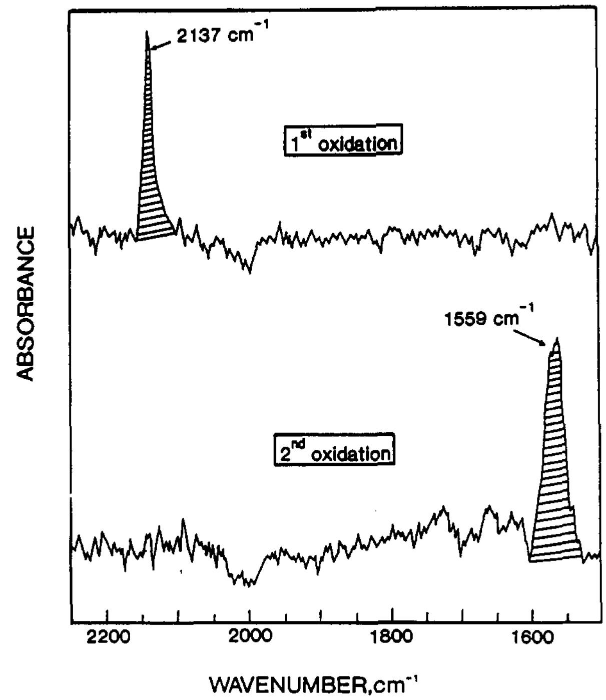


Figure 3. FTIR difference spectra obtained after the first two oxidations of 2.0 mM (OEP)Co in CH_2Cl_2, 0.2 M TBAP under 1 atm of CO. The first oxidation was carried out at 0.75 V and the second at 1.05 V. Both spectra are presented as the difference between the spectra of the electrooxidized species and neutral (OEP)Co under the same experimental conditions.

CH_2Cl_2 under a N_2 atmosphere and are located at $E_{1/2}$ = 0.67, 0.85, and 1.17 V vs SCE. The first oxidation was initially assigned as a Co(II) → Co(III) transition,[15] but later infrared, Raman, and ENDOR studies indicated that a Co(II) π cation radical is generated in noncoordinating media.[17-19]

The first oxidation of (OEP)Co (reaction I) shifts by −73 mV per 10-fold increase in P_{CO}, and this value may be compared with a theoretical slope of −59 mV for the case where one CO molecule is complexed to the product of the first oxidation, as shown in eq 4.

$$\text{(OEP)Co} + \text{CO} \rightleftarrows [\text{(OEP)Co(CO)}]^+ + e^- \qquad (4)$$

The second oxidation (reaction II) shifts by +61 mV per 10-fold increase in P_{CO}, and this slope may be compared to a theoretical +59 mV slope that would be obtained for an electrode reaction in which the CO molecule dissociates to give $[(OEP)Co]^{2+}$, as shown in eq 5.

$$[\text{(OEP)Co(CO)}]^+ \rightleftarrows [\text{(OEP)Co}]^{2+} + \text{CO} + e^- \qquad (5)$$

$E_{1/2}$ for the third oxidation of (OEP)Co (reaction III) is independent of the CO partial pressure and is also identical with the value obtained under a N_2 atmosphere. This lack of dependence on CO partial pressure is consistent with the electrode reaction given in eq 6, and this was confirmed by thin-layer UV-visible and FTIR spectroelectrochemistry.

$$[\text{(OEP)Co}]^{2+} \rightleftarrows [\text{(OEP)Co}]^{3+} + e^- \qquad (6)$$

The initial UV-visible spectra of (OEP)Co are independent of the gas above the solution (see Table I), indicating that neither CO nor N_2 interacts with the neutral complex. However, large spectral differences exist in the product generated after abstraction of one electron from (OEP)Co. The singly oxidized complex under a N_2 atmosphere has a substantially decreased Soret band (located at 377 nm) and a spectrum virtually identical with the one reported in the literature for $[(OEP)Co]^+Br^-$[15,18] or $[(OEP)Co]^+ClO_4^-$.[15,17,18] The latter two species have been characterized as Co(II) π cation radicals and have spectra that are quite different from the species generated after the abstraction of one electron from (OEP)Co under a CO atmosphere. This spectrum is shown in Figure 2 and has bands at 412, 529, and 560 nm. It resembles the spectrum of singly oxidized (OEP)Co in CH_2Cl_2 containing methanol[17] or H_2O[18] and is assigned as that of a genuine Co(III) complex, i.e. $[(OEP)Co^{III}(CO)]^+$.

