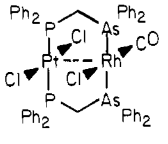
undergoes isomerization to **3** ($^{31}P\{^1H\}$ NMR: δ 16.4, $^1J(Pt,P)$ = 2880 Hz. IR: $\nu(CO)$ = 1965 cm^{-1}). The spectroscopic properties, particularly the carbonyl stretching frequencies, indicate that oxidative addition of Pt–Cl bond to the rhodium center has not occurred during these reactions.



3

The details of the structure **2** have been obtained by X-ray diffraction study.[5] A perspective drawing of the molecule is shown in Figure 1. Although the molecule has no crystallographically imposed symmetry, there is a virtual mirror plane passing through Pt, Rh, Cl(1) and the carbonyl group. The coordination about rhodium consists of a *trans*-Rh(CO)ClAs$_2$ group while at platinum it involves a *cis*-PtP$_2$Cl$_2$ unit. The Pt···Rh separation is 3.043 (1) Å, a value that is significantly longer than that expected for a Pt–Rh single bond.[6] Other interatomic distances for bonded atoms fall within the normal ranges.

A number of features of this structure are noteworthy. The metal–metal separation, 3.043 (1) Å, is comparable to those in other face-to-face dimers where a metal–metal single bond is absent.[4] Thus, the face-to-face structure seems to require a larger metal–metal separation than is apparently possible with a small-bite ligand like Ph$_2$Ppy. The arrangement of the bridging dapm ligands is unique for a face-to-face dimer. The trans/trans arrangement, as shown for **3**, is quite common for binuclear complexes,[4] and examples of a cis/cis unit are known.[7] The only cases where a cis/trans bridging arrangement has been seen previously are binuclear complexes where a five-coordinate metal center is bonded to a four-coordinate metal atom.[8] The complex as prepared appears to be isomerically pure with regard to the relative orientation of the rhodium carbonyl and chloride ligands toward the *cis*-PtP$_2$Cl$_2$ group. There is no evidence in the crystal structure for disorder of these groups, and in solution the spectroscopic properties do not indicate the presence of another isomer. Additionally there is no evidence for the formation of any head-to-tail isomers under the comparatively mild condition of our reactions. We have previously noted several examples of the formation of head-to-head/head-to-tail isomers with dapm as the bridging ligands.[9] The lack of isomerization of this type in the present case probably is a reflection of the relative inertness of the Pt(II)–P bond. It is unlikely that the relative orientation of these bridging ligands (i.e., head-to-head/head-to-tail isomerization) will have a marked effect on the metal–metal separation.

Acknowledgment. We thank the National Science Foundation (Grant CHE8217954) for financial support. F.E.W. was the holder of a University of California Regents' Fellowship.

Registry No. **2**·CH$_2$Cl$_2$, 88867-60-1; **3**, 88928-90-9; *cis*-(dapm)$_2$PtCl$_2$, 88867-61-2; Rh$_2(\mu$-Cl$)_2$(CO)$_4$, 14523-22-9; LPtCl$_2$ (L = 1,5-cyclooctadiene), 12080-32-9.

Supplementary Material Available: Listings of atomic fractional coordinates and temperature factors, bond lengths, bond angles, and crystallographic data for Rh(CO)Cl(μ-dapm)$_2$PtCl$_2$·CH$_2$Cl$_2$ (6 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of California
Davis, California 95616

Rosalvina R. Guimerans
Fred E. Wood
Alan L. Balch*

Received November 16, 1983

---

(5) Single crystals of *trans*-Rh(CO)Cl(μ-Ph$_2$AsCH$_2$PPh$_2$)$_2$-*cis*-PtCl$_2$·CH$_2$Cl$_2$ were grown by diffusion of diethyl ether into a dichloromethane solution of the complex. They belong to the space group $P2_1/c$ (No. 14) with a = 18.760 (3) Å, b = 11.610 (3) Å, c = 22.954 (6) Å, β = 92.81 (2)°, and Z = 4, at 140 K. Refinement yielded R = 3.8% for 6415 reflections with $F > 6\sigma(F)$ and 572 parameters.

