Studies on the Complexes of N, N'-Bis[o-(diphenylphosphino)benzylidene]ethylenediamine with Transition Metal Ions

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Abstract. The thermodynamic parameters for the interaction of Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, and Ag^+ with the new title ligand have been determined by titration calorimetry in 50% THF–methanol (V/V) at 25 °C. Ag^+ exhibited remarkably higher complexation selectivity. Ag^+ and several transition metal ions have been transported using this ligand as carrier in a bulk liquid membrane. Competitive Ag^+–M^{2+} transport studies have also been carried out for the same system. In this membrane transport study, high transport of Ag^+ was observed in both single and competitive Ag^+–M^{2+} transport studies. The complex formation of N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine (P_2N_2) with silver, [Ag(P_2N_2)] (NO_3), (**1**) is reported. Complex **1** has been characterized by X-ray crystallography. **1** is monoclinic, space group $P2_1/n$ (No. 14), with cell dimensions $a = 13.398(4)$ Å, $b = 12.577(5)$ Å, $c = 21.521(4)$ Å, $\beta = 100.14(2)$ Å, $V = 3570(2)$ Å^3 and $Z = 4$.

Key words: thermodynamic parameters, bulk liquid membrane transport, P_2N_2, crown ether, enthalpy change, stability constant.

1. Introduction

Interest in the development of techniques for the separation of heavy metal ions has increased in recent years. It is well known that metal ions can be transported across a liquid membrane [1]. With an ever increasing awareness of our energy demands, energy efficient membrane technology is proving to be a valuable approach in separation processes. The effectiveness of a membrane separation is determined by the flux of species through the membrane. Polymeric membranes have the disadvantages of usually producing higher fluxes and selectivities [2]. There are three types of membranes which are generally employed: bulk liquid membranes [3], emulsion liquid membranes [4], and polymer supported liquid membranes [5, 6]. In our previous papers [3, 4] we examined the influence of the structural variation within a series of crown ether carriers upon the selectivity and efficiency of the transport of metal ions across a bulk liquid membrane and an emulsion membrane.

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Silver has long been an important metal in commerce. It is valued for its resistance to corrosion and for its use in alloys and jewelry. The recovery of silver from waste solutions has commercial importance, and improved methods for accomplishing this are of interest. Legal limits have been placed on silver concentration in municipal water supplies. Improved means of lowering silver concentration are needed and the analysis and recovery of Ag^+ at low concentrations from solutions containing other cations at high concentration requires particularly selective carriers. Recently, there have been a few reports that sulfur-containing podands were exhibiting high transport selectivity for Ag^+ [7]. As a candidate for exhibiting high transport selectivity for Ag^+, we have chosen the ligand, N, N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine (P_2N_2):
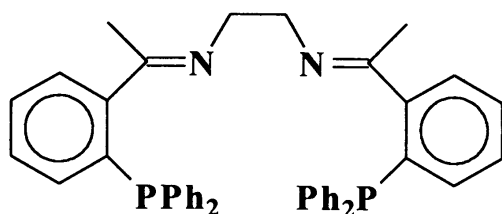
and determined ΔH, ΔS, and $\log K$ values for the $1:1$ interaction of P_2N_2 with Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} by titration calorimetry. In this study, we have focused on transport selectivity for Ag^+ over other transition metal ions in bulk liquid membrane by using the ligand (P_2N_2) as carrier.

2. Experimental

Liquid membrane transport experiments were conducted as reported earlier by using a bulk liquid membrane apparatus based on the concept of the Schulman bridge [8]. Two separate water phases were separated by a dichloromethane phase which constituted the membrane. The membrane consisted of 3.0 mL of 1.0 mM solution of the acyclic carrier in dichloromethane placed in the bottom of a glass vial (i.d. = 18 mm). The membrane was stirred at 25 °C for 24 h using a 13-mm Teflon-coated magnetic stirrer driven by a Hurst synchronous motor. The two water phases on top of the dichloromethane were separated by a length of glass tube which extended down into the dichloromethane layer. The water phases consisted of one 0.8 mL quantity of an aqueous cation solution (source phases) and the other 5.0 mL of distilled, deionized water (receiving phase). The solution of single salt source phase was 0.1 M $AgNO_3$/0.1 M of $M(NO_3)_2$. Each experiment was repeated three times in a chamber thermostated at 25 ± 1 °C. A 3 mL amount of the receiving phase was withdrawn by a syringe at the end of 24 h and the number of moles of cation was determined by atomic absorption spectrophotometer (Perkin Elmer Model 2380). The measured flux values (J_m = moles transported/sec m^2) were multiplied by 10^8 to obtain the J_m values in Table I. Each J_m value is the

