metal ion, through the use of eq 3 takes into consideration the

$$[M_f] = \frac{\alpha_L T_M}{\alpha_{ML} K_{ML}(T_L - T_M)} \quad (3)$$

$$\alpha_L = 1 + \beta_n^H[H^+]^n \quad (4)$$

$$\alpha_{ML} = 1 + \beta_{MH_nL}^H[H^+]^n \quad (5)$$

proton affinities of the ligand, α_L term, and other chelate species such as protonated metal complexes, α_{ML} term. For metal complexes where the predominate chelate species is ML across the p[H] range of interest, the α_{ML} term approaches unity and can be neglected in the calculation. The relative order of pM values given in Table IX holds only for the specified set of conditions, which include the metal ion concentration, ligand concentration, and p[H]. A higher ligand metal ion affinity is reflected by a greater pM value.

Table IX provides the value of pM calculated for each of the TMPHPG and EHPG ligands by employing a 10% excess of ligand at a physiologic p[H] of 7.4. Also provided are pM values for a variety of related multidentate ligands that have recently been investigated in this research group.[16,18] Since the stability constants of indium(III)-transferrin have not been accurately measured, the correlation between log K_{ML} values for the ligands of Table IX with iron(III) and indium(III) was employed to arrive at a reasonable estimate of log K_1* and log K_2* for indium(III)-transferrin.[1] The values of log K_1* and by K_2* estimated for indium(III)-transferrin are 18.2 and 17.4, respectively, at 25.0 °C, μ = 0.10 M, and [HCO_3^-] = 1.4 × 10^{-4} M. It is clear that the iron(III) and gallium(III) TMPHPG complexes would be expected to resist exchange of metal ion with transferrin in vivo. On the other hand, such an exchange is thermodynamically favorable for each of the indium(III) complexes.

Conclusions

Selective complexation of one isomer with a metal ion can be a useful method for the separation of diastereomeric ligand pairs. The metal ion must form a stable complex involving all the ligand donor groups and have distinct coordination preferences that may be less favorable in one diastereomer than in the other.

The more lipophilic EHPG analogues, *rac*- and *meso*-TMPHPG, with their dimethylated phenyl rings and a longer diamine bridge maintain a very high affinity for iron(III) and gallium(III) but form even weaker complexes with indium(III) than was found for *rac*- and *meso*-EHPG. The increased separation of the two chiral centers in the TMPHPG diastereomers, by an additional methylene group, generally reduced the differences in stability observed between the diastereomeric complexes. A further increase in the diamine alkyl chain length will undoubtedly serve to further isolate the two phenylglycine moieties and result in an additional decrease in the difference in metal ion affinity displayed by the diastereomers.

The most notable feature of these ligands is their relatively poor affinity for indium(III). Clearly the results of this work, and additional recent work conducted in this research group,[15,16] have demonstrated the lower relative affinity of indium(III) for hard phenolate oxygen donor atoms as compared to iron(III) and gallium(III). Ligands with a high affinity for indium(III) should be designed separately from those found useful for iron(III) and gallium(III). The design of these ligands needs to take into consideration the larger size of indium(III) as well as incorporation of softer coordinate donor groups.

Acknowledgment. This research was supported by the U.S. Public Health Service, National Cancer Institute, Grant No. CA-42925, and The Robert A. Welch Foundation, Grant No. A-259.

(27) L'Eplattenier, F.; Murase, I.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 837.
(28) Harris, W. E.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 713.
(29) Aisen, P.; Liebman, A.; Zweier, J. *J. Biol. Chem.* **1978**, *253*, 1930.
(30) Harris, W. R.; Pecoraro, V. L. *Biochemistry* **1983**, *22*, 292.

Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4, and Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701

Synthesis and Structure of the Norbornene Adduct of 1,3,5,2,4,6-Trithiatriazinium Tetrachloroaluminate [C_7H_{10}·S_3N_3][$AlCl_4$]

Allen Apblett,[†] Tristram Chivers,*[,†] A. Wallace Cordes,*[,‡] and Rainer Vollmerhaus[†]

Received October 4, 1990

The treatment of $(NSCl)_3$ with an excess of norbornene in dioxane at 0 °C produces C_7H_{10}·S_3N_3Cl (**1**). The addition of $AlCl_3$ or $AgAsF_6$ to a solution of this adduct in SO_2 yields [C_7H_{10}·S_3N_3]X [**2a**, X^- = $AlCl_4^-$; **2b**, X^- = AsF_6^-]. The ^{14}N NMR spectra of **2a**, **2b**, and [$S_3N_3Cl_2$]$AlCl_4$ are reported. The norbornene ligand was shown by X-ray crystallography to be attached to the $S_3N_3^+$ cation in **2a** via two sulfur atoms to give the exo-β isomer. The crystals of **2a** are triclinic, space group $P\bar{1}$, with a = 7.3572 (14) Å, b = 9.9771 (15) Å, c = 11.1178 (12) Å, α = 71.561 (11)°, β = 85.320 (13)°, γ = 80.133 (14)°, V = 762.4 (3) Å^3, and Z = 2. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at R = 0.029 and R_w = 0.035 for 2686 unique observed reflections. There are pronounced variations in the sulfur-nitrogen bond lengths in the S_3N_3 ring indicative of a structural weakness. The -N=S=N- unit [|d(S-N)| = 1.549 (3) Å] is linked to the three-coordinate sulfur atoms of the SNS moiety [|d(S-N)| = 1.627 (3) Å] by long S-N bonds [|d(S-N)| = 1.709 (3) Å]. Attempts to detach norbornene from the S_3N_3 ring in **2a** by heating or treatment with 2,3-dimethyl-1,4-butadiene resulted in loss of the -N=S=N- bridge to give the 2:1 adduct of norbornene and NS_2^+.

