YBr to ZrBr in the parent ZrBr structure, top curve. Thus, it is not the structure type but the presence of hydrogen in tetrahedral cavities that is significantly destabilizing in the transition from YXH to ZrXH.

Acknowledgment. Dr. J. D. Jorgenson provided invaluable assistance in the collection of the two neutron diffraction data sets at Argonne National Laboratory. The writing of this paper took place while J.D.C. was on leave at the Institut für Anorganische und Analytische Chemie, Justus-Liebig-Universität, Giessen, West Germany, under the auspices of the Alexander von Humboldt-Stiftung, Bonn, BRD. J.D.C. is indebted to Professor R. Hoppe and Dr. G. Meyer for many considerations in this regard.

Contribution No. 4134 from the Central Research and Development Department,
Experimental Station, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware 19898

A Cobalt Oxygen Carrier in Zeolite Y. A Molecular "Ship in a Bottle"

Norman Herron

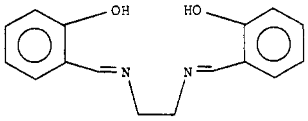
Received July 20, 1986

Cobalt(II) ion exchanged zeolite Y has been treated with a flexible Schiff base ligand, SALEN, so as to synthesize the Co(II) complex inside the pore structure of the zeolite itself. Such a complex is rigid and of such a size that it is physically entrapped inside the zeolite pores. The complex, as its pyridine adduct, shows affinity for dioxygen and forms 1:1 adducts. The O_2 binding equilibria are less favorable while the adducts show excellent resistance to autoxidation even at elevated temperatures. The oxygen adduct forms at a rate limited by diffusion of the oxygen into the zeolite and with a binding constant similar to the same species in solution. Hill plots of the oxygen binding behavior at four temperatures show slopes of 0.56, indicating a negative cooperativity between the cobalt binding sites. This behavior is interpreted as the superposition of the oxygen sorption behavior of the zeolite itself upon the sorption behavior of the complex. Apparent thermodynamics of binding show $\Delta H = -11.4$ kcal/mol and $\Delta S = -51$ eu. Attempts to prepare the same complex in the smaller pore zeolite 5A lead only to a selective removal of cobalt ions from the exterior surface of the zeolite crystallites.

While we are all familiar with reactions in mini- and microglassware, consider the extrapolation of the reaction vessel dimensions to its logical minimum. Eventually the vessel size becomes similar to the molecular size of the materials being prepared. At this level a new set of chemistries may be imposed on the reactants merely by the physical limitations of the vessel inside which such chemistry is constrained to occur. Such is the domain of intrazeolite chemistry where chambers and channels of molecular dimensions provide the rigid aluminosilicate framework within which reaction chemistry may be performed. Mobil's methanol to gasoline process is one example of the modified reactivity that results from constraining chemistry to occur inside such small vessels.[1a] We have shown selectivities approaching 50:1 in the selective hydrogenation of mixtures of cyclopentene and 4-methylcyclohexene using rhodium-containing zeolites.[1b] We now seek to demonstrate a relatively new idea in intrazeolite chemistry relating to supported metal catalyst species, namely, that a metal complex prepared inside a zeolite can have substantially different reactivity than its solution analogue.[2] We have prepared a complex where all of the individual components (metal ion plus various ligands) may easily pass in and out of the zeolite, but the final assembled coordination complex is too large and rigid to pass out once assembled inside.[3] The fundamental questions of how such entrapped "ship in a bottle" species[4] behave as compared to the identical species in free solution is a fascinating problem related to the variation of both structural and reaction chemistry with scale. We now report a preliminary study of the synthesis and oxygen binding behavior of a cobalt Schiff-base complex inside zeolite Y as compared to the behavior of the same material in free solution. While there are previous reports of oxygen-carrying species inside zeolites, these are all ionic species that are not true encapsulated complexes, and in most instances they have no solution phase equivalents for comparison.[5]

