disposal by the ZWO organization.

Registry No. $Br_2Sn_2[Mn(CO)_5]_4$, 56397-61-6.

Supplementary Material Available: Listing of structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907,
and from the Materials Physics Division, Atomic Energy Research Establishment, Harwell, Oxfordshire OX11 Ora, England

Crystal Structure of a Condensed Phosphatosilicate, Oxovanadium(IV) Diphosphatomonosilicate, $VO(SiP_2O_8)$

CATHERINE E. RICE,[1a] WILLIAM R. ROBINSON,*[1a] and BRUCE C. TOFIELD*[1b]

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Crystals of oxovanadium(IV) diphosphatomonosilicate, $VO(SiP_2O_8)$, are tetragonal, space group $P4/ncc$, $a = 8.747$ (2) Å, $c = 8.167$ (2) Å, and $Z = 4$. By use of Patterson and Fourier techniques, the structure has been solved from 1289 symmetry-independent structure factors collected on an automated diffractometer and refined to a weighted R of 0.031. The structure is composed of $V{=}O\cdots V{=}O\cdots V{=}O$ chains ($d(V{=}O) = 1.591$ (2) Å, $d(V\cdots O) = 2.492$ (2) Å) lying along the fourfold axes with parallel $Si(PO_4)_2Si(PO_4)_2Si$ chains along the $\bar{4}$ axes. These chains are joined by oxygen atoms of the PO_4 groups which complete the distorted VO_6 octahedra. A given PO_4 group is bonded to two V atoms ($d(P{-}O) = 1.492$ (1) Å, $d(V{-}O) = 1.977$ (1) Å) and two Si atoms ($d(P{-}O) = 1.572$ (1) Å, $d(Si{-}O) = 1.610$ (1) Å). All dimensions within the vanadium–oxygen octahedron and the diphosphatosilicate chain are similar to those observed in related compounds.

Introduction

Oxovanadium(IV) diphosphatomonosilicate was recently prepared[2] and appeared to be the first well-characterized compound containing a stoichiometric arrangement of condensed silicate and phosphate tetrahedra. The substitution of P^V for Si^{IV} in silicates or of Si^{IV} for P^V in phosphates is not, in fact, common in minerals (see ref 2) although a number of synthetic phosphosilicates with the apatite[3,4] or eulytine[5] structures, where the tetrahedra are not linked to one another, have been prepared. A very few phosphosilicates where there are no phosphate–silicate links but where the phosphate and silicate tetrahedra are crystallographically distinguished have also been characterized.[6,7]

The ease of preparation of $VO(SiP_2O_8)$[2] indicates, however, that phosphosilicates in general are not necessarily unstable and the stoichiometry (X_3O_8) of the tetrahedrally coordinated anion sublattice indicated a possibly novel arrangement compared to known silicate or phosphate structures. We have, therefore, undertaken the determination of the crystal structure of $VO(SiP_2O_8)$ to discover the anionic arrangement and also that of the VO^{2+} moiety. The latter is of interest because a magnetic ordering transition was observed[2] in $VO(SiP_2O_8)$ at 2.5 K.

Experimental Section

$VO(SiP_2O_8)$ was first prepared from the chemical transport of $VO(PO_3)_2$[8] with iodine in a quartz tube. Single crystals may also be prepared by chemical transport with chlorine, and polycrystalline $VO(SiP_2O_8)$ is formed from the direct combination of $VO(PO_3)_2$ with SiO_2.[2] A wedge-shaped crystal was selected from a sample of $VO(SiP_2O_8)$ produced during an attempt to transport $VO(PO_3)_2$ with I_2 in a quartz tube. The wedge was a rectangular plate measuring 0.229 mm parallel to the c axis of the tetragonal unit cell and 0.142 mm parallel to the a axis. The thickness of the plate parallel to b ranged from 0.057 mm at one end to 0.028 mm at the other.

Crystal Data: $VO(SiP_2O_8)$, mol wt 1139.92, $a = 8.747$ (2) Å, $c = 8.167$ (2) Å, $V = 624.8$ Å^3, $Z = 4$, $d_{measd} = 2.9$ (1) g cm^{-3},[8] $d_{calcd} = 3.03$ g cm^{-3}, Mo Kα radiation, λ 0.71069 Å, μ(Mo Kα) = 24.0 cm^{-1}; space group uniquely determined as $P4/ncc$ (No. 130) from diffraction symmetry and systematic absences ($hk0$, $h + k = 2n$; $0kl$, $l = 2n$; hhl, $l = 2n$).