Introduction

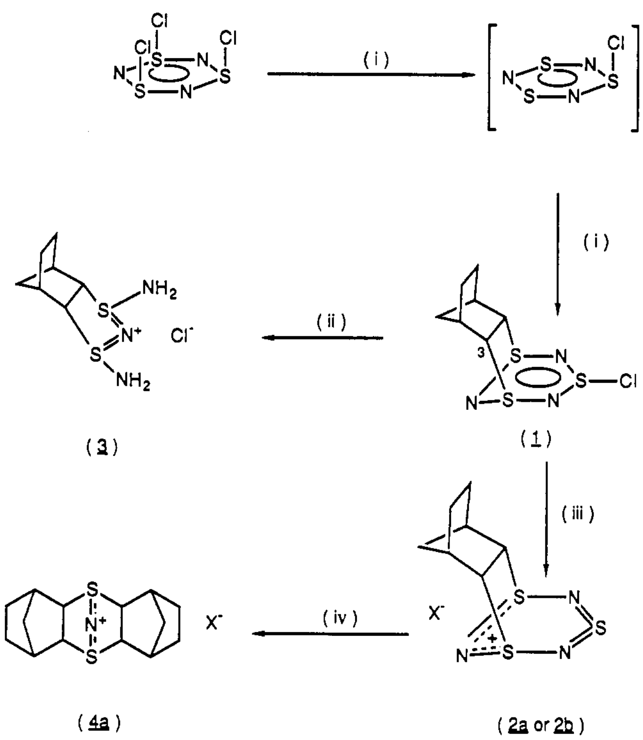
The $S_3N_3^+$ cation is conspicuous by its absence from the list of known monocyclic, binary sulfur-nitrogen (S-N) cations, which includes examples of five-, seven-, eight-, and ten-membered ring systems [$(S_3N_2^{\bullet+})_2$, $S_4N_3^+$, $S_4N_4^{2+}$, $S_5N_5^+$, respectively].[1] As an example of an antiaromatic 8-π-electron system, the molecular and electronic structures of $S_3N_3^+$ are of interest. Assuming D_{3h} symmetry, the monomeric cation is predicted to be a triplet, and thus highly reactive, on the basis of ab initio molecular orbital calculations.[2] Therefore, a distorted or associated structure is

† The University of Calgary.
‡ University of Arkansas.

(1) Chivers, T. *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 2, Chapter 29, pp 806-812.

0020-1669/91/1330-1392$02.50/0

Scheme I. Preparation and Thermolysis of the Norbornene Adduct of $S_3N_3^+$: (i) Norbornene; (ii) H_2O; (iii) $AlCl_3$ or $AgAsF_6$ in SO_2; (iv) 2,3-Dimethylbutadiene or Heat, X^- = $AlCl_4^-$ or AsF_6^-



likely, and the possibilities include (a) two 4-electron three-center bonds on the NSN and SNS moieties,[3] (b) a half-chair conformer,[4] or (c) a dimer.[5]

The isoelectronic 8-π-electron system $R_2PN_3S_2$, which has a singlet structure,[6] may be obtained by the thermal elimination of NSN from EN_5S_3,[7] but this process is symmetry forbidden for E = S^+.[8] Previous claims of the synthesis of "$[S_3N_3][SbCl_6]$"[9] and "S_3N_3Cl"[10] have been retracted[11,12] and attempts to prepare $S_3N_3^+$ by the chemical[13] or electrochemical[14] oxidation of $S_3N_3^-$ were unsuccessful. Banister et al. have proposed the initial formation of the adduct $C_7H_{10}{\cdot}S_3N_3Cl$ (**1**) in the reaction of $(NSCl)_3$ with an excess of norbornene from which they isolated and structurally characterized the hydrolysis product $[C_7H_{10}{\cdot}NS_2(NH_2)_2]Cl$ (**3**)[15] (see Scheme I). We have reinvestigated this system in order to isolate **1** and determine its usefulness as a source of the $S_3N_3^+$ cation.

We report here the synthesis and spectroscopic characterization of **1** and the corresponding salts $[C_7H_{10}{\cdot}S_3N_3]X$ (**2a**, X^- = $AlCl_4^-$; **2b**, X^- = AsF_6^-] and the X-ray structure of **2a**. Attempts to remove norbornene from the $S_3N_3^+$ ring in **2a** are also described briefly.

(2) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517.
(3) Bhattacharyya, A. A.; Bhattacharyya, A.; Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 7458.
(4) Zhu, J. K.; Gimarc, B. J. *Inorg. Chem.* **1983**, *22*, 1996.
(5) Boeré, R. T.; French, C. L.; Oakley, R. T.; Cordes, A. W.; Privett, J. A. J.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 7710.
(6) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.
(7) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. *Can. J. Chem.* **1984**, *62*, 712.
(8) Bestari, K. T.; Boeré, R. T.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 1579.
(9) Banister, A. J.; Padley, J. S. *J. Chem. Soc. A* **1969**, 658.
(10) Zborilova, L.; Touzin, J.; Navratilova, D.; Mrkosova, J. *Z. Chem.* **1972**, *12*, 27.
(11) Banister, A. J.; Dainty, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2658.
(12) Zborilova, L.; Gebauer, P. *Z. Chem.* **1979**, *19*, 32.
(13) Chivers, T.; Rao, M. N. S. *Can. J. Chem.* **1983**, *61*, 1957.
(14) (a) Chivers, T.; Hojo, M. *Inorg. Chem.* **1984**, *23*, 1526. (b) Fritz, H. P.; Bruchhaus, R.; Mews, R.; Höfs, H.-V. *Z. Anorg. Allg. Chem.* **1985**, *525*, 214.
(15) Hazell, A. C.; Hazell, R. G.; Banister, A. J.; Fielder, A. J. *Acta Crystallogr.* **1981**, *B37*, 177.

