sulfur to give $Ni(CO)(PPh_3)_3$ or PPh_3 to afford $Ni(\eta^2\text{-}COS)(PPh_3)_2$. A similar mechanism has been proposed for the formation of $Ni(\eta^2\text{-}CO_2)(L)_2$ ($L = PEt_3$, $P(n\text{-}Bu)_3$),[2] and the presence of $Ni(CO_2)(L)_3$ has been detected spectroscopically. The complex $Ni(\eta^2\text{-}CO_2)(L)_2$ is stable, whereas similar reactions with COS afford a mixture of metal carbonyls.[5]

Discussion

The stability of the species $M(\eta^2\text{-}COS)(L)_2$ ($L = PPh_3$) decreases in the order Pt > Pd > Ni. The platinum complex is stable in solution at low temperature, the palladium complex is stable in the solid state but decomposes upon dissolution, and the nickel complex has not been observed, although it is likely to be a transient intermediate in the observed carbonylation reaction. The reactions of ML_3 complexes with COS depend on the affinity of the metal center for carbon monoxide and sulfur, the species into which COS fragments upon C═S bond cleavage. Palladium and platinum have a higher affinity for sulfur than does nickel, and the formation of dithiocarbonates is favored. Nickl(0) complexes have a high affinity for π-acceptor ligands (e.g., $Ni(CO)_4$ is stable, $Pt(CO)_4$ is not), and $Ni(PPh_3)_3$ selectively binds the CO fragment. Although the preference of the metal center for a π-acceptor rather than a σ-donor ligand may be important in these reactions, kinetic factors are also important, as evidenced by the increased formation of $Pt(CO)(PPh_3)_3$ at higher temperature.

It is interesting that $Pt_2S(CO)(PPh_3)_3$ reacts with CS_2 to afford $Pt(CS_3)(PPh_3)_2$,[35] but addition of CS_2 to $Pt(PPh_3)_4$ affords $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$.[4] This complex is stable, and C–S bond cleavage to give $Pt_2S(CS)(PPh_3)_3$ does not occur. Hence, it is the greater stability of the coordinated C═S bond of CS_2 that prevents the formation of $Pt(CS_3)(PPh_3)_2$ from $Pt(PPh_3)_4$ and CS_2 by a pathway analogous to Scheme III. Both $Pt(S_2CNR)(PPh_3)_2$ and $Pt(S_2CNR)(RNC)(PPh_3)$ are formed from the reaction of $Pt(PPh_3)_4$ with SCNR (R = Me, Ph).[41] This reaction might proceed by a mechanism analogous to the one depicted in Scheme III. Cleavage of the dimer at both Pt–S bonds would account for the formation of both products.

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE80-09671). We thank Johnson-Matthey, Inc., Malvern, PA, for the loan of precious metal used in this study.

Registry No. $Pt(COS_2)(PPh_3)_2$, 25787-94-4; $Pt(CO_2S)(PPh_3)_2$, 81178-19-0; $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$, 15308-68-6; $Pd(\eta^2\text{-}COS)(P(p\text{-}C_6H_4CH_3)_3)_2$, 81178-20-3; $Pd(COS_2)(P(p\text{-}C_6H_4CH_3)_3)_2$, 81178-21-4; $Pd(\eta^2\text{-}COS)(PPh_3)_2$, 81178-22-5; $Pd(CO_2S)(P(p\text{-}C_6H_4CH_3)_3)_2$, 81178-23-6; $Ni(CO)(PPh_3)_3$, 15376-83-7; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Pt(\eta^2\text{-}COS)(PPh_3)_2$, 10210-51-2; $Pt_2S(CO)(PPh_3)_3$, 27664-43-3; $Pt(PPh_3)_4$, 14221-02-4; $Pt(O_2)(PPh_3)_2$, 15614-67-2; $Pd(P(p\text{-}C_6H_4CH_3)_3)_3$, 27903-26-0; $Pd(PPh_3)_3$, 28516-49-6; $Pd(O_2)(P(p\text{-}C_6H_4CH_3)_3)_2$, 81178-24-7; $Ni(PPh_3)_3$, 25136-46-3; COS, 463-58-1.

