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Synthesis and Nuclear Magnetic Resonance Spectra of ^{15}N-Enriched Sulfur-Nitrogen Compounds

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Received July 17, 1980

A simple synthesis of ^{15}N-enriched S_4N_4 from $^{15}NH_4Cl$ has been developed, and from it the following S–N compounds have been prepared: $S_4{*}N_3Cl$ and $Ph_3As{=}{*}N{-}S_3{*}N_3$ ($*N = 99\%\ ^{15}N$); $S_4{*}N_2$, $S_4{*}N_5Cl$, $S_3{*}N_3Cl_3$, $S_4{*}N_4Cl_2$, $S_4{*}N_5^-$, $S_3{*}N_3^-$, $S_4{*}N^-$, $Ph_3P{=}{*}N{-}S_3{*}N_3$, $Ph_3P{=}{*}N{-}S_3{*}N$, and 1,5-$(Ph_3P{=}{*}N)_2S_4{*}N_4$ ($*N = 30\%\ ^{15}N$). The ^{15}N NMR spectra of these compounds provide information concerning the structure and electronic distributions of S–N rings and cages in solution. The chemical shift data serve as a useful basis for monitoring the interconversions of S–N species.

Introduction

In the absence of a routine NMR probe, X-ray crystallography has been the only reliable method for establishing the molecular structure of sulfur–nitrogen compounds. Mason and co-workers[2a] have reported ^{14}N chemical shifts for a variety of *N*-sulfinylamines and *N*-sulfenamides and for S_4N_4,[2b] but the inherently broad lines observed for ^{14}N NMR spectra, e.g., S_4N_2 ($\Delta h_{1/2} = 110$ Hz)[3] and $S_4N_5^-$ ($\Delta h_{1/2} \approx 1600$ Hz),[4] severely limit the usefulness of such data in structural determinations. By contrast, the ^{15}N nucleus ($I = {}^1/_2$) gives rise to much narrower signals and is, in principle, a more useful probe for studying the structures of sulfur–nitrogen compounds.

Roberts and co-workers have demonstrated that natural-abundance ^{15}N NMR spectra of *N*-sulfinylamines (neat liquids or 3 M solutions in Me_2SO in 25-mm o.d. spinning tubes) can be obtained in 2–5 h with use of FT techniques.[5] However, the generally low solubility of many sulfur–nitrogen compounds, e.g., S_4N_4,[6] limits the application of natural-abundance (0.36%) ^{15}N NMR spectroscopy, even allowing for the benefits of pulse FT methods. Indeed the only example of the application of ^{15}N NMR spectroscopy to binary sulfur–nitrogen systems is the 1965 report by Logan and Jolly of the ^{15}N NMR spectrum of $S_4{*}N_3^+$ ($*N = 97.2\%\ ^{15}N$).[7]

We have therefore developed a simple synthesis of ^{15}N-enriched S_4N_4 and, from it, other sulfur–nitrogen derivatives starting from commercially available ^{15}N-labeled ammonium chloride. The method involves two steps, the first being the preparation of S_4N_3Cl according to the procedure of Logan and Jolly.[7] The reduction of S_4N_3Cl with iodide ion[8] in acetonitrile then affords S_4N_4 in an overall yield of 40–45% on the basis of nitrogen. In this paper we report the preparation and ^{15}N NMR spectra of a number of sulfur–nitrogen compounds of structural interest. Our objective has been to demonstrate the feasibility and utility of ^{15}N NMR spectroscopy as a structural tool and to establish a basis of chemical shift information from which to carry out more detailed studies on the electronic structures, reaction mechanisms, and possible fluxional behavior of sulfur–nitrogen compounds.

Experimental Section

Reagents. $^{15}NH_4Cl$ (30% and 99% ^{15}N) was obtained from Stohler Isotope Chemicals. The preparation of S_4N_3Cl followed closely the procedure described by Logan and Jolly,[7] but reaction times for the generation of $S_3N_2Cl_2$ were generally longer (48–72 h) than those reported.

