molecular rearrangements are clearly necessary for conversion of an *O,O*-nitrite to a *N*-nitrosyl (a transformation we have yet to observe for model complex **1**), suggesting that *N*-nitrite coordination may be more productive in denitrification mechanisms. Experiments designed to test this idea are in progress.

Preliminary investigation of the reactivity of **1** indicates that the coordinated nitrite is readily displaced. For example, addition of (PPN)Cl to a solution of **1** in CH_3CN resulted in quantitative formation of $[HB(t\text{-}Bupz)_3]CuCl$ (UV-vis).[10] In a reaction originally attempted in order to model the proton-induced dehydration suggested as the initial step in enzymatic nitrite reduction,[4] treatment of **1** with TMSOTf instead induced nitrite removal (presumably as the TMS ester) and formation of deep purple $[HB(t\text{-}Bupz)_3]CuOTf$ (**3**) (62%, Scheme I).[18] Compound **3** was also prepared independently by the reaction of $[HB(t\text{-}Bupz)_3]CuCl$ with AgOTf. An X-ray structure determination of **3**$\cdot C_7H_8$ revealed monodentate triflate bonding[19] to a Cu(II) ion that adopts a rare tetrahedral coordination geometry (Figure 3).[7,9c,20] The coordination sphere of the complex is similar to that of $[HB(3,5\text{-diisopropylpz})_3]CuCl$ (**4**),[9c] the only significant deviations from an ideal tetrahedral arrangement for **3** being intraligand angles between the pyrazole nitrogen donor atoms that are less than, and O1–Cu–N angles that are more than, 109.5° (average N–Cu–N = 97.2° and average O1–Cu–N = 121.2°). Like **4**, dihedral angles for **3** closely approach 90° (avg. 87.6°), in contrast to the lesser angles reported for other more distorted tetrahedral Cu(II) complexes.[20] EPR spectroscopic data for **3** (Figure 2c) and **4**[9c] in noncoordinating solvents are also similar, both compounds exhibiting signals that support retention of tetrahedral geometries in solution.[21]

Cyclic voltammetry of **3** in 0.1 M Bu_4NOTf in CH_2Cl_2/CH_3CN ($\sim$9:1) revealed an electrochemically quasi-reversible (ΔE_{pp} = 110 mV, greater values at scan rates >50 mV/s) and chemically reversible ($i_{pc}/i_{pa} \approx 1$) reduction with $E_{1/2} = +0.91$ V vs SCE. An identical cyclic voltammogram was obtained by starting with $[HB(t\text{-}Bupz)_3]Cu(CH_3CN)$ (**5**),[7] clearly identifying it as the reduction product. Only an irreversible reduction at +0.55 V was observed for **3** in the absence of added CH_3CN, suggesting that **5** is reversibly formed by reduction of a CH_3CN adduct of **3**. In support of this hypothesis, significant changes in the spectroscopic features of **3** (UV–vis, EPR) occur upon dissolution in CH_3CN, although we have not yet isolated and definitively characterized the apparent triflate substitution product. The redox potential for the **3**$\cdot CH_3CN \leftrightarrow$ **5** process is extraordinarily large and positive, presumably because geometric constraints (e.g. tetrahedral distortion) destabilize the Cu(II) state.[22] Future work will address this possibility as well as further aspects of the biomimetic reactivity of **1** and potential use of **5** as an oxidant and starting material for the synthesis of additional monocopper NiR model complexes.

Acknowledgment. I thank Professor Doyle Britton for his work on the X-ray structures of **1** and **3**, Christy Ruggiero for her help with EPR data collection, Professors Elinor T. Adman, Kenneth D. Karlin, and Bruce A. Averill for sending preprints (refs 3, 6b, and 4c, respectively), and the University of Minnesota for financial support.

Supplementary Material Available: Tables of atomic positional and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles for **1** and **3**$\cdot C_7H_8$ (20 pages). Ordering information is given on any current masthead page.