The two one-electron oxidations of $[(OEP)Co]^+$ and $[(OEP)Co(CO)]^+$ give products that have identical UV-visible spectra under N_2 or CO (see Figure 2 and Table I). The UV-visible data are thus consistent with the electrochemical results, which indicate that CO binds only to the singly oxidized complex, and this was confirmed by in situ FTIR spectroelectrochemistry.

The first oxidation of (OEP)Co produces a species that has a strong IR band at 2137 cm^{-1} and is assigned as the CO vibration of $[(OEP)Co(CO)]^+$. There are no discernible π-cation-radical bands in the region of 1540–1570 cm^{-1}. This contrasts with $[(OEP)Co^{II}]^+$ under N_2, which has a 1560-cm^{-1} band and has been assigned as a Co(II) π cation radical.[6,7]

A strong 1559-cm^{-1} band is present after controlled-potential oxidation of $[(OEP)Co(CO)]^+$ at 1.05 V (reaction II), and at the same time, there is a loss of the CO vibration (see Figure 3). These spectra indicate the generation of a porphyrin π cation radical only after loss of the CO axial ligand in the second oxidation. The π-cation-radical band disappears after the third oxidation of (OEP)Co, and an identical IR spectrum is obtained under CO or N_2 atmospheres. This agrees with the formation of a $[(OEP)Co^{III}]^{3+}$ product, as shown by the electrochemical and UV-visible data presented earlier.

In summary, all of the spectroscopic and electrochemical data are consistent with the formation of $[(OEP)Co^{III}(CO)]^+$ under a CO atmosphere. This compound has a well-defined Co(III) UV-visible spectrum and a strong CO vibration at 2137 cm^{-1}. The only previously characterized $[(OEP)M^{III}(CO)]^+$ complex is (OEP)Ir(CO)Cl, which has a 2056-cm^{-1} vibration in CH_2Cl_2 under N_2.[8] The $[(OEP)Co(CO)]^+$ derivative is relatively stable in CH_2Cl_2 under CO, but the carbon monoxide axial ligand is lost upon either reduction to give $(OEP)Co^{II}$ or oxidation to give $[(OEP)Co^{III}]^{2+}$.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (Grant No. CHE-8822881) and the National Institutes of Health (Grant No. GM-25172). We also acknowledge Dr. C. K. Chang for providing a sample of (OEP)Co.

Central Research Institute for Chemistry,
Hungarian Academy of Sciences, P.O. Box 17,
H-1525 Budapest, Hungary, and Department of Chemistry,
University of British Columbia, Vancouver, Canada V6T 1Y6

Syn and Anti Isomers of $Pd_2Cl_2(\mu\text{-dpmMe})_2$ (dpmMe = 1,1-Bis(diphenylphosphino)ethane)

Gabor Besenyei,[1a] Chung-Li Lee,[1b] Yun Xie,[1b]
and Brian R. James*,[1b]

Received December 20, 1990

Bis(diphenylphosphino)methane (dpm) is one of the most extensively used bidentate, bridging ligands within homo- and heterobimetallic complexes.[2] Replacement of one of the methylene hydrogens by a methyl group yields 1,1-bis(diphenyl-

---

[17] Salehi, A.; Oertling, W. A.; Babcock, G. T.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 5630.

[18] Oertling, W. A.; Salehi, A.; Chung, Y. C.; Leroi, G. E.; Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1987**, *91*, 5887.

