saturated six-membered rings of macrocyclic complexes is given in Table XIV. We conclude that an angle of near 140° is intrinsic to six-membered chelate rings containing –N–C–N– linkages and is not related in any way to the "bite" of the chelate required for optimal metal–ligand interactions.

The presence of the saturated atoms, C3 and C5, in the five-membered chelate rings does not induce a significant amount of strain in the six-membered rings as revealed by the torsion angles. The torsion angles (Table XI) are all small; the largest involving atoms in the six-membered rings is 2.5°. Similarly, the presence of the extensive conjugated systems does not induce any unreasonably large angular distortions involving C3 or C5. The smallest angle is C2–C3–N5, 104.5 (4)°; the largest is N9–C3–N5, 114.3 (4)°. Such small distortions are not expected to lead to enhanced reactivity.

Conclusions

In this paper we have presented two structures containing the previously unknown delocalized β-diazonato chelate ring, which is structurally similar to the β-dionato and β-diiminato rings and which shows increased nucleophilicity at the apical carbon when strained. This resonance structure remains intact upon oxidation of the 14-membered ring to a 16π-electron system in the nickel complex provided bulky groups such as trityl prevent cofacial approach of pairs of the complex. No rearrangement to the α-diimine resonance form observed in the cobalt(III) alkyl complex occurs. Thus it is shown that different metal coordination and substituents can stabilize different resonance isomers of the dihydrooctaaza[14]annulene macrocycle.

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Registry No. I, 60086-90-0; II, 67891-14-9; III, 67891-15-0; V, 67891-16-1; VII, 67891-17-2; VIII, 64057-23-4; IX, 67891-18-3; X, 67891-19-4; XI, 67891-20-7; XIII, 67891-21-8; Ph_3CBF_4, 341-02-6.

Supplementary Material Available: Tables listing observed and calculated structure factors for $Ni(C_{10}H_{18}N_8)$ and $Ni(C_{10}H_{20}N_{12})$ (20 pages). Ordering information is given on any current masthead page.

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Mixed Sulfur–Nitrogen–Selenium Compounds

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Se_4N_4 has been prepared in a new phase isostructural with S_4N_4. Its structure is reported together with the synthesis of two mixed sulfur–selenium–nitrogen compounds $(SSe_2N_2^+)_2(X^-)_2$ (X = Cl, Br). The proposed structure of the latter compounds is based on mass spectroscopic, IR, and ESR data. The existence of these mixed sulfur–nitrogen–selenium compounds is of particular significance in view of the attempts to prepare $(SeN)_x$, the analogue of superconducting $(SN)_x$.

Introduction

There have been many attempts to synthesize analogues of the superconducting polymer $(SN)_x$.[1] We have previously described short-chain oligomers involving polythiazyl chains as high as S_5N_4.[2] In contrast to $(SN)_x$ and its halogen modifications[3] these oligomers were not conducting. Extensive

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efforts have been made to prepare $(SeN)_x$ by routes similar to those used for $(SN)_x$. These efforts have not been successful, possibly because of the low volatility of Se_4N_4, which we originally believed might be partly related to the differences in the molecular packing of these two materials.[4] However, we have been able to synthesize Se_4N_4 in a new phase isostructural with that reported for S_4N_4,[5] but its volatility was not significantly improved. Thus we decided to investigate mixed (S, N, Se) compounds in the hope that these might lead more readily to stable polymers. Garcia-Fernandez[6] first reported such a compound, $Se_2N_2SCl_5$, but Bannister et al.[7] were unable to reproduce the synthesis. They suggested the compound was actually $Se_2S_4N_4Cl_2$, for which they described two structures, neither of which was well established. In this paper we report the preparation of two (SNSe) compounds $(SSe_2N_2Cl)_2$ and $(SSe_2N_2Br)_2$, for which we suggest a structure analogous to that of a similar well-established compound $(S_3N_2^+)_2(S_2O_6Cl^-)_2$.[8]

Experimental Section

General Information. All solvents were dried and distilled before use. The reactions were carried out in the absence of moisture either under vacuum or in a dry argon atmosphere. Elemental analyses were performed by Childers Laboratories and by The University of California Analytical Services, Berkeley, Calif.

