of pyrrolidine reveals the expected spectrum for D_{3h} symmetry, with two lines of approximate 2:1 intensity at −169.4 and −130.7 ppm, respectively. Unfortunately, the increased line widths often observed in organic solvents[2f] prevented determination of the $^2J_{\mathrm{W-O-W}}$ coupling constant for the anion in these organic solvents.

Summary. The significant features of the reaction of A-β-$SiW_9O_{34}^{10-}$ with ZrO^{2+} in acidic, aqueous solution may be summarized as follows:

1. The chemical behavior observed appears much more similar to that reported for A-α-$PW_9O_{34}^{9-}$ with M^{2+} or M^{4+} species, in that products of the composition $X_2W_{18}M_3$ are formed (at least under the acidic conditions of the present synthesis) rather than the XW_9M_3 (Keggin-like) structures that have been observed for M = V^{5+},[2b,2f] Mo^{6+},[1a] W^{6+},[1a] and Ti^{4+}.[3e]

2. The product $Si_2W_{18}[ZrOH]_3O_{68}^{11-}$ exhibits characteristics similar to those reported for $P_2W_{18}[CeO]_3O_{68}^{14-}$, formed by the reaction of A-α-$PW_9O_{34}^{9-}$ with Ce^{4+}. These include (a) retention of the isomeric form of the lacunary heteropolytungstate upon complexation with these M^{4+} ions and (b) the presence of an extra "belt" comprised of M–O–M (M = Ce) or M–OH–M (M = Zr) units—a feature peculiar to only these two $X_2W_{18}M_3$ systems.

3. The absence of any coordinating water or terminal M=O bonds in the $Si_2W_{18}[ZrOH]_3O_{68}^{11-}$ anion is a feature unique to this $X_2W_{18}M_3$ molecule and can be explained by the steric effects of the SiW_9O_{34} fragments on the relatively small zirconium atoms, "tucking" the Zr_3O_3 belt into the center of the structure and thereby "protecting" them from OH_x coordination despite the high oxophilicity of zirconium.

4. The "$Si_2W_{18}Zr_3$" composition and structure are retained in solution as demonstrated by multinuclear NMR, solution molecular weight measurements, and FAB mass spectrometry.

Acknowledgment. Support during the course of this work from NSF Grant CHE-8313459 and from Dreyfus Teacher-Scholar, Alfred P. Sloan, and Guggenheim (1985–1986) Fellowships to R.G.F. is gratefully acknowledged. The fast atom bombardment mass spectra were obtained as previously described[2h] on a VG analytical ZAB-HF ultrahigh-resolution 8-kV mass spectrometer with a Model 11250 data system at the University of Illinois at Urbana-Champaign with the assistance of Dr. J. C. Cook and Professor K. S. Suslick. T.J.R.W. thanks the University of Oregon for a visiting Associate Professorship during his sabbatical year (1987–1988).

Supplementary Material Available: Tables of crystal parameters and data collection and refinement details, anisotropic parameters, bond lengths and angles in the cations, and intramolecular bond angles in the $Si_2W_{18}Zr_3O_{71}^{14-}$ anion (12 pages); listings of observed vs calculated structure factors (59 pages). Ordering information is given on any current masthead page.

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Contribution from GTE Laboratories Incorporated, Waltham, Massachusetts 02254, and the Departments of Chemistry,
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Structural and Magnetic Studies of Electrochemically Crystallized Halides of 1,4,5,8-Tetraselenonaphthalene (TSeN)

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Experimental conditions are described for the growth of single crystals by anodic electrocrystallization of the isomorphous 1:1 chloride and bromide of 1,4,5,8-tetraselenonaphthalene (TSeN). A structural study was performed on the chloride for reasons of crystal quality, while physical studies were carried out on the more plentiful bromide, which was found to have a polycrystalline resistivity of 10^3–10^4 Ω cm. The chloride of TSeN, $[C_{10}H_4Se_4]Cl$, is an orthorhombic crystal of space group *Cmca* (D_{2h}^{18}; No. 64) with a = 19.110 (4) Å, b = 8.574 (2) Å, c = 13.437 (3) Å, V = 2201.6 Å^3, and Z = 8. The structure, solved by Patterson and difference-Fourier syntheses, is comprised of dimers of parallel TSeN cation radicals rather than infinite chains. Curie law behavior was observed in both static magnetic susceptibility and electron spin resonance studies of the bromide. The ESR spectral envelope is an example of an orthorhombic **g**-tensor system for which the intrinsic line width and the hyperfine anisotropy are much smaller than that of the **g** tensor. The line width of the solution ESR spectrum of the TSeN cation radical and the isotropic g value show a small solvent effect.

