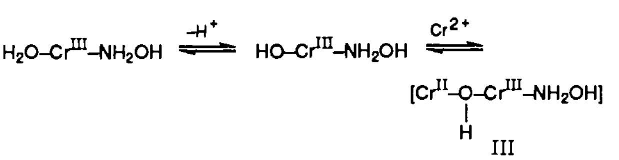
reactions must be more rapid than transfer from bromate, for the principal reduction product is Br^-, even when BrO_3^- is taken in excess. In this case, the further rapid oxidation of HNO_2 to NO_3^- accommodates the observed 3:2 stoichiometry.

Reduction by U(III) necessarily involves a pair of 1e⁻ transactions (sequence 7). An internal 2e⁻ shift is needed here as well,

$$[\mathrm{Cr^{I}{-}N{\equiv}O}]^{2+} \xrightarrow{\mathrm{U^{III}}} [\mathrm{Cr{-}N\overset{\bullet}{=}O}]^{+} \xrightarrow[\mathrm{3H^+}]{\mathrm{U^{III}}} [\mathrm{Cr^{III}{-}NH_2OH}]^{3+} \quad (7)$$

but we cannot say where in the sequence this occurs. The observed release of uncomplexed hydroxylamine is not wholly expected in view of the recorded[20] very slow aquation of the closely related Cr–N bond in $Cr(H_2O)_5(NH_3)^{3+}$ and the reported[21] persistence of Cr(III) complexes of hydroxylamine in aqueous solution. We suspect that aquation in this instance is catalyzed by traces of Cr(II) present in this strongly reducing solution (sequences 8,9).



$$\mathrm{H_2O{-}Cr^{III}{-}NH_2OH} \overset{-\mathrm{H^+}}{\rightleftharpoons} \mathrm{HO{-}Cr^{III}{-}NH_2OH} \overset{\mathrm{Cr^{2+}}}{\rightleftharpoons} [\mathrm{Cr^{II}{-}\underset{\displaystyle \mathrm{H}}{\underset{|}{O}}{-}Cr^{III}{-}NH_2OH}] \quad (8)$$

III

$$\mathrm{III} \rightarrow \mathrm{Cr^{III}{-}OH} + \mathrm{Cr^{2+}} + \mathrm{NH_2OH} \quad (9)$$

In sum, this study underscores the unique ability of the nitrosonium function to stabilize Cr(I), doubtless reflecting the capacity of this group to partake in strong metal-to-ligand back-bonding.[21] When this ligand is altered electronically, by either oxidation or reduction, rapid internal electron transfer generates the familiar tripositive state.

Acknowledgment. We thank Ms. Arla McPherson for technical assistance.

---

(20) Espenson, J. H.; Carlyle, D. W. *Inorg. Chem.* **1966**, *5*, 586. These workers report a half-life period of approximately 3000 h for this aquation at 45 °C.

(21) Ivashkovich, E. M.; Zhelekovskaya, L. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 33; *Chem. Abstr.* **1979**, *90*, 145161w.

(22) See, for example: Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

Contribution from the Department of Chemistry,
University of New Orleans,
New Orleans, Louisiana 70148

Synthesis and Crystal Structure of a Novel Layered Zintl Phase: $K_3Ga_3As_4$

Teresa L. T. Birdwhistell, Edwin D. Stevens,
and Charles J. O'Connor*

Received December 18, 1989

The semiconducting industry is actively searching for new types of semiconducting phases as well as new techniques for the preparation of crystalline and thin-film forms of known semiconducting phases. Of particular interest are the IV and III–V type semiconductors. A great deal of research has been reported on the methods of preparation of III–V type semiconductors.[1] Most of these techniques involve some sort of vapor-phase deposition to form structured films. For example, (AlGa)As/GaAs[2-6] and InP·(InGa/As) and (InGa)(AsP)[7-9] have been deposited via molecular beam epitaxy (MBE) and (AlGa)As/GaAs[10,11] have been prepared via organometallic vapor-phase epitaxy (OMVPE). The usual form of arsenic used for these preparations is AsH_3 or AsR_3 (where R is an organic group).[13,14] Other alternatives involve adducts of Ga–As complexes[15-18] or arsenic–organosilanes.[12] Because of the problems associated with AsH_3, new approaches to the formation of GaAs films are desirable.