Table I. ^{13}C and ^{14}N NMR Data for $C_7H_{10}{\cdot}S_3N_3Cl$ and $[C_7H_{10}{\cdot}S_3N_3]X$ (X^- = $AlCl_4^-$, AsF_6^-)

	$C_7H_{10}{\cdot}S_3N_3Cl$	$[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$	$[C_7H_{10}{\cdot}S_3N_3][AsF_6]$	assignment[c]
$\delta(^{13}C)^a$	28.0	28.4	28.3	C(6) and C(7)
	34.2	35.2	35.0	C(1) and C(2)
	39.0	41.4	41.3	C(3) and C(5)
	85.2	93.8	93.7	C(4)
$\delta(^{14}N)^b$	-135.6 (450)	-89.2 (385)	-88.5 (410)	N(2) and N(3)
	-259.0 (205)	-306.0 (705)	-305.9 (910)	N(1)

[a] ^{13}C chemical shifts are in ppm relative to Me_4Si. [b] ^{14}N chemical shifts are in ppm relative to external $MeNO_2$(l); $\upsilon_{1/2}$ values are given in parentheses. [c] See Figure 1 for atomic numbering scheme.

Experimental Section

Reagents and General Procedures. All reactions and the manipulation of moisture-sensitive products were performed under an atmosphere of dry N_2 (99.99%). Solvents were dried by heating under reflux with the appropriate drying agent: dioxane (sodium metal), $CFCl_3$ (P_4O_{10}), and SO_2 (molecular sieves). All solvents were distilled before use. Reactions were carried out either in one-necked side-arm flasks sealed with a rubber septum or in a double-bulb vessel equipped with a glass frit and J. Young valves.

The reagents $(NSCl)_3$[16] and $AgAsF_6$[17] were prepared by the literature procedures. The salt $S_3N_3Cl_2^+AlCl_4^-$ was generated in situ by treatment of $(NSCl)_3$ with 1 molar equiv of $AlCl_3$ in CCl_4.[18] Commercial samples of norbornene and 2,3-dimethyl-1,4-butadiene (Aldrich) were used as received. Commercial aluminum trichloride (MCB) was sublimed (140 °C/0.02 Torr) before use.

Instrumentation. Infrared spectra were recorded as Nujol mulls on CsI or KBr plates by using a Nicolet DX-5 FTIR spectrometer (4000–400 cm^{-1}) or a Perkin-Elmer 457 grating infrared spectrometer (400–200 cm^{-1}). ^{14}N and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer. All spectra were obtained in sealed 8-mm-o.d. tubes with SO_2 as solvent. These tubes were then placed inside a normal 10-mm-o.d. NMR tube and a lock solvent, $CDCl_3$ or D_2O, was then added to the space between the two tubes. For ^{14}N NMR spectra, internal dinitrogen was used as a reference and assigned a chemical shift of −71.6 ppm versus external nitromethane.[19] $CDCl_3$ was used as a reference for the ^{13}C spectra and assigned a chemical shift of 77.0 ppm versus Me_4Si. Mass spectra were obtained with a Kratos MS80 RFA instrument operating at 70 eV. Melting points were obtained in sealed capillaries, and values are uncorrected. Chemical analyses were performed by the Analytical Division of the Department of Chemistry, The University of Calgary, and Canadian Microanalytical Services, Vancouver, BC, Canada.

Preparation of $C_7H_{10}{\cdot}S_3N_3Cl$ (1). A solution of norbornene (2.82 g, 30 mmol) in 1,4-dioxane (10 mL) was added rapidly to solid $(NSCl)_3$ (0.81 g, 3.3 mmol) at 0 °C. The reaction mixture was stirred for 12 h, and then the bright yellow precipitate was separated by filtration, washed with 1,4-dioxane (3 × 10 mL) and identified as analytically pure $C_7H_{10}{\cdot}S_3N_3Cl$ (0.51 g, 1.9 mmol), mp 129 °C. Anal. Calcd for $C_7H_{10}ClN_3S_3$: C, 31.39; H, 3.76; N, 15.69. Found: C, 30.77; H, 4.05; N, 15.73. IR (cm^{-1}): 1461 m, 1309 m, 1295 s, 1246 m, 1216 m, 1114 m, 1040 m, 1000 m, 979 vs, 937 s, 915 m, 875 m, 747 s, 673 m, 608 s, 535 s, 501 s, 483 s, 470 s, 362 m, 278 m. NMR spectroscopic data are given in Table I.

Preparation of $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$ (2a). A mixture of $C_7H_{10}{\cdot}S_3N_3Cl$ (0.50 g, 1.87 mmol) and $AlCl_3$ (0.25 g, 1.87 mmol) was added to one side of a double-bulb vessel, and SO_2 (ca. 15 mL) was condensed onto the solids at −78 °C. The reaction mixture was warmed to 25 °C to give a dark orange solution, and crystallization was achieved by slow cooling of a saturated solution in SO_2 to 0 °C. Orange trapezoids of $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$ (2a) (0.45 g, 1.12 mmol), mp 116–119 °C dec, were separated by filtration. IR (cm^{-1}): 1309 m, 1300 s, 1250 m, 1221 m, 1197 m, 1178 m, 1170 m, 1120 m, 1046 s, 1031 m, 1021 s, 997 s, 989 s, 936

(16) Jolly, W. L.; Maguire, K. D. *Inorg. Synth.* **1967**, *9*, 102.
(17) Apblett, A.; Banister, A. J.; Biron, D.; Kendrick, A. G.; Passmore, J.; Schriver, M.; Stojanac, M. *Inorg. Chem.* **1986**, *25*, 4451.
(18) Salts of the $S_3N_3Cl_2^+$ cation are stable in solution in CCl_4, but apparently decompose in other solvents: (a) Mews, R.; Wagner, D.-L.; Glemser, O. *Z. Anorg. Allg. Chem.* **1975**, *412*, 148. (b) Gillespie, R. J.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1982**, *21*, 1296.
(19) McIntyre, D. D.; Apblett, A.; Lundberg, P.; Schmidt, K. J.; Vogel, H. J. *J. Magn. Reson.* **1989**, *83*, 377.