[19] Sandusky, P. O.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Am. Chem. Soc.* **1989**, *111*, 6437.

[1] (a) Central Research Institute for Chemistry. (b) University of British Columbia.

[2] Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

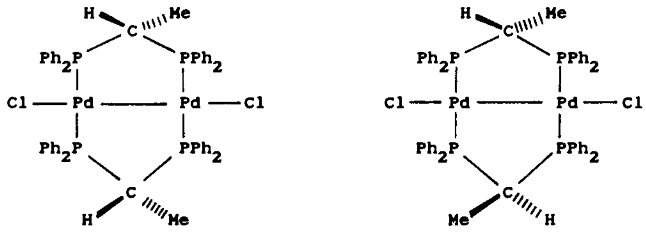
0020-1669/91/1330-2446$02.50/0

Table I. NMR and Other Spectral Data for Dinuclear Palladium–dpmMe Species[a]

complex	methine proton δ_H	methine proton J_{HH}	methine proton J_{HP}	methyl protons δ_H	methyl protons J_{HH}	methyl protons J_{HP}	$^{31}P\{^1H\}$ δ_P
anti-Pd$_2$ (*anti*-**1**)[b]	4.94 (q qn)	6.80	6.17	1.02 (d qn)	6.80	6.14	17.2 (b s)
syn-Pd$_2$ (*syn*-**1**)[c]	4.85 (q qn)	6.75	4.85	1.11 (d qn)	6.75	6.62	12.2 (s)
syn-Pd$_2$ (μ-CO)[d]	2.75 (un)			1.21 (un)			33.5 (s)
syn-Pd$_2$ (μ-SO_2)	4.50 (q qn)	7.20	6.90	1.04[e]			39.2 (s)
syn-Pd$_2$ (μ-S)	5.36 (q qn)	7.27	7.42	1.06 (d qn)	7.27	5.84	19.1 (s)
syn-Pd$_2$ (μ-SO)	5.39 (t q)	7.51	15.15	1.13 (d tr)	7.51	9.60	*f*
	4.17 (t q)	7.46	11.92	1.04 (d tr)	7.46	9.83	
syn-Pd$_2$ (μ-Se)	5.60 (q qn)	7.18	7.31	0.95 (d qn)	7.18	6.10	18.6 (s)
syn-Pd$_2$ (μ-O)	5.14 (q qn)	6.17	7.05	1.29 (d qn)	6.17	6.26	22.0 (s)
syn-Pd$_2$ (μ-SeO)	6.72 (t q)	7.23	16.05	1.10 (d tr)	7.23	9.79	*f*
	4.22 (t q)	7.12	10.94	1.02 (d tr)	7.12	10.25	

[a] *Pd*$_2$ = $Pd_2Cl_2(\mu\text{-dpmMe})_2$; data measured in CD_2Cl_2 or $CDCl_3$ at ~20 °C; ^{31}P shifts relative to 85% H_3PO_4, downfield being positive; b = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, un = unresolved multiplet; *J* in Hz; the integrations are correct. [b] δ_C 41.55 qn (*C*H, J_{CP} = 9.1), 14.92 s (C*C*H$_3$). ν(Pd–Cl), polyethylene: 252 cm^{-1} with sharp shoulder at 256 cm^{-1}. λ_{max}, nm (log ϵ (ϵ, M^{-1} cm^{-1})), CH_2Cl_2: 402 (3.97), 342 (4.32), 292 (4.48). [c] δ_C 41.60 qn (*C*H, J_{CP} = 9.8), 15.16 s (C*C*H$_3$). ν(Pd–Cl): 263 cm^{-1}. λ_{max}, mn (log ϵ): 398 (3.87), 340 (4.22), 286 (4.42). [d] ν(CO), CH_2Cl_2: 1726 cm^{-1}. [e] Overlaps with Me signals of *syn*-**1** present in solution. [f] An unanalyzed AA′BB′ pattern; see refs 3 and 7.