Another approach to the synthesis of III–V semiconductors is through the use of I–III–V Zintl phase materials as precursors. The reactivity of Zintl phase materials affords the possibility of solution-phase deposition of semiconducting films and perhaps the layering of metal–semiconductor deposition.[19,20] The reaction of a I–III–V Zintl phase with a III–VII salt (e.g., $GaCl_3$) would produce a III–V phase and a water-soluble alkali-metal halide.

Besides their potential for solution chemistry, the ternary Zintl phase materials are intrinsically interesting. In recent years a large number of crystal structures of ternary Zintl phase materials have been reported.[21-25] These materials display a wide range of structures, from discrete molecular units to one- or two-dimensional polymeric arrays. Despite the wealth of structural information that is unfolding, little is being done to explore the physical and chemical properties of these materials.

We have undertaken the synthesis of a series of I–III–V ternary Zintl phase materials, both as a preliminary step in the investigation of new synthetic routes to the preparation of III–V type semiconductors and for the purpose of investigating their electrical, magnetic, and structural properties. Several I–III–V Zintl phase materials have already appeared in the literature: $KGaSb_2$,[26] $K_3Al_2As_3$,[27] $Na_7Al_2Sb_5$,[28] $Na_2Al_2Sb_3$,[29] and $K_2Al_2Sb_3$.[29] The

---

(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Collins, D. M. Frontiers of Electronic Materials Processing. *AIP Conf. Proc.* **1986**, *138*, 140.

(2) Cho, A. Y.; Casey, H. C. *Appl. Phys. Lett.* **1974**, *25*, 288.

(3) Tsang, W. T.; Logan, R. A.; Salathe, R. P. *Appl. Phys. Lett.* **1979**, *34*, 413.

(4) Fujii, T.; Hiyamizu, S.; Wada, O.; Sugahara, T.; Yamakoshi, S.; Sakurai, T.; Hashimoto, H. *J. Cryst. Growth* **1983**, *61*, 393.

(5) Fujii, T.; Hiyamizu, S.; Yamakoshi, S.; Ishikawa, T. *J. Vac. Sci. Technol.* **1985**, *B3*, 776.

(6) Iwamura, H.; Saku, T.; Kobayashi, H.; Horikoshi, Y. *J. Appl. Phys.* **1983**, *54*, 2692.

(7) Tsang, W. T. *Appl. Phys. Lett.* **1984**, *44*, 288.

(8) Kawamura, Y.; Asahi, H.; Nagai, H. *J. Appl. Phys.* **1983**, *54*, 841.

(9) Masu, K.; Mishima, T.; Hiroi, S.; Konagai, S.; Takahashi, K. *J. Appl. Phys.* **1983**, *53*, 7558.

(10) André, J. P.; Brière, A.; Rocchi, M.; Riet, M. *J. Cryst. Growth* **1984**, *68*, 445.

(11) Hersee, S. D.; Hirtz, J. P.; Baldy, M.; Duchemin, J. P. *Electron. Lett.* **1982**, *18*, 1076.

(12) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. A. *Chem. Mater.* **1989**, *1*, 4.

(13) Leys, M. R. *Chemtronics* **1987**, *2*, 155.

(14) Stringfellow, G. B. *J. Electron. Mater.* **1988**, *17*, 327.

(15) Zaouk, A.; LeBugle, A.; Constant, G. J. *J. Cryst. Growth* **1979**, *46*, 415.

(16) Maury, F.; Constant, G. J.; Fontain, P.; Biberian, J. P. *J. Cryst. Growth* **1986**, *78*, 185.

(17) Maury, F.; Hammadi, A.; Constant, G. J. *J. Cryst. Growth* **1984**, *68*, 88.

(18) Byrne, E. K.; Theopold, K. H. *Science* **1988**, *241*, 332.