average of three separate determinations. The standard deviations are less than $\pm 15\%$. The J_m values given are valid for the CH_2Cl_2-source phase boundary. Blank experiments (no carrier present) were performed for each source salt solution to determine membrane leakage. No transport was detected for any of the M^{n+} studied under any of the source and receiving phase conditions when carrier was absent from the membrane phase. ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker WH-300 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8501 spectrometer. Elemental analyses were performed by the Basic Science Center, Korea. N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine was prepared using a modified literature method [12]. The metal solutions were prepared in deionized, distilled water from the highest grade materials available from the indicated suppliers. The chemicals used and their sources were: $Cu(NO_3)_2$, $Zn(NO_3)_2$ (Kanto, G.R); $Co(NO_3)_2$, $Cd(NO_3)_2$, $Mn(NO_3)_2$ (Junnsei, E.P); $Ni(NO_3)_2$, $AgNO_3$ (Hayashi, G.R); $Hg(CH_3COO)_2$: (Sigma ACS); CH_2Cl_2 (Fluka).

2.1. PREPARATION OF 1

A solution of $AgNO_3$(0.13 g, 0.8 mmol) in a 1:1 mixture of THF–EtOH (20 mL) was treated with P_2N_2(0.49 g, 0.8 mmol). The resulting mixture was stirred at room temperature for 24 h. The solution was filtered and slow evaporation furnished green prisms in 80% yield. mp. 201–203 °C (dec.). ^{1}H-NMR(300 MHz, $CDCl_3$) δ 8.40 (1H, s, CH), 7.73–6.95 (28H, m, ph), 3.57 (4H, s, CH_2); ^{31}P$\{^1$H$\}$-NMR (121.50 MHz, $CDCl_3$) δ 9.11 (dd, J_{Ag-P} = 506.9, JJ_{P-P} = 35.6 Hz); IR (on KBr pellet, cm^{-1}) 3414 (br), 3053 (m), 2888 (w), 2815 (m), 1641 (s), 1583 (w), 1556 (w), 1475 (m), 1433 (s), 1387 (vs), 1310 (vs), 1180 (w), 1156 (w), 1126 (w), 1096 (m), 1072 (w), 1032 (w), 998 (w), 916 (w), 882 (br), 748 (s), 696 (s), 540 (m), 507 (s). *Anal. Calcd*. for $C_{40}H_{34}N_3O_3P_2Ag$: C, 61.97; H, 4.39. *Found*: C, 61.14; 4.04.

2.2. CRYSTAL STRUCTURE DETERMINATION OF 1

A yellow crystal of compound **1** crystallized from THF/EtOH was mounted in a glass capillary in a random orientation. A summary of the crystal and X-ray structural analysis data for compound **1** is presented in Table II. All measurements were made on a Rigaku AFC65 diffractometer with graphite monochromated MoK_a(λ = 0.71069 Å) and a 12-kW rotating anode generator. From the systematic absence of $h\sigma 1(h + 1 \neq 2n)$ and $\sigma k\sigma(h \neq 2n)$, the space group could be determined to be monoclinic $P2_1/n$ (No. 14). The data were collected at a temperature of -120 ± 1 °C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50.0°. A total of 6663 reflections which were measured after every 150 reflections remained constant throughout data collection. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized position. The final cycle of full matrix least-squares refinement was based on 3836 observed reflection ($I > 3.00\sigma(I)$) and 242

Table I. Thermodynamic parameters for complexation of metal ion by ligand.