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Notes

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Reactions of Tetrasulfur Tetranitride [Cyclotetra(azathiene)] with Some Tin(II) and Tin(IV) Compounds

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Tetrasulfur tetranitride [cyclotetra(azathiene)] forms adducts with main-group and transition-metal halides.[1,2] Reactions in inert solvents precipitate complexes in which S_4N_4 acts as a mono- or bidentate ligand. In certain cases the products are adducts of disulfur dinitride. X-ray structures of $S_4N_4{\cdot}BF_3$,[3] $S_4N_4{\cdot}SbCl_5$,[4] and $S_4N_4{\cdot}AsF_5$[5] show unidentate donation through the nitrogen atom. In $S_4N_4{\cdot}CuCl$ pairs of S_4N_4 molecules act as bridging ligands between CuCl chains through 1,3-nitrogen atoms.[6]

Reaction between S_4N_4 and $SnCl_4$ was first reported at the turn of the century[7,8] to give a red precipitate of stoichiometry $SnCl_4{\cdot}2S_4N_4$, and this has been confirmed by more recent work.[10,11] The bromine analogue, $SnBr_4{\cdot}2S_4N_4$, forms from $S_4N_4H_4$ in ether or directly from S_4N_4 in hydrocarbon solvents.[11] Tin(II) chloride, on the other hand, has been reported to reduce S_4N_4 to $S_4N_4H_4$ in alcohol in early work[8] or to give no reaction in ether after 48 h at room temperature.[10]

The availability of more reactive tin(II) species such as dimethoxyltin(II) and bis(dimethylamino)tin(II) and spectroscopic techniques such as tin-119m Mössbauer spectroscopy has prompted us to reinvestigate the chemistry of S_4N_4 and tin.

Experimental Section

Tetrasulfur tetranitride was prepared by the method of Jolly.[12] Anhydrous $SnCl_2$, $SnBr_2$, and $SnCl_4$ were obtained from Alfa Inorganics, Beverly, MA, and anhydrous $SnBr_4$ was obtained from Apache Chemicals, Rockford, IL, and used without further purification. Tin(II) dimethoxide was prepared from $SnCl_2$,[13] and bis(dimethylamino)tin(II) was prepared by the method of Zeldin.[14] Carbon tetrachloride and dichloromethane were of reagent grade quality and were further dried over P_4O_{10}. Infrared spectra were recorded on a Beckman IR-12 spectrometer as Nujol or halocarbon mulls, and Mössbauer spectra were recorded with constant acceleration, cam-drive and Ranger Engineering instruments and were recorded vs. $Ca^{119m}SnO_3$ both as the source and standard for zero velocity at room temperature. All reactions were carried out in an inert atmosphere of dry nitrogen. Tin was determined gravimetrically as SnO_2, and halogens, nitrogen, carbon, and hydrogen were determined by

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Table I. Physical Properties and Tin-119m Mössbauer and Analytical Data for the Reaction Products of S_4N_4 with Tin Compounds

compd	Mössbauer data at 77 K, mm/s: IS (±0.06)	QS (±0.12)	Γ (±0.06)	Anal. data % found (calcd): Sn	Cl or Br	color	mp, °C
$SnCl_4 \cdot 2S_4N_4$	0.45		1.39	18.81	22.65 (Cl)	brick red	194–196
				(18.87)	(22.54)		
$SnBr_4 \cdot 2S_4N_4$	0.75		2.42	14.81	40.14 (Br)	scarlet red	290–300
				(14.71)	(39.61)		
$SnCl_2 \cdot S_2N_2$	2.03	3.77	1.71[a]	42.79	26.13 (Cl)	light orange	infusible <400
			1.93[b]	(42.13)	(25.17)		
	2.26[g]	4.46	2.00[a]				
			2.18[b]				
$SnBr_2 \cdot S_2N_2$	2.14	3.54	1.65[a]	33.01	43.30 (Br)	light yellow	infusible <400
			1.32[b]	(32.03)	(43.12)		
$Sn(OCH_3)_2 \cdot S_2N_2$	0.43		2.15	43.21	*c*	dull yellow	infusible <400
	0.13[g]	0.73	1.95[a]	(43.51)			
			2.08[b]				
$Sn[N(CH_3)_2]_2 \cdot S_2N_2$	0.63[d]	0.82	1.50	39.71	*e*		infusible <400
			1.52	(39.73)			
	0.60[f]		1.74				
	0.38[g]	0.76	1.29[a]				
			1.56[b]				