(6) A value of ca. 2.6 Å is to be expected on the basis of the Pd–Rh distance of 2.594 (1) Å found for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$.[2f]

(7) (a) Puddephatt, R. J.; Thomson, M. A.; Manojlović-Muir, L.; Muir, K. W.; Frew, A. A.; Brown, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, *805*. (b) Ling, S.-S. M.; Puddephatt, R. J.; Manojlović-Muir, L.; Muir, K. W. *Inorg. Chim. Acta* **1983**, *77*, L95.

(8) (a) Haines, R. J.; Meintjies, E.; Laing, M. *Inorg. Chim. Acta* **1979**, *36*, L403. (b) Anderson, M. P.; Pignolet, L. H. *Organometallics* **1983**, *2*, 1246. (c) Ladd, J. A.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.*, in press. (d) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500.

(9) Guimerans, R. R.; Balch, A. L. *Inorg. Chim. Acta* **1983**, *77*, L177.

Ambient- and Low-Temperature Crystal Structure of Vanadyl Hydrogen Phosphate, (VO)$_2$H$_4$P$_2$O$_9$

Sir:

Vanadium phosphorus oxides are known to act as heterogeneous catalysts in the oxidation of *n*-butane and *n*-butene to maleic anhydride.[1] A study of the crystal structures of these phosphates is valuable in understanding the mechanisms of the catalytic process. Recently, the crystal structure of the catalytically important compound (VO)$_2$P$_2$O$_7$ was reported.[2] This structure is built of double chains of VO$_6$ octahedra that share opposite corners along the chain and share edges across the chain. Pyrophosphate groups link the double chains into a three-dimensional network by sharing oxygen corners with vanadium.

The vanadyl pyrophosphate is formed from its precursor, (VO)$_2$H$_4$P$_2$O$_9$, by heating at 400 °C. A study of the precursor is important because it apparently controls the microstructure of the final catalyst. Recently, this precursor has been formulated as a hydrated pyrophosphate, i.e., (VO)$_2$P$_2$O$_7$·2H$_2$O, on the basis of thermogravimetric and infrared data.[3] Described here is the crystal growth and ambient- and low-temperature X-ray structure determinations of (VO)$_2$H$_4$P$_2$O$_9$. Although structurally related to (VO)$_2$P$_2$O$_7$, the precursor is composed of vanadyl hydrogen phosphate layers.

Crystals of (VO)$_2$H$_4$P$_2$O$_9$ were grown hydrothermally in a sealed gold tube under 3 kbar pressure by slowly cooling from 500 °C a mixture of VO$_2$ and 85% H$_3$PO$_4$ in mole ratio 1:1.2. X-ray powder diffraction, thermogravimetric analyses, and infrared data confirmed the material as the desired phase.

The crystal structure[4,5] consists of vanadyl hydrogen

---

(1) Bordes, E.; Courtine, P. *J. Catal.* **1979**, *57*, 236.

(2) Gorbunova, Yu. E.; Linde, S. A. *Sov. Phys.—Dokl.* (*Engl. Transl.*) **1979**, *24*, 138.

(3) Poli, G.; Resta, I.; Ruggeri, O.; Trifiro, F. *Appl. Catal.* **1981**, *1*, 395.

(4) Room-temperature crystal structure information: orthorhombic, space group *Pmmn*, a = 7.416 (1) Å, b = 9.592 (2) Å, c = 5.689 (1) Å, V = 404.7 Å^3, Z = 2; CAD4 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, θ–2θ scans, $2 < \theta < 30°$, 2501 reflections. An analytical absorption correction was applied with use of a Gaussian grid of 8 × 8 × 8; transmission factors ranged from 0.68 to 0.93. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques: 605 reflections with $I > 2\sigma(I)$, 58 variables (V, P, and O with anisotropic thermal parameters; H with isotropic parameters), anomalous dispersion correction for V and P, R = 0.022, R_w = 0.023. The hydrogen atom that forms the water molecule (H1) was refined reasonably well; parameters for the other hydrogen atom (H2) had higher standard deviations because of half-occupancy due to statistical disorder. An average isotropic thermal parameter was used for the hydrogen atoms in Figure 1. Oxygen atoms O2 and O3 initially exhibited relatively large B_{11} and B_{22} terms, respectively, when positioned on mirror planes (as shown in Figure 1). When these atoms were finally refined with half-occupancy in a position just off of their respective mirror planes, the thermal ellipsoids were reasonable and standard deviations and R factor were lowered. An ordered structure was not found with use of the room-temperature data in the lower symmetry space group $P2_12_12$.