Chart I



syn - 1 anti - 1

phosphino)ethane, abbreviated dpmMe to signify methylated dpm, and we have used this ligand with the aim of immobilizing Pd moieties on polymers for use in selective binding of CO in gas streams.[3] It is now clear that use of dpmMe adds a new dimension to the chemistry of tertiary-diphosphine-bridged systems, because of the existence of anti and syn isomers, which are illustrated in Chart I for $Pd_2Cl_2(\mu\text{-dpmMe})_2$ (**1**). We have earlier isolated and characterized (including an X-ray crystallographic analysis) **1** as the anti form,[3] and now wish to report on the syn form. Such isomers within solutions of $Ag_2(\mu\text{-dpmMe})_2^{2+}$ and $Hg_2(\mu\text{-dpmMe})_2^{4+}$ have been detected by NMR,[4,5] but assignments could not be made; our work describes the first isolation of both isomers within any dpmMe systems.

Results and Discussion

anti-**1** is prepared via a ligand-exchange reaction of the 2-(diphenylphosphino)pyridine complex $Pd_2Cl_2(\mu\text{-}Ph_2P(py))_2$ with dpmMe;[3] ^1H and $^{31}P\{^1H\}$ NMR data on the crude reaction product reveal the presence of the syn isomer (see Table I), which can be prepared in small yields by repeated workup of the residue obtained from the mother liquor from the *anti*-**1** synthesis, followed by final recrystallization from $CHCl_3$/MeOH at −10 °C. *syn*-**1** is best prepared, however, from the crude, yellow-orange product formed from $Pd_2Cl_2(\mu\text{-}Ph_2P(py))_2$;[3] this anti–syn mixture (~2:1) is treated with ~140 atm of CO at 20 °C to generate largely *syn*-$Pd_2Cl_2(\mu\text{-CO})(\mu\text{-dpmMe})_2$, analogous to the corresponding A-frame dpm complex.[2,6] Loss of the labile CO during the workup procedure (see Experimental Section) gives *syn*-**1**.

The synthetic procedure illustrates well the marked difference in reactivity of *syn*- and *anti*-**1** toward small molecules such as CO, SO_2, and H_2S. The anti isomer shows no reactivity toward these reagents under conditions where the syn isomer forms, respectively, the bridged-CO, -SO_2, and -S (with concomitant H_2 formation) A-frame species, with chemistry analogous to that of $Pd_2Cl_2(\mu\text{-dpm})_2$.[2,3,7] *syn*-**1**, like *anti*-**1**,[8] forms μ-Se and -O derivatives on reaction with elemental Se and *m*-chloroperbenzoic acid, respectively. Selected spectroscopic data for the various syn products and *anti*-**1** are given in Table I; the μ-S, -SO, -Se, and -SeO species have been isolated, while the other syn species have been formed in situ. In all the syn species, except the μ-SO and -SeO derivatives, the two CH (and Me) protons are equivalent, as are the P atoms, and the ^1H NMR splitting patterns (which show virtual coupling to the remote P atoms[3,8]) and singlet $^{31}P\{^1H\}$ resonances are as expected. The μ-SO and -SeO species have inequivalent CH (and Me) protons that each couple to the two adjacent P atoms, the data being consistent with pyramidal geometry at the chalcogen atom, as found for $Pd_2Cl_2(\mu\text{-dpm})_2(\mu\text{-SO})$.[7]

A quantitative explanation for the greatly enhanced reactivity of *syn*-**1** (vs *anti*-**1**) must await structural data on the syn isomer and its A-frame derivatives. In *anti*-**1**, the Me groups occupy the less sterically crowded pseudoequatorial positions of the fused five-membered chelate rings, which are both in a chair conformation;[3] the A-frame derivatives of $Pd_2Cl_2(\mu\text{-dpm})_2$ adopt boat conformations for both rings,[2,9] and if this holds for A-frame derivatives of *anti*-**1**, one Me group would necessarily be inside the boat, a sterically unfavorable location, and this could account for the decreased reactivity of *anti*-**1**.