Introduction

We recently reported the synthesis, purification, and crystal and molecular structure of the organoselenium π-donor 1,8:4,5-bis(diseleno)naphthalene (tetraselenonaphthalene, TSeN, **1**).[1] Cyclic voltammetry and the solution electron spin resonance (ESR) spectrum of the cation radical revealed the electron-transfer properties of TSeN. We now focus our attention on the structure and properties of the solid ion-radical salts, in particular the chloride and bromide of TSeN, our motivation for undertaking the synthesis of TSeN.[1]

We[2] and others[3] have attempted the synthesis of TSeN ion-radical salts by solution charge transfer. This experimentation to date has led to neither highly conductive solids nor to any crystals whose structures have been determined.[4] Since our initial hope was to prepare the solids $(TSeN)_2X$ and since electrocrystallization is the technique of choice for the superconducting tetrachalcogenofulvalene salts of this stoichiometry,[5] experimentation along these lines was initiated.

Electrocrystallization experiments were attempted with a variety of anions under many different conditions, but experimentally

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[⊥] Brandeis University.

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(4) Very recently, solution charge-transfer experiments at the University of Missouri—St. Louis have led to single crystals of a solid of the composition (by elemental analysis) $(TSeN)I_2$. Additionally, samples of a chloride and bromide of TSeN different (by X-ray powder diffraction) from those described herein have been obtained as well as a new trifluoroacetate. The electrical, magnetic, and structural properties of these solids will be discussed separately.

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Table I. Crystallographic Data for $[C_{10}H_4Se_4]Cl$ at 21 °C

$a = 19.110$ (4) Å
$b = 8.574$ (2) Å
$c = 13.437$ (3) Å
$V = 2201.6$ Å^3
$Z = 8$
fw: 475.4
space group: *Cmca* (D_{2h}^{18}, No. 64)
$\lambda = 0.71073$ Å
$\rho_{obs} = 2.83$ (1) g cm^{-3}
$\rho_{calc} = 2.869$ g cm^{-3}
$\mu = 134.0$ cm^{-1} (Mo K$\bar{\alpha}$)
transmission coeff: 0.635–1.000
$R(F_o) = 0.047$
$R_w(F_o) = 0.039$

useful quantities were obtained only for the chloride and bromide salts of TSeN. These salts were found to have 1:1 stoichiometry, and X-ray powder diffraction revealed them to be isomorphous. Hence, this work reports the preparation of these salts and our studies of their structural, electrical, and magnetic properties in the solid state. While most of these studies were carried out on the bromide because larger quantities were available, the crystals of the chloride were selected for X-ray study due to their better quality.

Experimental Section

General Procedures. TSeN was synthesized and purified as previously described.[1] Elemental analyses were performed by Galbraith Laboratories, Inc. Solvents for electrochemical crystal growth experiments were vacuum-distilled from calcium hydride and stored over molecular sieves. Static susceptibility measurements were performed on a SQUID device at the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology. ESR spectra were recorded on a Varian E-12 spectrometer operating at 9.27 GHz as previously described.[6,7] ESR sample size was 15 mg, and the polycrystalline samples of TSeN$^{\bullet+}$Br$^-$ were prepared by careful grinding and crushing of the electrocrystallized material.

