systematic variation of axial bases and macrocycles would help sort out their individual contributions.[14-16]

A substantial contribution to the ease of the Co–C bond homolysis in $C_6H_5CH_2Co([14]aneN_4)(H_2O)^{2+}$ comes from the large positive value of ΔS^{*}. This we attribute to the influence of the overall 2+ charge on the change in solvation of the benzyl group between the ground and transition states. The ΔS^{*} term is much smaller for the five neutral complexes in Table I.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract W-7405-Eng-82.

Supplementary Material Available: A table of the kinetic data and a plot of k_{obsd} against $[Cr^{2+}]$ at different temperatures (2 pages). Ordering information is given on any current masthead page.

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[14] The activation enthalpies for homolysis of a series of benzylcobaloximes and benzylcobalt porphyrin complexes containing bulky phosphines as axial ligands in toluene[15] and ethylene glycol[16] are all higher than the value for $C_6H_5CH_2Co(saloph)py$.

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Incipient Pentagonal-Pyramidal Coordination of Tellurium in a Macrocyclic Tetra(secondary amine) Complex

Sir:

Among the seven topologically distinct six-vertex polyhedra,[1,2] the octahedron (Figure 1) is found in the vast majority of six-coordinate complexes.[3] The trigonal prism (Figure 1) is found in some tris(dithiolene)[4] and a few other six-coordinate metal complexes.[5] Among the remaining five six-vertex polyhedra the C_{2v} 6,11,7-polyhedron (Figure 1)[6] and the pentagonal pyramid (Figure 1) may both be derived from AB_6E systems based on an underlying pentagonal bipyramid with a stereochemically active lone pair in an equatorial (6,11,7-polyhedron) and in an axial (pentagonal pyramid) position, respectively. The "distorted octahedron"[8] in the tellurium(IV) anion $[Me_2NCS_2TeBr_4]^-$ may be interpreted as a C_{2v} 6,11,7-polyhedron. This communication reports the first example of a pentagonal-pyramidal six-coordinate complex based on an underlying tellurium(IV) pentagonal bipyramid with a stereochemically active lone pair in an axial position. This complex was obtained serendipitously from an attempted preparation of (cyclen)Te isoelectronic with the known[9] (cyclen)PH.

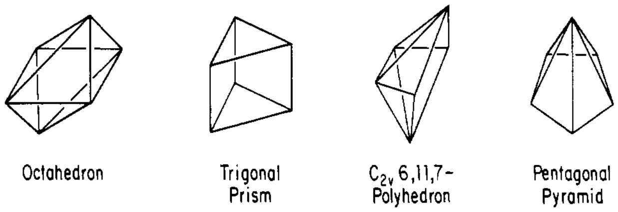

Figure 1. The four six-vertex polyhedra discussed in this paper.

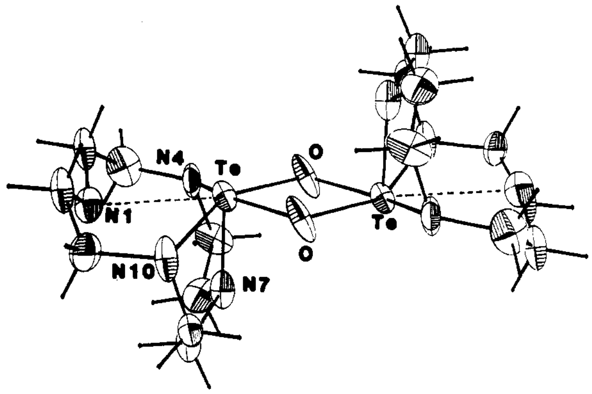

Figure 2. ORTEP diagram of the $[(C_8H_{16}N_4H_3)_2Te_2O_2]^{+2}$ cation in $[(C_8H_{16}N_4H_3)_2Te_2O_2]Cl_2{\cdot}4CHCl_3{\cdot}2CH_3OH$.

