metal center seems to be so electrophilic that the steric bulk of the entering nucleophile plays no significant role. In fact, the higher nucleophilicity of DMTU and TMTU, as a result of the inductive effects of the methyl substituents, seem to overcompensate for the decrease in $k_2$ expected as a result of increased steric hindrance.

The dependence of $k_2$ upon the basicity of the complexes is shown in Figure 2, where log $k_2$ is plotted against the p$K_a$ values of the aqua complexes. The least-squares fit for four of

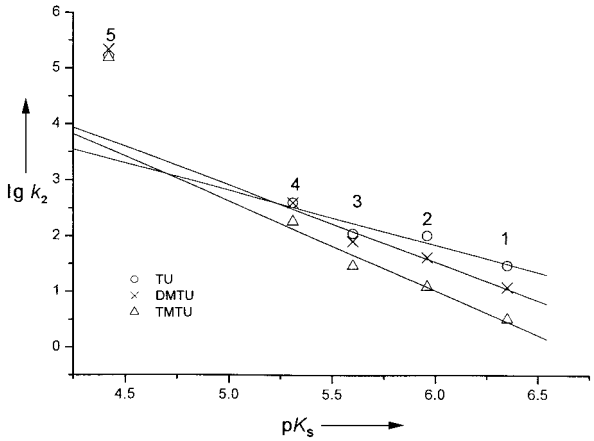


Figure 2. Plot of log $k_2$ versus the p$K_a$ of the aqua complexes at 25 °C for different entering nucleophiles TU ○, DMTU ×, and TMTU △. 1 = **aaa**, 2 = **apa**, 3 = **aap**, 4 = **pap**, and 5 = **ppp**.

the complexes (excluding **ppp**) resulted in reasonable straight lines with slopes of $-1.0 \pm 0.2$, $-1.4 \pm 0.2$, and $-1.6 \pm 0.2$ for the entering ligands TU, DMTU, and TMTU, respectively. The p$K_a$ values serve as a measure of the electron density around the $Pt^{II}$ center, which will control the electrophilicity of the metal center, the strength of the Pt–$OH_2$ bond, and therefore the acidity of the coordinated water molecule. The values of $k_2$ clearly depend on the basicity of the complexes; the rate of displacement of coordinated water increases with decreasing p$K_a$ value, that is, with the increasing electrophilicity of the metal center which controls the rate of the associative substitution process. The increase in reactivity from **aaa** to **pap** results from the increase in π-acceptor properties of the chelate, which decreases the electron density on the metal center and decreases the p$K_a$ value. The presence of the π-acceptor ligand(s) promotes the electrophilicity of the metal center and accounts for the observed correlation

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between $\lg k_2$ and $pK_a$. The more negative slopes observed in Figure 2 for the more sterically hindered nucleophiles DMTU and TMTU, results, as discussed above, from the smaller effect of steric hindrance on the reaction rate of the more electrophilic complexes.

The **ppp** complex is therefore unusually reactive in comparison to the other complexes and also does not fit into the $\lg k_2$ versus $pK_a$ relationship. The explanation offered for a similar system, where chloride was the leaving group, is that the strain on the ring system was the cause of the acceleration.[9] This is only one of the possible factors that can influence the process. From this study, we can conclude that the π-effect in this system is not just because of the addition or combination of the individual *cis* and *trans* effects. The formation of the two five-membered aromatic rings involving the $Pt^{II}$ center in the **ppp** complex is an important property that has a large influence on the observed reactivity; the presence of aromaticity allows for a much more extensive π-conjugated system. The consequence of this is a more electronically drained $Pt^{II}$ center, as also indicated by the trend in the $pK_a$ values, and a system capable of effectively stabilizing the five-coordinate transition state and/or intermediate through π back-bonding. A detailed study of the temperature and pressure dependencies of the investigated reactions has also been undertaken and the results will be reported in a forthcoming full report on this topic.

In summary, we have shown that it is possible to investigate the π-acceptor effect without the interference from the σ-donor effect that is much stronger and usually camouflages the π-effect. The π *cis* effect is certainly greater than the π *trans* effect. The investigation has revealed for the first time that the rate of substitution is inversely proportional to the basicity of the complex as a whole and not just that of the leaving or entering group. It has also shown that it is possible through π-acceptor effects to tune the $pK_a$ of the complex, which in turn controls the lability of the complex. Most important, however, is our finding that the electronic communication between the π-acceptor ligands as in the case of the **ppp** complex, is responsible for the drastic increase in lability observed in this particular case. It has recently been shown[10] that when this electronic communication between two aromatic rings is destroyed, the substitution rate is decreased by a factor of 60. The π-acceptor effects on their own (in the *cis* and/or *trans* position) are in the absence of such a direct communication of minor significance in affecting the lability of $d^8$ square-planar complexes.