Preparation of S_4N_4 from S_4N_3Cl. Finely powdered potassium iodide (2.34 g, 14.0 mmol) was added to a slurry of S_4N_3Cl (2.63 g, 12.7 mmol) in 75 mL of anhydrous acetonitrile, and the mixture was heated to reflux under an atmosphere of dry nitrogen. After 16 h at reflux, the intensely colored mixture was poured into an evaporating dish and left for ca. 48 h to allow the solvent and iodine to evaporate. The residual solid was then extracted with 3 × 200 mL of hot dichloroethane. Evaporation of the solvent from these extracts and fractional crystallization of the resulting mixture of S_4N_4 and c-S_8 from benzene yielded 1.49 g (8.12 mmol, 85%) of pure S_4N_4.

Preparation of ^{15}N-Labeled S–N Derivatives. ^{15}N-enriched $PNP^+S_4N_5^-$, $PNP^+S_3N_3^-$, and $PNP^+S_4N^-$ [$PNP^+ = (Ph_3P)_2N^+$] were all prepared according to a recently described procedure, starting from labeled S_4N_4.[9] $Ph_3P{=}N{-}S_3N_3$,[10] $(Ph_3P{=}N)_2S_4N_4$,[10] and $Ph_3P{=}N{-}S_3N$[11] were also prepared according to literature methods. $Ph_3As{=}N{-}S_3N_3$ was obtained by the reaction of Ph_3As with S_4N_4.[12] S_4N_2 was prepared by the reaction of S_4N_4 with sulfur in carbon disulfide.[3] $S_4N_4Cl_2$ was prepared by the chlorination of S_4N_4 at low temperature.[13] Partially labeled S_4N_5Cl was prepared by the reaction of unlabeled $Me_3Si{-}N{=}S{=}N{-}SiMe_3$[14] with ^{15}N-enriched $S_3N_3Cl_3$.[15]

Instrumentation. ^{15}N NMR spectra were recorded at 20.266 MHz on Bruker WP200 (at Kaiserslautern) Varian XL-200 (at Calgary) spectrometers, both operating in the FT mode. Solutions of varying molar (5×10^{-3}–10^{-1} M) and isotopic (30% and 99% ^{15}N) concentrations in chloroform or methylene chloride (except for S_4N_3Cl in 70% HNO_3, S_4N_5Cl in DMF, and $(Me_3SiN)_2S$ as neat liquid) were used. Samples were contained in 10-mm o.d. spinning tubes, and a 4-mm o.d. capillary containing ca. 2 M ${*}NH_4^+{*}NO_3^-$ ($*N = 95\%\ ^{15}N$) in acidified D_2O provided the field-frequency lock and external standard. NH_4NO_3 was itself calibrated against neat nitromethane, and chemical shift values are reported on the δ scale with liquid NH_3 at 25 °C as a reference point (on this scale $\delta(CH_3NO_2)$ is 380.23).[16] Useful spectra could usually be obtained with 50–500 scans, a pulse width of 10–20 μs, a relaxation delay of 30 s, 32 K data points, and

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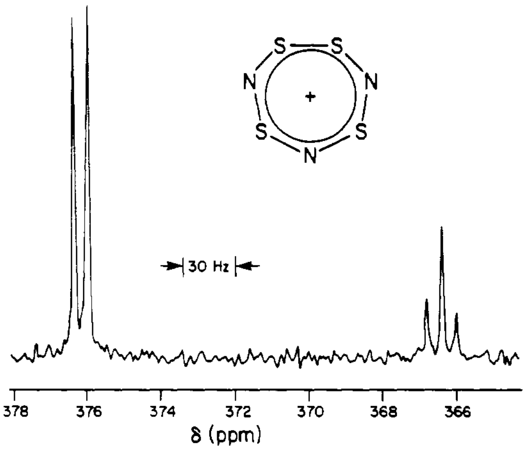

Figure 1. ^{15}N NMR spectrum of 99% ^{15}N-enriched S_4N_3Cl (ca. 2 × 10^{-1} M in 70% HNO_3, 2000 scans).