Preparation of Se_4N_4. Se_4N_4 was prepared by reaction of excess liquid NH_3 with $SeBr_4$ or $SeCl_4$ in a stainless steel bomb.[9] If the bomb was allowed to warm to room temperature, the stable phase of Se_4N_4 was obtained. However, if the bomb was heated to 70 °C overnight and then allowed to cool to room temperature, the metastable phase of Se_4N_4 isostructural with S_4N_4 crystallizes out.

Preparation of Bis[bis(trimethylsilyl)amino]sulfane, $[(SiMe_3)_2N]_2S$ (I).[18] A 32.3-g (0.2-mol) sample of $(SiMe_3)_2NH$ dissolved in 250 mL of ether was metallized with the equimolar amount of butyllithium solution. After the mixture was cooled to −78 °C, 6.1 mL (0.1 mol) of SCl_2 was slowly added with vigorous stirring. The precipitate (LiCl) was filtered off and the product recrystallized from methanol to give colorless air-stable crystals: mp 66 °C; yield 21 g (60%); ^1H NMR (CH_2Cl_2) δ 0.252 (singlet); IR (Nujol) 1266 (s), 1252 (s), 900 (vs), 842 (vs), 791 (s), 758 (m), (724 (m)), 676 (m), 647 (w), 617 (w), 493 (vw), 461 (vw) cm^{-1}.

Preparation of Thiodiselenazyl Chloride Dimer, $(SSe_2N_2Cl)_2$ (II). Over a period of 4 h a solution of 720 mg (2.04 mmol) of I in 25 mL of CH_2Cl_2 was dropped into a vigorously stirred suspension of 445 mg (2.02 mmol) of $SeCl_4$ and 225 mg (0.98 mmol) of Se_2Cl_2 in 25 mL of CH_2Cl_2. After 20 h of stirring, the deep violet precipitate was isolated on a frit and washed with CH_2Cl_2 until the solvent remained colorless. The crystal powder was dried under vacuum at room temperature for 2 h; yield 496 mg (98% according to eq 1). Anal. Calcd for $(SSe_2N_2Cl)_n$: Se, 62.31; N, 11.06; Cl, 13.98. Found: Se, 60.5; N, 10.6; Cl, 14.7.

Preparation of Thiodiselenazyl Bromide Dimer, $(SSe_2N_2Br)_2$ (III). A 1.32-g (3.75-mmol) sample of I was dissolved in 10 mL of CH_2Cl_2. To this vigorously stirred solution, 1.19 g (3 mmol) of $SeBr_4$ dissolved in 10 mL of CH_2Cl_2 was slowly added. The dark red-brown, slightly violet precipitate was washed and dried as described for II; yield 0.42 g (94% according to eq 1). Anal. Calcd for $(SSe_2N_2Br)_n$: Se, 53.01; N, 9.41; Br, 26.83. Found: Se, 52.8; N, 9.7; Br, 27.6.

Discussion

Structure of Se_4N_4. Although the molecular structures of Se_4N_4 and S_4N_4 are the same, their crystal structures belong to different space groups, reflecting the differences in molecular packing.[4] The Se_4N_4 molecules pack in an approximately body-centered cubic fashion, while the S_4N_4 molecules are almost cubic close packed. Recrystallization of the Se_4N_4 from liquid ammonia at 70 °C gives a new phase isostructural with S_4N_4. The X-ray powder pattern of this new phase is shown in Figure 1a. The pattern was indexed by comparison with S_4N_4 data, and the Appleman[10] least-squares technique was used to get the following lattice constants: a = 9.02 Å, b = 7.42 Å, c = 8.83 Å, β = 93.5°. These lattice constants were then used to calculate the powder pattern[11] of the new phase

