Structural Isomerism Involving an Ambidentate Ligand: the Synthesis and Characterization of Diselenocyanato[bis(diphenylphosphino)methane]palladium(II) and Cyano(selenocyanato)[diphenyl(diphenylphosphinomethyl)phosphine selenide]palladium(II)

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Abstract

The reaction, at 25 °C in methanol, between $[Pd(SeCN)_4]^{2-}$ and bis(diphenylphosphino)methane (dpm) has been found to produce cyano(selenocyanato) [diphenyl (diphenylphosphinomethyl) phosphine selenide]palladium(II), [Pd(dpmSe)(CN)(SeCN)], wherein the cyanide group is *trans* to an Se atom which has been inserted into one Pd–P bond, and the selenocyanate group is *trans* to the unchanged diphenylphosphino group. The structure has been confirmed by the results of a single crystal X-ray diffraction study. The structural isomer, $[Pd(dpm)(SeCN)_2]$, of the foregoing complex has also been prepared by the reaction of $Pd(C_2H_3O_2)_2$ with dpm, followed by reaction with KSeCN. Heating the $[Pd(dpm)(SeCN)_2]$ isomer converts it into [Pd(dpmSe)(CN)(SeCN)]. A mechanism is proposed for the isomerization which involves an intramolecular selenium atom insertion.

Introduction

The coordination chemistry of ambidentate ligands, especially the pseudohalides [1], has provided a rich mother lode of intriguing structural problems. The potential of these ligands to form linkage isomers is well documented [1]. We now wish to report an example of structural isomerism involving the ambidentate selenocyanate ion, $SeCN^-$.

This occurred serendipitously when our attempts to synthesize $[Pd(dpm)(SeCN)_2]$ (dpm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, bis(diphenylphosphino)methane) by a reaction between $[Pd(SeCN)_4]^{2-}$ and dpm yielded instead [Pd(dpmSe)(CN)(SeCN)] (dpmSe = $(C_6H_5)_2PCH_2P(Se)(C_6H_5)_2$, diphenyl(diphenylphosphinomethyl)phosphine selenide). We then succeeded in synthesizing the $[Pd(dpm)(SeCN)_2]$ structural isomer by an alternate route. In addition to providing the details of the synthesis and spectral characterization of both isomers, this paper also describes the structure determination, by single crystal X-ray diffraction, of the [Pd(dpmSe)(CN)(SeCN)] isomer and provides a mechanistic rationalization of its formation.

Experimental

All chemicals and solvents used were of reagent grade or better. Protective rubber gloves were worn during the handling of all selenium containing compounds.

Tetrabutylammonium Selenocyanate, $[(CH_3(CH_2)_3)_4N]SeCN$

This salt was prepared using the method employed by Burmeister and Williams [2]. The product, a white solid, was obtained in 76% yield and characterized by a strong, sharp ionic ν(CN) band in the infrared at 2080 cm^{-1}

Tetrabutylammonium Tetraselenocyanatopalladate(II), $[(CH_3(CH_2)_3)_4N]_2[Pd(SeCN)_4]$

This compound was synthesized from $[(CH_3(CH_2)_3)_4N]SeCN$ and $PdCl_2$, according to the procedure of Burmeister and Williams [2]. The red–orange product was obtained in 28% yield. The characteristic g(CN) band appeared at 2100 cm^{-1} in its infrared spectrum.

Cyano(selenocyanato)[diphenyl(diphenylphosphinomethyl)phosphine selenide]palladium(II), $[Pd\{(C_6H_5)_2PCH_2P(Se)(C_6H_5)_2\}(CN)(SeCN)]$

The procedure employed in the formation of this complex was similar to that reported by Meek *et al.* [3] for the synthesis of a series of [Pd($\overset{\frown}{L\;L'}$)(thiocyanate)$_2$] complexes involving bidentate ligands similar to dpm. In the present case, $[(CH_3(CH_2)_3)_4N]_2$-

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[Pd(Se(CN)$_4$] was used in place of the corresponding thiocyanato complex, and the reaction with dpm was carried out at 25 °C in methanol instead of absolute ethanol. The yellow–orange complex that resulted was obtained in 38% yield after recrystallization from acetone (melting point (m.p.) 239 °C, ν(CN) bands at 2138 (medium, sharp) and 2124 (strong, sharp) cm^{-1}). *Anal.* Calc. for [Pd{(C$_6$H$_5$)$_2$PCH$_2$P(Se)(C$_6$H$_5$)$_2$}(CN)(SeCN)]: C, 46.28; H, 3.16; N, 4.00. Found: C, 45.60; H, 3.40; N, 3.87%.