Preparation of the Bromide of TSeN. With use of a Pt-flag working electrode and Pt-gauze counter electrode, 200 mL of a solution of TSeN (5×10^{-4} M) and tetra-*n*-butylammonium bromide (0.08 M) in a 40:40:20 mixture (by volume) of bromobenzene, iodobenzene, and *N*,*N*-dimethylformamide (DMF) was electrolyzed for 35 days at 90 °C with a constant 750-mV potential across the cell. Green metallic reflecting crystals, 7.8 mg, were isolated from this experiment. Anal. Calcd for $C_{10}H_4Se_4Br$: C, 23.10; H, 0.78; Se, 60.75; Br, 15.37. Found: C, 23.31; H, 0.79; Se, 59.72; Br, 14.86. X-ray powder diffraction of this material revealed the following reflections (*d*, Å): 9.5, 6.7, 4.85, 3.86, 3.35, 3.17. An orthorhombic unit cell, with $a = 19.2$ Å, $b = 8.6$ Å, $c = 13.4$ Å, $V = 2210$ Å^3, and $\rho_{calc} = 3.12$ g cm^{-3}, is assigned. From the unit cell of TSeN$^{\bullet+}$Cl$^-$ given below and ionic radii of 1.81 and 1.96 Å for Cl$^-$ and Br$^-$, respectively, a unit cell volume of 2255 Å^3 and density of 3.06 g cm^{-3} may be estimated for TSeN$^{\bullet+}$Br$^-$. With use of a methylene iodide–bromoform mixture, a flotation density of 3.06 (3) g cm^{-3} is observed for TSeN$^{\bullet+}$Br$^-$.

Preparation of the Chloride of TSeN. With use of a Pt-wire working electrode and Pt-gauze counter electrode, a solution of TSeN (44 mg) and tetra-*n*-butylammonium chloride (0.10 M) in iodobenzene (90 mL) and DMF (10 mL) was electrolyzed at 60 °C for 50 days at a constant potential of 900 mV across the cell. Green reflective needles, 15 mg, were isolated from this experiment. X-ray powder diffraction of these crystals revealed the following (*d*, Å): 9.4, 7.6, 6.8, 5.1, 4.8, 4.07, 3.88, 3.80, 3.64, 3.36, 3.28, 3.17, 3.08. This pattern is completely indexed to the unit cell of the single-crystal study.

In addition to the green needles, the solids isolated from these experiments usually included black prisms with a flotation density of 2.57 g cm^{-3} whose powder patterns exhibit reflections at $d = 4.97$ and 4.63 Å. Neither of those reflections are found in the calculated pattern for TSeN$^+$Cl$^-$.

Structure Determination of $[C_{10}H_4Se_4]Cl$. Single crystals were grown as described above. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of good quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[8] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations.[9] Initial computational work was carried out on a NOVA 1200 computer using the Syntex XTL package. All final computational work was carried out on a VAX 8600 computer using the Enraf-Nonius SDP software package. Details of the structure analysis, in outline form, are presented in Table I, and atomic coordinates for all atoms appear in Table II. Attempts were made to explain the large U_{33} thermal parameter of the Cl$^-$ ion. Occupancy refinement suggested that the 1:1 formulation was correct. A model involving disorder of the chloride ion about $z = 0.5$ could not be refined successfully.

Table II. Atomic Coordinates for $[C_{10}H_4Se_4]Cl^{a,b}$

atom	*x*	*y*	*z*	*B*, Å^2
Se1	0.32828 (4)	0.67687 (8)	0.10329 (7)	2.93 (1)
Se2	0.32918 (4)	0.41231 (9)	0.14467 (7)	3.32 (2)
Cl	0.3192 (2)	0.500	0.500	10.3 (1)
C1	0.4638 (3)	0.8234 (8)	0.0901 (5)	2.4 (1)
C2	0.4270 (3)	0.6866 (8)	0.1088 (6)	2.1 (1)
C3	0.4631 (3)	0.5455 (7)	0.1281 (6)	1.9 (1)
C4	0.4270 (3)	0.4034 (8)	0.1444 (6)	2.2 (1)
C5	0.4636 (4)	0.2634 (8)	0.1592 (5)	2.5 (2)
H1	0.437 (3)	0.925 (7)	0.079 (5)	3 (2)
H5	0.435 (3)	0.161 (7)	0.161 (4)	2 (2)

[a] Atoms refined with use of anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] Numbers in parentheses in this and the following tables are estimated standard deviations in the least significant digit.