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Received July 26, 1991

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(18) $[HB(t\text{-}Bupz)_3]Cu(OTf)\cdot C_7H_8$ (**3**$\cdot C_7H_8$). Anal. Calcd for $C_{29}H_{42}BCuF_3N_6O_3S$: C, 50.77; H, 6.17; N, 12.25. Found: C, 49.05; H, 5.96; N, 12.40 (replicate analyses also gave low values for carbon, suggesting unavoidable partial loss of toluene solvate). UV–vis (CH_2Cl_2) [λ_{max}, nm (ϵ, cm^{-1} M^{-1}): 234 (7800), 256 (2600), 292 (sh, 1550), 434 (350), 550 (350). FTIR (KBr, cm^{-1}): 632, 731, 781, 1012 (ν_{SO}), 1058, 1198, 1236 (ν_{SO}), 1258, 1341 (ν_{SO}), 1367, 1501, 2511 (ν_{BH}), 2966. Crystal data for **3**$\cdot C_7H_8$ ($C_{29}H_{42}BCuF_3N_6O_3S$): size 0.35 × 0.30 × 0.15 mm, $M_r = 686.10$, space group $P2_1/n$ (No. 14), at −101 °C, $a = 10.367$ (6) Å, $b = 20.555$ (7) Å, $c = 15.39$ (1) Å, $\beta = 90.80$ (5)°, $V = 3279$ (6) Å^3, $Z = 4$, $\rho_{calcd} = 1.390$ cm^{-3}. For a total of 2809 unique, observed reflections with $I > 2\sigma(I)$ and 347 variables, the current discrepancy indices are $R = 0.076$ and $R_w = 0.076$. Full tables of bond lengths and angles, as well as atomic positional and thermal parameters for **3**$\cdot C_7H_8$ are provided in the supplementary material.

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A 3-Coordinate 4-Electron Phosphorus Donor[1]

A 3-coordinate phosphorus which can act as a 4-electron donor has never been observed. We have previously reported the synthesis, structure, chemistry[2-12] and electronic structure[13] of ADPnO[14] systems containing 3-coordinate, 10-electron pnictogen centers (10-Pn-3;[15] Pn = P, As, or Sb). The identity of the pnictogen center determines which of two general reactivity categories the molecules follow. The ring systems derived from either arsenic or antimony have been shown to form complexes with transition-metal centers which retain both the planar structure of the ADPnO ring and the hypervalent arrangement at the pnictogen center. Either 10-Pn-4[4,6] or 10-Pn-5[10] complexes can be formed depending on the number of metals which coordinate.

The phosphorus-derived ring system (ADPO) tends to show chemistry in which only a single lone pair of electrons from phosphorus is involved. Chemistry at the phosphorus of ADPO is generally accompanied by a reduction of the tridentate ligand backbone in ADPO by the second lone pair at the phosphorus center. This reduction leads to a folding of the ADPO ring systems in transition-metal complexes.[4,5,7,9-11,13] The unique reactivity of ADPO has been explained in terms of configuration mixing that transfers σ-electron density to the π-systems at phosphorus.[9-11,13]

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(14) The ADPnO acronym has been previously described and is used for simplicity in place of the name of the ring system it represents: 5-*a*za-2,8-*d*ioxa-1-*pn*ictabicyclo[3.3.0]*o*cta-2,4,6-triene. See ref 4, footnote 1d, for details.

(15) The *N*–X–*L* nomenclature system has been previously described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753): *N* valence electrons about a central atom X, with *L* ligands.