Data Collection. The crystal was mounted along the long dimension. Weissenberg and precession photographs confirmed the space group

Table I. Atomic Parameters with Estimated Standard Deviations in Parentheses

Parameter	V	P	Si	O(1)	O(2)	O(3)
x	$^1/_4$[a]	−0.071 07 (4)	$^3/_4$	$^1/_4$	0.411 49 (10)	−0.311 12 (11)
y	$^1/_4$	$-x/a$	$^1/_4$	$^1/_4$	0.402 42 (10)	0.389 44 (11)
z	0.353 33 (5)	$^1/_4$	$^1/_2$	0.548 17 (25)	0.307 91 (13)	0.389 15 (13)
β_{11}[b]	0.001 17 (2)	0.001 40 (2)	0.001 85 (2)	0.003 73 (12)	0.001 77 (10)	0.003 31 (10)
β_{22}	$=\beta_{11}$	$=\beta_{11}$	$=\beta_{11}$	$=\beta_{11}$	0.002 30 (10)	0.002 53 (9)
β_{33}	0.002 07 (4)	0.002 09 (5)	0.001 53 (7)	0.002 42 (20)	0.004 54 (12)	0.003 05 (11)
β_{12}	0.0	−0.000 12 (3)	0.0	0.0	−0.000 61 (6)	0.000 17 (8)
β_{13}	0.0	−0.000 18 (3)	0.0	0.0	−0.001 18 (9)	−0.001 07 (9)
β_{23}	0.0	$=\beta_{13}$	0.0	0.0	0.0034 (9)	0.001 06 (9)

[a] Entries with no esd's are fixed by the symmetry of the space group. [b] The form of the approximation is $f = f_0 \exp[-(\beta_{11}{}^2h^2 + \beta_{22}{}^2k^2 + \beta_{33}{}^2l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Molecular Dimensions

(a) Bond Distances, Å

V-O(1)	1.591 (2)	O(1)′-O(2)	2.876 (2)
V-O(2)	1.977 (1)	O(2)-O(2)‴	2.498 (2)
V-O(1)′	2.492 (2)	O(2)-O(3)	2.518 (1)
P′-O(2)	1.492 (1)	O(2)-O(3)′	2.502 (1)
P′-O(3)	1.572 (1)	O(3)-O(3)′	2.471 (2)
Si-O(3)	1.610 (1)	O(3)′-O(3)″	2.612 (2)
O(1)-O(2)	2.761 (2)	O(3)′-O(3)‴	2.663 (2)
O(2)-O(2)′	2.747 (1)		

(b) Bond Angles, Deg

O(1)-V-O(2)	100.81 (3)	O(3)-P′-O(3)′	103.56 (8)
O(2)-V-O(2)′	87.98 (2)	O(3)′-Si′-O(3)″	108.43 (4)
O(2)-V-O(2)″	158.37 (7)	O(3)″-Si′-O(3)‴	111.58 (7)
O(2)-P′-O(2)‴	113.04 (8)	V-O(2)-P′	146.36 (6)
O(2)-P′-O(3)	110.48 (5)	P′-O(3)-Si	142.21 (6)
O(2)-P′-O(3)′	109.44 (5)		

*P*4/*ncc* (No. 130) previously reported.[2]

Unit cell parameters and intensities were measured using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. An incident-beam collimator of 0.8 mm at a takeoff angle of 4° was used with a 4 mm × 4 mm receiving aperture located 173 mm from the crystal. The pulse height analyzer used with the scintillation counter was set to admit approximately 95% of the diffracted intensity. During data collection the crystal was aligned along a nonprincipal crystallographic direction in order to reduce the effects of multiple diffraction.[9] Unit cell parameters were determined by centering the Kα_1 reflections (λ 0.70926 Å) from 15 reflections with $74° < 2\theta < 82°$ at both positive and negative 2θ and taking the average as the diffraction angle.