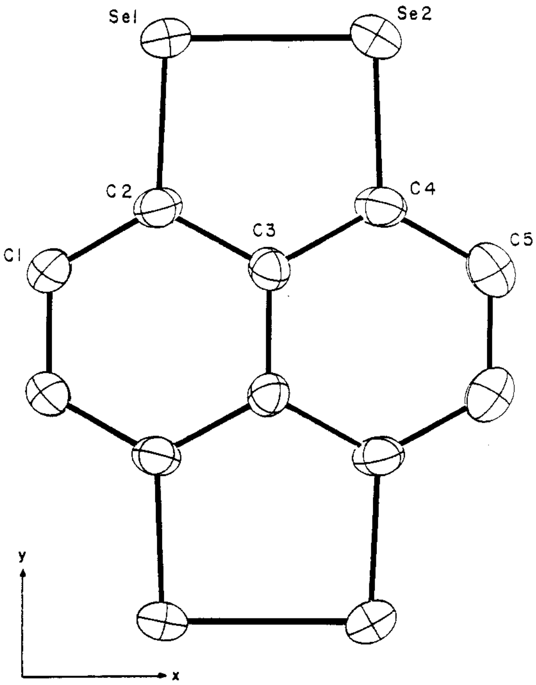

Figure 1. Structure of the molecular cation $[C_{10}H_4Se_4]^{\bullet+}$, showing the labeling scheme, and 50% probability ellipsoids, for atoms refined with anisotropic thermal parameters and the axis reference system used in the calculation of the principal components of the **g** tensor.

Results and Discussion

Preparation of the Salts. The low solubility of TSeN is a major problem in the electrocrystallization experiments, necessitating the use of both elevated temperatures and extended reaction times. Both galvanostatic and potentiostatic methods were attempted, and the results in the Experimental Section represent our best results to date. Only the bromide was typically prepared as a crystallographically homogeneous sample, and hence its properties were studied. The room-temperature resistivity of compacted samples of TSeN$^+$Br$^-$ was in the range 10^3–10^4 Ω cm.

Crystal and Molecular Structure of $[C_{10}H_4Se_4]Cl$. TSeN$^{\bullet+}$ forms by removal of an electron from the highest occupied molecular orbital of TSeN. When the molecular geometries of a neutral donor and its cation radical are compared, small but experimentally significant changes are noted as a result of the charge transfer. When the geometries of cation radicals of tetrathiafulvalene[10] and 4,4′-bithiopyranylidene[11] are compared to those of

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Table III. Bond Lengths (Å) and Angles (deg) for [$C_{10}H_4Se_4$]Cl

Se1-Se2	2.336 (1)	C2-C3	1.416 (8)
Se1-C2	1.889 (5)	C3-C3	1.410 (11)
Se2-C4	1.871 (6)	C3-C4	1.417 (8)
C1-C1	1.383 (12)	C4-C5	1.404 (9)
C1-C2	1.392 (8)	C5-C5	1.391 (13)
C1-H1	1.02 (6)	C5-H5	1.04 (6)
Se2-Se1-C2	91.5 (2)	C2-C3-C4	121.7 (5)
Se1-Se2-C4	92.7 (2)	C3-C3-C4	119.1 (3)
C1-C1-C2	120.4 (3)	Se2-C4-C3	116.9 (5)
C1-C1-H1	120 (4)	Se2-C4-C5	122.2 (4)
C2-C1-H1	120 (4)	C3-C4-C5	121.0 (6)
Se1-C2-C1	122.3 (5)	C4-C5-C5	119.9 (4)
Se1-C2-C3	117.2 (4)	C4-C5-H5	117 (3)
C1-C2-C3	120.4 (5)	C5-C5-H5	122 (3)
C2-C3-C3	119.2 (4)		