Experimental Section

Cobalt(II) ion exchange of zeolites CaNa-A (5A) and Na-Y (LZY-52) was carried out by following standard procedures.[6] A 10-g sample of zeolite in 1 L of distilled water was stirred with 0.2 g of cobaltous acetate at pH 6.5 for 4 h at 90 °C. The slurry was filtered and suction dried to give a pale pink powder, which, after being dried in a flow of dry oxygen at 400 °C, gives a blue purple solid with about one Co ion per eight supercages of the zeolite. These dried materials were treated with excess Schiff base ligand SALEN (1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene) (I) in an inert-atmosphere glovebox. This ligand



SALEN I

possesses two ionizable protons that are lost during complexation to a metal ion; thus, coordination to a divalent cation will result in the production of an electrically neutral complex and the liberation of two protons. Inside a zeolite, therefore, the released protons would become the charge compensators of the anionic zeolite framework, replacing the divalent metal ion in this capacity. The intimate mixtures of solids were heated to 120 °C for 30 min with continuous mixing during which time a yellow orange color developed. After cooling, the samples were Soxhlet-extracted with methylene chloride for 16 h in the inert atmosphere during which excess ligand and cobalt complex on the exterior of the zeolite crystallites were removed. The products were dried in vacuo at room temperature for at least 8 h and stored in the inert atmosphere. The samples were colored deep orange (zeolite Y) and blue (zeolite A).

Characterization of samples revealed the following: Chemical analysis of the zeolite Y sample shows between a 50% and 100% excess of the Schiff base ligand over the amount necessary to convert all of the cobalt to the complex. With zeolite A, essentially no ligand was detected by

---

(1) (a) Weisz, P. B. *Pure Appl. Chem.* **1980**, *52*, 2091. Smith, K. W.; Starr, W. C.; Chen, N. Y. *Oil Gas J.* **1980**, *78*(21), 75. (b) Corbin, D. R.; Seidel, W. C.; Abrams, L.; Herron, N.; Stucky, G. D.; Tolman, C. A. *Inorg. Chem.* **1985**, *24*, 1800.

(2) Camara, M. J.; Lunsford, J. H. *Inorg. Chem.* **1983**, *22*, 2498. Basset, J. M.; Theolier, A.; Commereuc, D.; Chauvin, Y. *J. Organomet. Chem.* **1985**, *279*, 147.

(3) Romanovsky, B. V. *Proc. Int. Symp. Zeolites Catal.* **1985**, 215. Meyer, G.; Wohrle, D.; Mohl, M.; Schulz-Ekloff, G. *Zeolites* **1984**, *4*, 80.

(4) This term was first used to describe $Ni(CO)_{n-4}L_n$ complexes entrapped in zeolite X. Herron, N.; Stucky, G. D.; Tolman, C. A. *Inorg. Chim. Acta* **1985**, *100*, 135.

(5) Howe, R. F.; Lunsford, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 5156. Howe, R. F.; Lunsford, J. H. *J. Phys. Chem.* **1975**, *79*, 1836. Schoonheydt, R. A.; Pelgrims, J. *J. Chem. Soc., Dalton Trans.* **1981**, 914. Winscom, C. J.; Lubitz, W.; Diegruber, H.; Moseler, R. *Stud. Surf. Sci. Catal.* **1982**, *12*, 14.

(6) Schoonheydt, R. A.; Van Wouke, D.; Vanhove, M. *J. Colloid Interface Sci.* **1981**, *83*, 279.

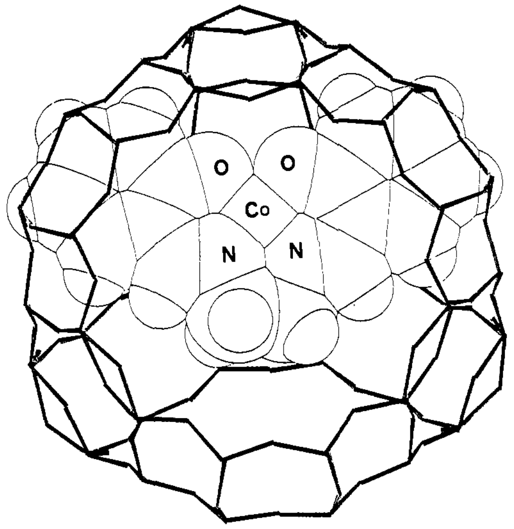


Figure 1. Pictorial representation of the CoSALEN adduct (space filling), inside the supercage of zeolite Y (sticks represent the bonds between tetrahedral atoms (Si/Al) and oxygen atoms). View is through one of the 12-ring windows of the supercage.