Table II. Crystallographic Data for $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$

chem formula: $AlC_7Cl_4H_{10}N_3S_3$	fw = 401.2
a = 7.3572 (14) Å	space group: $P\bar{1}$
b = 9.9771 (15) Å	T = 20(2) °C
c = 11.1178 (12) Å	λ = 0.71073 Å
α = 71.561 (11) Å	ρ_{calcd} = 1.75 g cm^{-3}
β = 85.320 (13) Å	R = 0.029
γ = 80.113 (14) Å	R_w = 0.035
V = 762.4 (3) Å^3	
Z = 2	

m, 914 m, 887 m, 870 m, 811 m, 747 s, 694 s, 676 s, 607 m, 591 s, 558 s, 530 s, 502 s, 490 s (ν_3 $AlCl_4^-$), 483 s, 464 s, 365 m, 354 m. Anal. Calcd for $C_7H_{10}AlCl_4N_3S_3$: C, 20.96; H, 2.51; N, 10.47. Found: C, 21.24; H, 2.68; N, 10.55. NMR spectroscopic data are given in Table I.

Preparation of $[C_7H_{10}{\cdot}S_3N_3][AsF_6]$ (2b). A mixture of $C_7H_{10}{\cdot}S_3N_3Cl$ (0.50 g, 1.87 mmol) and $AgAsF_6$ (0.56 g, 1.89 mmol) was added to one side of a double-bulb vessel, and SO_2 (20 mL) was condensed on to the solids at −78 °C. The reaction mixture was warmed to 25 °C to give a dark orange solution and a white precipitate of silver chloride, which was removed by filtration. A small amount (ca. 2 mL) of $CFCl_3$ was condensed into the orange solution and solvent was removed slowly from this solution by cooling the other bulb at −10 °C to give $[C_7H_{10}S_3N_3][AsF_6]$, (**2b**) (0.56 g, 1.33 mmol) as orange crystals contaminated with a small amount of silver chloride. The impure product was dissolved in SO_2 (10 mL) and filtered to remove AgCl. Slow evaporation of the solvent gave orange crystals of **2b**, mp 100 °C (dec. Anal. Calcd for $C_7H_{10}AsF_6N_3S_3$: C, 19.96; H, 2.39; N, 9.97. Found: C, 20.17; H, 2.45; N, 9.86. IR (cm^{-1}): 1312 m, 1303 s, 1175 m, 1122 m, 1049 s, 1027 s, 999 m, 991 s, 922 m, 870 m, 747 m, 742 m, 697 vs (ν_3 AsF_6^-), 589 s, 528 s, 494 m, 483 m, 465 s, 400 s (ν_4 AsF_6^-), 362 m, 353 m. NMR spectroscopic data are given in Table I.

X-ray Structural Analysis. A suitable orange trapezoid (0.30 × 0.50 × 0.50 mm) of **2a** was obtained by recrystallization from SO_2 and embedded in epoxy in a capillary tube. The structure was determined by the application of standard procedures, and pertinent crystallographic data are listed in Table II.

The unit cell was determined from the setting angles of 25 reflections with 16° > 2θ > 19°. Three reflections measured every hour were used to correct for 6% decay, which occurred during data collection from θ of 2° to 20° and 9% from 20° to 25°. All measurements were made by using an Enraf-Nonius CAD4 diffractometer, and calculations were done using the Enraf-Nonius system of programs. Mo Kα radiation, graphite monochromated, was employed, and $\omega/2\theta$ scans were used for data collection. An absorption correction was made on the basis of ψ scans. No general correction was made for extinction, however, the 1,1,-1 reflection was given zero weight because of extinction.

The structure was solved by direct methods and Fourier techniques. All non-H atoms were refined anisotropically. H atoms were constrained to idealized positions (C–H = 0.95 Å) with isotropic B values of 1.2 times the B value of the attached C atom. In the full-matrix least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma^2(I) + 0.04I^2]/4F^2$. Conventional atomic scattering factors, corrected for anomalous dispersion, were used.[20] Positional parameters are given in Table III, and selected interatomic distances and angles are given in Table IV.

Table III. Atomic Coordinates for Non-Hydrogen Atoms of $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$

	x	y	z	B_{eq}, Å^2
Cl(1)	0.4939 (2)	0.3194 (1)	0.44728 (9)	4.82 (2)
Cl(2)	0.7389 (1)	0.2453 (1)	0.1878 (1)	4.65 (2)
Cl(3)	0.3802 (2)	0.0608 (1)	0.3268 (1)	5.70 (3)
Cl(4)	0.2800 (2)	0.4193 (1)	0.16075 (9)	4.90 (2)
S(1)	0.9094 (1)	0.36568 (8)	0.65345 (8)	2.79 (2)
S(2)	0.9837 (1)	0.08302 (8)	0.74567 (8)	2.84 (2)
S(3)	0.9980 (1)	0.20679 (9)	0.48051 (8)	3.39 (2)
Al	0.4748 (1)	0.2621 (1)	0.27978 (9)	3.01 (2)
N(1)	0.8257 (4)	0.2221 (3)	0.7341 (3)	3.10 (6)
N(2)	1.0306 (4)	0.0713 (3)	0.5965 (2)	3.27 (6)
N(3)	0.9578 (4)	0.3550 (3)	0.5030 (2)	3.11 (6)
C(1)	1.1452 (4)	0.3196 (3)	0.7103 (3)	2.23 (6)
C(2)	1.1872 (4)	0.1543 (3)	0.7653 (3)	2.35 (7)
C(3)	1.2238 (5)	0.1299 (3)	0.9054 (3)	2.99 (8)
C(4)	1.0961 (5)	0.2542 (4)	0.9357 (3)	3.42 (8)
C(5)	1.1689 (5)	0.3696 (3)	0.8252 (3)	2.78 (7)
C(6)	1.3764 (5)	0.3371 (4)	0.8481 (3)	3.51 (8)
C(7)	1.4141 (5)	0.1740 (4)	0.9062 (3)	3.69 (9)