Diselenocyanato(bis(diphenylphosphino)methane)palladium(II), [Pd{(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$}(SeCN)$_2$]

One equivalent of Pd(C$_2$H$_3$O$_2$)$_2$ was dissolved in acetone. Solutions of dpm (1 equivalent, in CH$_2$Cl$_2$) and KSeCN (2 equivalents, in acetone) were added slowly. The reaction mixture was stirred for 1.5 h, whereupon the excess solvent was removed under reduced pressure. A dark yellow solid was isolated from diethyl ether in 73% yield (m.p. 180 °C, ν(CN) bands at 2130 and 2121 cm^{-1}). *Anal.* Calc. for [Pd{(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$}(SeCN)$_2$]: C, 46.28; H, 3.16; N, 4.00. Found: C, 44.12; H, 2.93; N, 3.75%.

Red Selenium

Potassium selenocyanate, KSeCN, was dissolved in a 1:1 ethanol:water solution (v/v). A 1:1 hydrochloric acid:water solution (v/v) was added dropwise very slowly, using a buret. The hydrogen cyanide gas, HCN, which was evolved in the reaction was bubbled into a 4–6% solution of sodium hypochlorite, NaOCl, and converted to sodium cyanide, NaCN. Precipitation of the red selenium metal occurred instantly.

Diphenyl(diphenylphosphinomethyl)phosphine selenide, (C$_6$H$_5$)$_2$PCH$_2$P(Se)(C$_6$H$_5$)$_2$

This ligand was prepared using the method of Grim and Walton [4]. A stream of N$_2$ gas was bubbled through 75 ml of toluene for 2 h to remove the oxygen. After reagent addition, the mixture was heated at reflux under N$_2$ for 2 h. The white product, exhibiting a melting point of 95–97 °C, was isolated in 43% yield and characterized by the ν(P=Se) band in its infrared spectrum at 530 cm^{-1}. *Anal.* Calc. for (C$_6$H$_5$)$_2$PCH$_2$P(Se)(C$_6$H$_5$)$_2$: C, 64.80; H, 4.79. Found: C, 64.72; H, 4.90%.

Diselenocyanato[diphenyl(diphenylphosphinomethyl)phosphine selenide]palladium(II), [Pd{(C$_6$H$_5$)$_2$PCH$_2$P(Se)(C$_6$H$_5$)$_2$}(SeCN)$_2$]

This complex was prepared by a method analogous to that used in the synthesis of [Pd(dpm)(SeCN)$_2$]. A dark red–orange solid, with a melting point of 195 °C, was isolated in 43% yield. The infrared spectrum showed the ν(CN) band at 2112 cm^{-1} and the ν(P=Se) band at 530 cm^{-1}. *Anal.* Calc. for [Pd{(C$_6$H$_5$)$_2$PCH$_2$P(Se)(C$_6$H$_5$)$_2$}(SeCN)$_2$]: C, 41.59; H, 2.84; N, 3.59. Found: C, 38.06; H, 2.76; N, 2.04%.

Infrared Measurements

Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Perkin-Elmer 180 Grating Infrared Spectrophotometer. Ten-fold abscissa scans were measured on the same instrument. Nujol mulls between KBr plates were used for all solid samples. Polystyrene film was used for daily calibration.

Elemental Analyses

Elemental microanalyses were carried out by Schwarzkopf Microanalytical Laboratory in Woodside, New York.

Melting Points

Melting point determinations were made on a Thomas Hoover Capillary Melting Point Apparatus.

X-ray Crystallography

Crystals of [Pd(dpmeSe)(CN)(SeCN)] suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution. The orange crystal was attached to a glass fiber with epoxy cement. Data were collected on a Nicolet R3 diffractometer, using graphite-monochromated Mo Kα radiation. Pertinent crystallographic parameters are summarized in Table I.