[a] Low-velocity wing of the doublet. [b] High-velocity wing of the doublet. [c] Anal. Calcd: C, 8.80; H, 2.20. Found: C, 8.84; H, 2.29. [d] Prepared in CH_2Cl_2 as solvent. [e] Anal. Calcd: N, 18.74. Found: N, 18.40. [f] Prepared in C_6H_6 as solvent. [g] Recorded at room temperature.

Instranal Laboratories, Rensselaer, NY.

Reaction of $SnCl_4$ and S_4N_4. A mixture of S_4N_4 (0.500 g, 2.72 mmol) and anhydrous $SnCl_4$ (0.095 g, 3.6 mmol) in dry CCl_4 (100 mL) was stirred for 48–72 h; a brick red solid was precipitated, filtered, and washed with CCl_4 to give $SnCl_4 \cdot 2S_4N_4$ in virtually quantitative yield based on S_4N_4. The brick red compound turns grayish at 192 °C and decomposes quickly to a deep red product at 194–196 °C (lit. mp 215–218 °C,[9] 200–202 °C[10]).

Reaction of $SnBr_4$ and S_4N_4. A slurry of S_4N_4 (0.500 g, 2.72 mmol) and anhydrous $SnBr_4$ (2.5 g, 5.6 mmol) in dry CCl_4 (100 mL) was stirred at room temperature. After 24 h a heavy scarlet red solid precipitated; the mixture was stirred for another 72 h and then filtered and washed with CCl_4. However, a 1:1 mole ratio of $SnBr_4$ and S_4N_4 stirred for 1 day gave only a small amount of the scarlet red solid; addition of excess of $SnBr_4$ almost immediately precipitated more. In the presence of excess $SnBr_4$, the reaction to form $SnBr_4 \cdot 2S_4N_4$ was nearly quantitative based on S_4N_4. The scarlet red compound turns yellow at 185 °C and melts completely between 290 and 300 °C (lit. mp 198–200 °C[10]).

Excess tin(IV) halides were used in both the above reactions in order to check whether a 1:1 product, $S_4N_4 \cdot SnX_4$, could be isolated, but only products of the composition $2S_4N_4 \cdot SnX_4$ were obtained.

Reaction of $SnCl_2$ and S_4N_4. A mixture of S_4N_4 (1.00 g, 5.44 mmol) and anhydrous $SnCl_2$ (1.08 g, 5.44 mmol) in dry CCl_4 (150 mL) was refluxed with stirring for 120 h, during which time the mixture slowly turned from yellowish to orange. After the mixture was cooled to room temperature, the solid $SnCl_2 \cdot S_2N_2$ was filtered and washed with the same solvent to give a yield of ~90% based on $SnCl_2$. The light orange solid did not melt at <400 °C.

Reaction of $SnBr_2$ and S_4N_4. A mixture of S_4N_4 (0.500 g, 2.72 mmol) and anhydrous $SnBr_2$ (0.760 g, 2.72 mmol) in dry CCl_4 (100 mL) was refluxed for 120 h; the color of the mixture gradually turned yellow to brownish. After cooling to room temperature, the reaction mixture was filtered and washed with CCl_4. The light yellow solid $SnBr_2 \cdot S_2N_2$ was produced in ~80% yield based on $SnBr_2$. The solid does not melt at <400 °C.

Reaction of Tin(II) Dimethoxide and S_4N_4. To tetrasulfur tetranitride (1.66 g, 9.02 mmol) in dry CH_2Cl_2 (150 mL) was added $Sn(OCH_3)_2$ (1.63 g, 9.02 mmol with stirring through a solids addition tube. The mixture was stirred for 1 week at room temperature and then filtered and washed. The dull yellow solid $Sn(OCH_3)_2 \cdot S_2N_2$ was obtained in ~80% yield. The solid does not melt at <400 °C.