chemical analysis. ESCA analysis of both samples showed a low Co concentration in the outer 50 Å of the zeolite crystallites, the surface concentration being some 10% of that in the starting ion-exchanged zeolites. Ratios Co/Al are

	5A	Y
bulk (chem anal.)	0.01	0.02
surface before SALEN (ESCA)	0.14	0.11
surface after SALEN (ESCA)	<0.01	0.01

X-ray powder diffraction patterns of the materials show excellent retention of the zeolite crystallinity with no additional features that could be ascribed to bulk crystalline CoSALEN. The diffuse reflectance visible spectrum of the complex in zeolite Y was almost identical with that of the same complex in free solution.

Results and Discussion

With the small pore 5A zeolite, the above data indicate that reaction of the cobalt(II) ions of the zeolite with the Schiff-base ligand occurs—but only with those ions that are on the exterior zeolite crystallite surfaces and not with those entrained within the zeolite pore system. As a result the complex, though formed, is easily removed by washing with organic solvent since, being uncharged, it is not electrostatically held to the anionic zeolite framework. This restriction to reaction only on the outer crystallite surfaces is a result of the pore size of zeolite 5A, which, at 5 Å, is much too small to allow the ligand access to the interior cobalt ions. Thus treatment of cation-exchanged zeolites with chelating ligands that are too large to access the zeolite interior represents a way to preferentially remove metal cations from the exterior crystallite surface. This contention is supported by the ESCA data on both samples (both zeolites A and Y), which show a considerable depletion of cobalt ions in the outer 50 Å of the crystallites. Such selective removal is of great importance to catalysis using metal ion containing zeolites where selectivity of the catalytic reaction tends to be dominated by exterior less selective surface active sites as these are subject to much less severe diffusion constraints than those sites within the body of the zeolite pore system.

With the zeolite Y, the pore dimensions (~8 Å) are sufficiently large to allow the SALEN ligand access to all cobalt sites within the supercage pore system. This presumes that the ligand is sufficiently flexible to twist its way through a very restrictive passage. As a result, the final material from this preparation shows a nonextractable color consistent with formation of the desired Schiff-base complexes. The nonextractability of the complex is a direct result of encapsulation within the supercages of the zeolite on the basis of size alone—it does indeed appear to be a true molecular "ship in a bottle". This size encapsulation arises from the rigid square-planar or square-pyramidal coordination geometry adopted by the metal/ligand complex such that the once flexible ligand, with a mimimum kinetic diameter of <6.5 Å, has been locked into a complex with a minimum kinetic diameter in excess of 9 Å—too large to exit from the ~8 Å zeolite pores. A pictorial representation of such a complex (based upon a superposition of the crystal structure of the CoSALEN pyridine adduct and the structure of zeolite Y) is shown in Figure 1. While chemical analysis shows an excess of free ligand inside the zeolite, this does not appear to be extractable despite the fact that it should still be flexible enough to be removed. Speculation suggests that this material is somehow trapped within the zeolite by pore blockage of its possible escape routes by the entrapped cobalt complexes. Indeed, when the ligand is adsorbed by simple sodium-Y zeolite where no complexation takes place, it may be completely removed (chemical analysis) by the Soxhlet-extraction procedure described above. In this case, no pore blockage occurs and the extraction procedure is effective.

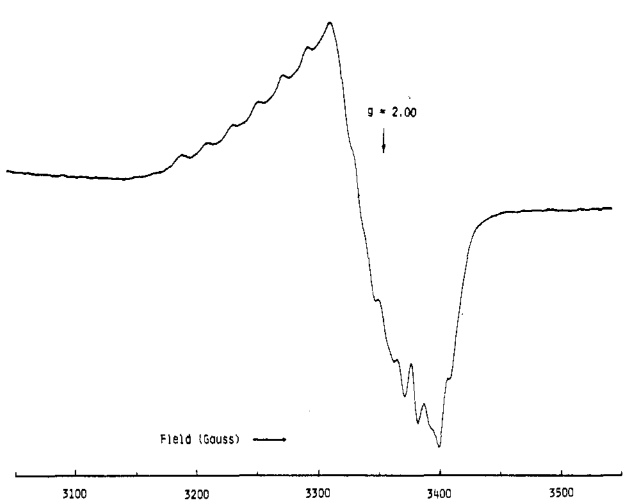


Figure 2. EPR spectrum of CoSALEN·py oxygen adduct inside zeolite Y at 298 K under 500 Torr of oxygen pressure.

