

Inorganica Chimica Acta 277 (1998) 1-7



Adducts of nitric oxide with cobaltous tetraphenylporphyrin and phthalocyanines: potential nitric oxide sorbents

John Wesley Owens ^{a,*}, Mildred Perry ^b, David W. Seybert ^c

* Department of Chemistry, Southern University, Baton Rouge, LA 70813, USA

^b Advanced Crosscutting Technologies Division, Federal Energy Technology Center, PO Box 109 40, Mailstop 922-273C Pittsburgh, PA 15236-0940, USA ^c Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA

Received 23 May 1997; revised 22 July 1997; accepted 1 September 1997

Abstract

Cobaltous tetraphenylporphyrin (Co(II)TPP) and cobaltous phthalocyanine (Co(II)Pc) complexes were studied in a variety of solvents, including water. The imidazole and nitrosyl adducts were synthesized and characterized by UV–Vis spectrophotometry and electron spin resonance spectroscopy. The imidazole adducts were subsequently exposed to nitric oxide to study the competitive interactions between nitrosyl and imidazole ligands in these cobaltous compounds. This is important, since it has been suggested that aqueous solutions of cobaltous porphyrins and phthalocyanines can serve as denitrification agents when bound to an immobilized imidazole modified silica gel (IMSG) substrate. Our results indicate that while nitric oxide binds both Co(II)TPP and Co(II)Pc in organic solvents in the absence of a bound imidazole ligand, it will not bind when imidazole is avially bound to the cobalt ion. Neither Co(II)TPP cor Co(II)Pc are water soluble and both will dimerize in water. A water soluble NO sorbert, which does not dimerize in water would be ideal for removing NO from flue gas streams. The Co(II)PcTs(IMSG) appears to meet these requirements. Preliminary results indicate that aqueous suspensions of Co(II)PcTs(IMSG) are capable of NO removal from a gas stream passed through these suspensions and may thus be suitable candidates for further development as NO sorbents for NO₄ abatement. @ 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt complexes; Porphyrin complexes; Nitric oxide complexes; Phthalocyanine complexes

1. Introduction

Nitric oxide (NO) and nitrogen dioxide (NO₂), collectively designated as NO₁, are two of the major pollutants emitted from coal-fired power plants. In the presence of organic peroxyl radicals generated from atmospheric hydrocarbons, NO and NO₂ can participate in a catalytic redox cycle resulting in the accumulation of ozone in the atmosphere [1]. Thus, there is a critical need to develop effective methods to reduce NO, emissions into the environment. Most of the present denitrification technologies, although effective. are relatively expensive, and new and more cost-efficient means of removing nitric oxide are desirable. The use of cobaltous phthalocyanines, Co(II)Pc and Co(II)PcTs (Ts = tetrasulfonate) and porphyrins, Co(II)TPP (TPP =tetraphenylporphyrin) as sorbents for nitric oxide has been examined by several investigators [2-6]. A thorough examination of the binding properties of these complexes with nitric oxide both in the presence and absence of other nitrogenous ligands is an important basic step toward the potential use of these complexes in NO removal strategies.

Cobaltous phthalocyanine was chosen for study because: (i) its nitrosyl adduct is relatively stable in air [2], (ii) it can act as a catalyst for the reduction of nitric oxide to N_2 . N₃O and NH₃ [3], and (iii) it can be attached to a silica gel substrate, which will prevent dimerization [2]. Co(II) TPP complexes share many of these same desirable properties, but the metallophthalocyanine systems tend to be more oxidatively stable than the corresponding porphyrin derivatives [6]. In fact, the binding of nitric oxide to a Co(II)-TPP(IMSG) complex (IMSG = imidazole modified silica gel, see Fig. 1) and to a Co(11) TPP/SiO2 complex has been examined previously by UV-Vis and IR spectrophotometry [6]. The results suggested that the IMSG cobalt complex moderately absorbed nitric oxide at ambient temperatures but effectively absorbed nitric oxide at elevated temperatures. Mochida et al. [3] and Ercolani et al. [4] observed a similar behavior for solid state Co(II)Pc treated with nitric oxide in air.

^{*} Corresponding author: Tel.: + 1-504-771 3750; e-mail: jowens 8960@aol.com

^{0020-1693/98/\$19.00 © 1998} Elsevier Science S.A. All rights reserved. *Pll* S0020-1693(97)05964-1



Fig. 1. (a) A diagram of Co(II) phthalocyanine immobilized on axially bound imidazole modified silica gel substrate (ImMSG) (adapted from Ref. [23]); (b) the structure of metallophthalocyanine (1.2).