Metal ion	ΔH, kcal/mol	$T\Delta S$, kcal/mol	$\log K$	ΔG, kal/mol
Cu^{2+}	−18.9	h	h	h
Cd^{2+}	−1.8	a	a	a
Zn^{2+}	−0.4	a	a	a
Ni^{2+}	−3.2	a	a	a
Co^{2+}	−2.8	a	a	a
Ag^{+}	−31.1	−25.7	3.96	−5.4

Titrate: 0.001 M ligand in 50% THF–MeOH.
Titrant: 0.01 M metal ion in 50% THF–MeOH.
a is the small amount of heat produced could not be used to determine thermodynamic parameters.
h is the value of $\log K$ could not be accurately determined by calorimetric methods.

variable parameters. The final converged agreement factors were $R_1 = 0.055$ and $R_w = 0.059$.

2.3. TITRATION CALORIMETRY

Typically, a run consisted of three sections: the initial heat capacity calibration, titration, and the final heat capacity calibration. The solution calorimeter used in this study is Tronac model 1250. The experimental procedure consists of titrating at 25 ± 0.02 °C in 50% (V/V) THF–methanol solution of 4 mM ligand with 40 mM metal nitrate. Heats of dilution are determined by titrating the mixed solution of the metal nitrate in 50% THF–methanol solution in the absence of the ligand; when this titration was repeated but with no metal nitrate in the titrant, the heat of dilution was negligible. Using the least squares program FS101 (Tronac, Inc.), values of $\log K, \Delta H$ and ΔS have been determined for complexation of the above metal ions by ligand.

3. Results and Discussion

The thermodynamic parameters of the ligand with Ag^+ and transition metal ions were determined by titration calorimetry. The numerical values of ΔH are listed in Table I.

According to Table I complexation of the cations with the ligand is exothermic and the $T\Delta S$ value is negative. These factors indicate that the interactions of the ligand with cations are enthalpy driven. No significant heat was produced for Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} with the ligand. Therefore, the binding strengths of these cations were expected to be very weak. Some heat was produced for Cu^{2+} with the ligand. We tried to calculate $\log K$ (stability constant), but unfortunately the $\log K$ could not be accurately determined by calorimetric methods. However, Ag^+ exhib-

Table II. Crystal and X-ray structural analysis data for compound **1**.

Empirical formula	$C_{40}H_{34}N_3O_3P_2Ag$
Molecular weight	774.54
Crystal color/habit	yellow/prismatic
Crystal system; space group	monoclinic; $P2_1/n$
$a/\text{Å}$	13.398(4)
$b/\text{Å}$	12.577(5)
$c/\text{Å}$	21.521(4)
$v/\text{Å}$	3570(2)
$D_c/\text{g cm}^{-3}$	1.441
$\mu(\text{Mo}K_\alpha)/\text{cm}^{-1}$	6.87
$F(000)$	1584
Reflection measured	6663
Observed reflections $[I > 3.00\sigma(I)]$	3836
Goodness of fit	1.78
R_1	0.055, $R_1 = \sum \|\|F_0\| - \|F_c\|\|/[\sum \|F_0\|]$
R_w	0.059, $R_w = \{[w(F_0^2 - F_c^2)^2]/[\sum_w F_0^2]\}^{1/2}$

ited a remarkably large enthalpy value. A large enthalpy value for Ag^+ with the ligand probably indicates strong complexation. Recombination of the ligand with the soft acid Ag^+ to form a complex of covalent nature is preferentially enthalpy driven. This result probably reflects the increased covalent character between soft acid and soft base in a Ag^+ complex of a ligand containing a phosphorus atom. According to X-ray crystallography, two phosphorus and two nitrogen atoms are participating in the coordination of Ag^+.