Reaction of Bis(dimethylamino)tin(II) and S_4N_4. To tetrasulfur tetranitride (2.10 g, 11.41 mmol) in dry CH_2Cl_2 (150 mL) was added $Sn[N(CH_3)_2]_2$ (2.35 g, 11.37 mmol) slowly through a solids addition tube with constant stirring. The mixture turned reddish brown immediately but was further stirred at room temperature for 120 h, filtered, and washed with CH_2Cl_2. The solid $(SN)_2Sn[N(CH_3)_2]_2$ product, formed in ~80% yield, does not melt at <400 °C.

Table II. Infrared Absorptions (cm^{-1})[a] for the $SnX_4 \cdot 2S_4N_4$ (X = Cl, Br) and $SnX_2 \cdot S_2N_2$ [X = Cl, Br, OCH_3, $N(CH_3)_2$] Complexes in the 2000–200-cm^{-1} Range

$SnCl_4 \cdot 2S_4N_4$	230 w, 330 s, 370 s, 420 m, 520 vs, 552 w, 572 w, 623 m, 685 m, 705 w, 725 w, 790 m, 798 m, 815 vs, 930 w, 970 vs, 1048 vs, 1410 s
$SnBr_4 \cdot 2S_4N_4$	230 m, 358 m, 422 m, 515 s, 550 w, 628 m, 665 m, 675 m, 705 w, 715 w, 782 vs, 928 m, 962 vs, 1042 vs, 1405 s
$SnCl_2 \cdot S_2N_2$	230 s, 250 w, 305 w, 355 w, 375 m, 385 m, 400 m, 420 w, 465 m, 520 w, 552 m, 560 w, 600 w, 650 m, 660 m, 705 m, 725 m, 785 s, 805 w, 845 m, 930 m, 955 s, 1020 br, m, 1045 w, 1078 m, 1210 br, m, 1400 s
$SnBr_2 \cdot S_2N_2$	370 br, sh, 390 m, 465 s, 520 w, 555 br, m, 600 w, 640 m, 650 m, 705 vw, 730 m, 795 s, 850 vw, 930 br, m, 960 m, 1025 s, 1080 s, 1100 br, s, 1160 m, 1220 br, m, 1265 m, 1410 s
$Sn(OCH_3)_2 \cdot S_2N_2$	390 s, 460 br, s, 520 w, 595 w, 655 w, 690 s, 740 m, 805 m, 920 s, 1025 vs, 1085 vs, 1260 m, 1380 m, 1470 s, 1650 m, 1710 m
$Sn[N(CH_3)_2]_2 \cdot S_2N_2$	360 m, 390 s, 440 s, 550 w, 585 m, 640 s, 650 s, 690 s, 735 s, 910 s, 1020 vs, 1085 vs, 1170 br, vs, 1260 m, 1365 m, 1430 m, 1465 m, 1650 vs, 1710 s

[a] Key: s = strong, m = medium, w = weak, br = broad, v = very, sh = shoulder.

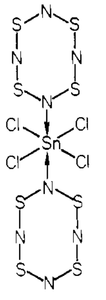
Reversing the order of addition of the equimolar quantities in CH_2Cl_2 gave a black solution which became dark red and then dark red-brown and precipitated a dark brown solid in quantitative yield.

Alcoholysis of the Aminotin(II) Product. $[(CH_3)_2N]_2SnS_2N_2$ (0.500 g, 1.68 mmol) was refluxed for 0.5 h in dry, oxygen-free methanol (100 mL) under N_2. The dark brown solid slowly dissolved with evolution of dimethylamine to give a light yellow solution. Evaporation of the solvent gave $(CH_3O)_2SnS_2N_2$ (0.43 g, 98% yield).

The Mössbauer parameters and analytical data of the complexes are given in Table I. The infrared spectral data are given in Table II.

