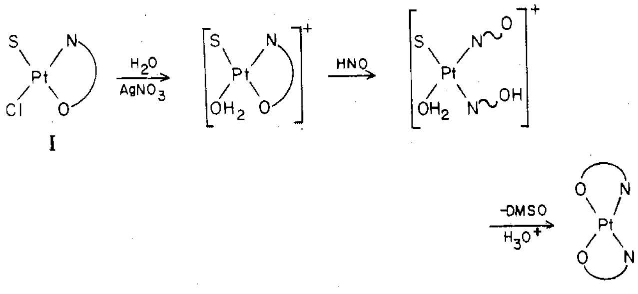
**Scheme IV.** Reaction Sequence Which Accounts for Isolation of *cis*-Pt(ala)$_2$ from I



methylamine species to a second species, whose chemical shift is nearly identical. At the same time, one peak due to $CH_3$ protons of aba continues to decline as a second peak grows.

Interpretation of the spectral changes shown in Figure 2 is summarized in Scheme III. The key observations are (a) that methylamine coordinates to platinum before any DMSO is lost and (b) that subsequent appearance of free DMSO is associated with the conversion of one species which contains coordinated methylamine to a second species which also contains coordinated methylamine. Direct displacement of DMSO by methylamine would have required simultaneous appearance of free DMSO and coordinated methylamine. Displacement of $OD^-$ by methylamine should not have led to displacement of DMSO at all. The observed increase in $^3J_{Pt-H}$ for $N-CH_3$ protons from 43 to 53 Hz on replacement of strongly bound trans DMSO by more weakly bound trans carboxylate further supports this interpretation. Finally, the loss of total DMSO-peak area can be attributed to deuterium exchange of the fairly acidic methyl protons of coordinated DMSO at the relatively high pH (~11) of the final solution.[8]

On the basis of this experiment, we conclude that *cis*-Pt(ala)$_2$ was probably obtained from I by Scheme IV. This conclusion emphasizes the great trans-labilizing effect of DMSO which, for this compound, more than compensates for the strong tendency of glycinate rings to remain intact.

**Acknowledgment.** We wish to acknowledge financial supprt for this project from the Research Corp. and National Science Foundation Grant No. 42192 which provided partial support for purchase of the Perkin-Elmer R-12B NMR spectrometer used in the project.

**Registry No.** K[Pt(DMSO)Cl$_3$], 21350-35-6; $K_2PtCl_4$, 10025-99-7; [Pt(aba)(DMSO)(DD$_2$)]NO$_3$, 60338-50-3; Pt(aba)(DMSO)Cl, 60338-48-9; Pt(gly)(DMSO)Cl (isomer I), 60383-64-4; Pt(gly)(DMSO)Cl (isomer II), 60338-47-8; methylamine, 74-89-5.

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## Stability of Polymeric Sulfur Nitride, $(SN)_x$, to Air, Oxygen, and Water Vapor

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Recently considerable interest has focused on the remarkable properties of polymeric sulfur nitride (polythiazyl), $(SN)_x$. Solid-state studies show $(SN)_x$ has the properties of a metal[3–8] down to low temperatures,[5] becoming superconducting near 0.3 K.[6] The discovery that this unique material forms oriented thin films[4] on a number of plastic substrates suggests its potential use in optical and microelectronic devices. With regard to the measurement of its chemical and solid-state properties, its stability in air is a matter of critical importance. In this note we report our observations on the stability of partly polymerized and completely polymerized, analytically pure crystals of $(SN)_x$ on exposure to several different atmospheres.

### Experimental Section

**Synthesis of $(SN)_x$.** The $(SN)_x$ crystals used in these studies were obtained by following *exactly* our previously described procedure.[9] This involved slowly growing crystals of $S_2N_2$ at 0 °C from the vapor phase during 48 h, followed by spontaneous room-temperature solid-state polymerization during 60 h. The lustrous, golden $(SN)_x$ crystals were then pumped in vacuo for (i) 2 h at room temperature, (ii) 1 h as the temperature was raised to 75 °C, and finally (iii) 2 h at 75 °C.

The $(SN)_x$ crystals were exposed to the air for 10 min or less during their weighing and loading in the appropriate pieces of apparatus described in the following paragraphs. These crystals are referred to as "unexposed crystals".

**Exposure of $(SN)_x$ to Air.** $(SN)_x$ crystals were placed in a 500-ml beaker covered loosely with filter paper to exclude dust and were permitted to stand undisturbed for 7 days at room temperature in normal laboratory lighting. The analytical results obtained after this time are given in Table I. The crystals underwent no detectable visual change. Similar results were obtained in duplicate experiments where time periods of 1, 2, and 48 h were employed.