All reflections in a quadrant of reciprocal space with $2\theta < 90°$ were collected. The θ–2θ scanning technique with a variable scan speed was used with a 2θ range of $(2.0 + 0.4 \tan°\theta)$ centered about the average peak position. Each reflection was first scanned at a rate of 20.1° min^{-1} to determine its approximate intensity. Reflections were then scanned twice at a slower rate necessary to accumulate a minimum net count of 1000 counts above background. The maximum rate for this slower scan was 6.7° min^{-1} while the minimum rate was 0.9° min^{-1}. Those reflections which were too weak to give the desired net count were scanned twice at the minimum speed. If the results of two slow scans were statistically different, the slow scans were repeated. Background counts were made for one-fourth of the scan time at each end of both scans. Three standard reflections were monitored after measurement of every 60 reflections. These standards did not change significantly during the course of data collection.

Integrated intensities, I, were obtained using the expression $I = C - 2B$, where C is the sum of the counts collected during the two slower scans and B is the sum of the background counts during these scans. A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = [C + 4B]^{1/2}$. The data were corrected for Lorentz–polarization effects. The crystals were measured using a microscope with a micrometer eyepiece and the appropriate absorption corrections applied.[10] Averaging of equivalent reflections gave 1289 independent reflections. I was set equal to $\sigma(I)/2$ for 66 of these reflections which were taken as unobserved ($I_{\text{obsd}} < \sigma(I)$).

Structure Analysis. A Patterson map[11] located the vanadium atoms in position 4c and the phosphorus and silicon atoms in positions 8f and 4b, respectively. A subsequent Fourier map located the oxygen positions. Three weighted refinement cycles of the scale factor, all variable atomic parameters, and isotropic temperature factors reduced R_1 ($R_1 = \sum|F_o - F_c|/|F_o|$) to 0.061 and R_2 ($R_2 = [\sum w|F_o - F_c|^2]^{1/2}/[\sum w|F_o|^2]^{1/2}$) to 0.043. Five subsequent refinement cycles of the scale factor, all variable atomic positions, anisotropic temperature factors, and an isotropic extinction correction reduced R_1 to 0.040 and R_2 to 0.031. Final shifts in the parameters were less than 10% of the estimated standard deviations of the individual parameters. The standard deviation of an observation of unit weight was 3.04. Weights were assigned as $w = 1/\sigma^2(F) = 4F_o{}^2/\sigma^2(F_o{}^2)$. Scattering factors were those of Ibers[12] for V^0, Si^0, P^0, and O^0 with real and imaginary anomalous scattering corrections applied for all atoms.[13] The extinction correction was of the form $F_c{}^{\text{cor}} = F_c/[1 + sF_o]^{1/2}$ with a final s value of 3.24 (9) × 10^{-5}.

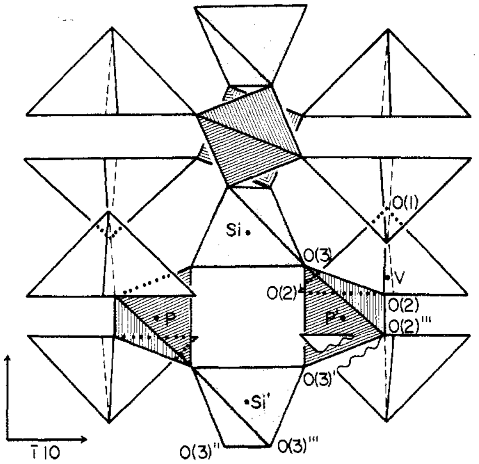

Figure 1. Projection of the structure of VO(SiP$_2$O$_8$) on the 110 plane. SiO$_4$ tetrahedra are dot shaded; PO$_4$ tetrahedra, line shaded; and VO$_5$ square pyramids, open.

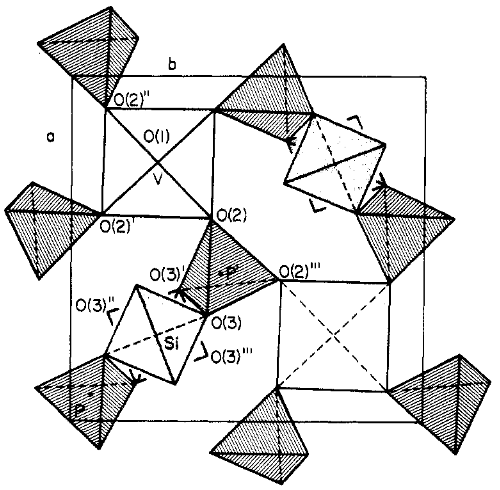

Figure 2. Projection of the structure of VO(SiP$_2$O$_8$) on the 001 plane. SiO$_4$ tetrahedra are dot shaded; PO$_4$ tetrahedra, line shaded; and VO$_5$ square pyramids, open.