As well as marked differences in reactivity, *syn*- and *anti*-**1** may be distinguished by differences in their $^{31}P\{^1H\}$ shifts,[10] the ^1H shifts and J_{HP} values for the methine protons, ν(Pd-Cl) values, and electronic spectra (Table I).

The binding of CO and SO_2 by *syn*-**1** is reversible at ~20 °C, and under these gases at 1 atm total pressure in $CHCl_3$, about 50% conversion to the respective A-frame product is observed; the affinity for these gases is 500–1000 times less than that shown by $Pd_2Cl_2(\mu\text{-dpm})_2$ under corresponding conditions[3,6,9] and must result from steric constraints imposed by incorporation of the Me groups. The Me groups, via interactions with ortho hydrogens, might inhibit rotation of the Ph groups about the P–C bond,[3] and this could hinder axial approach of the gas to the metal. Qual-

---

(3) Lee, C.-L.; Yang, Y.-P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220.

(4) van der Ploeg, A. F. M. J.; van Koten, G. *Inorg. Chlm. Acta* **1981**, *51*, 225.

(5) Dean, P. A. W.; Srivastava, R. S. *Can. J. Chem.* **1985**, *63*, 2829.

(6) Lee, C.-L.; James, B. R.; Nelson, D. A.; Hallen, R. T. *Organometallics* **1984**, *3*, 1360.

(7) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622.

(8) Besenyei, G.; Lee, C.-L.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1750.

(9) Balch, A.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(10) The broad singlet of *anti*-**1** (half-width 2.8 ppm at 25 °C) splits at −40 °C into two multiplets centered at 22.1 and 11.8 ppm; the P atoms in the solid-state structure are inequivalent.[3] The nature of the process(es) leading to the "averaged" ^{31}P signal is not established, but is likely related to fluxionality witin the chelate rings. In $Au_2Cl_2(\mu\text{-}Ph_2PC_3H_4PPh_2)_2$, where the P atoms are joined via a cyclopropylidene group, chloride dissociation and exchange in solution lead to equivalence within the P (and H) atoms;[11] chloride dissociation is not observed in our Pd_2 systems.

(11) Schmidbauer, H.; Pollok, Th.; Herr, R.; Wagner, F. E.; Bau, R.; Riede, J.; Mueller, G. *Organometallics* **1986**, *5*, 566.

itatively, the off-rates for the gases appear much faster than in the dpm systems, and this could be of value in gas separation technology.[12] The H_2S reaction at 1 atm and 20 °C, as in the dpm system,[13] is complete in minutes.

syn-**1** in $CHCl_3$ isomerizes very slowly to the anti form ($t_{1/2} \sim 15$ days). Within the A-frame products of **1**, however, the syn species are preferred; thus, the μ-Se and -SeO derivatives of *anti*-**1** spontaneously convert to the syn forms.[14] Of note, the syn form of an A-frame species, in a boat conformation with both Me groups pseudoequatorial, allows for minimum steric interactions (just the two methine hydrogens) for the bridged moiety.

The synthesis of *syn*-**1** from *anti*-**1** is clearly based on preferred formation of the *syn*-μ-CO species.

Experimental Section

The sources of the materials, syntheses of the precursor complexes, and instrumentation used have been described earlier.[3,6,8]

***syn*-1 and Derivatives.** What proved to be a 2:1 mixture of *anti*- and *syn*-**1** was prepared as described in ref 3 to the stage of precipitation by addition of Et_2O. This mixture (1.07 g, 1 mmol) was dissolved in 25 mL of CH_2Cl_2 and the solution exposed to ~140 atm CO for 60 h at -20 °C without stirring. The CO was then released and the solution volume reduced to 5 mL by evacuation; addition of 20 mL of Et_2O precipitated yellow crystals (0.81 g) that contained a syn-anti mixture in about a 4:1 ratio by ^1H NMR. Dissolution in 3 mL of $CHCl_3$ and reprecipitation by addition of 10 mL of MeOH gave 0.33 g of a material with 95% syn content.