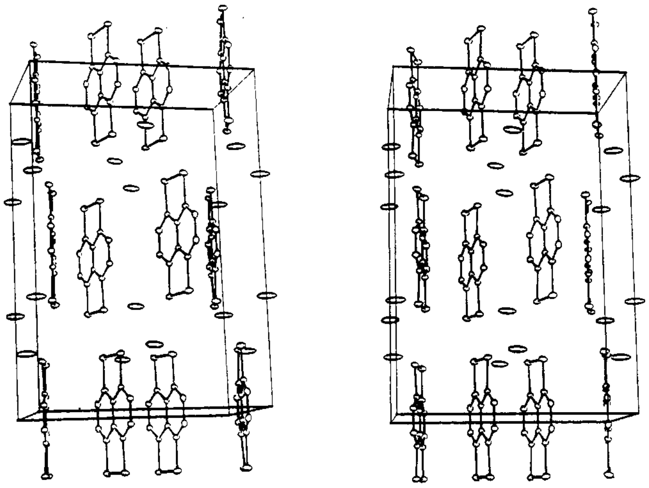

Figure 2. Stereoview of the unit cell for [$C_{10}H_4Se_4$]Cl (*a* vertical, *c* horizontal).

neutral analogues, double bonds are longer and single bonds are shorter after oxidation.

The structure of the TSeN molecular cation, which has crystallographic *m* symmetry, is shown in Figure 1. Bond lengths and angles (Table III) lie very near to those values observed for neutral TSeN.[1] The Se-Se bond lengths in the molecular cation are 0.028 (2) Å shorter and the Se-C bond lengths 0.016-0.044 (8) Å shorter than those observed in the neutral molecule. The carbon atoms form a plane with no deviations >0.033 (7) Å; the Se atoms deviate from this plane by 0.127 (1) Å (Se1) and 0.012 (1) Å (Se2). The C-Se-Se-C torsion angle is -3.5 (3)°. The packing of the molecules is shown in Figure 2. It can be seen that the molecules form parallel "dimer pairs" along the *b* axis. The shortest intradimer Se1-Se2 distance is 3.42 Å, while the shortest interdimer Se1-Se2 distance is 3.67 Å. The individual chains along the *b* axis are not interconnected by short contacts but rather are isolated by the chloride ions. The Se-Se and Se-C bond lengths observed herein for TSeN$^{\bullet+}$Cl$^-$ are similar to those previously reported for partially oxidized cations of 1,5,9,10-tetraselenoanthracene[12] and tetraselenotetracene.[13]

Magnetic Properties of TSeN$^{\bullet+}$Br$^-$. (a) Static Susceptibility. A SQUID device was used to study the static susceptibility of TSeN$^{\bullet+}$Br$^+$ over the temperature range 6-300 K. Curie law behavior was observed, and the concentration of spin-$^1/_2$ species was found to be 2×10^{21} spins mol^{-1}.

(b) ESR. The single crystals obtained were too small (i.e., contained too few paramagnetic species) to allow single-crystal ESR studies to be performed. However, it was possible to record a polycrystalline ESR spectral envelope, which is shown in Figure 3. This envelope is a textbook example of an orthorhombic g-tensor system for which the intrinsic line width and the hyperfine anisotropy are much smaller than that of the g tensor.[14] The ESR spectrum of this material was studied as a function of temperature from 77 to 300 K. There is a very slight narrowing of the overall width of the spectral envelope, due to a very slight temperature dependence of the values of the principal components of the **g** tensor. The observation of a resolved anisotropic **g**-tensor spectrum, as shown in Figure 3, is consistent with the spin count as measured by static susceptibility (i.e., a dilute magnetic system in which the individual magnetic spins are held rigidly in space).[6,7] In contrast, for solids in which there is one spin per molecule, Heisenberg spin-spin exchange effects[15] would narrow the spectral envelope and wash out the turning points at the two extremes of the spectrum. In the case of dilute magnetic solids in which the magnetic species are in motion (e.g., excitonic solids), the spectral envelope would be narrowed also.

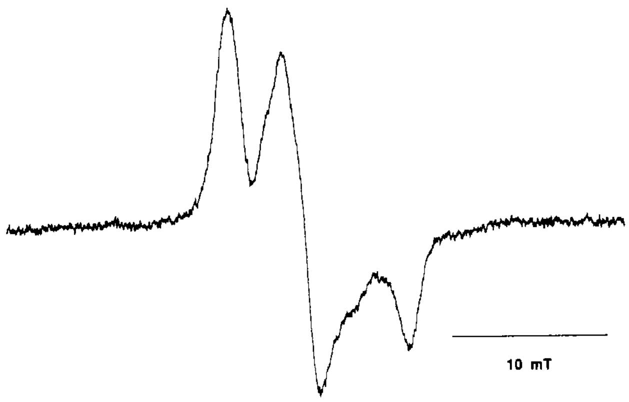

Figure 3. Room-temperature ESR spectral envelope of polycrystalline TSeN$^+$Br$^-$ prepared electrochemically.