The crystal structure was solved and refined using the SHELXTL (Version 4.0) Program Library (Nicolet Corp., Madison, Wis.). A profile fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required.

The position of the palladium atom was obtained by direct methods. All other non-hydrogen atoms were located by difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using blocked-cascade, least-squares refinement methods. The hydrogen atom positions were calculated in idealized positions on the basis of d (C–H) = 0.96 Å, and thermal parameters equal to 1.2 times the isotropic equivalent value for the atom to which the hydrogen atom was attached.

An ORTEP plot of the structure of the [Pd(dpmSe)(CN)(SeCN)] complex is shown in Fig. 1. Atomic coordinates are given in Table II. Important bond distances and angles are shown in Table III.

Discussion

The results of what had been expected to be a rather straightforward reaction between [Pd(SeCN)$_4$]$^{2-}$ and dpm were somewhat startling. Instead of the anticipated [Pd(dpm)(SeCN)$_2$] product, the crystal structure of the species actually

TABLE I. Crystal and Intensity Data Collection Summary for [Pd(dpmSe)(CN)(SeCN)]

Molecular formula	$PdSe_2P_2C_{27}H_{22}N_2$
Molecular weight	700.72
a (Å)	11.537(3)
b (Å)	12.815(4)
c (Å)	19.104(6)
V (Å^3)	2824(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
ρ (calc.) (g/cm^3)	1.65
Z	4
Radiation	Mo Kα (graphite-monochromated)
Absorption coefficient, μ(Mo Kα) (cm^{-1})	33.29
Temperature (°C)	24 ± 2
Scan speed (°/min)	4.5–20.0
Scan type	$\theta - 2\theta$
Scan range	$2.0 + (\alpha_1 - \alpha_2)$
Standards Monitored (x standards every y reflections), x/y	3/150
2θ Limits (°)	3.0–45.0
Reflections collected	$h, k, \pm l$
No. reflections collected	4245
Unique reflections	3404
Unique reflections used	3123 with $F_o > 2.0\sigma(F_o)$
Weighting factor, g[a]	0.00098
R (F)[b]	0.057
R (F_w)[c]	0.062
Highest peak on final difference map (e/Å^3)[d]	0.94

[a] Weight $= 1/[\sigma^2(F) + |g|(F^2)]$. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = [\Sigma w^{1/2}(|F_o| - |F_c|)]/\Sigma w^{1/2}(F_o)$. [d] Peak is 0.98 Å from Pd.

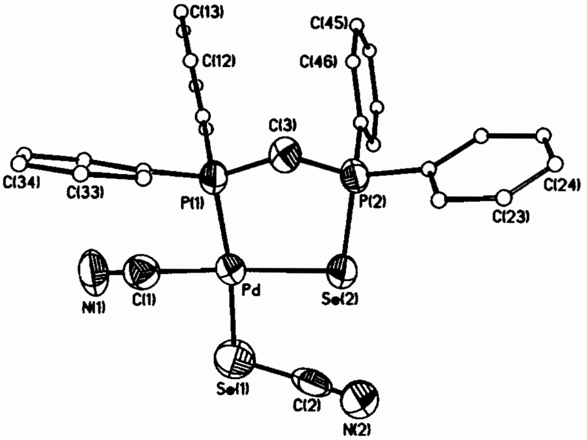


Fig. 1. Molecular structure and labeling scheme for [Pd(dpmSe)(CN)(SeCN)]. Hydrogen atoms have been deleted. Thermal ellipsoids are shown at the 50% probability level.