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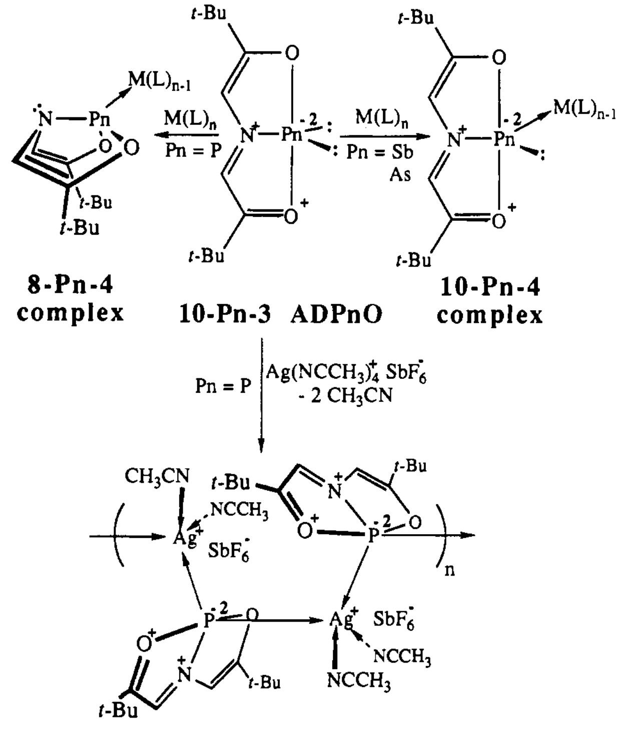
This electronic effect gives a delicate balance between the 8-P-3 and 10-P-3 forms of ADPO. Recently, we synthesized a unique compound in which ADPO formed a 10-P-4 complex with silver.[12] This result is an exception to the general reactivity pattern of ADPO and suggests that silver does not disturb the delicate electronic balance in ADPO. Demonstration of chemical reactivity for both phosphorus lone pairs of electrons should be possible in spite of all previous results to the contrary.[4,5,7,9-11,13]



1

We now report the synthesis of an adduct in which the 3-coordinate phosphorus of ADPO acts as a 4-electron donor while maintaining its planar geometry. The reaction between ADPO and $Ag(CH_3CN)_4{}^+SbF_6{}^-$ in 1:1 ratio leads to yellow crystalline **1** in 76% yield.[16] Compound **1** is readily soluble in CH_2Cl_2, but decomposes slowly in solution at room temperature. Most donor solvents (e.g. THF and CH_3CN) displace ADPO from the coordination sphere of silver as indicated by ^1H NMR shifts. The complex is insoluble in hexane or toluene.

The ^1H and ^{13}C NMR chemical shift values (CD_2Cl_2) for the ADPO moiety in **1** are very close to those of uncomplexed ADPO. However, the $^3J_{P-H}$ coupling constant of 18.1 Hz for the ring protons is clearly different from that for free ADPO (9.6 Hz) and follows the same trend seen for other metal complexes of ADPO.[4,5,9-11] When a solution is cooled, the ring ^1H NMR resonances broaden and shift slightly downfield [δ 7.94 (20 °C) → 8.08(−90 °C)]. The phosphorus coupling to these protons becomes unresolvable at about −80 °C. The ^{31}P NMR spectrum of **1** shows a broad singlet at δ 152. This ^{31}P signal becomes broader and moves to 139 ppm at −90 °C. This low-temperature chemical shift value is identical to the chemical shift observed for **1** in a solid-state ^{31}P NMR spectrum. These data indicate a weak interaction between silver and phosphorus centers which leads to exchange at room temperature.

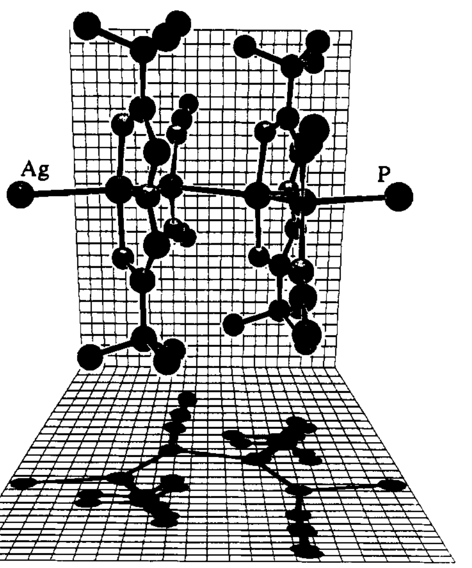


Figure 1. KANVAS[18] drawing of an ADPO–Ag polymer fragment in **1**. Hydrogens have been omitted for clarity.