**Exposure of $(SN)_x$ to Dry Oxygen.** Commercial grade oxygen (Airco, Inc., 99.5% $O_2$, 0.5% Ar) was passed through a drying train consisting of Linde 4A molecular sieve, followed by silica gel (Fisher; Grade 42, 6–16 mesh), before being allowed to contact the $(SN)_x$ crystals held in a 20-ml bulb connected to the oxygen supply by a "T"-tube. The oxygen flow was maintained for 7 days and was vented to the air through a paraffin oil bubbler. After 7 days at room temperature in normal laboratory lighting there was no visual change in the appearance of the $(SN)_x$ crystals. Pertinent analytical data are given in Table I.

**Exposure of $(SN)_x$ to Moist Oxygen.** This experiment was carried out as described for the experiment using dry oxygen except that the drying train was replaced by a bubbler fitted with a fine glass frit and filled with distilled water. The oxygen was saturated with water by passing it through the bubbler held at 0 °C (vapor pressure of water at 0 °C 4.6 Torr). No change in appearance of the $(SN)_x$ was noted. Pertinent analytical data are given in Table I.

**Exposure of $(SN)_x$ to Water Vapor.** The $(SN)_x$ crystals were held in a previously evacuated tube at room temperature in normal laboratory lighting for 7 days under a constant atmosphere of 4.6 Torr of water vapor, maintained by a bulb of degassed, distilled water held at 0 °C, which was connected to the tube containing the $(SN)_x$. No change in appearance of the $(SN)_x$ crystals was noted. Pertinent analytical data are given in Table I.

**Exposure of Incompletely Polymerized $S_2N_2$ to Air.** Golden $(SN)_x$ crystals, obtained by the solid-state room-temperature polymerization of $S_2N_2$ for a period of only 27 h, were exposed, without any previous pumping or heating treatment, to the normal laboratory atmosphere for 1 h in a dish covered loosely with filter paper. The crystals

Table I. Elemental Analyses[a]

| | Wt used, g | % S | % N | % C | % H | % O |
|---|---|---|---|---|---|---|
| Calcd for $(SN)_x$ | | 69.59 | 30.41 | | | |
| Unexposed crystals | | 69.50[c] | 30.29 | [b] | [b] | |
| Exposed to air for 7 days | 0.1100 | 69.11[c] | 30.36 | [b] | [b] | |
| | | 69.54[d] | 30.17 | 0.21 | 0.09 | [e] |
| Exposed to dry oxygen for 7 days | 0.1248 | 69.01[c] | 30.57 | [b] | [b] | |
| | | 69.52[d] | 30.33 | 0.29 | 0.03 | [e] |
| Exposed to moist oxygen for 7 days | 0.1234 | 69.16[c] | 30.32 | [b] | [b] | |
| | | 69.60[d] | 30.24 | 0.10 | 0.03 | [e] |
| Exposed to 4.6 Torr water vapor for 7 days | 0.1216 | 69.13[c] | 30.56 | [b] | [b] | |
| | | 69.60[d] | 30.46 | 0.01 | <0.01 | [e] |
| Incompletely polymerized crystals exposed to air for 1 h (random sampling) | 0.0702 | 68.98[c] | 30.56 | 0.06 | 0.16 | |
| | 0.0711 | 68.79[d] | 29.95 | 0.67 | 0.10 | 0.46 |
| | 0.0699 | 67.09[f] | 31.14 | 0.10 | 0.06 | 2.23 |
| Incompletely polymerized crystals exposed to air for 1 h (visibly tarnished) | 0.0505 | 64.66[c] | 30.43 | [b] | [b] | |
| Incompletely polymerized crystals exposed to air for 1 h (visibly less tarnished) | 0.1011 | 69.00[c] | 30.15 | [b] | [b] | |

[a] In addition to the data given here, analytical results carried out on 45 separate preparations of $(SN)_x$ crystals, using the same method we report here, yielded an average of 69.35% S and 30.46% N, with root-mean-square deviations of 0.07% and 0.02%, respectively. The dimensions of the $(SN)_x$ crystals used in all experiments reported in this communication were in the range 0.5–1.5 mm. [b] Reported as "zero". [c] Analysis performed by Schwarzkopf Microanalytical Laboratory. [d] Analysis performed by Galbraith Laboratories, Inc. [e] Reported as "none or trace". [f] Analysis performed by Huffman Laboratories, Inc.

possessed the iodine-like odor commonly associated with $S_2N_2$. At the end of this time, approximately one-third of the crystals were coated with a gray-white film. The surfaces of the remaining crystals were noticeably less tarnished. A random selection of crystals was taken for analysis as well as a hand-picked sample consisting of obviously tarnished crystals and also a hand-picked sample consisting of less tarnished crystals. Each batch of crystals was then placed in a Pyrex glass tube, quickly evacuated, sealed, and mailed to the commercial analytical laboratories. Analytical data are given in Table I.