Table IV. Principal Components of the **g** Tensor from the Polycrystalline ESR Spectral Envelopes of TSeN$^{\bullet+}$Br$^-$

	g_1	g_2	g_3	$\langle g \rangle$	lw, G
296 K	2.0850	2.0481	2.0084	2.0472	121.5
111 K	2.0825	2.0498	2.0075	2.0466	118.0
TSeN$^+$ (calcd)[a]	2.06968	2.05227	2.00232	2.04107	

[a] $g_1 = g_{yy}$; $g_2 = g_{xx}$; $g_3 = g_{zz}$.

Table V. Values of the Isotropic g Tensor and Spectral Line Widths for TSeN$^{\bullet+}$ in Various Solvents at Room Temperature

solvent	isotropic g tensor	lw, G
bromobenzene	2.04302	5.37
trifluoroacetic acid	2.04297	5.70
methylene chloride	2.04239	10.05

Table IV summarizes the principal components of the **g** tensor for TSeN$^{\bullet+}$Br$^-$ at 296 and 111 K. Also shown in Table IV are the calculated principal components for the TSeN$^{\bullet+}$ **g** tensor from the energy weighted maximum overlap (EWMO) technique, which was first proposed by Linderberg and Ohrn.[16] For more information about this technique and its use to calculate anisotropic g tensors, see ref 17.

Isotropic *g* Value for TSeN$^{\bullet+}$Br$^-$. In previous work,[1,2] we reported the isotropic *g* value for TSeN$^{\bullet+}$ as 2.0425 at room temperature. This measurement was taken in solutions of methylene chloride. Subsequent studies have indicated that some sort of complex is formed in methylene chloride solutions that leads to

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a shift in the isotropic *g* value and an increase in the observed line width, as shown in Table V.

Conclusions

Single crystals of ion-radical salts of the π-donor TSeN have been obtained for the first time. The 1:1 salts $TSeN^{\bullet+}X^-$ (X = Cl, Br) have isomorphous crystal structures. The structure of $TSeN^{\bullet+}Cl^-$ reveals dimers of parallel cation radicals as well as the changes in molecular geometry that occur on electron loss from TSeN. $TSeN^{\bullet+}Br^-$, an electrical semiconductor, exhibits Curie law paramagnetism in both static susceptibility and electron spin resonance studies. The detailed assessment of the potential of TSeN as a precursor to ion-radical salts with novel solid-state properties requires investigations beyond this initial study, and such research has been initiated.[4]

Supplementary Material Available: Table S-I, presenting experimental details for the structure determination, and Table S-II, listing thermal parameters (3 pages); a table of observed and calculated structure amplitudes (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, Department of Chemistry, Rider College, Lawrenceville, New Jersey 08648, and Department of Physics, Nuclear Research Center, "Demokritos", Athens, Greece

Chloride-Induced Assembly of Manganese(II) Complexes Having Oligomeric and Chain Structures