(19) Haushalter, R. C. *Angew. Chemie* **1983**, *95*, 560.

(20) Haushalter, R. C.; Krauss, L. J. *Thin Solid Films* **1983**, *102*, 2312.

(21) Schäfer, H. *Annu. Rev. Mater. Sci.* **1985**, *15*, 1.

(22) Schäfer, H.; Eisenmann, B.; Muller, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 694 and references therein.

(23) von Schnering, H. G. *Bol. Soc. Quim.* **1988**, *33*, 41.

(24) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(25) Lii, K.-H.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *67*, 374.

(26) Cordier, G.; Ochman, H.; Schäfer, H. *J. Less Common Met.* **1986**, *119*, 291–296.

(27) Cordier, G.; Ochman, H.; Schäfer, H. *Rev. Chim. Miner.* **1985**, *22*, 58–63.

(28) Cordier, G.; Ochman, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1984**, *517*, 118.

(29) Cordier, G.; Ochman, H.; Schäfer, H. *Rev. Chim. Miner.* **1984**, *12*, 282–291.

0020-1669/90/1329-3892$02.50/0

Table I. Crystal Data and Measurement Conditions for $K_3Ga_3As_4$

$K_3Ga_3As_4$	fw 626.1
$a = 6.597$ (2) Å	space group *Pnna* (No. 52)
$b = 14.792$ (4) Å	λ(Mo Kα) = 0.709 30 Å
$c = 10.589$ (3) Å	μ(Mo Kα) = 209.5 cm^{-1}
$V = 1033.5$ (5) Å^3	trans coeff = 0.14–1.00
$Z = 4$	$R = 0.071$
$T = 100$ (5) K	$R_w = 0.060$

physical properties of these materials are currently under investigation. We report here on the preparation, crystal structure, and physical properties of a new two-dimensional layered polymeric Zintl phase material: $K_3Ga_3As_4$.

Experimental Section

Synthesis. $K_3Ga_3As_4$ was prepared by direct combination of the elements at elevated temperatures. In a typical preparation, a dry quartz or Vycor tube was charged with 0.44 g of K (11 mmol), 0.24 g of Ga (3.4 mmol), and 0.56 g of As (7.5 mmol). The sample tube was evacuated at a pressure of approximately 0.005 Torr for at least 1.5 h and then sealed under vacuum. The sample tube was placed inside a larger diameter tube, which was similarly evacuated and sealed. The sample was heated at 750 °C in a tube furnace for 10 h and then cooled to ambient temperature over a 40-h period. A metallic black crystalline product was obtained. Side reactions produce an orange powder that was readily isolated from the $K_3Ga_3As_4$ product by mechanical separation. No attempt was made to identify the orange powder. The metallic black crystalline $K_3Ga_3As_4$ can be isolated in approximately 85% yield (based on Ga).

Resistivity Measurements. Resistivity measurements on pressed pellets were made by using a linear four-probe method.[30] The current was supplied by a Keithley Model 224 programmable current source, and the voltage drop across the sample was measured with a Keithley Model 181 digital nanovoltmeter.

Crystallography. Single crystals of $K_3Ga_3As_4$ were separated under a protective coat of hydrocarbon oil and examined by using a microscope. An irregular crystalline plate was attached to a glass fiber by using silicon grease, rapidly transferred from the oil to an Enraf-Nonius CAD-4 diffractometer, and cooled to 100 (5) K with a stream of cold N_2 gas. Unit cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with $37° \leq 2\theta \leq 61°$. Systematic absences $0kl$, $k + l = 2n + 1$, $h0l$, $h + l = 2n + 1$, and $hk0$, $h = 2n + 1$, indicated space group *Pnna*. A total of 9170 reflections were measured from six symmetry-related octants to a maximum 2θ of 60° by using θ–2θ scans. Three standard reflections measured at 2-h intervals showed a 14% decline in intensity during data collection, and a decay correction was applied on the basis of a second-order polynomial least-squares fit to the intensity standards. The data were corrected for Lorentz and polarization effects and empirically for absorption on the basis of ψ scans of four reflections. Equivalent symmetry-related reflections were averaged yielding a final data set of 1536 unique reflections with an interval agreement factor of $R_I(F^2) = 0.052$. Only 654 reflections in the final set had $I > 3\sigma(I)$. The relatively high value of R_I is attributed to the platelike habit of the crystals, resulting in large absorption effects, and to a relatively large number of weak intensities in the data set.