Table IV. Bond Lengths (Å) and Bond Angles (deg) for $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$

Distances			
S(1)–N(1)	1.625 (3)	C(1)–C(5)	1.544 (4)
S(2)–N(1)	1.629 (3)	C(2)–C(3)	1.538 (4)
S(1)–N(3)	1.715 (3)	C(3)–C(4)	1.532 (5)
S(2)–N(2)	1.703 (3)	C(4)–C(5)	1.528 (5)
S(3)–N(2)	1.545 (3)	C(3)–C(7)	1.539 (5)
S(3)–N(3)	1.553 (3)	C(5)–C(6)	1.531 (5)
S(1)–C(1)	1.829 (3)	Al–Cl(1)	2.135 (1)
S(2)–C(2)	1.821 (3)	Al–Cl(2)	2.127 (1)
C(1)–C(2)	1.553 (4)	Al–Cl(3)	2.134 (1)
C(6)–C(7)	1.534 (5)	Al–Cl(4)	2.120 (1)
Angles			
N(1)–S(1)–N(3)	106.8 (1)	C(2)–C(3)–C(4)	103.2 (3)
N(1)–S(2)–N(2)	107.0 (1)	C(1)–C(5)–C(4)	102.5 (2)
N(2)–S(3)–N(3)	118.7 (1)	C(2)–C(3)–C(7)	105.7 (3)
N(1)–S(1)–C(1)	100.5 (1)	C(1)–C(5)–C(6)	105.3 (2)
N(2)–S(2)–C(2)	100.4 (1)	C(4)–C(3)–C(7)	101.1 (3)
N(3)–S(1)–C(1)	98.2 (1)	C(4)–C(5)–C(6)	101.9 (3)
N(2)–S(2)–C(2)	99.2 (1)	C(3)–C(4)–C(5)	94.6 (2)
S(1)–N(1)–S(2)	109.4 (2)	C(5)–C(6)–C(7)	103.9 (3)
S(2)–N(2)–S(3)	120.1 (2)	C(3)–C(7)–C(6)	103.0 (3)
S(1)–N(3)–S(3)	119.9 (2)	Cl(1)–Al–Cl(2)	109.85 (6)
S(1)–C(1)–C(2)	107.5 (2)	Cl(1)–Al–Cl(3)	110.24 (6)
S(2)–C(2)–C(1)	107.7 (2)	Cl(1)–Al–Cl(4)	108.30 (6)
S(1)–C(1)–C(5)	113.4 (2)	Cl(2)–Al–Cl(3)	108.48 (6)
S(2)–C(2)–C(3)	112.5 (2)	Cl(2)–Al–Cl(4)	111.58 (6)
C(2)–C(1)–C(5)	103.0 (2)	Cl(3)–Al–Cl(4)	108.38 (6)
C(1)–C(2)–C(3)	103.1 (2)		

Results and Discussion

Preparation of $C_7H_{10}{\cdot}S_3N_3Cl$ (1). Banister et al. isolated the hydrolysis product $[C_7H_{10}{\cdot}NS_2(NH_2)_2]Cl$ (**3**) from the reaction of $(NSCl)_3$ with an excess of norbornene in 1,4-dioxane.[15] They speculated that norbornene dechlorinates $(NSCl)_3$ to give S_3N_3Cl, which undergoes an S,S-cycloaddition with norbornene to give $C_7H_{10}{\cdot}S_3N_3Cl$ (**1**) (Scheme I). In this investigation, we have obtained the adduct **1** as a yellow, moisture-sensitive solid in ca. 60% by carrying out the reaction of $(NSCl)_3$ with an excess of norbornene in a minimum amount of 1,4-dioxane at 0 °C. The ^{13}C and ^{14}N NMR data for **1** (see Table I) indicate that the norbornene ligand is symmetrically S,S′-bonded to the S_3N_3 ring. This adduct **1** is insoluble in most organic solvents and is sparingly soluble in SO_2.

Preparation of $[C_7H_{10}{\cdot}S_3N_3]X$ (2a, X^- = $AlCl_4$; 2b, X^- = AsF_6^-). The salts $[C_7H_{10}{\cdot}S_3N_3]X$ (**2a**, X^- = $AlCl_4$; **2b**, X^- = AsF_6^-) were readily obtained as moisture-sensitive, orange crystals by the treatment of **1** with aluminum trichloride or silver hexafluoroarsenate in SO_2. These salts were easily purified by recrystallization from SO_2. The ^{13}C and ^{14}N NMR data for **2a** and **2b** are compared with those of **1** in Table I. The ^{13}C NMR spectra of **2a** and **2b** are consistent with the retention of the symmetrical S,S′-attachment of norbornene to the S_3N_3 ring, and the ^{13}C chemical shifts of the pairs of equivalent carbon atoms are shifted downfield slightly compared to the corresponding values for **1**. The downfield shift for the unique carbon atom, C(4), in **2a** and **2b** is more pronounced. The ^{14}N NMR spectra of $C_7H_{10}{\cdot}S_3N_3^+$ salts exhibit two signals at ca. −89 and −306 ppm corresponding to the pair of equivalent nitrogens and the unique nitrogen atom, respectively. As indicated in Figure 2 these NMR spectra display a close resemblance to the ^{14}N NMR spectrum of the $S_3N_3Cl_2^+$ cation[21] suggesting a similar structure. Although the structure

(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(21) Apblett, A.; Chivers, T.; Fait, J. F. *Inorg. Chem.* **1990**, *29*, 1643.