From Table I it can be seen that the percent nitrogen in the material is apparently not a very sensitive criterion for judging the purity of the $(SN)_x$ since it is essentially invariant in all samples, even when the percent sulfur in a sample decreased and the oxygen content increased. This suggests that the main initial reaction which occurs between the incompletely polymerized material and air may be the replacement of one sulfur atom by two oxygen atoms, which, of course, have the same atomic weight as sulfur. This would not, therefore, affect the observed percentage of nitrogen in a sample.

## Results and Discussion

We have previously reported[9] a convenient method for reproducibly synthesizing analytically pure crystals of $(SN)_x$ in high yield. This involves the solid-state polymerization of disulfur dinitride, $S_2N_2$, which occurs spontaneously at room temperature, viz.

$$xS_2N_2 \rightarrow 2(SN)_x$$

In this note we have demonstrated that conventional elemental analyses (Table I) performed by three different commercial analytical laboratories as well as visual observations can detect no reaction between crystals of completely polymerized, analytically pure polymeric sulfur nitride, $(SN)_x$, prepared by our synthetic method,[9] when they are exposed for 7 days at room temperature to (i) normal laboratory atmosphere (1 atm pressure), (ii) dry oxygen (1 atm pressure), (iii) moist oxygen (1 atm pressure), and (iv) water vapor (4.6 Torr). These observations do not preclude the possibility that fresh $(SN)_x$ surfaces when removed from vacuum and placed in the air may become covered with a very thin, nonvisible surface coating of oxidation and/or hydrolysis products. Indeed, after many weeks' exposure to air, the crystals do slowly become tarnished, particularly at the dark ends which are made up of the polymer chain-terminating groups.

It is particularly important to note that crystals of $(SN)_x$ which still contain significant amounts of unpolymerized and/or partly polymerized $S_2N_2$ are apparently very much more reactive to air (Table I), reacting significantly during periods as short as 1 h. The presence of contaminants in the $(SN)_x$ such as $S_2N_2$, $S_4N_4$, etc. cannot, of course, be detected by elemental analyses, since they have the same empirical formula as $(SN)_x$. It should be stressed that lustrous, golden crystals of partly or incompletely polymerized $S_2N_2$ which visually appear identical with completely polymerized $(SN)_x$ may still contain significant quantities of $S_2N_2$,[9] which can be removed by pumping in vacuo. We therefore strongly recommend that before any physical or chemical studies are carried out on crystalline $(SN)_x$, it be heated at approximately 75 °C with constant pumping in vacuo as we have described previously,[9] in order simultaneously to promote polymerization of oligomeric $(SN)_y$ or $S_2N_2$ and to remove any traces of unpolymerized $S_2N_2$. Unless this is done, misleading observations on physical or chemical properties of $(SN)_x$ may be obtained.

**Acknowledgment.** This research was supported in part by the National Science Foundation through the Laboratory for Research on the Structure of Matter and through Grants No. GH-39303 and No. GP-41766X and by the Advanced Research Projects Agency through Grant No. DAHC 15-72-C-0174.

**Registry No.** $(SN)_x$, 12033-56-6; $S_2N_2$, 25474-92-4; $H_2O$, 7732-18-5.

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## New Route to the Preparation of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$

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A binuclear complex, $\mu$-carbonato-bis(pentaamminecobalt(III)) sulfate tetrahydrate, has been reported by Kremer and Mac-Coll[1] and Kranig.[2] They have obtained this salt by mixing $CoSO_4$, $(NH_4)_2CO_3$, and $NH_4OH$ at low temperatures and bubbling air through the mixture for a period of 24 h.

It has been shown[3,4] that in the reaction of aquopentaamminecobalt(III) ion with carbon dioxide, hydroxopentaamminecobalt(III) species, which is in equilibrium with the aquopentaamminecobalt(III) ion in aqueous solution, plays an important role in the rate-determining step. In the process of carbon dioxide uptake, formation of $[(NH_3)_5CoCO_3H]^{2+}$ has been proposed as a possible intermediate step. Now, in the same way that a proton is split from this intermediate to form the $[(NH_3)_5CoCO_3]^+$ ion, we could also imagine the splitting of a water molecule between the above-mentioned intermediate and the $[(NH_3)_5CoOH]^{2+}$ ion, to form a binuclear complex

$$[(NH_3)_5CoCO_3H]^{2+} + [HOCo(NH_3)_5]^{2+} \rightarrow [(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + H_2O$$