This work describes the behavior of cobaltous phthalocyanine and porphyrin complexes in water and in a variety of nitrogenous solvents. The reactions of cobaltous phthalocyanines and porphyrins bearing a nitrosyl and/or an imidazole ligand were investigated to provide a better understanding of the competitive binding of nitric oxide to cobalt complexes. The central questions surrounding these cobaltous phthalocyanines, and porphyrins are: (i) does nitric oxide bind? (ii) If so, are these nitrosyl complexes stable in air? (iii) Does the presence of axial imidazole(s) affect the binding of nitric oxide? The information presented in this report might help to explain the observed facile binding of nitric oxide to: Co(II)TPP(IMSG) reported by Tsuji et al. [6] as well as contribute to the development of more efficient sorbents for nitrie oxide.

The UV=Vis spectrum was taken and compared with literature values (when possible) for each of the following compounds: Co(II)TPP, Co(II)TPP(Im), Co(II)TPP(NO), Co(II)Pe, Co(II)Pe(Im), Co(II)PeTs and Co(II)PeTs (Im). Some of these complexes were also characterized by electron spin resonance spectroscopy. The behavior of the imidazole adducts in the presence of nitric oxide is closely examined.

2. Experimental

2.1. Synthetic procedures

Tetraphenylporphyrin and phthalocyanine were purchased from Porphyrin Products (Logan, Utah) and used without additional purification. The Co(II)TPP complex was prepared by the N.N-dimethylformamide method [7]. Cobalt phthalocyanine tetrasulfonate was synthesized by a published procedure [8]. Imidazole adducts were prepared by direct addition of this ligand at room temperature into solvents containing metalloporphyrin or metallophthalocyanine and stirring for 24 h in the absence of air. This procedure was first reported by Cariati et al. [9]. Nitrosyl adducts were prepared under anaerobic conditions by bubbling 90% NO in N₂ into various solvents containing the metalloporphyrin and metallophthalocyanine complexes under study and monitoring the position of the Soret band. The imidazole modified silica gel was prepared following a procedure reported by Burwell [10]. Pyridine, N,N-dimethylformamide, toluene, dichloromethane and quinoline were purchased from Aldrich, deoxygenated with nitrogen, dried over CaO, and used without further purification.

2.2. Spectroscopic procedures

UV-Vis spectra were obtained on a Cary 17 spectrophotometer. The nitrosyl complexes were examined in quartz cuvettes which had been sealed under anaerobic conditions. The ESR spectra were recorded on a Varian E3 spectrometer at X band liquid nitrogen temperature device. All of the complexes were examined at 77 K. g-values were verified using a gauss meter and the following equation [11]:

$$g_1 = g_2 \left(H_2 / H_1 \right)$$

.. ...

2.3. NO removal experiments

Removal of NO from a simulated flue gas were conducted using a gas bubbler column (diameter = 5.5 cm, height = 21 cm) equipped with a sparger on the inlet line. NO was introduced at a rate of 450 ml min⁻¹ at ambient temperature from a calibrated mixture of NO/N₂ containing 490 ppm NO into an aqueous solution (500 ml), and NO concentration in the outlet stream was monitored with a Thermo Electron model 10 NO analyzer. Experiments were performed using either Co(II)PcTs (0.75 mM) or Co(II)PcTs \cdot IMSG (2.2 mM). All experiments used a 5 mM *N*-2-hydroxyethyl piperazine-*N'*-2-ethane sulfonic acid (HEPES) buffer at pH 7.0.

3. Results and discussion

3.1. Electronic characterization of porphyrins and phthalocyanines

Cobalt tetraphenylporphyrins exhibit electronic spectra characteristic of most porphyrins (see Fig. 2). The Soret band occurs at 417 nm, the Q bands at 527 (Q_B) and 595 nm (Q_a), and several smaller bands appear near 660, 885 and 1055 nm [12,13]. These latter three bands are associated with metal \rightarrow porphyrin ring or porphyrin ring \rightarrow metal charge transfer transitions. The Soret and Q bands arise from $\pi \rightarrow \pi^*$ porphyrin ring transitions, with the Soret band arising from the addition of the $a_{1u}(\pi) \rightarrow e_{\mu}(\pi^*)$ and the $b_{1u}(\pi) \rightarrow e_{\mu}(\pi^*)$ transitions [14,15].