The final atomic parameters listed in Table I were used along with the variance–covariance matrix to calculate the distances, angles, and estimated standard deviations reported in Table II. Observed and calculated structure factor amplitudes are listed as the supplementary material.

Discussion

As shown in Figures 1 and 2, the crystal structure of $VO(SiP_2O_8)$ is composed of chains of slightly distorted corner-sharing VO_6 octahedra lying along the fourfold axes of the unit cell and $Si(PO_4)_2Si(PO_4)_2Si$ chains lying along the $\bar{4}$ axes. Both kinds of chains are connected to four chains of the other type by corner sharing of phosphate tetrahedra. Vanadium has crystallographically imposed fourfold symmetry; silicon, $\bar{4}$ symmetry; and phosphorus, twofold symmetry since it is located on a twofold axis perpendicular to the $\bar{4}$ axis.

This arrangement is quite similar to that found in $VO(MoO_4)$[14] and α-$VO(SO_4)$,[15] for example, although in these compounds each tetrahedral anion has all four oxygen atoms linked to (separate) vanadium atoms and there are no condensed-anion chains. The vanadium atoms are linked only indirectly via a V–O–X–O–V (X = P, Mo, S) pathway which explains why the magnetic ordering temperatures observed in $VO(SiP_2O_8)$[2] and $VO(SO_4)$[15] are low. The nature of the ordering phenomena and the reasons for their presence in $VO(SiP_2O_8)$ and $VO(SO_4)$, but apparent absence in $VO(PO_3)_2$,[8] which also has V–O–P–O–V links,[16] must await further study.

The interatomic distances and angles in Table II indicate that the vanadium sits in an almost regular octahedron of oxygen atoms with unique oxygen–oxygen distances of 2.747 (1), 2.761 (2), and 2.876 (2) Å. The vanadium ions are cooperatively displaced along the fourfold axis from the plane of the four symmetry-related oxygen atoms by 0.371 Å giving one short vanadium–oxygen bond (1.591 (2) Å) characteristic of the vanadyl ion, VO^{2+}. Chains of such vanadium–oxygen octahedra are a structural feature of anhydrous vanadyl ion compounds: $VO(Se_2O_5)$,[17] α-$VO(SO_4)$,[15] $VO(MoO_4)$,[14] and $VO(PO_3)_2$[16] also have linear chains, and β-$VO(SO_4)$[18] has zigzag chains.

Short vanadium–oxygen distances are characteristic of vanadyl oxyanion salts in general, and in the silicates haradaite ($Sr(VO)Si_2O_6$),[19] cavansite, and pentagonite (dimorphs of $Ca(VO)Si_4O_{10}\cdot 4H_2O$),[20] distances of 1.573 (5), 1.597 (22), and 1.565 (27) Å are observed, respectively. This bond length varies by about 0.1 Å and the distances observed in the chain compounds are 1.591 (2) Å ($VO(SiP_2O_8)$), 1.594 (17) Å (β-$VO(SO_4)$),[18] 1.605 (6), 1.619 (7), and 1.621 (4) Å ($VO(Se_2O_5)$),[17] 1.63 (3) Å (α-$VO(SO_4)$)[15] and 1.677 (16) Å ($VO(MoO_4)$).[14]

Vanadium is also bonded to four oxygens from separate phosphate groups related by the fourfold axis with a vanadium–oxygen distance of 1.977 (1) Å. The corresponding distances in the vanadyl salts noted above range from 1.958 (8) to 2.056 (18) Å. The octahedron is completed by a sixth oxygen lying along the fourfold axis 2.492 (2) Å from the vanadium. The position of this oxygen trans to the short vanadium–oxygen bond is highly variable ranging from 2.284 (17) Å in α-$VO(SO_4)$to 2.588 (17) Å in $VO(MoO_4)$, and it seems reasonable to describe the vanadium as being in approximately square-pyramidal coordination by oxygen. In cavansite the sixth position is filled by the oxygen of a water molecule 2.887 (33) Å from the vanadium while the sixth position in pentagonite is vacant.