TABLE II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

Atom	x	y	z	U[a]
Pd	8514(1)	1299(1)	−519(1)	51(1)
Se(1)	8565(2)	1124(1)	−1795(1)	100(1)
Se(2)	7359(1)	−271(1)	−359(1)	63(1)
P(1)	8661(3)	1621(2)	642(1)	47(1)
P(2)	7600(3)	−476(2)	756(1)	48(1)
N(1)	9982(10)	3283(8)	−810(7)	69(5)
N(2)	7197(12)	−761(9)	−2131(6)	101(5)
C(1)	9460(10)	2581(9)	−714(6)	66(4)
C(2)	7753(12)	−53(10)	−1994(6)	74(3)
C(3)	7623(9)	802(7)	1130(5)	43(3)
C(11)	10076(8)	1319(8)	986(3)	48(4)
C(12)	10286(11)	1494(11)	1685(6)	87(6)
C(13)	11413(12)	1286(12)	1953(7)	100(6)
C(14)	12264(12)	933(11)	1499(8)	104(6)
C(15)	12000(10)	733(11)	836(8)	83(6)
C(16)	10928(10)	938(10)	557(7)	72(5)
C(31)	8376(10)	2933(7)	941(5)	53(4)
C(32)	7325(12)	3269(9)	1194(7)	60(5)
C(33)	7174(14)	4398(10)	1392(9)	113(8)
C(34)	8067(13)	4996(10)	1317(8)	119(8)
C(35)	9104(14)	4664(11)	1090(9)	122(8)
C(36)	9268(13)	3632(10)	884(7)	90(6)
C(21)	6419(10)	−1216(7)	1103(5)	53(4)
C(22)	5290(10)	−638(10)	1113(8)	94(6)
C(23)	4405(13)	−1453(11)	1337(9)	123(8)
C(24)	4571(13)	−2404(11)	1570(97)	91(6)
C(25)	5619(14)	−2799(11)	1567(9)	111(8)
C(26)	6556(11)	−2213(6)	1362(7)	92(6)
C(41)	6919(9)	−1162(8)	968(6)	36(4)
C(42)	9500(12)	−1744(10)	469(8)	97(6)
C(43)	10477(15)	−2243(13)	679(13)	133(10)
C(44)	10923(16)	−2209(14)	1327(12)	129(10)
C(45)	10341(11)	−1623(9)	1826(6)	36(6)
C(46)	9334(10)	−1117(10)	1648(7)	75(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

isolated (Fig. 1) showed that a selenium atom had been inserted into one Pd–P bond, yielding cyano(selenocyanato)[diphenyl(diphenylphosphinomethyl)phosphine selenide]palladium(II), [Pd(dpmSe)(CN)(SeCN)], with the remaining Se-bound selenocyanate group *trans* to the 'normal' diphenylphosphino group and a cyanide *trans* to the P=Se group. In accord with this structure, two distinct ν(CN) stretching bands were observed in the infrared spectrum of the complex [2138 cm^{-1} (Pd–CN) and 2124 cm^{-1} (Pd–SeCN)].

The stability of five-membered rings in saturated systems is well known and occurrences of phosphine selenide formation have previously been documented [5]. Thus, the observed product should be relatively favorable thermodynamically. It is, however, important to note that the same insertion process does not occur for the analogous thiocyanate complex [3],

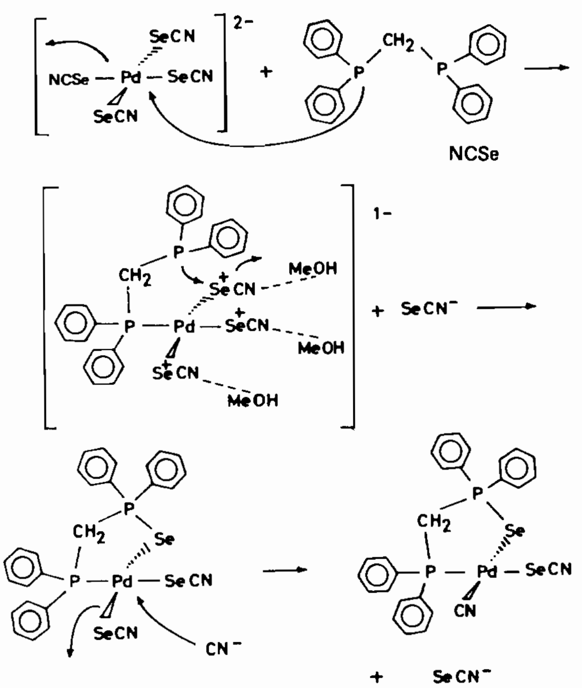
TABLE III. Selected Bond Distances and Angles for [Pd(dpmSe)(CN)(SeCN)]