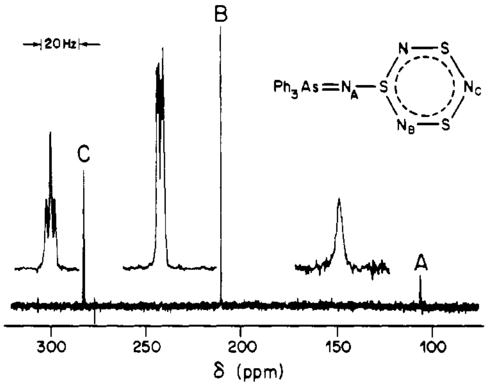

Figure 2. ^{15}N NMR spectrum of 99% ^{15}N-enriched $Ph_3As{=}N{-}S_3N_3$ (ca. 2 × 10^{-1} M in $CHCl_3$, 1800 scans).

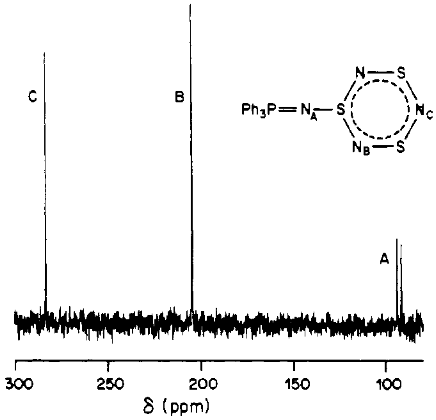

Figure 3. ^{15}N NMR spectrum of 30% ^{15}N-enriched $Ph_3P{=}N{-}S_3N_3$ (ca. 2 × 10^{-1} M in $CHCl_3$, 400 scans).

a spectral width of 10 KHz. The probe temperature was held constant at ca. 24 °C.

Results and Discussion

The ^{15}N NMR parameters of the representative sulfur-nitrogen cations, anions, and neutral compounds studied in this investigation are summarized in Table I. Spectra which illustrate particular points of interest are shown in Figures 1–4. Only in the case of $Me_3SiNSNSiMe_3$, as a neat liquid, was it possible to obtain an ^{15}N NMR spectrum at the natural abundance level. For other compounds, 30% ^{15}N NMR enrichment was sufficient to obtain good spectra on ca. 10^{-2} M solutions in a reasonable period of time. These spectra provide chemical shifts but not ^{15}N–^{15}N coupling constants. Although some incipient fine structure was observed it could not be resolved from the predominantly singlet resonances ($\Delta h_{1/2} <$ 1.5 Hz). The presence of 10^{-1} M tris(acetylacetonato)chromium(III), [Cr(acac)$_3$], in solutions of S_4N_4 in $CHCl_3$ greatly shortens the ^{15}N relaxation time without causing significant contact shifts (<3 ppm)[17] or line broadening ($\Delta h_{1/2} \approx$ 3–4 Hz). Thus, samples containing the relaxation agent required no pulse delay (as opposed to a 30-s delay for normal spectra), thereby significantly reducing the accumulation time required for routine analysis. However, it should be noted that the use of such agents precludes the observation of ^{15}N–^{15}N coupling constants, which are generally quite small ($|^2J_{NN}| \approx$ 1–8 Hz; see the following section).