The thermodynamic properties of the ligand are expected to induce the transport selectivity of Ag^+. Single and binary transport of Ag^+ towards other ions was performed in bulk liquid membrane. The transport rates are listed in Table III:

Results from the present study for the transport of Ag^+ using the ligand carrier are given in Table III. Very little transport of other transition metal ions occurs when the ligand is used as carrier. In the carrier-facilitated transport process in which macrocyclic ligand carriers participate, a complex forms between the macrocyclic carriers and cation. Therefore, the stability of the complex plays a role in determining the rate at which the cation moves through the membrane [9]. Kirch and Lehn [10] concluded that the value of log K for highest transport was between 5.5 and 6. Lamb *et al.* [11] observed that there is an optimum log K(CH$_3$OH) value for M^{n+}-macrocycle interaction of which M^{n+} transport is greatest. The transport of M^{n+} decreases rapidly as the log K(CH$_3$OH) value becomes less than the optimum value. The optimum log K(CH$_3$OH) values were found to be 5.5–6.0 for monovalent cations and 6.5–7.0 for divalent cations. The value of stability constant (log K) for the Ag^+–ligand interaction is 3.96. This is to be expected because of the weak interaction between other transition metal ions and the ligand.

Table III. Transport of single ions and binary transport of Ag^+ and M^{2+} simultaneously by bulk liquid membrane containing the ligand as carrier.

Single metal ion	Flux ($\times 10^{-8}$ mol sec^{-1}m^{-2})	Binary metal ion	Flux ($\times 10^{-8}$ mol sec^{-1}m^{-2})
Ag^+	379.6	Ag^+/Cu^{2+}	526.3[a]
Cu^{2+}	6.8	Ag^+/Mn^{2+}	356.6[a]
Mn^{2+}	a	Ag^+/Ni^{2+}	435.8[a]
Ni^{2+}	1.0	Ag^+/Co^{2+}	539.4[a]
Co^{2+}	a	Ag^+/Zn^{2+}	571.7[a]
Zn^{2+}	0.6	Ag^+/Pb^{2+}	473.6[a]
Pb^{2+}	a	Ag^+/Cd^{2+}	458.5[a]
Cd^{2+}	3.6	Ag^+/Hg^{2+}	0.7/1967.7
Hg^{2+}	2610.1		

[a] No transport, transport condition: source phase (aqueous solution of metal nitrate–single(0.1 M M(NO$_3$))$_n$), (0.1 M AgNO$_3$ plus 0.1 M M(NO$_3$)$_2$ in water–binary metal ion): membrane phase (CHCl$_3$) 1.0 mM carrier; receiving phase(deionized water).

In the case of Ag^+, transport of Ag^+ occurs very rapidly when the same ligand is used as carrier. Because two NO_3^- anions must accompany one transition metal ion during transport, while only one NO_3^- anion per Ag^+ cation is necessary for Ag^+ transport. The number of anions per cation which must be dehydrated for transport to occur significantly affects the distribution coefficient of the transported moiety [13]. The ΔH value for the Ag^+ – ligand interaction is higher than those for other transition metal ion – ligand interactions. The transport of Hg^{2+} occurs remarkably rapidly but massive precipitates form in the CHCl$_3$ layer. We could not determine ΔH because of the precipitates formed in the solution.

In order to determine the transport selectivity of the system under conditions of binary transport of cations, the measurements were carried out by placing equimolar amounts of Ag^+ and transition metal ions in the source phase. Table III lists competitive transport experimental data for binary systems containing Ag^+ and one other metal ion. A striking feature of the data in Table III is the almost universal transport selectivity demonstrated by the ligand for Ag^+ over the other metal ions.