(22) Cordes, A. W.; Craig, S. L.; Privett, J. A. J.; Oakley, R. T.; Boeré, R. T. *Acta Crystallogr.* **1986**, *C42*, 508.

(23) Chivers, T.; Fielding, L.; Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1979**, *18*, 3379.

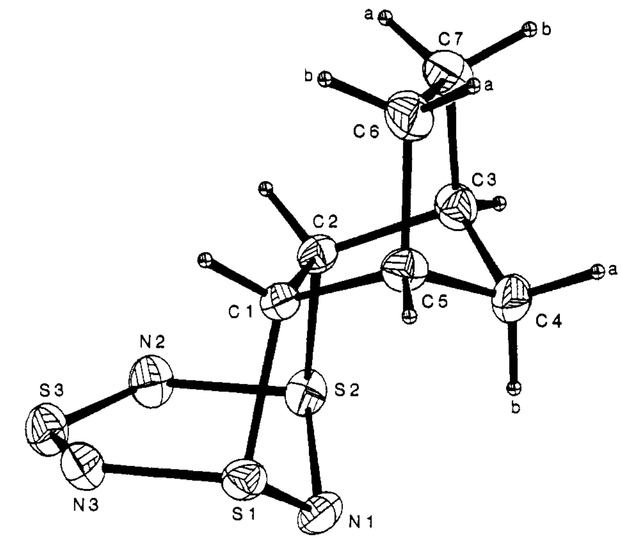


Figure 1. ORTEP plot (30% probability ellipsoids) and atomic numbering scheme for the cation $[C_7H_{10}{\cdot}S_3N_3]^+$ in **2a**.

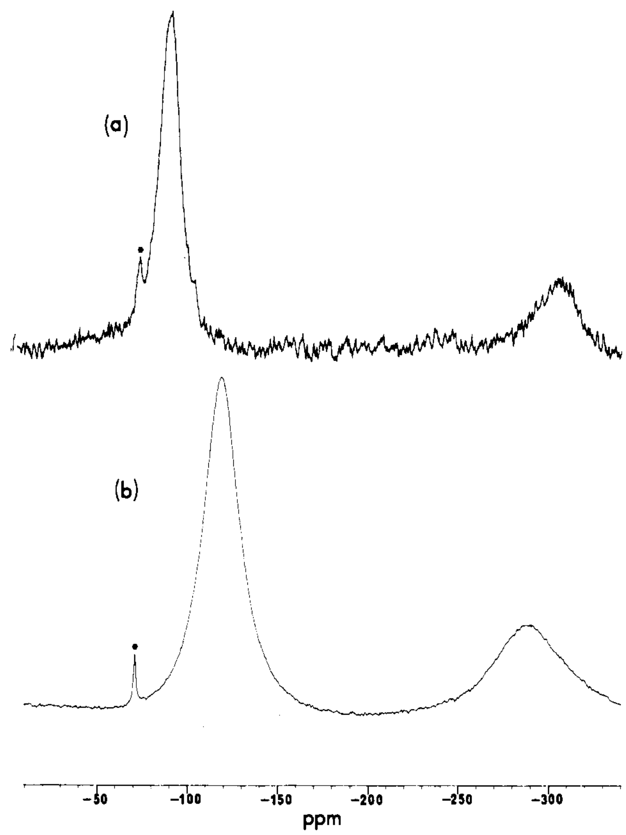


Figure 2. ^{14}N NMR spectra of (a) $C_7H_{10}S_3N_3^+AsF_6^-$ and (b) $S_3N_3Cl_2^+AlCl_4^-$ in SO_2. The peaks marked with an asterisk are due to dissolved N_2.

of the $S_3N_3Cl_2^+$ cation is unknown, it is likely that it involves a cis arrangement of the chlorine atoms attached to sulfur.

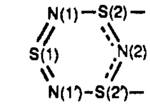
A comparison of the IR spectra of **1**, **2a**, and **2b** with that of norbornane reveals strong bands characteristic of the S_3N_3 ring at 1040–1050, 980–990, 675, 500, and 465–470 cm^{-1} for the adducts.

Crystal and Molecular Structure of $[C_7H_{10}{\cdot}S_3N_3][AlCl_4]$ (2a). An ORTEP drawing of the cation in **2a** with the atomic numbering scheme is displayed in Figure 1 and the bond lengths and bond angles are given in Table IV. The X-ray structural determination confirms that addition of norbornene to the six-membered S_3N_3 ring occurs in a 1,3-fashion across two of the sulfur atoms to give the exo-β isomer. A similar mode of addition and stereochemistry have been found for the norbornadiene adducts of other 8-π-electron six-membered rings, e.g. $Ph_2PN_3S_2{\cdot}C_7H_8$[6] and $PhCN_3S_2{\cdot}C_7H_8$.[24] There are pronounced variations in the S–N bond lengths of the S_3N_3 ring in **2a** that are reminiscent of the structures of the cation $S_4N_5^+$ (in which an NSN unit bridges the $S_3N_3^+$ cation)[23,24] and the related bicyclic molecules ES_3N_5 (E = PhC,[25] Me_2NC,[26] ClC,[27] F_3CC,[28] F_2P[29]) in which the NEN moiety bridges the S_3N_3 ring. Thus the sulfur-diimide (–N=S=N–) unit in **2a** [$|d(S–N)|$ = 1.549 (3) Å] is linked to the SNS moiety [$|d(S–N)|$ = 1.627 (3) Å] by long S–N bonds [$|d(S–N)|$ = 1.709 (3) Å]. These S–N bond lengths are compared with the corresponding values for $S_4N_5^+$ and ES_3N_5 in Table V.