Table I. Tellurium Coordination Polyhedron in $[(cyclenH_3)_2Te_2(\mu\text{-}O)_2]Cl_2{\cdot}2MeOH{\cdot}4CHCl_3$

	Distances (Å)		
	Apical		
Te–N7	1.996 (22)		
	Basal		
Te–O1	1.998 (13)	Te–N1	2.703 (18)
Te–O1′	1.998 (13)	Te–N10	2.424 (19)
Te–N4	2.472 (18)		
	Nonbonding		
Te–Te	3.107 (2)		
	Angles (deg)		
	Apical–Basal		
N7–Te–O1	92.3 (7)	N7–Te–N1	83.1 (7)
N7–Te–O1′	91.5 (7)	N7–Te–N10	79.0 (7)
N7–Te–N4	77.6 (7)		
	Adjacent Basal–Basal		
O1–Te–O1′	77.3 (6)	N1–Te–N10	67.6 (5)
O1′–Te–N4	73.2 (6)	N10–Te–O1	73.8 (6)
N4–Te–N1	67.9 (6)		
	Nonadjacent Basal–Basal		
O1–Te–N4	148.4 (6)	N1–Te–O1	141.3 (6)
O1′–Te–N1	141.0 (5)	N10–Te–O1′	149.0 (6)
N4–Te–N10	131.5 (6)		

A solution of $(CF_3CH_2O)_4Te$[10] was obtained by treatment of 2.0 g (7.4 mmol) of $TeCl_4$ in 50 mL of tetrahydrofuran and 20 mL of pentane at −72 °C with a mixture of 3.34 g (33.4 mmol) of CF_3CH_2OH and 3.4 g (33.4 mmol) of triethylamine. After the mixture was warmed slowly to room temperature over a period of 5 h, the precipitate of $[Et_3NH]Cl$ was removed by filtration of 0 °C. The filtrate was cooled to −20 °C and then treated with 1.2 g (7 mmol) of 1,4,7,10-tetraazacyclododecane ($cyclenH_4$). After the mixture was stirred for 12 h, the white precipitate was filtered. Suitable rhombohedral crystals for X-ray diffraction were obtained by crystallization from a mixture of chloroform and methanol. These white crystals, shown by the structure determination to have the stoichiometry $[(C_8H_{16}N_4H_3)_2Te_2O_2]Cl_2{\cdot}4CHCl_3{\cdot}2MeOH$, are efflorescent, losing the coordinated solvent molecules and their crystallinity upon drying. The crystals were therefore kept moist with the solvent mixture during the structure determination. Elemental analysis on the dry noncrystalline material gave values close to those expected for the solvent-free formulation $[(C_8H_{16}N_4H_3)_2Te_2O_2]Cl_2$. Anal. Calcd: C, 27.4;

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H, 5.4; N, 16.0; Cl 10.1. Found: C, 25.9; H, 5.5; N, 15.0; Cl, 9.5.

The compound $[(C_8H_{16}N_4H_3)_2Te_2O_2]Cl_2 \cdot 4CHCl_3 \cdot 2CH_3OH$ forms monoclinic crystals: space group $P2_1/c$; $a = 10.430$ (3) Å, $b = 15.633$ (9) Å, $c = 15.407$ (6) Å, $\beta = 107.76$ (3)°; $V = 2392.4$ (18) Å^3; $Z = 2$, $d_{calcd} = 1.724$ g/cm^3. Least-squares refinement using the 1943 observed reflections revealed the structure depicted in Figure 2 ($R = 0.080$ and $R_w = 0.098$). The hydrogen atoms could not be unambiguously located. Oxidation state and bond distance considerations suggest the presence of hydrogen atoms on N1, N4, and N10 but not on N7 or the bridging oxygen atoms. The two tellurium atoms in the $[(C_8H_{16}N_4H_3)_2Te_2O_2]^{2+}$ cation are not within bonding distance (Te–Te = 3.107 (2) Å) and are bridged by two μ-oxygen atoms in a manner similar to that in the binuclear tellurate(VI) anion $Te_2O_6(OH)_4^{4-}$.[11]