The material, as prepared as a dry powder, shows no EPR activity down to 100 K, suggesting that the complex may be high-spin, which is known in certain solvents.[7] Attempts to force the complex over to the more normal and EPR-detectable low-spin form[8] by addition of pyridine were unsuccessful. The reason remains unclear, but the fact that pyridine is able to coordinate is confirmed by the oxygen adsorption behavior reported below. The apparent retention of a high-spin configuration for the unoxygenated complex as its five-coordinate pyridine adduct was an unexpected consequence of the restriction of the complex within the confines of the zeolite framework.

Adsorption of oxygen at 760 Torr and 100 K by the dry solid before pyridine treatment produces a very weak axial EPR signal reminiscent of solution-phase oxygen adducts in noncoordinating solvents.[9] The binding constant for oxygen is clearly very low since the weak signal is only observed at low temperature—again consistent with the equivalent solution behavior.[9,10] When this material is treated with pyridine and then the excess base is removed by evacuation, the oxygen binding behavior improves dramatically. Exposure of the solid to oxygen at room temperature generates an EPR signal shown in Figure 2. The signal is interesting from two viewpoints: First, the fact that the signal is axial and not isotropic even at 298K indicates that the complex is not free to tumble and rotate inside the zeolite cavities but is rather locked into position as in a true crystal. Inspection of Figure 1 demonstrates the reasonableness of this conclusion. Second, the EPR parameters $g_{\parallel} = 2.0780$, $g_{\perp} = 2.0204$, $A_{\parallel} = 21$ G, and $A_{\perp} = 11.3$ G are very similar to those of the same complex in

---

(7) Migita, K.; Chikira, M. *J. Chem. Soc., Dalton Trans.* **1983**, 2281.
(8) Cockle, S. A.; Hill, H. A. O.; Williams, R. J. P. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 131.
(9) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(10) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.

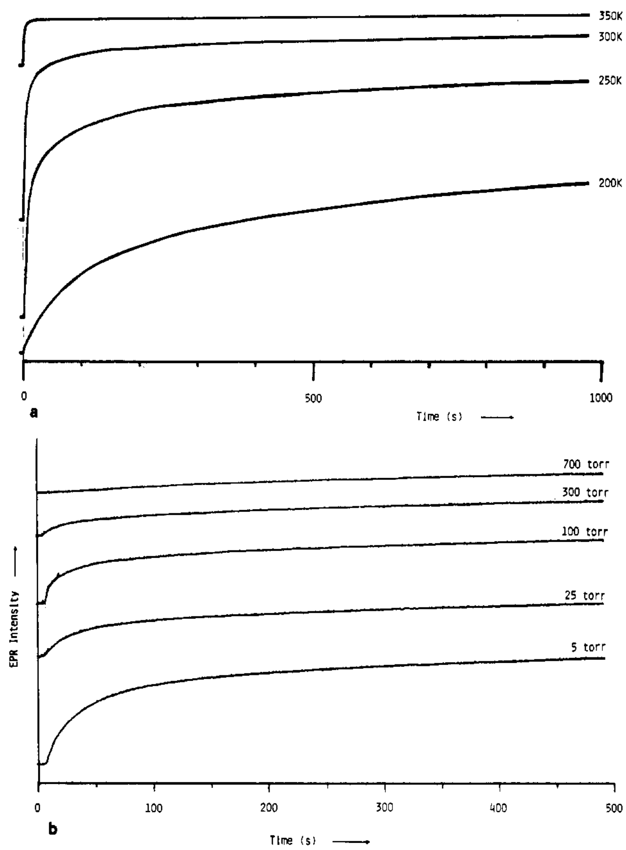


Figure 3. Kinetics of the growth of EPR signal intensity from the CoSALEN·py oxygen adduct: (a) as a function of sample temperature; (b) as a function of applied oxygen pressure.