Table V. S–N Bond Lengths (Å) for $[C_7H_{10}{\cdot}S_3N_3]^+$ and Some Bridged S_3N_3 Structures[a]

	d[S(1)–N(1)]	d[S(2)–N(1)]	d[S(2)–N(2)]	ref
$[C_7H_{10}{\cdot}S_3N_3]^+$	1.549 (3)	1.709 (3)	1.627 (3)	this work
$[S_4N_5]Cl$	1.551 (4)	1.682 (4)	1.629 (5)	23
$[S_4N_5]AsF_6$	1.548 (7)	1.688 (6)	1.612 (7)	24
$PhCN_5S_3$	1.547 (2)	1.728 (2)	1.630 (2)	25
$Me_2NCN_5S_3$	1.540 (3)	1.747 (3)	1.626 (4)	26
$ClCN_5S_3$	1.550 (2)	1.731 (2)	1.633 (2)	27
$F_3CCN_5S_3$	1.545 (2)	1.725 (2)	1.630 (2)	28
$F_2PN_5S_3$	1.550 (9)	1.692 (8)	1.622 (6)	29

[a] Mean values for chemically equivalent S–N bonds are given. The numbering scheme for these bonds is indicated below.



The S(1)–N(3)–S(3)–N(2)–S(2) moiety in **2a** in planar to with 0.06 Å and N(1) lies out of this plane by 0.845 (3) Å so that the dihedral angle between the S_3N_2 and SNS planes is 62.1°. The endocyclic bond angles at nitrogen in the –N=S=N– unit are ca. 120° while that at the unique nitrogen, N(1), is 109.4 (1)°. The endocyclic bond angles at the three-coordinate sulfur atoms are ca. 107° while that at the unique sulfur atom, S(3), is 118.7 (1)°.

The structural weakness indicated by the long S–N bonds connecting the –N=S=N– unit to the three-coordinate sulfur atoms is reflected in the mass spectra and the chemical reactivity (vide infra) of **2a** and **2b**. The peak with the highest *m/e* value in the mass spectra corresponds to $C_7H_{10}{\cdot}NS_2^+$, i.e. the loss of the N_2S bridge from the parent cation, $C_7H_{10}{\cdot}S_3N_3^+$.

Chemical Reactivity of $C_7H_{10}{\cdot}S_3N_3^+$ Salts. In an attempt to detach the norbornene fragment from the $S_3N_3^+$ ring the salts **2a** and **2b** were treated with 2,3-dimethyl-1,3-butadiene in SO_2 and the reaction was monitored by ^{13}C NMR spectroscopy. In both cases, the final product exhibited four ^{13}C NMR signals at 29.5, 34.3, 42.0, and 71.3 ppm, and the same species was obtained upon heating **2a** at ca. 100 °C for several hours. This product is tentatively identified as the 2:1 adduct of norbornene with the NS_2^+ cation, i.e. $(C_7H_{10})_2{\cdot}S_2N^+$,[30] formed via loss of the N_2S bridge from $C_7H_{10}{\cdot}S_3N_3^+$ (Scheme I). The formation of the 2:1 adduct rather than the 1:1 adduct $C_7H_{10}{\cdot}S_2N^+$ is puzzling. However, it is clear that the fragmentation of the S_3N_3 ring in **2a** and **2b** is a facile process, and the preparation of salts of the free $S_3N_3^+$ cation will require an alternative approach.

(24) Isenberg, W.; Mews, R. *Z. Naturforsch.* **1982**, *37b*, 1388.
(25) Boeré, R. T.; Cordes, A. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1985**, 929.
(26) Chivers, T.; Edelmann, F.; Richardson, J. F.; Smith, N. R. M.; Treu, O. Jr.; Trsic, M. *Inorg. Chem.* **1986**, *25*, 2119.
(27) Banister, A. J.; Clegg, W.; Gorrell, I. B.; Hauptman, Z. V.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1611.
(28) Maggiulli, R.; Mews, R.; Stohrer, W.-D.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1881.
(29) Appel, R.; Ruppert, I.; Weiss, J. *Z. Anorg. Allg. Chem.* **1974**, *406*, 329.
(30) The ^{13}C NMR chemical shifts for $(C_7H_{10})_2NS_2^+$ prepared directly from NS_2^+ and norbornene are 28.3, 33.1, 40.8, and 71.3 ppm. The reason for the systematic error of 1.2 ppm between these values and our data is not apparent. (a) Burford, N.; Johnson, J. P.; Passmore, J.; Schriver, M. J.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1986**, 967. (b) Schriver, M. J. Ph.D. Thesis, University of New Brunswick, Canada, 1989.

Conclusions

Norbornene adducts of the $S_3N_3^+$ cation are readily obtained by the reaction of $(NSCl)_3$ with an excess of norbornene in 1,4-dioxane followed by treatment of $C_7H_{10}{\cdot}S_3N_3Cl$ so formed with a chloride ion acceptor or silver salt. Although the structural data for one of these adducts indicate localized π-bonding at opposite ends of the S_3N_3 ring, it is likely that the structure of the unattached $S_3N_3^+$ cation will be significantly different from that of the adduct.[31] The structural weakness implied by the variations in S–N bond lengths in the adduct is reflected in the facile loss of the –NSN– bridge.