The most interesting feature of this structure is the tellurium coordination polyhedron. The relevant bond distances and angles are summarized in Table I. This tellurium coordination polyhedron may be viewed as a pentagonal pyramid with O1, O1′, N4, N1, and N10 in the basal plane and the deprotonated nitrogen atom N7 in the apical position. The standard deviation of the five basal atoms from planarity is 0.18 Å, and the atoms Te and N7 are displaced on opposite sides of the best plane of the five basal atoms by 0.20 and 1.78 Å, respectively. The average of the five apical–basal angles, i.e. those involving N7, (Table I) is slightly acute (84.7°), indicating that the lone pair in the axial position of the original pentagonal bipyramid is slightly more sterically demanding than the N7 in the other axial position. The five adjacent basal–basal angles (Table I) range from 67.7 to 77.3° as compared with the 72° expected for a regular pentagon base. This deviation from ideal 5-fold symmetry is rather small considering the constraints imposed by the four fused five-membered chelate rings formed by the coordinated macrocylic tetraamine. These constraints also make one of the distances from the central Te to the basal nitrogens (i.e., N1) significantly longer (2.703 (18) Å) than the distances to the other two basal nitrogens (N4 and N10) suggesting that the Te–N1 bond is appreciably weaker than the Te–N4 and Te–N10 bonds so that the pentagonal-pyramidal coordination can be described as "incipient".

This preliminary result suggests that the structures of crystalline products from reactions of tellurium(IV) derivatives with macrocyclic poly(secondary amines) might be a fertile source of unusual coordination polyhedra derived from larger underlying polyhedra with stereochemically active lone pairs and that such products merit more detailed attention.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-82-12166.

Supplementary Material Available: Tables II–V, listing crystal data, positional parameters, anisotropic thermal parameters, and bond angles and distances for $TeCl_7O_2N_4C_{11}H_{25}$, and an ORTEP diagram of the $[(C_8H_{16}N_4H_3)_2Te_2O_2]^{2+}$ cation showing the four $CHCl_3$ molecules of crystallization (5 pages); tables of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.

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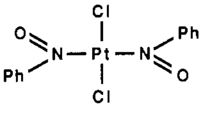
Molecular Structure of (μ-η^1-Nitrosobenzene-*N*)(μ-η^2-nitrosobenzene-*N,O*)(η^1-nitrosobenzene-*N*)tris(trimethylphosphine)diplatinum(II), a Complex Containing Three Linkage Isomers of Nitrosobenzene

Sir:

Aliphatic and aromatic nitro compounds may be reduced to amines with metal hydrides,[1,2] with hydrogen in the presence of a transition-metal catalyst,[3] or by catalytic hydrogenation.[4] These reductions may proceed through an intermediate nitroso compound, although such intermediates have never been structurally characterized. Several examples of transition-metal nitroso compounds exist.[5-13] The nitroso group may be bound η^1 to the metal through nitrogen as a σ base (I)[5-7] or may bridge two metal centers in an η^1 or η^2 fashion (II).[8-10] The reaction between $Pt(C_2H_4)(PPh_3)_2$ and nitrosobenzene results in side on η^2 coordination of the N–O group (III).[11] This complex inserts substrates into the Pt–N bond to give nitrones (IV).[12] Some studies suggest that nitroso groups may coordinate to a metal through the oxygen atom,[13] though this has never been established crystallographically.



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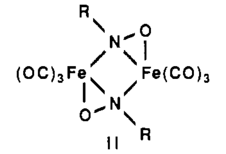

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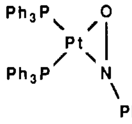

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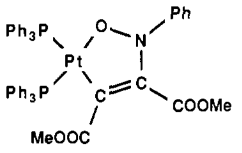

IV

We attempted to catalytically reduce nitrobenzene to aniline with the highly reactive platinum dihydride $PtH_2(PMe_3)_2$ (**1**).[14] When 10 equiv of nitrobenzene was added to a solution of **1** (0.06 M in THF) under a hydrogen atmosphere, the yellow solution became dark brown. No gas evolution was apparent. The reaction solution was paramagnetic, and NMR spectra could not be obtained.[15] Reduction of the solution volume to 1 mL and addition

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