0020-1669/84/1323-1308$01.50/0

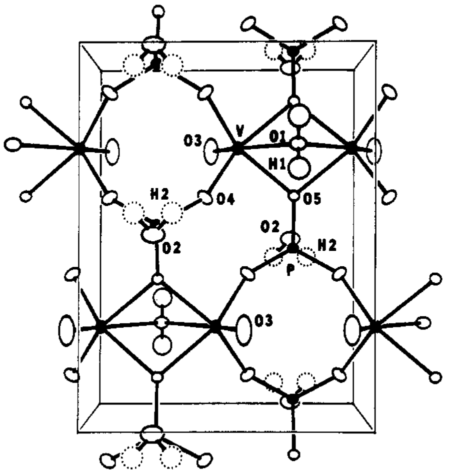


Figure 1. ORTEP drawing of a section of a layer in $(VO)_2H_4P_2O_9$ at room temperature. Selected bond distances (Å) are as follows: V–V, 3.094; V–O3, 1.587; V–O1, 2.336; O1–H1, 0.78; O2–H2, 0.69.

phosphate layers stacked along the c axis and held together by interlayer hydrogen bonding. Figure 1 shows a section of one layer (at room temperature) containing pairs of face-sharing VO_6 octahedra. Although each vanadium atom has available one electron for metal–metal bonding, a V–V bond does not exist in this compound. One of the face-shared oxygen atoms (O1) is from a water molecule that bridges the two vanadyl groups. The four remaining oxygen atoms of each octahedron are shared with phosphate tetrahedra. These tetrahedra are oriented with a pseudo threefold axis perpendicular to the plane of the layers, and only the basal oxygen atoms of these trigonal pyramids are shared with vanadium. The remaining hydrogen atoms are bound to the apical oxygen atoms of the phosphate groups.

Each hydrogen atom of a shared water molecule is hydrogen bonded to an apical phosphate oxygen atom in an adjacent layer. Also, the covalently bonded hydrogen atoms on these apical oxygen atoms are hydrogen bonded to vanadyl oxygen atoms of a neighboring layer. At ambient temperature, vanadyl oxygen, apical phosphate oxygen, and associated hydrogen atoms each are statistically disordered between two equivalent positions and an average structure results. Disordered hydrogen atom (H2) sites are represented by dotted circles and disordered oxygen atoms (O2 and O3) by elongated thermal ellipsoids[4] in Figure 1. At lower temperatures (i.e., ~−130 °C), these hydrogen and oxygen atoms are ordered. A doubling of the c axis occurs at the lower temperature because atomic ordering occurs not only within the layers but also between adjacent layers. The unit cell of the ordered structure contains two stacked layers. Sections of these two layers are shown in Figure 2.

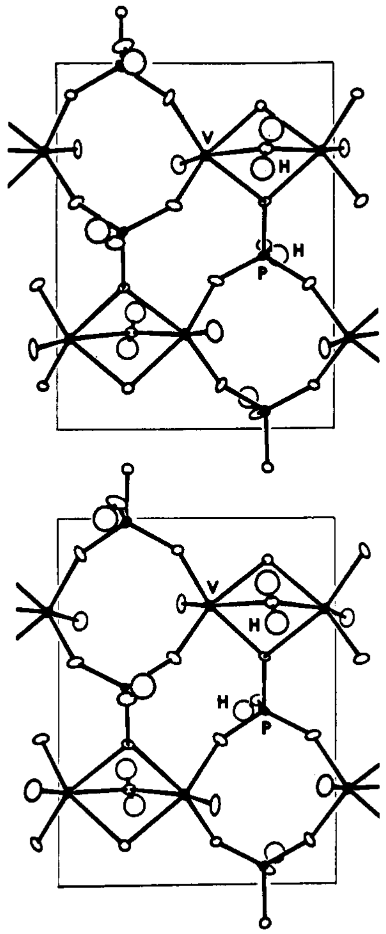


Figure 2. ORTEP drawing showing sections of the two ordered layers in the unit cell of $(VO)_2H_4P_2O_9$ at −130 °C.