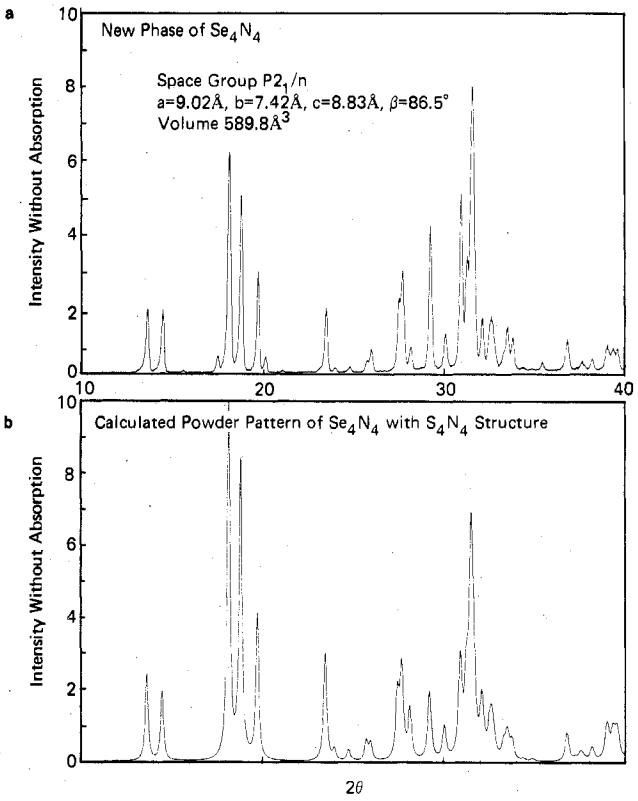

Figure 1. (a) Experimental X-ray powder pattern of the new phase of Se_4N_4. (b) Calculated powder pattern of Se_4N_4 assuming same structure as S_4N_4.

Table I. Mass Spectrum of Se_4N_4

m/e	m/e
480 (Se_6, 29)	240 (Se_3, 48)
400 (Se_5, 40)	188 (N_2Se_2, 28)
376 (N_4Se_4, 33)	174 (NSe_2, 100)
320 (Se_4, 29)	160 (Se_2, 97)
282 (N_3Se_3, 71)	94 (NSe, 91)
268 (N_2Se_3, 35)	80 (Se, 67)
254 (NSe_3, 72)	

Beam Energy 70 eV

(Figure 1b), assuming the atoms had the same coordinates as in S_4N_4. The agreement between the calculated and experimental pattern justifies these assumptions. The new phase is metastable relative to the usual Se_4N_4 phase to which it reverts on heating. Both phases are insoluble in organic solvents and are violently explosive. Attempts to pyrolyze this new phase to give $(SeN)_x$ were no more successful than previous attempts[1] with the normal phase. Like the normal phase, it is poorly volatile even when heated under vacuum at temperatures as high as 220 °C, where it slowly decomposes in the solid state to give N_2 and Se. The mass spectrum given in Table I shows Se_2N_2 to be present in the vapor phase; however, it is not as significant as S_2N_2 in the vapor above S_4N_4.[12] Other species which might be expected to be significant in building $(SeN)_x$ chains such as Se_4N_4, Se_3N_3, and SeN are quite prevalent, again suggesting that the lack of volatility is the prime cause of our lack of success. Attempts to spontaneously polymerize Se_4N_4 in the presence of bromine vapor, as we reported for S_4N_4,[13] were also unsuccessful.

Silylated sulfur diimines, R–NSNSiMe$_3$ (R = SiMe$_3$ or alkyl), are convenient starting materials for the syntheses of either SN chains[2,14,15] or rings.[16] Similarly, compounds of the

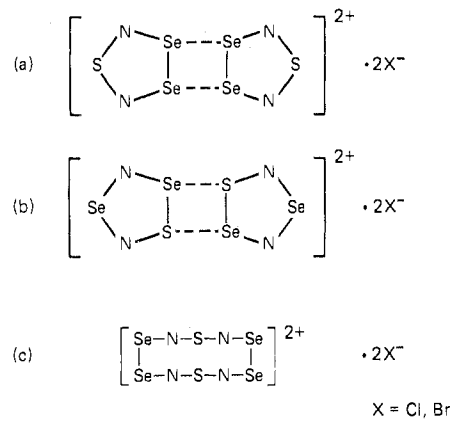

Figure 2. Possible structures of $(SSe_2N_2X)_2$.