In order to examine the possibility of the occurrence of this reaction, $[Co(NH_3)_5H_2O]I_3$, prepared according to the method described by Schlessinger,[5] was employed as a starting material in the reaction

$$2[Co(NH_3)_5H_2O]I_3 + 3Ag_2CO_3 + 2(NH_4)_2SO_4 \xrightarrow[H_2O]{CO_2} 6AgI\downarrow + 2(NH_4)_2CO_3 + [(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$$

Reaction of $[Co(NH_3)_5H_2O]I_3$ (32.7 mmol), $(NH_4)_2SO_4$ (65.7 mmol), and $Ag_2CO_3$ (48.9 mmol) in 200 ml of water at 0 °C, with constant stirring and bubbling of $CO_2$ gas for a period of 2 h, produced an oily liquid, which was then crystallized into deep red crystals, by addition of absolute alcohol. An acidified solution of this product showed no reaction with $K_2S_2O_8$, therefore excluding $[Co(NH_3)_5H_2O]ISO_4$ as a possible reaction product. Yield of the binuclear complex was 49%, based on the amount of $[Co(NH_3)_5H_2O]I_3$ used. Anal. Calcd: $NH_3$, 27.75; Co, 19.19; $SO_4$, 31.38. Found: $NH_3$, 27.50; Co, 19.10; $SO_4$, 31.40. A sample of this complex salt (0.5 g) was heated at 600 °C to a constant weight (0.2501 g). The loss of weight according to the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O \rightarrow 2CoSO_4 + 10NH_3 + CO_2 + {}^1/_2O_2 + 4H_2O$$

corresponded to 49.98% volatiles ($NH_3$, $CO_2$, $H_2O$, and $O_2$) in the compound (calcd 49.34%). In addition, the deep violet residue ($CoSO_4$) was analyzed for its sulfate content (exptl 61.57%; calcd 61.93%).

Potentiometric titration of a $1.63 \times 10^{-3}$ M solution of the complex, which showed an initial pH of 7.2, gave a mole ratio of $H^+$:Co equal to 0.93 which is consistent with the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + 2H^+ \xrightarrow{H_2O} 2[(NH_3)_5CoH_2O]^{3+} + CO_2$$

The electronic spectrum of the complex showed a d–d transition at 505 m$\mu$ (log $\epsilon$ = 2.14) and a shoulder growing at 350 m$\mu$ on a uv band consistent with the data expected of a $N_5Co$–O–CO–O chromophore.[6] The near-uv band showed a maximum at 255 m$\mu$.

Adding $H_2SO_4$ to the complex for a complete conversion to the $[(NH_3)_5CoH_2O]^{3+}$ ion shifted the bands to 490 m$\mu$ (log $\epsilon$ = 1.69) and 340 m$\mu$, respectively, which are values reported for the aquopentaamminecobalt(III) complex ion.[7]

The DTA curve of the complex was obtained by a Netzch 404 instrument. It showed, against Kaolin as reference, three endothermic peaks at 170, 310, and 490 °C corresponding to the loss of water of crystallization, ammonia, and carbon dioxide, respectively.

These experimental data conclusively prove the formation of a binuclear complex. Furthermore, this reaction is found to be a more convenient synthetic procedure for the formation of the binuclear complex and probably would be suitable for the preparation of similar complexes of Rh and Ir.

**Registry No.** $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2$, 49731-04-6; $[Co(NH_3)_5H_2O]I_3$, 15612-06-3.

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## Correlation of Electron Paramagnetic Resonance Line Intensities with Magnetic Moments for Some Spin-Crossover Systems

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In 1973 we reported observation of separate paramagnetic resonance (EPR) lines due to the $S = {}^1/_2$ and $S = {}^5/_2$ states in the spin-crossover system of tris(dicyclohexyldithiocarbamato)iron(III) (CHDF) at room temperature and 127 K.[1] Identification of these lines was based primarily on the temperature dependence of the line intensities. In particular we identified a broad asymmetric line at $g_{\mathrm{eff}} \simeq 4.3$ that decreased in intensity at low temperature as due to the $S = {}^5/_2$ state; this is consistent with the observation that shortening the metal–ligand bond[2] and decreasing the thermal energy available favors the low-spin case. Also, theory predicts a broad line in the region of $g_{\mathrm{eff}} \simeq 4.3$ for reasonable values of the fine-structure parameters in the $S = {}^5/_2$ system.[3]

Recently Hall and Hendrickson[4] have reported EPR spectra of similar compounds at much lower temperatures than were

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