free solution containing pyridine axial ligand,[11] $g_\parallel = 2.082$, $g_\perp = 1.995$, $A_\parallel = 17.4$ G, and $A_\perp = 10.5$ G (50% pyridine/50% dichloromethane solvent). The larger Co hyperfine couplings found for the present zeolite-entrapped system may indicate a higher spin density at the metal ion in the zeolite "solvent" than in true solution. The overall close similarity of the zeolite and solution spectra indicate that the entrapped complex is not subject to any severe structural distortions as a result of being inside the zeolite. The EPR signal may be quantitatively reversed by simple evacuation of the sample at room temperature and then regenerated quantitatively by reexposure to oxygen of the original partial pressure. This extremely clean, reversible formation of a 1:1 Pauling type[9] Co:O_2 adduct at these temperatures should be compared with the behavior of the same complex in solution, where relatively rapid autoxidation to peroxo dimer species occurs,[12] and with the behavior of solid CoSALEN itself, which forms the peroxo dimer species exclusively.[13] Consideration of the "ship in a bottle" nature of the zeolite species indicates that such a peroxo dimerization process is precluded in this case by the very effective site isolation on the basis of complex size. In addition, any other oxidative process for complex destruction that involves a bimolecular intermediate cannot occur, and this may be a major reason for the excellent longevity of the entrapped complexes.

The zeolite-entrapped pyridine-bound complex as a dry solid was placed in the EPR cavity while attached to a mini vacuum line, and the changes in EPR spectra following introduction of molecular oxygen of various partial pressures were monitored. With the magnetic field fixed to the position of the peak maximum in Figure 2 and the growth in signal intensity plotted as a function of time after introduction of oxygen, plots such as those in Figure 3 were obtained. These plots give a measure of the kinetics of equilibrium attainment as a function of temperature (Figure 3a) or of oxygen pressure (Figure 3b) and follow classical diffusion behavior extremely well,[14] indicating that the kinetic process being monitored is diffusion of oxygen into the zeolite pores. Comparison to the rate of oxygenation of solid crystalline CoSALEN[1] with $t_{1/2} = 240$ s at 298 K shows that the present zeolite system is much more accessible, $t_{1/2} = 7$ s. Significantly, the very rapid ($t_{1/2} = {\sim}1$ s) attainment of equilibrium at 350 K is followed by a strict leveling of the signal indicating a very autoxidation- and dimerization-resistant oxygen adduct, which survives intact even at this elevated temperature. Indeed, cycling the material between the oxygenated and unoxygenated states can be repeated for many hours (>24) with no detectable decrease in the signal intensity at 298 K.

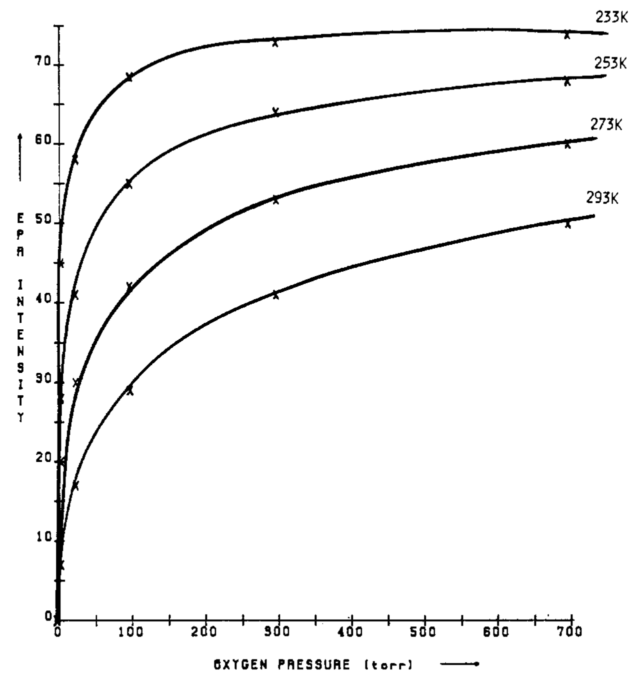


Figure 4. Oxygen adsorption isotherms for CoSALEN·py in zeolite Y.