The structure was determined with MULTAN80,[31] with the four highest peaks in the E map corresponding to the As and Ga positions. Positions of the K atoms were determined in a subsequent difference Fourier summation map. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$ and $\sigma^2(F^2) = \sigma_{cs}^2 + (0.02F^2)^2$, including anisotropic temperature factors for all atoms converged at $R = 0.071$ and $R_w(F) = 0.060$ for 47 variables and 654 reflections. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*. All computer programs used for data collection, reduction, and refinement were from the CAD4-SDP package. Crystal data are reported in Table I.

Results and Discussion

Unlike some of the ternary Zintl phases containing chalcogenides, $K_3Ga_3As_4$ is insoluble in polar solvents such as liquid ammonia or ethylenediamine. The material is extremely air sensitive, being readily oxidized by either air or water.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters of $K_3Ga_3As_4$

atom	x	y	z	B,[a] Å^2
As(1)	0.5411 (5)	0.1365 (3)	0.1932 (3)	0.67 (6)
As(2)	0.0407 (5)	0.1758 (3)	0.4047 (3)	0.65 (6)
Ga(1)	0.8083 (7)	0.2500	0.2500	0.79 (9)
Ga(2)	0.4025 (5)	0.2166 (3)	0.3889 (3)	0.71 (7)
K(1)	0.0593 (12)	0.0923 (6)	0.1202 (7)	1.12 (13)
K(2)	0.7500	0.0000	0.4219 (12)	1.11 (16)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2(\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Selected Distances (Å) and Angles (deg) in $K_3Ga_3As_4$[a]

	Bonding Distances		
Ga(1)–As(1)	2.507 (2)	K(1)–As(1)	3.336 (3)
Ga(1)–As(2)	2.498 (1)	K(1)–As(1)	3.385 (3)
Ga(2)–As(1)	2.556 (2)	K(1)–As(2)	3.259 (3)
Ga(2)–As(1)	2.512 (2)	K(2)–As(1)	3.441 (3)
Ga(2)–As(2)	2.467 (2)	K(2)–As(2)	3.237 (1)
Ga(2)–As(2)	2.444 (2)	K(2)–As(2)	3.470 (2)
	Nonbonding Distances		
Ga(1)–Ga(2)	3.094 (2)	Ga(1)–K(1)	3.174 (3)
Ga(2)–Ga(2)	3.102 (2)		
	Angles		
As(1)–Ga(1)–As(1)	90.66 (7)	As(1)–Ga(2)–As(2)	106.75 (6)
As(1)–Ga(1)–As(2)	107.15 (4)	As(1)–Ga(2)–As(2)	118.49 (6)
As(1)–Ga(1)–As(2)	124.62 (4)	As(1)–Ga(2)–As(2)	125.96 (6)
As(2)–Ga(1)–As(2)	104.27 (7)	As(1)–Ga(2)–As(2)	112.76 (6)
As(1)–Ga(2)–As(1)	89.42 (6)	As(2)–Ga(2)–As(2)	103.86 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