(a) Bond distances (Å)			
Pd–Se(1)	2.450(2)	Pd–Se(2)	2.433(2)
Pd–P(1)	2.262(3)	Pd–C(1)	2.006(12)
Se(1)–C(2)	1.816(13)	P(1)–C(3)	1.844(10)
Se(2)–P(2)	2.164(3)	P(2)–C(3)	1.787(9)
N(1)–C(1)	1.097(16)	C(2)–N(2)	1.142(18)
(b) Bond angles (°)			
Se(1)–Pd–Se(2)	93.4(1)	P(1)–C(3)–P(2)	109.2(5)
Se(2)–Pd–P(1)	94.0(1)	Se(1)–Pd–P(1)	172.3(1)
Se(2)–Pd–C(1)	176.5(3)	Se(1)–Pd–C(1)	83.0(3)
Pd–Se(1)–C(2)	105.8(4)	P(1)–Pd–C(1)	89.6(3)
Pd–P(1)–C(3)	110.0(3)	Pd–Se(2)–P(2)	98.8(1)
Se(2)–P(2)–C(3)	106.5(3)	Se(1)–C(2)–N(2)	176.5(12)
Pd–C(1)–N(1)	178.8(12)		

probably due to the greater bond strength of the C–S bond relative to the C–Se bond, and, more importantly, was not observed to occur for any of the other similar selenocyanate complexes ($[Pd\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}(SeCN)_2]$, where $n = 2, 3, 4$) that were examined in a related study [6].

A review of the work done by Songstad and Stangeland [7] suggested that solvation effects due to interactions of the nitrogen end of the selenocyanate with a protic solvent (in this case, methanol) could account for the observed reaction sequence. Because of this association, Songstad and Stangeland have proposed that a substantial positive charge is induced on the selenium atom causing it to act as an electrophile.

A mechanism which employs these principles was postulated (see Scheme 1). A study of the validity of this mechanism and its implications yielded some interesting results. The first step involved running the reaction in a non-protic solvent (acetone). The product thus obtained was once again that of the monophosphine selenide. From this it was concluded that, although solvent interactions may have some effect on monophosphine selenide formation, there are other factors which provide much stronger influences on product determination. It was also suspected that the incorporated selenium atom may have originated from free selenocyanate in solution. This hypothesis was disproved by employing palladium(II) acetate as the starting material and adding two equivalents of potassium selenocyanate to the mixture after coordination to dpm had taken place. The monophosphine selenide structure was not observed. Instead, the originally anticipated diselenocyanate complex, $[Pd(dpm)(SeCN)_2]$, was produced. This material was subsequently heated at reflux for 18 hours and reisolated as a gold solid. Its infrared spectrum showed strong, sharp bands at 2143 and 2134 cm^{-1}, indicative of cyanide and selenocyanate coordination, respectively. Although the positions of these bands are not identical to those observed in the original monophosphine selenide complex, the peak shapes are very similar and an asymmetric broadening to the right side of the selenocyanate band is exhibited in both spectra. It is interesting to note that heating [Pd(dpmSe)(CN)(SeCN)] at reflux in methanol produced no apparent change in structure at all and formation of the diphosphine diselenide structure $[Pd(dpmSe_2)(CN)_2]$, was not observed. In fact, the ν(CN) bands of the recovered material were identical to those of the initial product. This can be explained as a tendency to minimize ring strain. For



Scheme 1.

TABLE IV. Bond Angles in Analogous Thiocyanate and Selenocyanate Palladium(II) Complexes

Ligand	SCN^- [8]	$SeCN^-$
dpm	73.3(5)° P–Pd–P	94.0(1)° [this work] P–Pd–Se
dpe[a]	85.1(1)° P–Pd–P	85.1(1)° [6] P–Pd–P
dpp[b]	89.0(1)° P–Pd–P	90.9(1)° [6] P–Pd–P