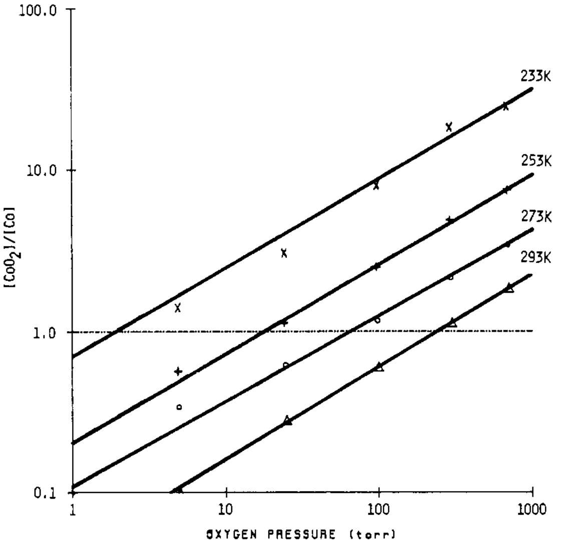


Figure 5. Hill plots of oxygen binding to CoSALEN·py in zeolite Y.

These very structurally stable monomeric adducts may be further characterized by estimating their oxygen binding affinity from data such as that in Figure 3b. From the signal intensity at equilibrium under each oxygen partial pressure, an oxygen

---

(11) Abel, E. W.; Pratt, J. N.; Whelan, R. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 901.

(12) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946. Ochiai, E. I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1727.

(13) Barkelew, C. H.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 2257. Hughes, E. W.; Wilmarth, W. K.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 2273.

(14) Breck, D. W. In *Zeolite Molecular Sieves*; Wiley: New York, 1974.

Table I. Apparent Oxygen Binding Constants for CoSALEN·py in Zeolite Na-Y

temp, K	K_{O_2}, Torr^{-1}	$P_{1/2}$, Torr	$P_{1/2}$(CoSALEN),[a] Torr
233	0.53	1.9	0.04
253	0.056	17.7	0.36
273	0.012	80.1	2.21
293	0.0033	305.5	10.5

[a] Data for free CoSALEN in pyridine solvent calculated from thermodynamic data in ref 18.

absorption isotherm may be constructed as in Figure 4. From such data, Hill plots[15] may be constructed, Figure 5, which in turn give the apparent oxygen binding constants listed in Table I. The Hill plots show slopes of 0.56 ± 0.02, indicating a negative cooperativity between the Co binding sites.[10] This translates as meaning that as oxygen is bound by the first cobalt sites, subsequent binding by further sites is inhibited. This is the reverse of the behavior displayed by hemoglobin.[10] The explanation of such an observation is not clear but may simply be a manifestation of the oxygen adsorption behavior of the zeolite itself, which tends to "pump" oxygen so as to have a higher effective oxygen concentration inside the pores than the externally applied oxygen pressure would imply.[14] This effect is more pronounced at lower oxygen pressures and so from the cobalt complex's point of view, the perceived oxygen pressure is not varying linearly with the applied oxygen pressure, with the deviation being such as to skew the Hill plot to a slope of less than 1. This behavior of the zeolite in raising the effective concentration of a reagent (oxygen) at an active site (cobalt) is very reminiscent of the function of the protein in creating an active site in an enzyme. In this way the zeolite may be considered an inorganic protein as we and others have previously suggested.[16,17]

Finally a van't Hoff plot of this data gives an excellent straight line ($R = 0.997$) from which $\Delta H = -11.4 \pm 0.5$ kcal/mol and $\Delta S = -51 \pm 2$ eu are deduced (standard state of 1 Torr). For comparison the equivalent complex in solution has $\Delta H = -12.4$ kcal/mol and $\Delta S = -47$ eu,[18] implying that inside the zeolite the lower binding constants (see Table I) result from a reduced exothermicity. This effect is consistent with the oxygen being bound inside the zeolite cavity at a restrictive binding site where the sterics of interaction of bound oxygen with the zeolite walls will be important.