Table I. Selected Bond Distances and Angles for **1** and ADPO[a]

property	1	ADPO
P–Ag	243.4 (5), 257.4 (5)	
P–O	177.5 (12), 183.9 (13)	179.2 (2), 183.5 (2)
P–N	172.8 (14)	170.3 (2)
$C–C_{ring}$	137.1 (22), 134.7 (23)	134.2 (4), 133.7 (4)
C–N	135.1 (18), 129.3 (21)	137.5 (3), 138.2 (3)
C–O	134.2 (20), 132.2 (21)	133.1 (4), 132.8 (4)
O–P–O	167.7 (6)	167.7 (1)
N–P–O	84.7 (6), 83.0 (6)	84.2 (1), 83.5 (1)
P–Ag–P	106.1 (1)	
Ag–P–N	118.3 (5), 109.9 (5)	
Ag–P–Ag	131.5 (2)	

[a] Bond distances in pm and angles in degrees.

The X-ray crystal structure of **1** shows a polymeric structure with a silver–phosphorus backbone.[17] The phosphorus has the unusual role of acting as a 4-electron donor which bridges tetrahedral silver centers. This arrangement leads to a zigzag polymeric chain as depicted in Figure 1. The Ag–P distances (Table I) of 257.4 (5) and 243.4 (5) pm show a slight asymmetry. The tetrahedral silver centers contrast the square-planar silver center previously observed for an ADPO/Ag(I) 4:1 complex.[12]

The phosphorus center in **1** is best described as trigonal bipyramidal (tbp) in which the equatorial sites are occupied by the nitrogen and two silver centers and the ligand oxygen atoms are in the apical positions. The trigonal aspect of the geometry at phosphorus is readily apparent from the shadow on the lower plane of Figure 1. The planar nature of the ADPO rings is evident from both the direct view and the shadow in Figure 1. The geometry of the ADPO fragment is very similar to that of uncomplexed ADPO. The Ag–P–Ag angle of 131.5 (2)° for **1** is significantly larger than the value expected for ideal tbp geometry but follows the same trend as the 10-Pn-5 complexes of ADAsO and ADSbO.[10]

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(16) Solid ADPO (0.803 g, 3.32 mmol) was added at room temperature to $[Ag(CH_3CN)_4]^+SbF_6^-$ (1.7 g, 3.34 mmol) in CH_3CN (40 mL) and stirred for 1 h. The volatiles were removed under vacuum to obtain an orange residue. This residue was dissolved in CH_2Cl_2 and filtered, and hexane was added to the filtrate. Yellow crystals of **1** were obtained by cooling to −25 °C; 1.69 g, 76% yield. Mp: 127–128 °C dec (color darkens around 115 °C). NMR data in CD_2Cl_2: ^1H δ 1.31 (s, 18 H), 2.21 (s, 6 H), 7.94 (d, $^3J_{PH}$ = 18.1 Hz, 2 H); $^{13}C\{^1H\}$ δ 2.4 (s, CH_3CN), 27.8 (d, J_{PC} = 1.2 Hz, $(CH_3)_3C$), 34.8 (d, J_{PC} = 8.5 Hz, $C(CH_3)_3$), 115.0 (s, NC), 119.4 (s, CH_3CN), 172.7 (s, CO); ^{31}P δ 152. Satisfactory (±0.4%) C, H, N analyses were obtained.

(17) Crystal data for **1** at 203 K with Mo Kα radiation: a = 736.0 (2) pm, b = 1464.4 (3) pm, c = 2284.4 (4) pm, orthorhombic, $P2_12_12_1$, Z = 4, 1030 unique reflection with $I > 3\sigma(I)$. The final R factors were R = 0.051 and R_w = 0.037. The largest residual density in the final difference Fourier map was 0.83 e/Å^3 near an acetonitrile nitrogen. Further details of the crystal structure are available in the supplementary material.