Metallophthalocyanines exhibit spectra which include a Soret band appearing near 320 nm, and Q_{β} and Q_{α} bands occurring near 615 and 660 nm, respectively (Fig. 3) [16,17]. These bands arise from the same transitions as those for porphyrins. The Soret band, very intense for porphyrin complexes, is usually broad and featureless in the phthalocyanine spectra and is usually not as sensitive to the nature of the axial ligand.

3.2. Reactions with imidazole in various solvents

3.2.1. Co(II) porphyrins

A spectrophotometric titration of Co(II) TPP with imidazole in toluene is shown in Fig. 4. Coordination of imidazole produces a red shift of the beta band from 527 to 555 nm. The Soret band also shifts from 417 to 431 nm while the bands initially appearing near 660 and 885 nm are shifted to the red (see Fig. 2(a),(b)). When the concentration ratio of imidazole to Co(II) TPP exceeds 10:1, three new bands appear at 421 (a shoulder of the 431 nm band), 515 and 555 nm. A neat solution of imidazole exhibits no absorbance in this region. The band appearing near 421 nm is a shoulder of the more intense Soret band at 431 nm. Others have reported the existence of bands near 422, 515, 550 and 595 nm in the spectrum of Co(II) TPP(Im) [6]; however, there has been no report of a band appearing near 431 nm.

Ligand numbers can be determined utilizing the following equation [18]:

$$\log(A - A_0) / (A_x - A) = n \log[\operatorname{Im}] + \log K \tag{1}$$

where A_0 is the absorbance before any ligand has been added. A_z is the absorbance when the maximum amount of ligand has been added, A is any absorbance value between these two extremes, and n is equal to the number of ligands bound. This equation is valid under isosbestic conditions and a plot of $\log(A - A_0)/(A_z - A)$ versus $\log[\text{Im}]$ for Co(II) TPP yields a slope of 1.0, indicating that only one imidazole ligand binds (see Fig. 4). K_1 is calculated as 1.02×10^4 , indicating that the reaction below lies far to the right:

$$\operatorname{Co}(\operatorname{II})\operatorname{TPP} + n\operatorname{Im} \to \operatorname{Co}(\operatorname{II})\operatorname{TPP}(\operatorname{Im})_n$$
 (2)

where n = 1.



Fig. 2. (a) UV–Vis spectrum of 5.0×10^{-6} M Co(II)TPP in toluene (+++); (b) 5.0×10^{-6} M Co(II)TPP(Im) in dichloromethane (------); (c) after deoxygenation of (b) with nitrogen and bubbling with NO for 30 min in a dry box (-----).



Fig. 3. (a) UV-Vis spectrum of 1.0×10^{-6} M Co(11)PcTs in water (····); (b) 1.0×10^{-6} M Co(11)PcTs(Im)₂ in water (-----); (c) after deoxygenation of (b) with nitrogen and bubbling with NO for 30 min in a dry box (-----).



Fig. 4. Spectrophotometric titration of 1.25×10^{-5} M Co(11) TPP with imidacole in toluene. The initial imidazole concentrations are 0.025, 0.050, 0.25, 0.50 and 2.5 mM, respectively.

3.2.2. Co(II) phihalocyanines

Cobalt(II) phthalocyanine was found to be soluble in quinoline. N.N-dimethylformamide (DMF) and pyridine; however, it is not soluble in water. The Soret electronic band positions for Co(II)Pc in these organic solvents appear primarily between 300-450 nm. Because of its unique solubility



Fig. 5. Spectrophotometric titration of 1.0×10^{-6} MCo(11)PeTs in water at 670 nm. Imidazole concentrations were varied as follows: 0.1, 0.375, 1.0, 3.75 and 10 mM, respectively.

in water, Co(II)PcTs was chosen for further investigation in this study.