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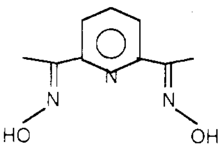
The planar tridentate ligand 2,6-diacetylpyridine dioxime (H_2dapd) forms complexes with Mn(II) having stoichiometries that are determined by the nature of the counterion. The monomeric bis chelate complex $Mn(H_2dapd)_2X_2$ forms with outer-sphere counterions X = Br^- (3) and ClO_4^- (2). However, with Cl^- a discrete oligomeric complex, $[Mn(H_2dapd)Cl_2]_n$, probably dimeric ($n = 2$) or tetrameric ($n = 4$), forms in nonprotic solvents like DMF, while only a monomeric Mn(II) complex forms in protic solvents. This is in equilibrium with a linear-chain polymer $n = \infty$ (**1**) in the solid state. Compound **1** crystallizes in the monoclinic space group *Cc* [$Z = 4$, $a = 17.843$ (3) Å, $b = 10.422$ (2) Å, $c = 6.809$ (1) Å, $\beta = 106.49$ (0)°]. Mn coordinates to form pentagonal bipyramids $Mn(N_3Cl_2)Cl_2$ in which each chloride occupies axial and equatorial sites on adjacent monomer units in the helical chains. Variable-temperature magnetic susceptibility indicates weak ferromagnetic coupling in **1** ($\mu_{eff} = 8.40\ \mu_B$ at 4.2 K and 6.02 μ_B at 294 K), with an effective spin-exchange temperature of $T_0 = 5$ K ($J = 0.2\ cm^{-1}$), using a one-dimensional linear-chain classical model. This contrasts with the monomeric complex **2**, which exhibits a temperature-independent moment 5.94–5.81 μ_B between 294 and 4.2 K, indicating no intermolecular coupling. The oligomeric complex of **1** in DMF also exhibits ferromagnetic coupling, as seen by the EPR-active paramagnetic ground state. Possible structures are discussed. The weaker ionic bonding between Mn(II) and Br^- and ClO_4^- vs Cl^- accounts for the formation of the bis chelate complexes **2** and **3**. The capacity for Cl^- to spontaneously assemble an oligomeric Mn(II) cluster in solution is compared with the special requirement for Cl^- for assembly of the polynuclear manganese complex responsible for photosynthetic water oxidation.

Introduction

Oximes are well-known chelating agents that form a variety of metal complexes. 2,6-Diacetylpyridine dioxime (H_2dapd) is



H_2dapd

a particularly interesting planar N,N,N-donor chelating ligand. Fe(II) and Ni(II) form mononuclear complexes with this ligand.[1-3] McCormic et al.[4] have isolated the monomeric, five-coordinate copper complex $[Cu(Hdapd)(Cl)_2]$ and the dimeric dication $[Cu(Hdapd)]_2^{2+}$. Complexes with Mn(II) and H_2dapd have not yet been reported. We were prompted to study the coordination chemistry of this ligand because of the opportunity for formation of discrete Mn aggregates dictated by the incomplete coordination presented by the planar tridentate ligand. Tetrameric and dimeric manganese sites are of biological importance in the enzymes responsible for photosynthetic water oxidation[5] and within the pseudocatalase of *L. planatarum*,[6] respectively. In this study we report the synthesis of manganese(II) complexes with H_2dapd and provide EPR, X-ray crystallographic, and magnetic susceptibility evidence for the special capability of chloride for inducing assembly of an oligomeric Mn(II) complex in aprotic solvents and a linear-chain polymer in the solid state. This is discussed in relation to the chloride requirement observed for photooxidation of the manganese enzyme in photosynthetic water oxidation.

Table I. Crystallographic Data for **1**

chem formula	$C_9H_{11}Cl_2MnN_3O_2$	fw	319.1
a	17.843 (3) Å	space group	*Cc*
b	10.422 (2) Å	*T*	296 K
c	6.809 (1) Å	λ	0.710 69 Å
β	106.49 (1)°	ρ_{calc}	1.75 g/cm^3
V	1214.1 (4) Å^3	μ	15.7 cm^{-1}
Z	4	trans coeff	0.458–0.552
$R(F_o)$	0.039	$R_w(F_o)$	0.045

Experimental Section

2,6-Diacetylpyridine Dioxime (H_2dapd) ($C_9H_{11}N_3O_2$). The ligand was prepared from hydroxylamine hydrochloride and 2,6-diacetylpyridine by a literature procedure.[7]

$[Mn(H_2dapd)Cl_2]_n$ (1). H_2dapd (0.01 mol) was dissolved in ethanol (50 mL). To this solution was added $MnCl_2\cdot4H_2O$ (0.01 mol) and the solution refluxed for 1 h and cooled to form a yellow precipitate. Crystals for X-ray crystallography studies were obtained by slowing boiling off excess ethanol from a dilute solution of the compound. For analysis, the compound was recrystallized from a mixture of ethanol–DMF (1:1). Anal. Calcd for $(C_9H_{11}N_3O_2)MnCl_2$: C, 33.86; H, 3.45; N, 13.17; Mn, 17.25. Found: C, 33.68; H, 3.44; N, 12.71; Mn, 17.75.

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