Table I. ^{15}N NMR Parameters of Sulfur-Nitrogen Species

compd	% N	solvent	chemical shift[a]
$Me_3SiNSNSiMe_3$	0.36	neat liquid	321.3 (s)
S_4N_4	99	$CHCl_3$	123.2 (s)
S_4N_2	30	$CHCl_3$	266.3 (s)
$S_4N_3^+$	99	HNO_3	376.1 (2 N, d, $^2J_{NN}$ = 8.5 Hz), 366.4 (1 N, tr, $^2J_{NN}$ = 8.5 Hz)
$Ph_3P{=}N{-}S_3N_3$	30	$CHCl_3$	282.5 (1 N, s), 203.5 (2 N, d, $^3J_{PN}$ = 4.3 Hz), 92.0 (1 N, d $^1J_{PN}$ = 48.9 Hz)
$Ph_3As{=}N{-}S_3N_3$	99	$CHCl_3$	282.6 (1 N, tr, $^2J_{NN}$ = 2.2 Hz), 209.6 (2 N, d of d, $^2J_{NN}$ = 2.2 Hz), $^2J_{NN}$ = 0.7 Hz) 104.9 (1 N, s)[b]
$Ph_3P{=}NSNSS$	30	$CHCl_3$	472.0 (1 N, s), 86.9 (1 N, d, $^1J_{PN}$ = 58.0 Hz)
1,5-$(Ph_3P{=}N)_2S_4N_4$	30	$CHCl_3$	159.8 (2 N, s), 153.6 (2 N, d, $^3J_{PN}$ = 4.3 Hz), 86.2 (1 N, d, $^1J_{PN}$ = 43.9 Hz), 82.1 (1 N, d, $^1J_{PN}$ = 47.6 Hz)
$Cl_2S_4N_4$	30	$CHCl_3$	231.5 (s, br)
$Cl_3S_3N_3$	30	$CHCl_3$	118.5 (s)
S_4N_5Cl	30[c]	DMF	225.1 (2 N, s), 39.3 (1 N, s)
$S_4N_5^-$	30	$CHCl_3$	138.7 (4 N, s), 53.3 (1 N, s)
$S_3N_3^-$	30	$CHCl_3$	148.4 (s)
S_4N^-	30	$CHCl_3$	212.8 (s)

[a] In ppm; positive values are downfield of NH_3(l) at 25 °C. [b] See text. [c] Only two of the four equivalent nitrogens are labeled.

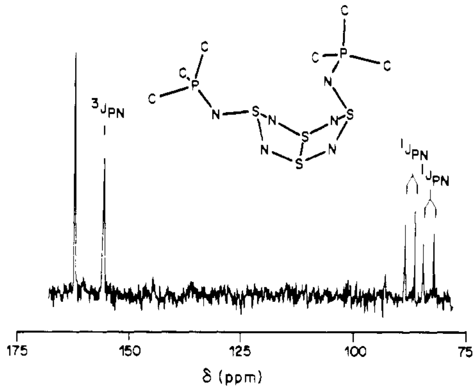

Figure 4. ^{15}N NMR spectrum of 30% ^{15}N-enriched $(Ph_3{=}N)_2S_4N_4$ (ca. 10^{-1} M in $CHCl_3$, 800 scans).

Spin–Spin Coupling, $^2J_{^{15}N-^{15}N}$, in Sulfur Nitrides. In order to assess the range of values to be expected for ^{15}N–^{15}N coupling constants, we have examined a few molecules enriched with 99% ^{15}N. Figure 1 illustrates the effect of two-bond

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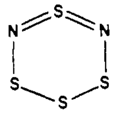
coupling for the $S_4{}^{15}N_3{}^+$ cation. The expected doublet–triplet pattern, consistent with the known planar structure,[18] is observed. The chemical shifts (376.1 and 366.4 ppm) are similar to those reported by Logan and Jolly[7] (335 and 343 ppm downfield of 5.7 M $^{15}NH_4Cl$ in 0.1 M HCl) as are the $^2J_{^{15}N-^{15}N}$ values (8.5 vs. 7 Hz), but considerably better resolution was possible on more dilute solutions with use of FT methods.