### *Experimental Section*

The ligands diethylenetriamine, bis(2-pyridylmethyl)amine, and terpyridine were obtained from Aldrich and used without further purification. *N*-(pyridyl-2-methyl)-1,2-diaminoethane was synthesized according to the literature method,[11a] whereas 2,6-bis(aminomethyl)pyridine was prepared following a method used to synthesize 6-(aminomethyl)-2,-2′-bipyridine by using 2,6-bis(bromomethyl)pyridine as starting material.[11b,c] Synthesis of **aaa** and **ppp** was performed according to literature methods.[11d,e] The preparation of the chloroplatinum precursor for **pap**, **aap**, and **apa** was performed according to a procedure similar to that used for the preparation of the chloro complex of **ppp**.[11f] The latter two were treated with silver triflate to produce the required aqua complexes. For **pap**, the chloro complex was hydrolyzed using sodium hydroxide to give the hydroxy complex which was precipitated from solution with the help of excess sodium perchlorate. Microanalysis and $^1H$ NMR spectra were used to check the purity of all the complexes. An Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system was used in all kinetic measurements.

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[1] a) J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, *2nd ed.*, Wiley-VCH, New York, **1997**, p. 51; b) M. L. Tobe, J. Burgers, *Inorganic Reaction Mechanisms*, Addison-Wesley Longman, Essex, **1999**, p. 54.

[2] a) G. Feraone, V. Ricevuto, R. Romeo, M. Trozzi, *Inorg. Chem.* **1970**, *9*, 1525 – 1528; b) M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto, U. Bellico, *Inorg. Chim. Acta* **1979**, *34*, 169 – 174; c) F. Basolo, *Coord. Chem. Rev.* **1996**, *154*, 151 – 161.

[3] a) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, B. L. Shaw, *J. Chem. Soc.* **1961**, 2207 – 2215; b) V. Ricevuto, R. Romeo, M. Trozzi, *J. Chem. Soc. Dalton Trans.* **1972**, 1857 – 1862; c) V. Ricevuto, R. Romeo, M. Trozzi, *J. Chem. Soc. Dalton Trans.* **1974**, 927 – 929.

[4] R. van Eldik, D. A. Palmer, H. Kelm, *Inorg. Chem.* **1979**, *18*, 572 – 577.

[5] a) R. Romeo, A. Grassi, L. M. Scolaro, *Inorg. Chem.* **1992**, *31*, 4383 – 4390; b) M. R. Plutino, L. M. Scolaro, R. Romeo, A. Grassi, *Inorg. Chem.* **2000**, *39*, 2712 – 2720.

[6] a) R. Romeo, M. L. Tobe, *Inorg. Chem.* **1974**, *13*, 1991 – 1996; b) R. Gosling, M. L. Tobe, *Inorg. Chem.* **1983**, *22*, 1235 – 1244; c) R. Romeo, M. L. Scolaro, N. Nastasi, G. Arena, *Inorg. Chem.* **1996**, *35*, 5087 – 5096; d) O. F. Wendt, L. I. Elding, *J. Chem. Soc. Dalton Trans.* **1997**, 4725 – 4731.

[7] a) J. K. Burdett, *Inorg. Chem.* **1975**, *14*, 931; b) J. K. Burdett, *Inorg. Chem.* **1977**, *16*, 3013 – 3024.

[8] F. Basolo, R. G. Pearson, *Mechanisms of Inorganic Reactions*, *2nd ed.*, Wiley, New York, **1967**, p. 355.

[9] F. Basolo, H. B. Gray, R. G. Pearson, *J. Am. Chem. Soc.* **1960**, *82*, 4200 – 4203.

[10] R. Romeo, M. R. Plutoni, L. M. Scolaro, S. Stoccoro, G. Minghetti, *Inorg. Chem.* **2000**, *39*, 4749 – 4755.

[11] a) J. D. Barger, R. D. Zachariasen, J. K. Romary, *J. Inorg. Nucl. Chem.* **1969**, *31*, 1019 – 1022; b) R. Ziessel, J.-M. Lehn, *Helv. Chim. Acta* **1990**, *73*, 1149 – 1162; c) W. Baker, K. M. Buggle, J. F. W. McOmie, D. A. M. Watkins, *J. Chem. Soc.* **1958**, 3594 – 3603; d) D. P. Fairlie, W. G. Jackson, B. W. Skelton, H. Wen, A. H. White, W. A. Wickramasinghe, T. C. Woon, H. Taube, *Inorg. Chem.* **1997**, *36*, 1020 – 1028; e) G. Annibale, P. Bergamini, V. Bertolasi, M. Cattabriga, A. Lazzaro, A. Marchi, G. Vertuani, *J. Chem. Soc. Dalton Trans.* **1999**, 3877 – 3882; f) G. Annibale, M. Brandolisi, B. Pitteri, *Polyhedron* **1995**, *14*, 451 – 453.

[12] R. Romeo, M. Cusumano, *Inorg. Chim. Acta* **1981**, *49*, 167 – 171.


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