type $SiMe_3(R)NSN(R)SiMe_3$ are useful for introducing divalent sulfur.[17] The compound $(SiMe_3)_2NSN(SiMe_3)_2$ (I) was first prepared in poor yield (<10%) by Wannagat et al.[18] Using a modified reaction, we have increased the yield to about 60%. Reaction of I with $SeCl_4$ or $SeBr_4$ in CH_2Cl_2 gave dark purple, highly insoluble precipitates. Both materials are crystalline powders with elemental compositions corresponding to $(SSe_2N_2Cl)_n$ (II) and $(SSe_2N_2Br)_n$ (III). Distillation of the CH_2Cl_2 reaction solution gave $Me_3SiCl(Me_3SiBr)$ and $(Me_3Si{-}N)S$ as side products. Their relative ratio (~14:3) as measured by ^1H NMR of the solution is consistent with reaction 1 (where X = Cl, Br). According to reaction 1, part

$$4SeX_4 + 5[(SiMe_3)_2N]_2S \rightarrow (SSe_2N_2X)_2 + 3(Me_3SiN)_2S + 14Me_3SiX \quad (1)$$

of the $(Me_3Si)_2NSN(SiMe_3)_2$ is oxidized to $Me_3SiNSNSiMe_3$, and the oxidation state of the selenium halide is decreased. Consequently, the yield would be expected to be increased by using a 2:1 mixture of SeX_4 and Se_2X_2 to achieve an average selenium oxidation state of 2.5. In fact, if the synthesis is carried out according to reaction 2 (where X = Cl, Br), the

$$2SeX_4 + Se_2X_2 + 2[(SiMe_3)_2N]_2S \rightarrow (SSe_2N_2X)_2 + 8Me_3SiX \quad (2)$$

yield is approximately 100%. The chloride (II) and particularly the bromide (III) exhibit surprisingly high thermal stability. They decompose exothermically, but not explosively, without melting starting at 175 (II) and 200 °C (III). They dissolve readily in sulfuric or chlorosulfonic acid to make dark green solutions, indicating decomposition. The insolubility of both II and III in all common organic solvents suggests either an ionic or a polymeric structure. This high insolubility prevented us from obtaining suitable crystals of either material for X-ray studies. Nevertheless, a molecular structure can be elucidated from ESR, IR, and mass spectrometric data which is consistent with that of analogous thiazyl compounds. Thus the most likely structure of II and III is shown in Figure 2a. The analogous salt[8] $(S_3N_2^+)_2(S_2O_6Cl^-)_2$ has been shown to contain two 1,2-dithiolium cations[19] which are linked by pairs of sulfur atoms in a four-center, two-electron bond. Such a dimeric structure for II and III is consistent with the absence of any ESR signal[20] from the powders. The IR spectra of II and III (Table II) in the range 4000–350 cm^{-1} are almost identical. This indicates the absence of SCl or SBr bonds, supporting an ionic structure and tending to exclude a covalent polymeric structure. The IR spectra in the region 900–1000 cm^{-1} shown in Table II are very similar to that of $(S_3N_2Cl)_n$, which is also believed to contain the $S_6N_4^{2+}$ cation.[8] The bands at 972 and 941 cm^{-1} (II), 975 and 941 cm^{-1} (III), and 964 and 944 cm^{-1} in $(S_3N_2Cl)_n$ can be assigned to ν(sym) and ν(asym) of the NSN moiety. These bands are approximately

Table II. IR Spectra (Nujol, cm^{-1}) and Raman Spectra (powder, cm^{-1})

$(SSe_2N_2Cl)_2$ (II)		$(SSe_2N_2Br)_2$ (III)	$(S_3N_2Cl)_2$[5]
IR	Raman	IR	IR
972 s	972 vw	975 s	964 s
941 s	945 w	941 s	944 vs
801 w			745 w
			716 sh, s
720 w		720 w	708 vs
617 vs	618 w	618 vs	699 sh, s
588 m	567? vw	585 m	583 s
			569 w
472 w	471 w	475 w	456 w
	463 m		
356 vs	354 w	355 vs	431 m
	258 s		
	195 w		
	110 vs		