The ^{15}N NMR spectrum of $Ph_3As{=}^{15}N{-}S_3{}^{15}N_3$ (see Figure 2) is readily interpreted in terms of the known solid-state structure.[19] The broad signal ($\Delta h_{1/2} \approx 3$ Hz) at 104.9 ppm is attributed to the exocyclic nitrogen, N_A, the broadening being due to quadrupole relaxation from the adjacent ^{75}As nucleus ($I = {}^3/_2$; 100%). The triplet at 282.6 ppm ($^2J_{^{15}N-^{15}N} = 2.2$ Hz) is assigned to the unique nitrogen, N_C, in the S_3N_3 ring. The middle signal at 209.6 ppm is a doublet of doublets attributed to the pair of equivalent nitrogens, N_B, coupled to N_C ($^2J_{^{15}N-^{15}N} = 2.2$ Hz) and N_A ($^2J_{^{15}N-^{15}N} = 0.7$ Hz). It is noteworthy that the $^2J_{^{15}N-^{15}N}$ coupling constants for the neutral compound are significantly smaller than those found for the $S_4N_3{}^+$ cation. The corresponding phosphorus compound $Ph_3P{=}{*}N{-}S_3{*}N_3$ (*N = 30% ^{15}N), which has a solid-state structure similar to the arsenic derivative,[20] also exhibited three well-separated signals (Figure 3). In this compound the signal for the exocyclic nitrogen, N_A, is a well-resolved doublet due to the coupling $^1J_{^{31}P-^{15}N} = 48.9$ Hz. A doublet is also observed at 203.5 ppm due to the three-bond coupling $^3J_{^{31}P-^{15}N} = 4.3$ Hz. The similarity of the chemical shifts of the endocyclic nitrogens in the $Ph_3E{=}N{-}S_3N_3$ (E = P, As) suggest that the NMR technique will be a useful diagnostic structural probe for other monosubstituted S_3N_3 derivatives.

^{15}N Chemical Shifts in Sulfur Nitrides. The sulfur nitride derivatives studied in this work exhibit a very broad range of chemical shifts, and it would be premature at this time to attempt the interpretation of this data in terms of particular effects. Nonetheless, some qualitative statements can be made. The ^{15}N shifts of S_4N_4 (123.2 ppm) and S_4N_2 (266.3 ppm) agree well with the ^{14}N values obtained earlier (131 ppm for S_4N_4[2] and 270 ppm for S_4N_2[3]). The singlet observed for S_4N_2 is in the region generally expected for sulfur diimides (e.g.; $Me_3Si{-}N{=}S{=}N{-}SiMe_3$, 321.3 ppm; $Ph{-}N{=}S{=}N{-}Ph$, 306 ppm[2c]) and supports the proposed six-membered structure **1**.[3]



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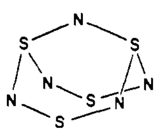
The structures of the sulfur–nitrogen cages $S_4N_5{}^-$[21] and $S_4N_5{}^+$[15] are closely related to that of S_4N_4 except that one of the transannular S–S bonds is bridged by N^- or N^+. In $S_4N_5{}^-$ the unbridged S–S distance is ca. 2.71 Å[21] and in $S_4N_5{}^+$ it is 4.0 Å.[15] Consistent with the cage structure **2** the ^{15}N NMR spectrum of $S_4N_5{}^-$ shows two signals with an intensity ratio of 4:1 at 138.7 and 53.3 ppm, corresponding to the four equivalent nitrogens and the unique bridging nitrogen, N_B, respectively. In $S_4N_5{}^+$, prepared from unlabeled $Me_3Si{-}N{=}S{=}N{-}SiMe_3$ and labeled $S_3N_3Cl_3$, only two of the four equivalent nitrogens and the bridging nitrogen N_B are enriched; the signals corresponding to these two types of nitrogen are observed at 225.1 and 39.3 ppm, respectively. Thus, in both the cation and the anion, the bridging nitrogens are found to high field of the four nonbridging atoms, a trend which is consistent with recent charge density calculations, which indicate the primary effect of the bridging nitrogen is to withdraw electron density from the S_4N_4 unit.[15b] The shifts for the anionic series $S_4N_5{}^-$ (weighted average = 121.6 ppm), $S_3N_3{}^-$ (148.4 ppm), and S_4N^- (212.8 ppm) can also be correlated with the calculated charge densities on nitrogen,[9b,15b,22] but the correspondence may be fortuitous. The effect of excited-state mixing and bond polarity on the ^{15}N shifts of sulfur nitrides is by no means clear. For example, a comparison of the chemical shifts of the S_3N_3 resonances in $Ph_3E{=}N{-}S_3N_3$ (λ_{max} for E = P is 478 nm and for E = As is 488 nm) and in $S_3N_3{}^-$ (λ_{max} = 360 nm) would suggest an inverse dependence of the HOMO → LUMO excitation energy on δ, whereas the relative shifts of the S_3N nitrogen in $Ph_3P{=}N{-}S{-}N{=}S{=}S$ (**3**) (λ_{max} = 491 nm) and in S_4N^- (**4**) (λ_{max} = 582 nm) would indicate a direct dependence. Obviously the subject of δ/λ correlations is more complex in these molecules than in simple chromophores (e.g., $N{=}S{=}O$), and a proper explanation must await a more complete understanding of the nature of the electronic excitations, the bond polarities, and charge densities found in sulfur–nitrogen systems.