Results and Discussion

The bisadducts of S_4N_4 with tin(IV) chloride and bromide are high melting, highly red-colored solids as previously reported.[7-11] Their precipitation from CCl_4 is enhanced by the presence of excess tin(IV) halide. The tin-119m Mössbauer isomer shifts (IS) are consistent with hexacoordination at tin[15] but cannot distinguish whether sulfur or nitrogen donor atoms are being used. Ligands in which the donor atom holds more than one subsitutent atom are usually found to take trans positions, in the octahedron,[16] and the crystal structures of $SbCl_5{\cdot}S_4N_4$,[4] $AF_5{\cdot}S_4N_4$,[5] $CuCl{\cdot}S_4N_4$,[6] and $S_4N_4{\cdot}BF_3$[3] show that the nitrogen is functioning as the donor atom. Thus we reason by analogy that the tin(IV) complexes have the structure



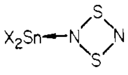
A

and this conclusion is supported by the number of observed metal–halide absorptions in the far-infrared region which lie at 330 s (lit. 309,[11] 304[9]) cm^{-1} for the chloride and 230 m (lit. 220[11]) cm^{-1} for the bromide. The cis configuration would be expected to give rise to three bands.[16]

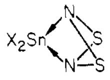
The tin(II) adducts of the simple binary SN species are being reported here for the first time. The four products formed after long reaction times are infusible solids whose analytical data specify the formulas $SnX_2S_2N_2$. Their infrared spectra differ sufficiently from those of the SnX_4 adducts[9,10] to suggest different structures. The bis(dimethylamino)tin(II) disulfur dinitride product undergoes alcoholysis in refluxing methanol (eq 1) At least two types of structures are possible,

$$[(CH_3)_2N]_2SnS_2N_2 + 2CH_3OH \rightarrow (CH_3O)_2SnS_2N_2 + 2(CH_3)_2NH \quad (1)$$

the first involving the four-membered S_2N_2 ring as a uni- (B)



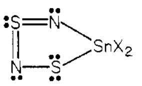
B



C

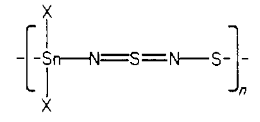
or bidentate (C) donor to the tin(II) atom. Precedence for structure B is found for the $SbCl_5$ derivatives[17] where crystal structure data are available for $2SbCl_5{\cdot}S_2N_2$ in which both nitrogen atoms are engaged in donation to antimony.[18] The chelating S_2N_2 ring as in structure C is found in the copper complexes, $X_2Cu{\cdot}S_2N_2$.[19,20]

A second structural type would result from insertion into the S_2N_2 ring to give the oxidative addition product



D

The action of lead(II) iodide in S_4N_4 in liquid ammonia gives a monoamine of lead dithionitrosyl, $Pb(NS)_2{\cdot}NH_3$, in which the lead is bonded to sulfur and nitrogen in a five-membered ring, as in structure D.[21] Other oligomeric or polymeric forms forms (E) are presumably possible but have no precedence in the literature.[1,2]

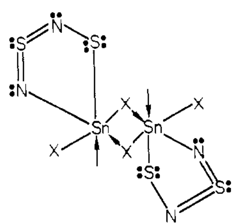


E

The products from the tin(II) starting materials are slightly colored, infusible solids which precipitate from chlorocarbon solvents after long stirring times at reflux for the halides and at ambient temperature for the tin(II) methoxide and dimethylamino derivative.

The tin-119 Mössbauer data for the $X_2SnS_2N_2$ species fall into two distinct sets for the X = Cl and Br compounds on the one hand, and the X = OCH_3 and $N(CH_3)_2$ compounds on the other (see Table I). Both sets of data include IS values clearly in the tin(IV) region, thus ruling out tin(II) structures B and C for these products. With regard to the former two compounds, there is neither any precedent in the tin Mössbauer literature[15,22] for the combination of high IS values in the tin(IV) range and high quadrupole splitting (QS) values observed here, nor are there data available for dihalotin compounds bound to nitrogen or sulfur, excepting for the $X_2Sn[S_2CN(C_2H_5)_2]_2$ derivatives in which X = Cl (IS = 0.78)[23] and Br (0.90,[23] 0.95[24] mm s^{-1}) and in which there is no resolvable QS. These dithiocarbamates are six-coordinated in the solid state.[25] The IS and QS are values for our dihalides reflect a four-coordinated tin environment with extremely polarizing ligands producing a severe distortion in the electric field at the tin atom. It is not known at this writing whether structures such as D or E will have these properties. Additional coordination by nitrogen or sulfur atoms would account for the high QS values observed but would be expected to lower the IS to values below those recorded. Thus we favor structures D or E for the $X_2Sn{\cdot}S_2N_2$ compounds, which on the basis of their infusible nature and the observation of strong ambient-temperature Mössbauer spectra probably are polymeric as in E.