In this membrane, highly selective transport of Ag^+ was observed in both single and binary cation mixtures. Incorporation of the ligand which are selective for Ag^+ into the liquid membrane may be used to remove Ag^+ from environmental systems. In broader sense, these experiments demonstrate the potential application to selective removal, concentration, purification of Ag^+ or other metallic elements from mixtures.
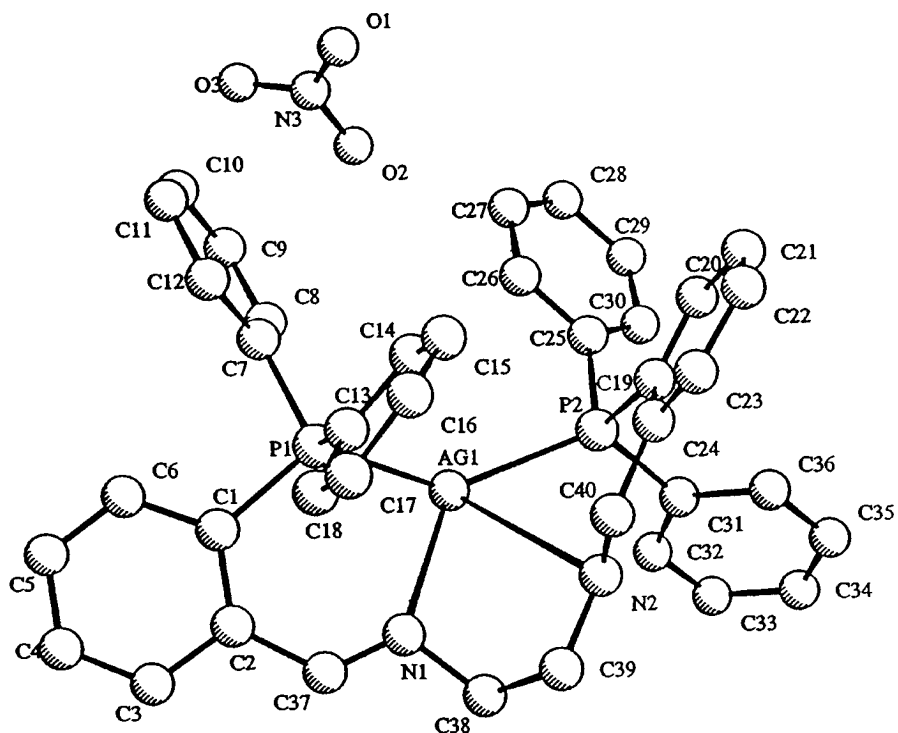
Figure 1. Molecular structure of the complex cation **1** showing the atom numbering scheme.

Table IV. Selected bond lengths (Å) and angles(deg) for complex **1**.

Ag(1)—P(1)	2.433 (2)	Ag(1)—N(1)	2.557 (6)
Ag(1)—P(2)	2.396 (2)	Ag(1)—N(2)	3.058 (6)
P(1)—C(1)	1.830 (7)	C(2)—C(37)	1.46 (1)
P(2)—C(1)	1.845 (7)	C(24)—C(40)	1.46 (1)
N(1)—C(37)	1.268 (9)	C(38)—C(39)	1.51 (1)
N(1)—C(38)	1.461 (9)	N(2)—C(40)	1.253 (9)
N(2)—C(39)	1.478 (9)	Ag(1)—P(1)—N(1)	54.7 (1)
P(2)—Ag(1)—P(1)	133.88 (7)	Ag(1)—P(2)—N(2)	68.2 (1)
P(2)—Ag(1)—N(1)	127.6 (1)	Ag(1)—N(1)—N(2)	66.5 (2)
P(2)—Ag(1)—N(2)	65.1 (1)	Ag(1)—N(1)—P(1)	51.0 (1)
P(1)—Ag(1)—N(1)	74.3	N(2)—N(1)—P(1)	97.2 (2)
P(1)—Ag(1)—N(2)	109.6 (1)	N(1)—N(2)—P(2)	96.2 (2)
N(1)—Ag(1)—N(2)	63.4 (2)	N(1)—N(2)—Ag(1)	50.1 (2)
O(2)—Ag(1)—N(2)	140.1 (2)	P(2)—N(2)—Ag(1)	46.68 (9)
O(3)—Ag(1)—N(2)	100.8 (2)		