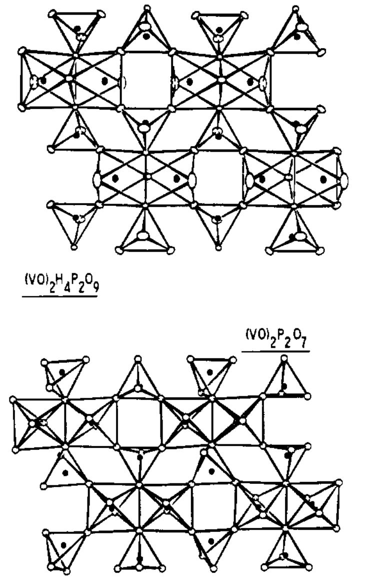


Figure 3. Comparison of $(VO)_2H_4P_2O_9$ and $(VO)_2P_2O_7$ in terms of connected octahedra and tetrahedra. Only half of each pyrophosphate group is shown for $(VO)_2P_2O_7$.

A structural relationship between $(VO)_2H_4P_2O_9$ and $(VO)_2P_2O_7$ is clearly evident from this study. Figure 3 compares the two structures in terms of connected octahedra and tetrahedra. For clarity, only half of each pyrophosphate group is pictured for $(VO)_2P_2O_7$. In this compound, the double chains of edge-sharing VO_6 octahedra run perpendicular to the plane of the drawing. On the basis of a study of the two structures and a minimum energy requirement, a mechanism

---

(5) Low-temperature (−130 °C) crystal structure: monoclinic, space group $P2_1/c$, a = 11.159 (2) Å, b = 7.401 (1) Å, c = 11.360 (2) Å, β = 120.73 (2)°, V = 2(403.2) Å^3, Z = 4; Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, ω scans, $2 < \theta < 27.5°$, 1950 reflections. An analytical absorption correction was applied with use of a Gaussian grid of 8 × 8 × 8; transmission factors ranged from 0.53 to 0.92. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques: 1646 reflections with $I > 2\sigma(I)$, 152 variables (V, P, and O with anisotropic thermal parameters; H with isotropic parameters), anomalous dispersion correction for V and P, R = 0.068, R_w = 0.092. At −100 °C, an incommensurate ordering along the b axis of the room-temperature cell was evidenced from axial oscillation photographs. Because the data for the ordered structure were collected near this temperature (i.e., −130 °C), the high residuals were attributed to background noise arising from a partially disordered atomic arrangement. For this reason, the hydrogen atoms were not refined as well as would have been expected. An average isotropic thermal parameter was used for the hydrogen atoms in Figure 2.

for conversion to the pyrophosphate is postulated. This involves loss of the bridging H_2O molecule with movement of the resulting square pyramids around the edge-shared "hinge" to a position where vanadyl groups are parallel. Half of the vanadyl oxygen atoms are slightly shifted, giving rise to the edge-shared octahedral arrangement where the octahedral dimers have vanadyl bonds pointing in opposite directions.[2] After proton migration, half of the phosphate tetrahedra each lose an apical oxygen atom in the form of an H_2O molecule. These coordinately unsaturated PO_3 units invert and interact with PO_4 tetrahedra above or below to form pyrophosphate groups. This mechanism leaves all V–O–P connections intact and involves primarily the breaking of weak V–OH_2 and P–OH_2 bonds. Although a structural change occurs on an atomic level, no change in particle morphology was observed in scanning electron micrographs taken before and after the structural conversion.

Acknowledgment. The authors thank R. Jakeman for valuable discussions and M. Sweeten for technical assistance.

Registry No. $(VO)_2H_4P_2O_9$, 89415-02-1.

Supplementary Material Available: Listings of positional and thermal parameters and interatomic distances (2 pages). Ordering information is given on any current masthead page.

---

(6) Contribution No. 3424.