Additional coordination to the tin atom is necessary to account for the Mössbauer data for the methoxy and dimethylamino derivatives. Here the IS values demand a six-coordinated tin(IV) atom surrounded by electronegative atoms and the strong ambient-temperature spectra demand a polymeric structure. The additional coordination could arise from the methoxy oxygen or amino nitrogen atoms in the ligand moieties which could engage in bridging the SnS_2N_2 heterocycles of structure D to form an associated polymer



F

or cross-link the polymer chains of structure E

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(20) This formulation indicates a +2 oxidation state for the metal, although the product can only be made from Cu(I).[19] This complex may actually be $X_2CuS_2N_2H$ derived from the +1 oxidation state.[1]

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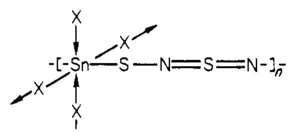

G

The nitrogen or sulfur atoms of the S_2N_2 moiety could also participate in bridging to tin as the nitrogen atoms in the dimeric 5,5-dimethyl-1,3λ^4,2,4,5-dithiadiazastannole do.[26] Methoxy bridging occurs in trimethyltin(IV) methoxide,[27] and we have recently proposed bridging by dimethylamino groups in tin(IV) amines on the basis of variable-temperature Mössbauer studies.[28] There is no precedent, however, for the latter structure (G), and the former structure (F) would appear to be more likely in the dihalo derivatives. The bridged or cross-linked structures F and G would account for the insoluble and infusible nature of these products, however. Infrared data is of limited utility, other than to confirm the presence of the OCH_3 and $N(CH_3)_2$ groupings from the ν(C–H) and δ(C–H) absorptions.

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Registry No. $SnCl_4{\cdot}2S_4N_4$, 24046-65-9; $SnBr_4{\cdot}2S_4N_4$, 67735-19-7; $SnCl_2{\cdot}S_2N_2$, 81245-11-6; $SnBr_2{\cdot}S_2N_2$, 81245-12-7; $Sn(OCH_3)_2{\cdot}S_2N_2$, 81245-15-0; $(SN)_2Sn[N(CH_3)_2]_2$, 81245-17-2; S_4N_4, 28950-34-7; $SnCl_4$, 7646-78-8; $SnBr_4$, 7789-67-5; $SnCl_2$, 7772-99-8; $SnBr_2$, 10031-24-0; $Sn(OCH_3)_2$, 37182-97-1; $Sn[N(CH_3)_2]_2$, 81245-13-8.

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Crystal and Molecular Structure of $[Nd(tren)_2(CH_3CN)](ClO_4)_3$

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Lanthanide coordination chemistry is dominated by oxygen-donor ligands, especially by chelate ligands such as β-diketonates or EDTA. However, recently several nitrogen-bonded complexes have been well characterized. As with oxygen-donor ligands, amine complexes are generally more stable for chelating ligands. For example, pyridine complexes exist only in solution, while complexes with ethylenediamine or 1,10-phenanthroline can be isolated.[1] In addition, Forsberg and co-workers have recently added compounds of the type $Ln(tren)X_3$ [tren = $N(CH_2CH_2NH_2)_3$] and $Ln(tren)_2X_3$ to the list of lanthanide amine complexes.[2,3] We are interested in the structures of these compounds and their possible use as template compounds in macrocycle synthesis.