The syntheses of the *syn*-μ-S and -Se complexes and oxidation of these to the monooxo derivatives by using *t*-BuOOH follow the procedures described in refs 7 and 8 for the dpm analogues. For convenience, mixtures of *anti*- and *syn*-**1** were generally used as precursors, but the pure syn products were readily isolated from the $CHCl_3$/MeOH reprecipitation procedure described above. All the isolated complexes gave satisfactory elemental analyses. The *syn*-μ-O species, formed in situ at -50 °C by using *m*-chloroperbenzoic acid,[8] remained sufficiently stable at ~20 °C to record the ^1H NMR spectrum at this temperature, while the *anti*-μ-O species[14] decomposed above -25 °C.

Acknowledgment. We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (operating grant to B.R.J. and an International Scientific Exchange award to G.B.), and the Isaak Walton Killam Foundation for a postdoctoral fellowship (to C.-L.L.) administered by the University of British Columbia. Johnson Matthey Ltd. generously provided a loan of Pd.

---

(12) Lyke, S. E.; Lilga, M. A.; Nelson, D. A.; James, B. R.; Lee, C.-L. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 517.

(13) Barnabas, F.; Sallin, D.; James, B. R. *Can. J. Chem.* **1989**, *67*, 2009.

(14) Besenyei, G.; James, B. R. Work in progress.

Contribution from the Departments of Chemistry
and Biochemistry, Sinsheimer Laboratories,
University of California, Santa Cruz, California 95064,
and University of California, Davis, California 95616

Synthesis, Structure, and Properties of Potassium Bis(L-cysteinato-*N*,*S*)nickelate(II) Sesquihydrate

Narayan Baidya, Dije Ndreu, Marilyn M. Olmstead,
and Pradip K. Mascharak*

Received December 4, 1990

Introduction

The existence of Ni-S ligation at the Ni site(s) of the [NiFeS] hydrogenases,[1-4] as demonstrated by recent spectroscopic studies,[5-7] has raised new interest in the structure and coordination chemistry of monomeric nickel complexes with S-containing ligands. Model studies have indicated that the unusual redox properties of the nickel site arise from the presence of soft thiolato S atoms in the first coordination sphere of nickel.[8-10] Structural and spectroscopic parameters of the cysteinato complexes of nickel therefore deserve special attention. Despite earlier reports,[11-16] precise structural information on such complexes is yet unavailable. As part of our systematic analogue studies,[10,17,18] we report here the synthesis and structure of potassium bis(L-cysteinato-*N*,*S*)nickelate(II) sesquihydrate (**1**). Synthetic procedures that yield impure samples of this complex have been published by other groups. The present procedures allow isolation of pure material. The ^1H and ^{13}C spectra of **1** are also discussed.

Experimental Section

Preparation of Compounds. L-Cysteine and L-cysteine ethyl ester hydrochloride were purchased from Aldrich Chemical Co. In the following preparations, all operations were performed under a pure dinitrogen atmosphere.

$K_2[Ni(SCH_2CH(NH_2)COO)_2]\cdot 1.5H_2O$ (1). To a solution of dipotassium cysteinate ($KSCH_2CH(NH_2)COOK$), prepared from 0.61 g (5 mmol) of L-cysteine and 0.58 g (10.3 mmol) of KOH in 20 mL of ethanol, was added with stirring a solution of 0.29 g (1 mmol) of nickel nitrate hexahydrate in 5 mL of ethanol. The initial brown mixture turned cloudy and a flocculent green precipitate appeared within 10 min. After

---

* To whom correspondence should be addressed at the University of California, Santa Cruz.