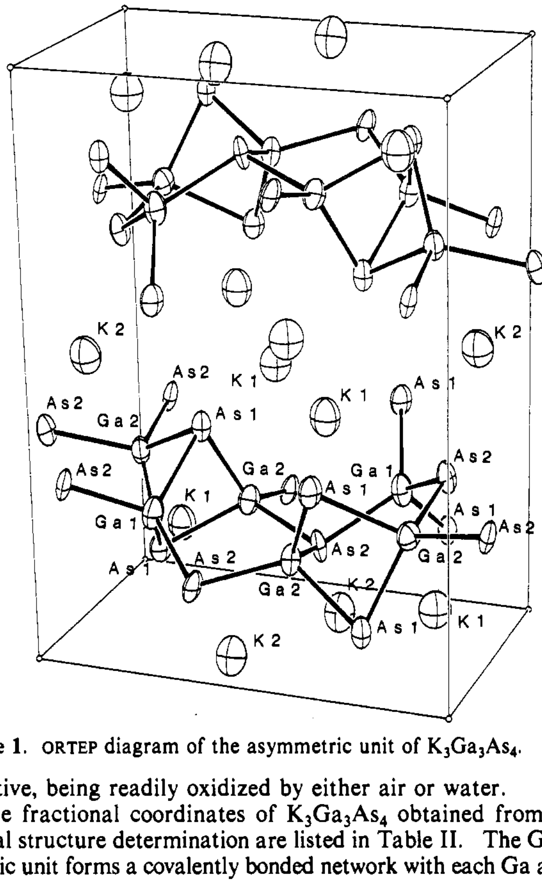


Figure 1. ORTEP diagram of the asymmetric unit of $K_3Ga_3As_4$.

The fractional coordinates of $K_3Ga_3As_4$ obtained from the crystal structure determination are listed in Table II. The GaAs anionic unit forms a covalently bonded network with each Ga atom bonded to four As atoms and each As atom bonded to three Ga atoms. An ORTEP diagram[32] of the packing of the $Ga_3As_4{}^{3-}$ anionic

---

(30) Standard F374-84 in the 1986 ASTM Annual Book of Standards, Vol. 10.05.

(31) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN80, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England, and Louvain, Belgium, 1980.

(32) Johnson, C. K. ORTEPII. Report ORNL-5188; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

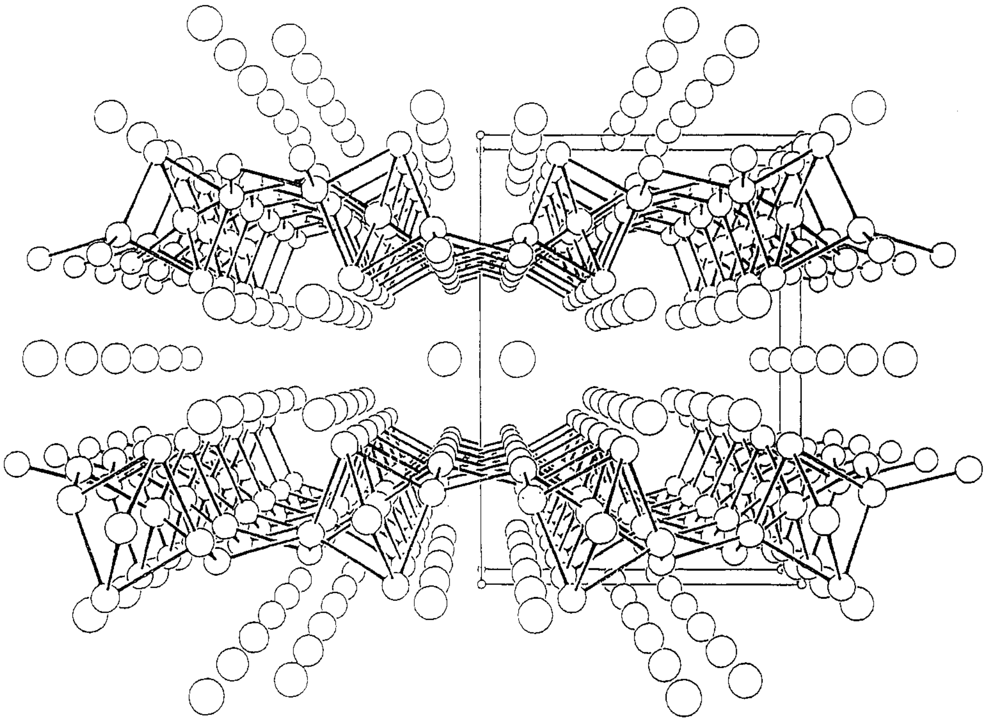


Figure 2. Structural diagram showing the layered nature of the gallium arsenide sheets insulated by potassium sheets.

unit in the unit cell is illustrated in Figure 1. Selected bond distances and angles are listed in Table III.