3.1. Synthesis and molecular structure of 1

The ligand, P_2N_2, appears to react with many transition metal ions. However, we have focused on the derivative of silver(I) as silver ion exhibited a markedly large enthalpy value with the ligand, thus providing a template by the strong complexation. The addition of 1 molar equiv. of P_2N_2 to a stirred solution of $AgNO_3$ in THF-EtOH gave a green solution. The complex of **1** is a green crystalline solid that is air stable and is soluble in $CHCl_3$ and THF. The infrared spectrum of **1** shows a strong absorption band due to the imino group ($\nu_{C=N}$) at 1641 cm^{-1}. The ^{1}H-NMR spectrum of **1** is consistent with the proposed structure: the methyne and methylene protons appear as two distinct singlets at $\delta 8.40$ and 3.57, respectively. The values are comparable to those of corresponding hydrogen atoms in related complexes [12]. The ^{31}P$\{^1$H$\}$-NMR spectrum shows an AB pattern ($J_{Ag-P} = 506.7$ Hz, $J_{P-P} = 35.6$ Hz) and is consistent with the distorted tetrahedral structure. The structure was subsequently confirmed by a single-crystal X-ray diffraction study. Slow diffusion of EtOH into a tetrahydrofuran solution of **1** yielded green single crystals of X-ray quality. The crystal structure of **1** consists of well-separated anions and cations. A PLUTO drawing of **1** is found in Figure 1, while selected bond lengths and angle can be found in Table IV. The cation has a distorted tetrahedral geometry and has an approximate C_2 axis along the bisector of the P—Ag—P angle. The Ag—N(2) bond distance of 3.06 Å is extremely long and suggests that the imine is only weakly coordinated to the metal center. This distance is typical of Ag—N distances in a related ferrocenyl–silver compound. The Cu—P distances range from 2.396(2) to 2.433(2) Å, and the average value of 2.415 Å falls within the range of values (2.35 to 2.43 Å) observed for Ag(I) complexes [14] having two monodentate phosphorus ligands. The chelate 'bite' angles, P(1)—Ag—N(1) = $74.3(1)°$, P(2)—Ag—N(2) = $63.4(2)°$, N(1)—Ag—N(2) = $63.4(2)°$, are considerably smaller than ideal tetrahedral angles and result in a large P(1)—Ag—P(2) angle of $133.88(7)°$. The C=N, C—N, and C—C distances within the chelate rings are close to the values which have been found in the [Cu(P_2N_2)]ClO$_4$ complex [12].

In summary, Ag^+ exhibited markedly large enthalpy value for the ligand P_2N_2; the large enthalpy value of Ag^+ for the ligand indicates the strong complexation. Fast Ag^+ transport also occurs when the ligand is used as carrier. The tetradentate ligand P_2N_2 has been shown to function as a chelating agent for Ag^+ ion. Crystallographic evidence suggests that the ligand is coordinated to silver ion in a distorted tetrahedral geometry.

References

1. J. P. Behr, M. C. Kirch, and J. M. Lehn: *Am. Chem. Soc.* **107**, 241 (1985).
2. J. D. Way, R. D. Noble, T. M. Flynn and E. D. Solan: *J. Membr. Sci*. **12**, 239 (1982).
3. M. H. Cho, K. H. Son Woo, M. Y. Heo, I. C. J. Yoon, and S. J. Kim: *Bull. Korean Chem. Soc.* **9**, 5 (1998).
4. M. H. Cho, H. S. Chun, J. H. Kim: *Bull. Korean Chem. Soc. Sci.* **12**, 5(1991).
5. R. W. Baker, M. E. Tuttle, D. J. Kelly, and H. K. Lonsdale: *J. Memb. Sci*. **2**, 213 (1977).
6. C. F. Reusch and E. L. Cussef: *Aiche. J.* **19**, 4 (1973).
7. S. S. Lee, J. H. Jung, S. H. Yu and Ni. H. Cho: *Thermochim. Acta* **259**, 133 (1995).
8. J. L. Toner, R. C. Helgesom and D. J. Cram: *J. Am. Chem. Soc.* **101**, 494 (1979).
9. J. D. Lamb, R. M. Izatt and J. J. Christensen: *Progress in Macrocyclic Chemistry* **2**, 42–74.
10. M. Kirch and J. M. Lehn: *Angew. Chem. Int. Ed. Engl.* **14**, 555 (1975)
11. J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asey and R. M. Izatt: *J. Am. Chem. Soc.* **102**, 6820 (1980).
12. J. C. Jeffery, T. B. Rauchfuss and P. A. Tucker: *Inorg. Chem.* **19**, 3306 (1990).
13. R. M. Izatt, D. V. Dearden, P. R. Brown, J. S. Bradshaw, J. D. Lamb and J. J. Christensen: *J. Am. Chem. Soc.* **105**, 1785 (1983).
14. P. W. R. Corfield and H. M. M. Shearer: *Acta Crystallogr.* **20**, 502 (1966).