A spectrophotometric titration of Co(11)PcTs (Ts = tetrasulfonate) with imidazole at 670 nm in aqueous solution displayed good isosbestic points (Fig. 5), and application of Eq. (1) to the data yielded n = 2.1 and a $K_2 = 4.3 \times 10^6$. The

magnitude of K_2 indicates that the following reaction lies far to the right, and that two ligands are axially bound.

$$Co(II)PcTs + nIm \rightarrow Co(II)PcTs(Im)_n$$
(3)

An analogous titration of Co(11)PcTs was also carried out with 1-methylimidazole, since this ligand should more closely approximate the ligand character of the ImMSG complex. The results of this latter titration (data not shown) were comparable to the results obtained with imidazole (n=2.1and $K_2=2.2\times10^2$). Solutions of Co(11)Pc have been shown previously to bind two identical nitrogenous ligands when the ligand concentration is high [9]. Results of this study are in good agreement with previous reports. The Co(11)PcTs complex was characterized by UV-Vis spectrophotometry and ESR spectroscopy.

The ESR spectra of the Co(II)PcTs diimidazole adduct complex appears in Fig. 6. This spectrum of the diimidazole complex is well defined and clearly contains all eight lines associated with the hyperfine splitting by the I = 7/2 nucleus. Each hyperfine line is further divided by the 1:2:3:2:1 superhyperfine splitting pattern associated with the presence of two nitrogen atoms (I = 1), indicating that the two imidazole ligands are coordinated to the cobalt ion. This same splitting pattern was originally observed and characterized by Walker [19] for Co(II)TPP(quinoline)₂, and has also been reported by Cariati et al. for Co(II)Pc(Py)₂[9].

Fig. 3(a), (b) contains the UV-Vis spectra for Co(II)PcTs and its imidazole adduct. Fig. 3(c) contains the



Fig. 6. ESR spectrum of Co(II)PcTs(Im)₂ in toluene at 77 K.

spectrum of the Co(II)PcTs(Im) complex upon treatment with NO (this is discussed later). Upon the addition of imidazole to Co(II)PcTs, the Soret band shifts from 320 to 350 nm, and the Q_{α} band shifts from 660 to 665 nm. The Q_{β} band, which appears as an inflection (630–650 nm) of the more intense 660 nm band in the Co(II)PcTs spectrum is clearly present at 615 nm in the spectrum of the imidazole adduct.

3.3. Reactions with nitric oxide

3.3.1. Solvent

The UV-Vis band positions for nitric oxide in various solvents were examined. A quintet of peaks (338, 350, 361, 375 and 390 nm) appears when nitric oxide is dissolved in water, pyridine or dimethylformamide. Only two peaks appear when nitric oxide is dissolved in quinoline (480 and 375 nm). The origin of these peaks is likely related to the presence of one or more of the following species: dinitrogen tetraoxide (N₂O₄), dinitrogen pentaoxide (N₂O₅) and dinitrogen oxide (N₂O) [2]; NO₂ and NO₂⁻ may also be present [3]. Springborg et al. [20] have assigned the band near 350 nm to the presence of the NO₂⁻ ion.

3.3.2. Porphyrins and phthalocyanines

The addition of nitric oxide alone to Co(II)TPP in dichloromethane causes a red shift in the position of the Soret band from 417 to 441 nm (Fig. 7(a),(b)). The position of this band is 10 nm higher than that observed for Co(II)TPP(Im) (431 nm, with a shoulder at 421 nm; see Fig. 7(a)). This could mean that the Co-N bond order is higher in the nitrosyl adduct than in the imidazole adduct. A higher bond order would be expected for the nitrosyl adduct because of the ability of the ligand orbitals to participate in backbonding with the d orbitals on the cobalt ion [21]. These complexes were characterized by UV-Vis spectrophotometry and ESR spectroscopy.

The band positions obtained upon addition of nitric oxide to Co(II)PcTs in water are shown in Table 1. There is a red shift of both the Q_{α} and Q_{β} bands in each of the solvents when NO is introduced. The behavior of cobaltous phthalocyanine complexes with nitric oxide is different from that observed for cobaltous porphyrins. The Soret band of cobaltous phthalocyanine complexes appears to be more sensitive, and the Q bands less sensitive, to the nature of the ligand. The nitrosyl ligand produces a much larger shift in the position of the Soret band than does the imidazole ligand.

The ESR spectra of both the Co(II)Pc(NO) and Co(II)PcTs(NO) complexes were silent. One possible reason for this is that the normal d^7 low spin arrangement expected for a cobalt nitrosyl complex has been changed to low spin d^6 by electron transfer from the metal to the nitrosyl group. This kind of behavior has been observed previously in cobalt nitrosyl complexes [22]. Such a low spin d^6 electronic arrangement would not be ESR active.