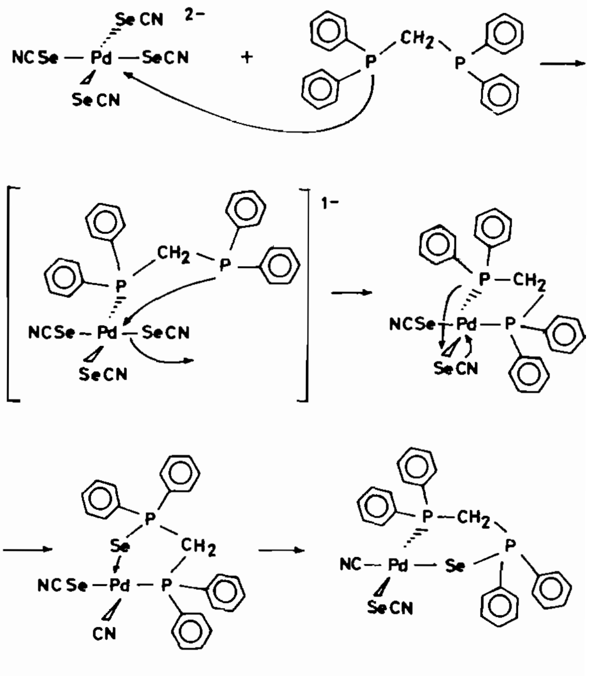
[a] $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$. [b] $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$.

example, in the case of thiocyanate coordination, the P–Pd–P bond angle for the dpm complex has been determined to be 73.3° [8] while [Pd(dpmSe)(CN)(SeCN)] has a P–Pd–Se bond angle of 94.0° (see Table IV).

The final aspects of the mechanistic study involved the synthesis of another hypothesized intermediate, $[Pd(dpmSe)(SeCN)_2]$, and the possibility that selenium may be a better *trans* director than phosphine. The complex was prepared by adding one equivalent of dpmSe and two equivalents of potassium selenocyanate to a solution of palladium(II) acetate in acetone The addition of CN^- to a solution of $[Pd(dpmSe)(SeCN)_2]$ in acetone caused no displacement of selenocyanate. It was thus concluded that the postulated solvent assisted mechanism was, in fact, not adequate in accounting for the observed product formation.

Based on these new data, an alternate reaction pathway was proposed (see Scheme 2). Initial attack of dpm on the palladium center presumably results in the formation of a reaction intermediate, $[Pd(dpm)(SeCN)_2]$. Support for this mechanism arises from the fact that, as described earlier, this intermediate can be synthesized relatively easily. Infrared analyses indicated that a mixture of the two complexes, $[Pd(dpm)(SeCN)_2]$ and [Pd(dpmSe)(CN)(SeCN)], can be trapped by running the reaction at low temperature (0 °C). This is evidenced by the presence of three bands in the ν(CN) region of the spectrum of the isolated mixture (2148, 2140, and 2127 cm^{-1}). The bands are indeed shifted to some extent, but this is probably due to crystal lattice effects or solvent influences.

The next step is presumed to involve abstraction of a selenium atom by one of the phosphine groups. The concept of an intramolecular rearrangement correlates well with the fact that monophosphine selenide formation occurs when, as noted above, $[Pd(dpm)(SeCN)_2]$ is heated. The final step in the reaction sequence employs the strong *trans* directing property of CN^-, which has been well established. This would explain the *trans* relationship between selenium and cyanide observed in the crystal structure (see Fig. 1). The argument for relief of ring strain still holds true for the intermediate four-membered ring and provides the rationalization for why monophosphine selenide formation is not observed in the other bis(diphenylphosphino) complexes.



Scheme 2.

Acknowledgement

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References

1 A. M. Golub, H. Köhler and V. V. Skopenko, 'Chemistry of Pseudohalides', Elsevier, Amsterdam, 1986.
2 J. L. Burmeister and L. E. Williams, *Inorg. Chem., 5,* 1113 (1966).
3 D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc., 92,* 5351 (1970).
4 S. O. Grim and E. D. Walton, *Inorg. Chem., 19,* 1982 (1980).
5 P. Nicpon and D. W. Meek, *Inorg. Chem., 31,* 1297 (1966).
6 C. A. Grygon, J. L. Burmeister and W. C. Fultz, unpublished results.
7 J. Songstad and L. J. Stangeland, *Acta Chem. Scand., 24,* 804 (1970).
8 G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc., 97,* 1059 (1975).