The novel phosphatosilicate chain consists of four-membered rings of tetrahedra ($P_2Si_2O_{12}$) linked via apical Si atoms. The $Si_2P_2O_{12}$ units possess crystallographic 222 symmetry. Each silicon atom is surrounded by an approximate tetrahedron of bridging oxygens while each phosphorus is bonded tetrahedrally to two bridging and to two terminal oxygens. Each of these terminal oxygens constitutes one of the fourfold related oxygen atoms in different VO_6 octahedra.

Such an arrangement allows both phosphate and silicate tetrahedra to achieve ratios of terminal to bridging oxygens commonly found in phosphates and silicates. Although three bridging oxygen atoms are found, for example, in the rare earth pentaphosphates,[21] most condensed phosphates are either pyrophosphates or else linear or cyclic metaphosphates with two terminal and two bridging oxygen atoms per tetrahedron. And although condensed layer and chain silicates with one or two terminal oxygens are not uncommon (indeed the vanadyl ion containing mineral haradaite, $Sr(VO)Si_2O_6$, is a linear metasilicate[19]), silicate tetrahedra with all four oxygens in a bridging role occur in the many framework silicates and aluminosilicates.

Four-membered rings of tetrahedra are commonly found in framework structures but the isolated chain system as found in $VO(SiP_2O_8)$ is unknown in either phosphate or silicate systems. In coesite[22] and the feldspars[23] such rings are linked via oxygen atoms and all oxygen atoms provide links to other tetrahedra. Linkage through oxygen is also found in vlasovite ($Na_4Zr_2(Si_8O_{22})$),[24] where there are $(Si_4O_{11})_\infty$ ribbons, and cavansite, ($Ca(VO)(Si_4O_{10})\cdot 4H_2O$),[20] a sheet silicate. Discrete rings occur in kainosite ($Ca_2(Y,Ln)_2[Si_4O_{12}]CO_3\cdot H_2O$),[25] in taramellite ($Ba_2(Fe,Ti,Mg)_2H_2[O_2(Si_4O_{12})]$),[26] and in several cyclic tetrametaphosphates.[27] Linkage of four-membered rings by Si or Al atoms, in the manner found in $VO(SiP_2O_8)$, may be discerned in framework structures such as sodalite and analcime,[23] but again all oxygens have a bridging role to provide links in three dimensions to other tetrahedra.

The dimensions within the $Si_2P_2O_{12}$ unit agree closely with corresponding dimensions in P_4O_{12} and Si_4O_{12} systems. Thus, the silicon–oxygen distance of 1.610 (1) Å equals the average silicon–oxygen distance of 1.612 Å reported in ref 28 for 10 silicates. This distance is close to those observed in the discrete Si_4O_{12} rings in kainosite[25] and taramellite[26] and in the chains of Si_4O_{12} rings in coesite[22] and vlasovite.[24] The Si–O–P angle of 142.21 (6)° is in a range found in both Si_4O_4 and P_4O_4 rings.

The phosphorus–oxygen distances are close to average phosphorus–oxygen distances in cyclic and linear metaphosphates. The phosphorus to bridging oxygen distance of 1.572 (1) Å is slightly shorter than the average values of 1.608 and 1.594 Å reported by Baur[29] while the terminal phosphorus–oxygen distance of 1.492 (1) Å is slightly longer than the average of 1.480 Å for cyclic metaphosphates but very close to the average of 1.489 Å for linear metaphosphates. As in other cyclic and linear metaphosphate systems,[29] the O–P–O angles increase in the order of O(b)–P–O(b) < O–P–O(b) < O–P–O where O(b) indicates a bridging oxygen and O a terminal oxygen.

None of the structural features observed in this work suggest that condensed phosphatosilicates are inherently unstable. The limited number of examples of such systems may simply reflect a lack of preparative effort in this area. The example of $VO(SiP_2O_8)$ indicates that arrangements of tetrahedra in patterns not found either in phosphates or in (alumino) silicates may be expected.