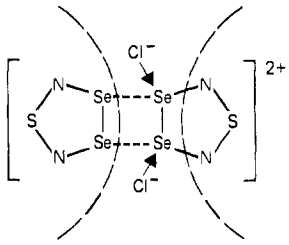

Figure 3. Cleavage of $(SSe_2N_2Cl)_2$ to give fragments observed in the mass spectrum.

the same for all three compounds, but the other bands in II and III are shifted. Whereas the band at 431 cm^{-1} in the IR spectrum of $(S_3N_2Cl)_2$ probably can be assigned to an S–S stretch mode, the bands at 356 cm^{-1} (IR) and 354 cm^{-1} (Raman)[21] in II may result from an Se–Se stretch which is expected in the region 260–370 cm^{-1}.[22]

Mass spectra[23] show SSe_2N_2 and Se_2Cl_2 to be the principal molecular species in the vapor phase when II is heated to ~80 °C. These results are also consistent with our proposed structure (Figure 2a), which might be expected to volatilize by cleavage of the weak interion Se bonds accompanied by simultaneous attachment of the chlorine atoms to selenium and elimination of Se_2Cl_2, as shown in Figure 3. No SN, SeN, or SeSN peaks containing chlorine were observed in the mass spectra. Other structures such as those shown in Figure 2b or 2c or even ionic polymeric structures may be considered. However, they do not appear to be as consistent with the IR and mass spectrometric data.

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Registry No. I, 18243-89-5; II, 68070-51-9; III, 68070-50-8; Se_4N_4, 12033-88-4; $(SiMe_3)_2NH$, 999-97-3; SCl_2, 10545-99-0; $SeCl_4$, 10026-03-6; Se_2Cl_2, 10025-68-0; $SeBr_4$, 7789-65-3.

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Crystalline Beryllium Hydride

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Crystalline BeH_2 was prepared by high-pressure compaction–fusion of amorphous BeH_2 catalyzed by 0.5–2.5 mol % lithium. Pressures of at least 2.75 kbar (at 200 °C) as well as temperatures exceeding 130 °C (at 6.2 kbar) were required for the transformation. This was accompanied by an increase in density from 0.62–0.65 g/cm^3 for amorphous BeH_2 to 0.77–0.78 g/cm^3. Two separate crystalline phases were identified. X-ray diffraction patterns of the low-temperature phase were indexed for a hexagonal unit cell with dimensions a = 4.20 Å and c = 6.76 Å with a theoretical density of 0.82 g/cm^3.

Introduction

All preparations of beryllium hydride reported to date give amorphous, polymeric solids containing hydrogen-bridged BeH_2Be groups.[1-3] The insolubility and nonvolatile character of BeH_2 is consistent with long chains having many repeating monomer units. Unlike the related covalent hydrides MgH_2[4] and AlH_3,[5] no crystalline form of nonsolvated BeH_2 has been reported. Holley and co-workers[6] obtained X-ray diffraction patterns for BeH_2 etherates containing about 60 wt % BeH_2. X-ray powder patterns have been published for $BeH_2 \cdot 0.21Et_2O$,[7] but there is no evidence that any of these data represent the $(BeH_2)_n$ structure itself.

We report the production and characterization of nonsolvated crystalline BeH_2 by the compaction–fusion of amorphous BeH_2, catalyzed by 0.5–2.5 mol % lithium.

Experimental Section

All experiments were conducted under a moisture-free nitrogen atmosphere. Owing to the pyrophoric nature of beryllium alkyls and the toxicity of the products, a glovebox was employed in transferring reactants to the pyrolysis and compaction apparatus.[8] Solvents were dried by conventional methods.