(18) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

Compared to the bis(metal) phosphinidenes, **1** probably does not enjoy any substantial stabilization from pπ–dπ interactions.[10,19-23] The weak Ag–P interaction and the close P–O interaction (as in free ADPO) indicate the preference for the hypervalent bonding arrangement over Ag → P back-bonding. Also, as observed previously, ADPO does not form pnictinidene-like complexes with $CpMn(CO)_2$ fragments as do the heavier members of the ADPnO series.[10]

Attempts are currently under way to isolate monomeric $ADPO[Ag^+(CH_3CN)_3]_2(SbF_6^-)_2$ (**2**), and other metal complexes of planar ADPO. Preliminary data indicate the formation of **2** in solution, but attempted crystallization lead to the formation of **1** and $Ag^+(CH_3CN)_4SbF_6^-$.

Acknowledgment. The excellent technical assistance of Hugh A. Craig and William J. Marshall made this work possible. Fredric Davidson kindly provided the NMR spectroscopic results reported herein.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination on **1** including a description of the experimental procedures, tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and distances and angles, and ORTEP structure drawings (7 pages). Ordering information is given on any current masthead page.

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Received September 12, 1991

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Articles

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Siderophore Chemistry of Vanadium. Kinetics and Equilibrium of Interaction between Vanadium(IV) and Desferrioxamine B in Aqueous Acidic Solutions[†]

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Received July 3, 1991

The kinetics and equilibrium of interaction between vanadyl sulfate and a natural trihydroxamate-based siderophore, desferrioxamine B methanesulfonate, were studied spectrophotometrically in acidic aqueous perchlorate solutions of 2.0 M ionic strength. The bi-, tetra-, and hexadentate-bonded complexes were formed under these conditions, and their stability constants were calculated. The rate constants for the formation and hydrolysis of the bi- and tetradentate complexes were estimated. The formation of the bidentate complex proceeds via two parallel pathways involving the hydrolyzed and unhydrolyzed vanadyl–aquo species. The hydrolyzed form was found to react with the siderophore ca. 10^5 times faster than the unhydrolyzed form.

Introduction

Numerous living organisms are capable of selectively concentrating various trace elements against an extreme concentration gradient due to the participation of low molecular weight molecules that are involved as the carriers. Tunicates, a certain type of sessile marine organism, are for example known to concentrate vanadium 10^8-fold over the sea water level of ca. 0.1 ppb.[1] Although vanadium is the principal metal stored in the vanadocytes, iron was also found to be present as a constituent.[2,3] A possible common mechanism for transport and storage of these two metals was considered, since in human organisms the same proteins appear to be involved with both metals.[4] Although during the last two decades the chemistry of vanadium attracted great interest, the biochemical role of this essential trace element is still poorly understood compared to the other first-row transition metals.[5] Its eventual better understanding, at least in part, depends on our understanding of the coordination chemistry of vanadium in its different oxidation states.

In a previous communication[6] we have reported on the mechanism of the interaction between VO_2^+ ion and desferrioxamine B in strongly acidic medium. Desferrioxamine B, $NH_2(CH_2)_5\{N(OH)C(O)(CH_2)_2C(O)N(H)(CH_2)_5\}_2N(OH)C(O)CH_3 = H_3DFB$, is a linear trihydroxamate-based siderophore produced by certain microorganisms[7] and besides iron(III) also very strongly chelates vanadium ions.[6,8,9] This siderophore is currently used as a drug in the treatment of patients suffering from Cooley's anemmia[10] or chronic dialysis.[11] Therefore, the obtained results may be of some relevance in predicting a potential disturbance in the vanadium balance in these patients as a consequence of the administration the drug. Hence, it seemed worthwhile to undertake a study of the interaction between vanadium in its 4+ oxidation state and desferrioxamine B, the results of which are presented in this report. Apart from their eventual biological application, the results throw some more light on the intimate mechanism of the substitution reactions at the V(IV) metal ion center. Besides the new kinetic data on this system, our results also augment a previous study[8] regarding the equilibrium constants of the system, which has been published during the preparation of this paper.

[†] Taken in part from I.B.-H.'s Ph.D. Thesis.

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