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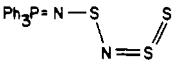

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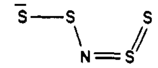

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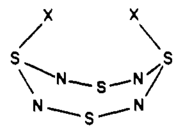
Conformational Studies of the Disubstituted S_4N_4 Derivatives 1,5-$(Ph_3P{=}N)_2S_4N_4$ and $Cl_2S_4N_4$. The X-ray structural determination of $(Ph_3P{=}N)_2S_4N_4$ has shown that the two substituents are in different (*axial*, *equatorial*) orientations.[10] The ^{15}N NMR spectrum of this compound (see Table I and Figure 4) shows that this conformation is preserved in solution. Two signals are observed at 86.2 and 82.1 ppm for the nonequivalent exocyclic substituents (the two phosphorus atoms are also inequivalent, $\delta_P(CDCl_3)$, external reference H_3PO_4) = 23.6 and 18.1 ppm). Each of these signals is a doublet due to coupling with phosphorus ($^1J_{^{31}P-^{15}N} \approx 46$ Hz; cf. 49 Hz in $Ph_3P{=}N{-}S_3N_3$). Two further signals at 160.8 and 153.8 ppm are assigned to the nonequivalent pairs of endocyclic nitrogens; one of these signals is resolved into a doublet resulting from the three-bond coupling to phosphorus ($^3J_{^{31}P-^{15}N} = 4.3$ Hz; cf. 4.3 Hz in $Ph_3P{=}N{-}S_3N_3$). Thus it appears that the two ligated sulfurs are not free to undergo configurational inversion in solution. Presumably the *axial–axial* conformer **5** is too sterically strained, and *equatorial–equatorial* isomer **6** imposes a strongly repulsive interaction between the partly "antibonding" lone pairs on the substituted sulfurs. In contrast, the ^{15}N NMR spectrum of $Cl_2S_4{*}N_4$ shows all four nitrogens to be equivalent,[25] as are the fluorines in $F_2S_4N_4$.[13] In these latter molecules the S–S bond is expected to be



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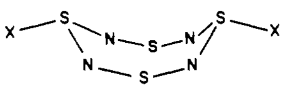

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weaker,[10,23] and the molecules consequently are less puckered, i.e., approaching the structure of the $S_4N_4^{2+}$ dication.[24] In such a conformation the cross-ring interactions between 1,5 sulfurs and their ligands will be less restrictive, and equilibration of the ligand orientations can occur.

Conclusion

The broad range of chemical shifts exhibited by the compounds examined in this preliminary study illustrate the sensitivity of the ^{15}N nucleus to changes in molecular and electronic environment. Although the interpretation of these shifts is not straightforward, the information presented here provides an empirical basis for the identification of both new and known sulfur–nitrogen species. The complex solution chemistry of sulfur–nitrogen derivatives can now be routinely monitored in ^{15}N NMR spectroscopy, and the study of the fluxional behavior of sulfur–nitrogen rings and cages (e.g., $S_4N_5^{\pm}$ and S_5N_6[23]) can be pursued. We are currently investigating these possiblities.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the University of Calgary, and NATO (Research Grant No. 1744) for financial support. The assistance of Dr. R. Yamdagni in obtaining the NMR spectra and helpful discussions with Dr. W. G. Laidlaw are gratefully acknowledged. We also thank Dr. J. Mason for her comments on the manuscript.