The structure of $K_3Ga_3As_4$ is composed of layers of K^+ ions and covalently bonded sheets of $[Ga_3As_4{}^{3-}]_\infty$ alternating in the *b* direction (Figure 2). Within the anionic sheets, each Ga atom is bonded to four As atoms at the corners of a distorted tetrahedron. Three $GaAs_4$ tetrahedra, one centered at Ga(1) and two centered at Ga(2) atoms, share a common edge [As(1)-As(1)]. Corner sharing links groups of three tetrahedra together in both the *a* and *c* directions, forming the infinite two-dimensional anionic sheet. The average Ga-As bond distance is 2.497 Å compared with 2.448 Å with GaAs. The average As-Ga-As angle is 108.4° although there is substantial variation from the average, most noticeably in the angles to the shared edge, which are 90.66 (7) and 89.42 (7)°.

The As atoms are bonded to three Ga atoms in an orientation that directs the filled lone-pair orbitals approximately perpendicular to the sheet and toward the layer of K^+ ions. The average K⋯As contact distance is 3.36 Å compared with average distances of 3.46 Å in K_2SiAs_2 and KSi_3As_3 and 3.47 Å in KAs.

The gross structure of the $[Ga_3As_4{}^{3-}]_\infty$ sheets can also be described in two different ways, depending on the angle at which the structure is viewed. When viewed parallel to the layers, the structure appears to contain trigonal-bipyramidal clusters with As atoms occupying the axial positions and Ga atoms occupying the equatorial positions. These $Ga_3As_2{}^{3+}$ clusters are structurally similar to the $Bi_5{}^{3+}$ and $Pb_2{}^{2-}$ Zintl ions. Each equatorial Ga atom in the cluster is linked to two other clusters through a bridging As atom.

When the structure is viewed perpendicular to the layers, a two-dimensional network of six-membered rings is apparent. This type of structure is well-known, appearing in materials such as metallic arsenic and Zintl phases such as $CaSi_2$[21] and KSnAs.[25] In $K_3Ga_3As_4$ pairs of six-membered rings are "tied together" by bridging As atoms. A similar structure has been observed for $M_2Al_2Sb_3$ (M = Na, K), in which the six-membered rings are bridged by As_2 moieties.[29]

Zintl phase materials are formally classified as semiconductors. $K_3Ga_3As_4$ has the appearance of a semiconductor: it is a dark metallic gray solid and opaque in appearance. The resistivity measurements on pressed pellets of $K_3Ga_3As_4$ indicate that the activation energy for elevation of electrons into the conduction band is sufficiently large that a calibrated current ($i \geq 0.1$ mA at V = 1 mV) may not be passed through the material at room temperature and the material behaves as a semiconductor with a band gap ≥2 eV.

We are in the process of preparing and characterizing a variety of I-III-V Zintl phase materials and will report on their structural and resistivity properties.

Acknowledgment. C.J.O. wishes to acknowledge support from a grant from the Louisiana Education Quality Support Fund, administered by the Board of Regents of the state of Louisiana, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of anisotropic thermal parameters and complete crystal data (2 pages); a listing of observed and calculated stucture factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Water Oxidation by $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$. An Oxygen-Labeling Study

Daniel Geselowitz and Thomas J. Meyer*

Received November 28, 1989

Introduction

The complex $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ can be oxidized chemically or electrochemically to the [V,V] state, which undergoes autoreduction to the [III,IV] state, in water, accompanied by the appearance of dioxygen.[1-3] In order to understand

---

(1) (a) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855. (b) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029.

(2) (a) Rotzinger, F. P.; Muravalli, S.; Comke, P.; Hurst, J. K.; Grätzel, M.; Pern, F.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619. (b) Nazeeruddin, M. K.; Rotzinger, F. P.; Comte, P.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1988**, 872.

0020-1669/90/1329-3894$02.50/0 © 1990 American Chemical Society