(1) (a) Moura, J. J. G.; Moura, I.; Teixeira, M.; Xavier, A. V.; Fauque, G. D.; LeGall, J. *Met. Ions. Biol. Syst.* **1988**, *23*, 285. (b) Moura, J. J. G.; Teixeira, M.; Moura, I.; LeGall, J. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988; Chapter 9. (c) Moura, J. J. G.; Teixeira, M. Moura, I.; Xavier, A. V.; LeGall, J. *J. Mol. Catal.* **1984**, *23*, 303.

(2) (a) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297. (b) Cammack, R.; Fernandez, V. M.; Schneider, K. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988; Chapter 8. (c) Cammack, R.; Hall, D. O.; Rao, K. K. In *Microbial Gas Metabolism: Mechanistic, Metabolic and Biotechnological Aspects*; Poole, R. K., Dow, C., Eds.; Academic Press: New York, 1985; Chapter 4.

(3) (a) Bastian, N. R.; Wink, D. A.; Wackett, L. P.; Livingston, D. J.; Jordan, L. M.; Fox, J.; Orme-Johnson, W. H.; Walsh, C. T. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., *Ed.*; VCH: New York, 1988; Chapter 10. (b) Walsh, C. T.; Orme-Johnson, W. H. *Biochemistry* **1987**, *26*, 4901.

(4) Hausinger, R. P. *Microbiol. Rev.* **1987**, *51*, 22.

(5) (a) Maroney, M. J.; Colpas, G. J.; Bagyinka, C. *J. Am. Chem. Soc.* **1990**, *112*, 7067. (b) Colpas, G. J.; Maroney, M. J.; Bagyinka, C.; Kumar, M.; Willis, W. S.; Suib, S. L.; Baidya, N.; Mascharak, P. K. *Inorg. Chem.* **1991**, *30*, 920. (c) Maroney, M. J.; Colpas, G. J.; Bagyinka, C.; Baidya, N.; Mascharak, P. K. Submitted for publication.

(6) Eidsness, M. K.; Sullivan, R. J.; Scott, R. A. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988; Chapter 4.

(7) (a) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062. (b) Scott, R. A.; Wallin, S. A.; Czechowski, M.; Der Vartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864.

(8) (a) Krüger, H. J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955. (b) Krüger, H. J.; Holm, R. J. *Inorg. Chem.* **1989**, *28*, 1148; **1987**, *26*, 3645. (c) Snyder, B. S.; Rao, C. P.; Holm, R. H. *Aust. J. Chem.* **1986**, *39*, 963.

(9) Fox, S.; Wang, Y.; Silver, A.; Millar, M. *J. Am. Chem. Soc.* **1990**, *112*, 3218.

(10) (a) Baidya, N.; Stephan, D. W.; Campagna, C. F.; Mascharak, P. K. *Inorg. Chim. Acta* **1990**, *177*, 233. (b) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1991**, *30*, 929. (c) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1989**, *28*, 3426.

(11) Vinicheniko, I. G.; Zegzhda, G. D.; Maiboroda, O. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1985**, *30*, 997.

(12) Sovago, I.; Gergely, A.; Harman, B.; Kiss, T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1629.

(13) Levason, W.; McAuliffe, C. A. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 123.

(14) Letter, J. E., Jr.; Jordan, R. B. *J. Am. Chem. Soc.* **1975**, *97*, 2381.

(15) Srivastava, S. K.; Raju, E. V.; Mathur, H. B. *J. Inorg. Nucl. Chem.* **1973**, *35*, 253.

(16) Lenz, G. R.; Martell, A. E. *Biochemistry* **1964**, *3*, 745.

(17) Rosenfield, S. G.; Armstrong, W. H.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3014.

(18) (a) Rosenfield, S. G.; Wong, M. L. Y.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 4119. (b) Rosenfield, S. G.; Berends, H. P.; Gelmini, L.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 2792.

0020-1669/91/1330-2448$02.50/0