Equipment. Compaction–fusion of BeH_2 was carried out using (1) piston-mold and (2) hydrostatic equipment. Piston-molds were cylinders, 1.27-cm i.d. × 6.35-cm o.d. × 7.62-cm length, fitted with close-tolerance, polished plungers. They were constructed from case-hardened ASTM 440C steel, enclosed by a 1500-W electrical heater and metal bellows through which dry nitrogen could be circulated. Cooling was provided by pumping water through tubing coiled around the mold. Pressure was supplied by a 50-ton hydraulic (platen) press. Temperature was measured by a thermocouple inserted in a well, drilled axially halfway down the piston.

The hydrostatic compaction–fusion equipment consisted of a Harwood Engineering Co. 13.8 kbar pneumatically operated pressure-generating unit and pressure vessels. One of the vessels was 15.24-cm o.d. × 2.54-cm i.d. × 26.67-cm length; the other was 40.64 cm o.d. × 5.08-cm i.d. × 50.8-cm length. Both were rated at 13.8 kbar. Pressure was measured using a bulk modulus cell with a pneumatic transmitter and receiver–recorder. The pressure vessels were heated electrically and cooled by circulating water through coils wound around them. Temperatures were measured by thermocouples attached to the surface and also positioned in the plug closure at the end of each vessel. The hydraulic fluid consisted of a mixture of white gasoline containing 15 vol % Esso Univis P48 oil, which will not solidify at pressures well above 6.9 kbar. The pressure vessels were operated behind a barricade made of 1.27-cm steel plate.

Analytical Measurements. X-ray powder data were obtained with a Philips Norelco X-ray unit, using a 114.6 mm diameter camera with Ni-filtered Cu Kα radiation. Intensities were estimated visually. Densities were measured by a sink–float technique, employing benzene, *n*-nonane, mesitylene, and methylcyclohexane at varying temperatures. The density of the sample was obtained from the solvent temperature–density relationship at the point of sink–float equilibrium. Methods for determination of hydride hydrogen, beryllium alkyls and alkoxides, and chloride are described in a preceding paper.[3] Analysis for lithium was carried out by flame photometry of the acid hydrolysate.

Preparation of Lithium-Doped BeH_2. Lithium was introduced into amorphous BeH_2 in two different ways: (a) by mechanical mixing of the solids, preferably by grinding them together, and (b) by adding an alkyllithium compound to the $(t\text{-Bu})_2Be \cdot Et_2O$ prior to solution pyrolysis. In a typical pyrolysis experiment, 0.41 g (6.3 mmol) of *n*-butyllithium (as a 22% solution in hexane) was mixed with 50 g (253 mmol) of $(t\text{-Bu})_2Be \cdot Et_2O$ and the mixture added to well-stirred dodecane as quickly as possible while maintaining a temperature of 200 ± 5 °C. After 10 minutes, the resulting slurry was cooled quickly and filtered, and the solids were washed with 200 mL of petroleum ether and dried for 1 h in vacuo at 100 °C. The BeH_2 product (94.1 wt % purity) was a white-to-gray powder (d = 0.66 g/cm^3), which reacted slowly with moist air or water.

Crystallization of BeH_2 by Compaction–Fusion. A. With the Piston-Mold Unit. A retainer plug was placed in the bottom of the mold and the Li-doped BeH_2 powder added in several increments, tamping down well after each addition, until 0.4–0.5 g was charged. The piston and bellows assembly were fitted in place and positioned between the platens of the hydraulic press. The predetermined pressure was applied and the mold heated to the desired temperature, while the pressure was held constant. After the pressure and temperature were maintained for a set time, the mold was cooled either slowly or quickly, by circulating water through the cooling coil. When the temperature reached about 60 °C, pressure was released, the unit disassembled, and the BeH_2 pellet pressed into a nitrogen-flushed container. It was then broken up or pulverized for density determination and analysis.

B. Using Hydrostatic Compaction. A 1.9-cm o.d. × 0.051-cm wall × 10.2-cm flat-bottom seamless aluminum capsule was placed in a close-fitting, tapered split mold and 3–4 g of the Li-doped BeH_2 powder introduced and precompacted with a piston at 1.4 kbar. This was done in several increments to obtain efficient capsule loading. (Capsules employed with the large pressure vessel were 4.45-cm o.d.

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