Fig. 7. (a) UV=Vis spectrum of 1.0×10^{-6} M Co(II)TPP(Im) in toluene (_____); (b) 1.0×10^{-6} M Co(II)TPP(NO) in toluene (_____); (c) after heating (b) in air for 30 min at 80°C (····).

Table 1 Electronic band positions for Co(11) tetraphenylporphyrins and Co(11) phthalocyanines

Tetraphenylporphyrin (in dichloromethane) Co(11)TPP	Band positions (nm)				
	417	\$27		595	660
Co(11)TPP(1m)	431	515	555	<u>598</u>	660
Co(11)TPP(NO)	441			598	658
Co(TPP)(Im)(NO) *	431	515	555	598	660
Phthalocyanine (in water)					
Co(II)PeTs	320	444	615		660
Co(11)PeTs(1m),	350	444	615		665
Co(II)PcTs(NO)	350	445	617		670
Co(11)PeTs(1m);(NO) *	350	444	615	640	665

^a The reaction of nitric oxide with Co(11) TPP, Co(11) TPP(1m), Co(11) PCTs and Co(11) PcTs(1m)₂ took place by bubbling nitric oxide for 30 min into solutions containing the imidazole adducts. Whereas the nitric oxide adduct formed readily in the absence of imidazole, there was no definite binding of NO in the presence of a bound imidazole ligand.

3.3.3. Complexes containing the imidazole ligand

The importance of the behavior of nitric oxide toward cobaltous porphyrins and phthalocyanines lies in the fact that such porphyrin and/or phthalocyanine complexes can be attached to an imidazole silica gel and potentially used to remove nitric oxide from flue gas. Examination of the reaction between NO and the Co(11)TPP(Im) complex indicates that NO does not bind. No change was observed in the position of the usually sensitive Soret band (431, 421 nm, shoulder) when NO was introduced (see Fig. 2(c)). Had a nitrosyl ligand bound the Co(II)TPP(Im) complex, a new band should have appeared near 441 nm. When NO binds Co(TPP), the Soret clearly shifts to 441 nm (see Figs. 2 and 7(b), and Table 1).

The visible spectrum observed for the addition of nitric oxide to the cobaltous phthalocyanine tetrasulfonate imidazole adduct in water does produce a small change in the spectrum (Fig. 3(c)). There are no noticeable shifts in the positions of the major bands, so it is not likely that the NO molecule binds $Co(11)PcTs(1m)_2$. Although exposure of NO to the $Co(11)PcTs(1m)_2$ complex does produce a weak band near 640 nm, the ESR spectrum remained unchanged. There is no evidence to support the coordination of a NO molecule to the $Co(11)PcTs(1m)_2$ complex. It is possible that the NO molecule could be absorbed somehow onto the phthalocyanine moiety.

3.3.4. Removal of NO from a gas stream

Preliminary experiments were conducted at ambient temperature to determine whether Co(II)PcTs either in solution or adsorbed onto ImMSG was effective as an NO sorbent. When a stream of NO (490 ppm) was passed through an aqueous solution of Co(II)PcTs, initial removal of NO was approximately 27%. The reaction is completely reversible. This removal capacity decreased in a first-order manner with a $T_{1/2}$ of 160 min, indicative of NO binding and progressive saturation of these binding sties. In contrast, when the same experiment was repeated with an aqueous suspension of Co(II) PcTs adsorbed onto IMSG, the initial removal rate of NO from the gas stream was approximately 12%, but this removal rate remained constant over a 4.5 h period. The absence of any loss of NO removal capacity could indicate a catalytic process, possibly involving NO oxidation caused by trace contamination with molecular oxygen. Control experiments using IMSG at comparable levels showed 0% removal of NO from the outlet stream. Further studies must be carried out to more adequately characterize the nature of this NO removal process, but these preliminary results clearly suggest the feasibility of using an immobilized Co(II)PcTs matrix for oxidation of NO from gas streams.