(31) The structure of the norbornadiene adduct of the 8-π-electron system $Ph_2PN_3S_2$ shows substantial differences in ring conformation, bond lengths, and bond angles compared to that of $Ph_2PN_3S_2$.[6]

Acknowledgment. We are grateful to Dr. R. Yamdagni for assistance with the measurement of the ^{13}C and ^{14}N NMR spectra and Dr. M. J. Schriver (Dalhousie University) for providing the unpublished ^{13}C NMR data for $(C_7H_{10})_2{\cdot}NS_2^+$. We thank the NSERC (Canada), the National Science Foundation, and the State of Arkansas for financial support.

Supplementary Material Available: Listings of crystallographic parameters, thermal parameters, hydrogen atom parameters, and least-squares planes (5 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Dioxygen Adducts of Nickel(II) and Cobalt(II) Dioxopentaazamacrocyclic Complexes: Kinetics, Stabilities, and Hydroxylation of the Ligands in the Nickel Dioxygen Complexes

Dian Chen, Ramunas J. Motekaitis, and Arthur E. Martell*

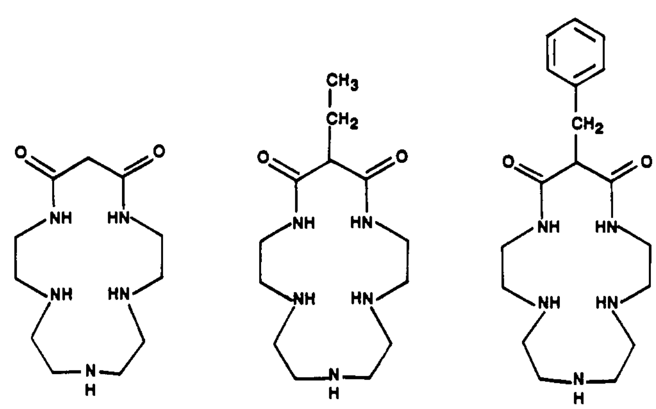
Received August 2, 1990

The macrocyclic ligands 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, 15-ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, and 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione have been prepared, and the stability constants of their Cu(II), Ni(II), and Co(II) complexes have been determined potentiometrically. The dioxygen affinities of the Ni(II) and Co(II) complexes have been measured as a function of partial pressure of dioxygen and temperature. The nickel(II) macrocycles form 1:1, superoxo-type dioxygen complexes, while the Co(II) complexes of the same ligands form 2:1 peroxo-bridged binuclear dioxygen adducts. Equilibrium constants (K_{O_2}), $\Delta H°$, and $\Delta S°$ of dioxygenation are reported. All dioxygen complex formation reactions are strongly exothermic with strongly negative entropy changes. Both nickel and cobalt dioxygen complexes undergo facile degradation in aqueous solution but have significant lifetime for determination of oxygenation constants by dioxygen sorption measurements. The cobalt(II) complexes have higher dioxygen affinities than the nickel(II) complexes with the same ligands. The rates of dioxygen complex formation and degradation have been measured qualitatively and semiquantitatively by UV-visible absorbance studies. The result of this investigation confirms the previous discovery of the formation of dioxygen adducts from nickel(II) complexes, but they are found to undergo irreversible degradation too rapidly to be employed for dioxygen separation or transport. All three Ni(II) dioxygen complexes studied hydroxylate the macrocyclic ligand at the electron-rich 15-carbon position, thus providing new examples of oxygen insertion (monooxygenase-like activity) by the activation of coordinated dioxygen.

Introduction

The recent reports by Kimura et al.[1a-f] that the Ni(II) complexes of dioxopentaazamacrocyclic ligands form stable dioxygen adducts is of considerable interest in view of the fact that such complexes are the first nickel(II) dioxygen carriers to be described. The possibility that these Ni(II) macrocyclic complexes may be employed for the separation of dioxygen from air deserves further investigation, especially in view of the report[1a] that they may undergo several oxygenation and deoxygenation cycles. An even more unique characteristic is the reported endothermic nature of the formation of these nickel dioxygen complexes, which was suggested[1a] as the possible reason for their unusual properties.

In view of the novelty of these nickel(II) dioxygen complexes, it was considered worthwhile to carry out equilibrium and kinetic studies on their formation and to compare their properties with those of the corresponding cobalt dioxygen complexes involving the same ligands. The three ligands selected for this study seem particularly effective in forming stable nickel(II) dioxygen complexes: 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOH (**1**), and its derivatives with ethyl and benzyl groups at the 15-position, to give 15-ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOET (**2**), and 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOBZ (**3**), respectively.



1 PNOH, L 2 PNOET, L' 3 PNOBZ, L''

(1) (a) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497. (b) Kimura, E.; Machida, R. *J. Chem. Soc., Chem. Commun.* **1984**, 499. (c) Kushi, Y.; Machida, R.; Kimura, E. *J. Chem. Soc., Chem. Commun.* **1985**, 216. (d) Kimura, E.; Anan, H.; Toike, T.; Shiro, M. *J. Org. Chem.* **1989**, *54*, 3998. (e) Kimura, E.; Sakonaka, A.; Machida, R. *J. Am. Chem. Soc.* **1982**, *104*, 4255. (f) Machida, R.; Kimura, E.; Kushi, Y. *Inorg. Chem.* **1986**, *25*, 3461.

Experimental Section

Materials. The malonic acid and substituted malonic acid esters employed in the following syntheses, diethyl malonate, diethyl ethylmalonate, and diethyl benzylmalonate, were obtained as pure substances from Aldrich Chemical Co. Tetraethylenepentamine was purified as described in the literature.[2]

1,4,7,10,13-Pentaazacyclohexadecane-14,16-dione, PNOH (1), was prepared by a modification of the method of Kimura et al.[1] ^1H NMR ($CDCl_3$–Me_4Si): δ 1.83 (s, 3 H, CH_2NHCH_2), 2.71–2.91 (m, 12 H,

(2) Jonassen, H. B.; Frey, F. W.; Schaafsma, A. *J. Phys. Chem.* **1957**, *61*, 504.