In conclusion, it has been shown that a molecular "ship in a bottle" complex can be made so that it carries oxygen as a cargo and that such a material is much more stable toward irreversible oxidation than the equivalent solution-phase species. Unusual effects on the magnetic properties and oxygen binding behavior of the complex as a result of the zeolite environment are manifest, and the striking analogies between zeolite-encapsulated active sites and natural enzyme systems are reinforced. We have identified a number of other oxygen carrier systems inside zeolites with properties similar to those reported above, and these will be reported in a full publication in the near future together with a detailed analysis of the oxygen adsorption kinetics and thermodynamics.

Acknowledgment. The contributions of W. E. Farneth to oxygen sorption measurements, L. Abrams to fitting the diffusion kinetics, and W. R. Bachman to running the EPR spectra are appreciated. J. Nicholson and R. D. Farlee constructed the mini vacuum line/EPR facility, P. E. Bierstedt obtained the ESCA data, and J. B. Jensen prepared a number of the complexes reported. Their contributions and the insights of C. A. Tolman are likewise appreciated.

---

(15) Hill, A. V. *J. Physiol.* (*London*) **1910**, *40*, IV–VII. See also ref 10, p 158.

(16) Herron, N.; Tolman, C. A.; Stucky, G. D. *J. Chem. Soc., Chem. Commun.*, in press.

(17) Dyer, A.; Hayes, G. G.; Phillips, G. O.; Townsend, R. P. *ACS Symp. Ser.* **1973**, *No. 121*, 299.

(18) Tauzher, G.; Amiconi, G.; Antonini, E.; Brunori, M.; Costa, G. *Nature* (*London*) *New Biol.* **1973**, *241*, 222.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Heterobimetallic Complexes of Rhodium with Platinum, Silver, and Gold Containing Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

Robert J. McNair and Louis H. Pignolet*

Received June 9, 1986

Several new heterobimetallic compounds that contain bridging PNP ligands have been synthesized. The reactions of $[Rh(PNP)_2]BF_4$ with $Pt(PPh_3)_2(C_2H_4)$ and $Ag(PPh_3)(NO_3)$ led to the formation of $[RhPt(\mu\text{-}PPh_2)(\mu\text{-}PNP)(PN)(PPh_3)](BF_4)_2$ (**1**) and $[RhAg(\mu\text{-}PNP)_2](BF_4)(NO_3)$ (**2**), respectively. The reactions of $[RhAu(\mu\text{-}PNP)_2](BF_4)(NO_3)$ with CO and HCl gas and with aqueous HBr gave $[RhAu(\mu\text{-}PNP)_2(CO)_2](BF_4)(NO_3)$ (**3**) and $[RhAu(\mu\text{-}PNP)_2X]BF_4$ with X = Cl (**4**) and Br (**5**), respectively. Compound **1** was characterized by single-crystal X-ray diffraction [$P2_1/c$, $a = 15.921$ (9) Å, $b = 16.128$ (3) Å, $c = 33.326$ (9) Å, $\beta = 101.44$ (2)°, $Z = 4$, $\rho = 1.439$ g cm^{-3}, $R = 0.063$] and was found to have bridging diphenylphosphido and PNP ligands and a PN [2-[(diphenylphosphino)methyl]pyridine] ligand chelated to the Rh. The Rh–Pt distance [2.708 (1) Å] is consistent with a metal–metal bond. The PN and PPh_2 ligands resulted from cleavage of a phosphorus–carbon bond of a PNP ligand. The other compounds **2**–**5** were characterized in solution by ^{31}P and ^1H NMR spectroscopy and by IR spectroscopy. They all have bis(μ-PNP) structures.

Introduction

Heterobimetallic complexes in which two metals are held in close proximity by bridging P–P or P–N ligands have received considerable attention in recent years.[1-34] Interest in such mixed-metal compounds stems from their potential use in catalysis and organometallic-based synthetic chemistry. These compounds

---

(1) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet L. H., Ed.; Plenum: New York, 1983; p 167.

(2) Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5272.

(3) Guimerans, R. R.; Wood, F E.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 1307.

(4) Farr, J. P.; Olmstead, M. M.; Rutherford, N. M.; Wood, F. E.; Balch, A. L. *Organometallics* **1983**, *2*, 1758.

(5) Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

0020-1669/86/1325-4717$01.50/0 © 1986 American Chemical Society