4. Conclusions

The work presented here suggests that organic solutions of Co(II) TPP and Co(II) Pc will bind NO molecules. Neither of these compounds is water soluble, and both compounds tend to dimerize in water at high concentrations. These two factors limit their effectiveness as NO absorbers. The water soluble Co(II)PcTs complex effectively removes NO from a gas stream (27% removal) but will dimerize at high concentrations. Immobilization of the Co(II)PcTs complex on ImMSG appears to be ideal; it is water-soluble and will not dimerize. The imidazole ligand occupies the fifth coordination site in the Co(II)PcTs(ImMSG) complex, leaving the final coordination site available for a nitrosyl molecule. This report offers evidence that the mobile Co(II)PcTs complex binds two imidazole ligands at its axial positions. The second imidazole ligand appears to be highly cooperative. However, the fully coordinated Co(II)PcTs(Im)₂ complex does not bind NO in aqueous solution. Our preliminary data suggest that aqueous solutions of immobilized Co(II)PcTs(Im-MSG) can effect a sustained 12% NO removal efficiency for time periods greater than 4.5 h. It seems likely that aqueous solutions of this complex can potentially be exploited for NO removal from flue gas.

Acknowledgements

The authors would like to thank the Chemistry Department of Southern University and the Department of Chemistry and Biochemistry of Duquesne University for the use of their facilities. A sincere thanks is also given to the personnel and staff of the Flue Gas Cleanup Division of the Pittsburgh Energy Technology Center, Pittsburgh, PA. We especially thank Dr R.A. Diffenbach for his assistance in conducting the preliminary NO removal experiments. J.W.O. and D.W.S. were supported by the Oak Ridge Associated Universities Faculty Research Participation Program. J.W.O. also wishes to thank the Health Research Centers and the Research Centers at Minority Institutions Program (NIH-RCMI, G12 RRO9104-04) at Southern University for the use of their facilities.

References

- [1] J.H. Seinfeld, Science, 243 (1989) 745.
- [2] C.M. van den Bleek, J.W. Eek, J. Reedijk and P.J. van den Berg. Int Chem. Eng. Symp. Ser., 57 (1980) R1.
- [3] I. Mochida, K. Takeyoshi, H. Fujitsu and K. Takeshita, J. Mol. Catal., 3 (1977/78) 417.
- [4] C. Ercolani, C. Neri and C. Sartori, J. Chem. Soc. A. (1968) 2123.
- [5] K. Tsuji, H. Fujitsu, K. Takeshita and I. Mochida, J. Mol. Catal., 9 (1980) 389.
- [6] K. Tsuji, M. Imaizumi, A. Oyoshi, I. Mochida, H. Fujitsu and K. Takeshita, Inorg. Chem., 21 (1982) 721.
- [7] J.W. Buchler, in D. Dolphin (ed.), The Porphyrins, Vol. 1, Academic Press, New York, 1978, p. 389, Part A.
- [8] J.H. Weber and D.H. Busch, Inorg. Chem., 4 (1965) 469.
- [9] F. Cariati, D. Galizzoli, F. Morazzi and C. Busetto, J. Chem. Soc., Dalton Trans., (1974) 556.
- [10] R.L. Burwell, CHEMTECH, 370 (1974).
- [11] J.E. Wertz and J.R. Bolton, Electron Spin Resonance: Elementary Theory and Practical Applications, McGraw Hill, New York, 1972.
- [12] R.J.P. Williams and D.W. Smith, Struct. Bonding (Berlin), 7 (1970) 2648.
- [13] J. Owens and C.J. O'Connor, Coord. Chem., 84 (1988) 1.
- [14] M. Gouterman, in D. Dolphin (ed.), The Porphyrins, Vol. 3, Part A. Academic Press, New York, 1978, Ch. 1.
- [15] M.W. Makinen and A.K. Churg, in H.B. Gray and A.B.P. Lever (eds.), Iron Porphyrins, Part I, Elsevier, New York, 1983, p. 101.
- [16] P. Day, H.A.O. Hill and M.G. Price, J. Chem. Soc. A., (1968) 90.
- [17] C.C. Leznoff and A.B.P. Lever, Phthalocyanine Properties and Applications, VCH, New York, 1989, p. 133.
- [18] D. Brault and M. Rougee, Biochem. Biophys. Res. Commun. 57 (1974) 654.
- [19] F.A. Walker, J. Am. Chem. Soc., 92 (1970) 4235.
- [20] J. Springborg, P.C. Wilkins and R.G. Wilkins, Acta Chem. Scand., 43 (1989) 967.
- [21] H. Hugheey, Inorganic Chemistry, Harper and Row, New York, 3rd edn., 1983.
- [22] W.R. Scheidt and J.L. Hoard, J. Chem. Soc., 95 (1973) 8281.
- [23] R.L. Burwell, O. Leal, D.L. Anderson, H. Bowman and F. Basolo, J. Am. Chem. Soc., 97 (1975) 5125.