Central Research and Development Department[6]
E. I. du Pont de Nemours and Company
Experimental Station
Wilmington, Delaware 19898

C. C. Torardi*
J. C. Calabrese

Received January 9, 1984

Articles

Contribution from the Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia, and Institut für Physikalische Chemie, Westfälische Wilhems-Universitat, Münster D-4400, West Germany

EPR and Optical Spectra of $CuCl_4^{2-}$ Doped into Single Crystals of Several Zinc(II) Host Lattices

ROBERT J. DEETH,[†] MICHAEL A. HITCHMAN,*[†] GERHARD LEHMANN,[‡] and HUBERT SACHS[‡]

Received June 1, 1983

The EPR and electronic spectra of copper-doped diethylenediammonium hexachlorozincate(II), $(enH_2)_2Zn[Cu]Cl_6$, cesium tetrachlorozincate(II), and rubidium tetrachlorozincate(II) are reported and in each case suggest the presence of distorted-tetrahedral $CuCl_4^{2-}$ ions. At 77 K the EPR spectrum of $(enH_2)_2Zn[Cu]Cl_6$ exhibits both copper hyperfine and chlorine superhyperfine structure. As with other pseudotetrahedral copper(II) complexes the hyperfine parameters cannot be explained satisfactorily from the simple equations generally used for planar and distorted-octahedral complexes. The principal axis of each superhyperfine tensor apparently deviates significantly from the chlorine–copper bond direction, and it is suggested that this is probably because the ligands do not lie along the molecular x and y axes. The molecular **g** tensor of $(enH_2)_2Zn[Cu]Cl_6$ is highly rhombic, with the d_{z^2} orbital making a significant contribution to the metal part of the ground-state wave function. Angular-overlap calculations suggest that the rhombic perturbation to the ligand field in this compound is caused by a substantial difference between the angles subtended by the chlorine ligands at the copper ion, and the distortions estimated for the $CuCl_4^{2-}$ ions present in all three complexes are interpreted in terms of Jahn–Teller and lattice-induced perturbations.

Introduction

The compounds of copper(II) exhibit an unusually wide range of stereochemistries.[1] Moreover, these complexes tend to be quite plastic:[2] that is, they can often be readily deformed so that factors such as crystal packing and hydrogen bonding may strongly influence the geometry of any particular molecule. This is the case, for instance, for the $CuCl_4^{2-}$ ion, which exhibits a stereochemistry ranging from near-tetrahedral in $((CH_3)_3NH)_3Cu_2Cl_7$[3] to square planar in, for instance, $[C_6H_5C_2H_4N(CH_3)H_2]CuCl_4$.[4] There are many examples of intermediate geometries, with the majority of tetrachlorocuprates having a flattened tetrahedral ligand arrangement of approximately D_{2d} symmetry.[5] The stereochemistry of copper(II) complexes is thought to be strongly influenced by the Jahn–Teller effect, which predicts that a regular tetrahedral geometry should be unstable. Qualitatively, the geometries observed for the $CuCl_4^{2-}$ ion may be rationalized in terms of a distortion along one component of the active Jahn–Teller mode of E symmetry,[6] with the final structure being determined by a balance between the ligand field stabilization of the square-planar geometry and the destabilizing effect of ligand–ligand repulsions.

Because of its relative simplicity and wide range of stereochemistries, the electronic structure of the $CuCl_4^{2-}$ ion has been the subject of numerous theoretical studies, from detailed molecular orbital calculations[7,8] through simple angular-overlap[9-11] and crystal field[12] calculations. Experimentally,

---

[†] University of Tasmania.
[‡] Westfälische Wilhems-Universitat.

(1) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 43. Hathaway, B. J. *Struct. Bonding (Berlin) 14*, **1973**, 49.
(2) Gays, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melrick, M.; Serator, M.; Valach, F. *Coord. Chem. Rev.* **1976**, *19*, 253. Hathaway, B. J. *Ibid.* **1981**, *35*, 211.
(3) Clay, R. M.; Murray-Rust, P.; Murray-Rust, J. *J. Chem. Soc., Dalton Trans.* **1973**, 593.
(4) Harlow, R. L.; Wells, W. J., III; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.
(5) For a review of all aspects of chlorocuprate chemistry see: Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.
(6) Bacci, M. *Chem. Phys.* **1979**, *40*, 237.
(7) Ros, P.; Shuit, G. C. G. *Theor. Chim. Acta* **1966**, *4*, 1.
(8) Demuynck, J.; Veillard, A.; Wahlgren, U. *J. Am. Chem. Soc.* **1973**, *95*, 5563.
(9) Day, P.; Jørgensen, C. K. *J. Chem. Soc.* **1964**, 6226.