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Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Structural Characterization of Bis[dichloroaquo(pyridine *N*-oxide)copper(II)]

EVA DIXON ESTES and DEREK J. HODGSON*

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The crystal and molecular structure of bis[dichloroaquo(pyridine *N*-oxide)copper(II)], $[Cu(pyO)(H_2O)Cl_2]_2$, has been determined from three-dimensional x-ray data collected by counter methods. The material crystallizes in the space group $P\bar{1}$ of the triclinic system with one dimeric formula unit in a cell of dimensions $a = 7.976$ (2), $b = 9.469$ (3), $c = 5.906$ (1) Å; $\alpha = 81.02$ (2), $\beta = 96.38$ (2), and $\gamma = 98.77$ (3)°. The observed and calculated densities are 1.88 and 1.899 g cm^{-3}, respectively. Least-squares refinement of the structure based on 2335 independent reflections has led to an R factor (on F) of 0.051. The structure consists of oxygen-bridged dimers with a Cu–Cu' separation of 3.272 (1) Å and a Cu–O–Cu' angle of 109.4 (1)°. The coordination about the copper atoms is tetragonal pyramidal with two chlorine and two oxygen atoms forming the base and a water oxygen atom at the apex. The observed magnetic and conductivity properties of the complex are readily understood in the light of the observed structure.

Introduction

A number of 1:1 and 2:1 complexes of pyridine *N*-oxide and copper halides have been prepared and characterized.[1-9] The abnormally low room-temperature magnetic moments of these complexes suggested a dimeric or polymeric structure with the bridging oxygen atoms of the pyridine *N*-oxide ligands providing a pathway for a superexchange mechanism. Subsequent structure determinations indicated that the 2:1 complexes $[Cu(pyO)_2Cl_2]_2$ and $[Cu(pyO)_2Br_2]_2$ are dimeric[8,9] with one pyridine *N*-oxide ligand acting as a bridge and the other as a monodentate ligand. In $[Cu(pyO)_2Cl_2]_2$ the coordination at the copper atom is tetragonal pyramidal[9] with the terminal pyridine *N*-oxide ligand in the apical position; in $[Cu(pyO)_2Br_2]_2$ the coordination at the copper atom is trigonal bipyramidal[8] with the terminal pyridine *N*-oxide ligand in an equatorial position.

In the 1:1 complexes $[Cu(pyO)Cl_2]_x$ and $[Cu(pyO)Br_2]_x$, the geometry around the copper is tetragonal pyramidal with the pyridine *N*-oxide ligand bridging two copper atoms, but the apical position is now occupied by a distant halide atom from an adjacent dimer, forming infinite chains of dimers.[6,7]

The complexes $[Cu(pyO)_2Cl_2]_2$, $[Cu(pyO)Cl_2]_x$, and $[Cu(pyO)Br_2]_x$, which have similar geometries at the copper centers, show[10] a correlation between the Cu–O–Cu bridging angle, ϕ, and the singlet–triplet splitting, $2J$, which is like that reported for hydroxo-bridged copper dimers, namely, that as ϕ increases $2J$ decreases.[11]

Kokoszka and coworkers have determined the magnetic[12,13] and conductometric[14] properties of the complex dichloroaquo(pyridine *N*-oxide)copper(II), $Cu(pyO)(H_2O)Cl_2$, which they proposed should be of the 2:1 structure type with a water molecule replacing the nonbridging pyridine *N*-oxide ligand. The large negative $2J$ value of -885 cm^{-1} is almost identical with the value[15] of -880 cm^{-1} reported for $[Cu(pyO)_2Cl_2]_2$, which suggests that the complexes may have very similar geometries. However, the unusually high conductivity[14] of the aquo complex suggests that there may be an additional pathway for magnetic exchange. In order to investigate this possibility and to further our understanding of the relationship between the structural and magnetic properties of copper(II) complexes, we have undertaken a complete three-dimensional analysis of the crystal structure of $[Cu(pyO)(H_2O)Cl_2]_2$.

Experimental Section

Bright green crystals of $[Cu(pyO)(H_2O)Cl_2]_2$ were prepared by the following method. Pyridine *N*-oxide was added dropwise to a concentrated solution of $CuCl_2{\cdot}2H_2O$ in approximately 50 ml of hot ethanol until a yellow-green precipitate formed. Water was then added dropwise until the precipitate redissolved. Crystals were obtained from the filtered solution after standing for a few days.

On the basis of precession and Weissenberg photographs, the crystals were assigned to the triclinic system. No systematic absences were observed, which implies that the space group is either $P1$ or $P\bar{1}$. The latter space group was chosen and subsequent refinement of the structure indicated that this choice is the correct one. The cell constants, obtained by the least-squares method of Busing and Levy,[16] are $a = 7.976$ (2), $b = 9.469$ (3), $c = 5.906$ (1) Å; $\alpha = 81.02$ (2), $\beta = 96.38$ (2), and $\gamma = 98.77$ (3)°. A density of 1.899 g cm^{-3}