There has been a continuing interest in the use of lanthanide ions as shift reagents in NMR spectroscopy. During the last decade,[4] lanthanide shift reagents have been actively investigated and utilized in simplifying complex NMR spectra. The utility of these compounds has been hampered to some extent by the simplifying assumptions that must be made—including the geometries. It would be extremely interesting to have a substitutionally inert lanthanide complex formed by an amine macrocycle such as can be envisioned from $Ln(tren)_2$ as a precursor. This paper reports the structural chacterization of $[Nd(tren)_2(CH_3CN)](ClO_4)_3$, as the first step in this project.

Experimental Section

Manipulation of moisture-sensitive materials was accomplished with Schlenk techniques and the use of a Vacuum Atmospheres HE-93-A glovebox with recirculating moisture-free argon atmosphere. Elemental analyses were performed by the Microanalytical Laboratory, University of California, Berkeley, CA. Infrared spectra were obtained on a Perkin-Elmer 597 spectrophotometer (Nujol mulls).

Materials. Acetonitrile (CH_3CN) was distilled from P_2O_5; benzene from potassium–benzophenone ketyl. The tren $[N(CH_2CH_2NH_2)_3]$ was extracted from crude triethylenetetramine.[2] Crystalline 16-cyclam was a generous gift from William Smith.[5]

Neodymium perchlorate $[Nd(ClO_3)_3]$ was prepared by addition of excess Nd_2O_3 to 70% $HClO_4$.[6] The excess Nd_2O_3 was removed by filtration and the solution evaporated to dryness. Residual H_2O was removed by heating to ~250 °C under vacuum for 3 days. Some reversion to the oxide was evidenced by the presence of blue among the pink perchlorate. This contaminant was conveniently left behind during an extraction into acetonitrile. Evaporation of the solution left a compound of formula $Nd(ClO_4)_3(CH_3CN)_4$. Anal. Calcd for $Nd(ClO_4)_3(CH_3CN)_4$: C, 15.83; H, 1.98; N, 9.27; Nd, 23.78. Found: C, 16.23; H, 2.26; N, 9.23; Nd, 24.88.

$[Nd(16\text{-}aneN_4)][ClO_4]_3$. The combination of $Nd(ClO_4)_3(CH_3CN)_4$ and 16-cyclam (16-aneN_4) in a 1:2 molar ratio leads to an intractable blue solid that was not characterized. The similar reaction in a 1:1 molar ratio leads to the formation of an acetonitrile-soluble material of formula $[Nd(16\text{-cyclam})](ClO_4)_3$, and single crystals were obtained from CH_3CN solutions. Anal. Calcd for $NdC_{12}H_{24}Cl_3O_{12}N_4$: C, 21.47; H, 4.17; N, 8.35; Nd, 21.51. Found: C, 21.71; H, 4.23; N, 8.80; Nd, 21.11.

For an apparently orthorhombic single crystal, 5355 X-ray diffraction data were collected for $4° \le 2\theta \le 55°$. The unit cell size and contents are a = 18.192 (2) Å, b = 15.762 (2) c = 8.096 (1) Å, and Z = 4. Refinements in space group $Pn2_1a$ or its centric alternative *Pnma* did not lead to a successful solution of the structure, apparently due to a major disorder involving closely related isomers of the cation. Complete solution of this structure has been abandoned, but we are able to report that the Nd^{3+} ion is seven- or eight-coordinate with coordination by four 16-cyclam nitrogen atoms, one oxygen atom from each of two of the perchlorate anions, and one or two oxygen atoms from the remaining perchlorate anion. The Nd–N and Nd–O bond lengths are about 2.5 Å.

$[Nd(tren)_2(CH_3CN)](ClO_4)_3$. This complex, originally reported as $Nd(tren)_2(ClO_4)_3$, was prepared after the method of Forsberg.[3] Crystals suitable for diffraction were obtained by the addition of benzene to a concentrated acetonitrile solution of the complex. After 2 days of standing at room temperature, the clear pink solution yielded several large, well-formed crystals. Infrared spectroscopy revealed the presence of acetonitrile (ν_{CN} = 2262 cm^{-1}).

Data Collection, Solution, and Refinement[7]

The absences identified with the precession camera (hkl, $h + k$

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