Registry No. $Me_3SiNSNSiMe_3$, 18156-25-7; S_4N_4, 28950-34-7; S_4N_2, 32607-15-1; $S_4N_3^+$, 29631-23-0; $Ph_3P{=}NS_3N_3$, 33082-06-3; $Ph_3As{=}NS_3N_3$, 63212-45-3; $Ph_3P{=}NSNSS$, 73845-61-1; 1,5-$(Ph_3P{=}N)_2S_4N_4$, 72144-79-7; $Cl_2S_4N_4$, 71699-97-3; $Cl_3S_3N_3$, 5964-00-1; S_4N_5Cl, 67954-28-3; $S_4N_5^-$, 58858-09-6; $S_3N_3^-$, 65107-36-0; S_4N^-, 51330-98-4; S_4N_3Cl, 12015-30-4; ^{15}N, 14390-96-6.

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Ferromagnetic Exchange Coupling in Polynuclear Copper(I)–Copper(II) Complexes with Penicillamine and Related Ligands

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Received May 8, 1980

Crystalline derivatives of mixed-valence Cu(I)–Cu(II) cluster complexes of composition $[Cu^{II}_6Cu^{I}_8L_{12}Cl]^{5-}$, where L is deprotonated α-mercaptoisobutyric acid or D-penicillamine, were obtained with $Co(NH_3)_6^{3+}$ as counterions. The magnetic moments of these complexes have been measured in the temperature range from 2.5 to 300 K and in magnetic fields up to 2.0 T. A ferromagnetic interaction was observed which is interpreted as due to *intra*cluster-exchange interactions between the spins of the six paramagnetic Cu(II) atoms which are located at the apices of a slightly deformed octahedron with edges of ~0.67 nm. A theoretical model is discussed which describes the interaction of spins in a locally isolated, symmetrical arrangement. A model of isotropic Heisenberg nearest-neighbor-exchange interactions for an octahedral arrangement of spins gives a good fit with the experimental data for an exchange constant J/k_B on the order of 7 K.

Introduction

Mixed-valence copper complexes of composition $[Cu^{II}_6Cu^{I}_8L_{12}Cl]^z$ have been synthesized with three thiolate ligands (L), viz., D-penicillamine[2,3] [$H_2Pen = HSC(CH_3)_2CH(NH_3^+)COO^-$; $z = 5-$], β,β-dimethylcysteamine[4,5] [$HDMC = HSC(CH_3)_2CH_2NH_2$; $z = 7+$], and α-mercaptoisobutyric acid[6] [$H_2MIBA = HSC(CH_3)_2COOH$; $z = 5-$]. These complexes have been characterized by X-ray diffraction, and their geometries have been described.[2-6] They have a number of structural features in common (Figure 1). A single chlorine atom lies at the center of a cube of eight Cu(I) atoms. This Cu^{I}_8 cube is inscribed into an icosahedron of 12 sulfur atoms, so that each Cu(I) atom lies at the center of a triangular face of this S_{12} icosahedron. Above each of the six faces of the Cu^{I}_8 cube lies a Cu(II) atom. The Cu(II) atoms lie also above a S–S edge of the sulfur icosahedron. Each sulfur atom forms a bridge between two Cu(I) atoms and one Cu(II) atom. The bidentate ligands chelate the Cu(II) atoms resulting in cis planar four-coordination ($Cu^{II}N_2S_2$ for H_2Pen and HDMC; $Cu^{II}S_2O_2$ for H_2MIBA). The methyl substituents are essential as they protect the Cu(I) sites sterically.[3] The six Cu(II) atoms occupy the vertices of a slightly deformed octahedron with edges of approximately 0.67 nm.[2-6]

These compounds are unique examples of systems in which a large number (six) of relatively isolated paramagnetic centers are symmetrically arranged in a single molecule.

The ESR spectra of the H_2Pen[3] and HDMC[5] complexes are poorly resolved. Most likely this is due to intramolecular interactions between the paramagnetic Cu(II) atoms. We will discuss a very general approach to the description of the magnetic *intra*cluster-exchange interactions in polynuclear paramagnetic complexes. The calculations are carried out in detail for a regular octahedral arrangement of spins. The analysis of the data on the temperature dependence of the magnetic susceptibility for the H_2Pen and for the H_2MIBA complexes based on this model reveals the existence of a ferromagnetic interaction. The magnetic field dependence of the magnetization data at our lowest temperatures indicates that the lowest level is characterized by a spin quantum number $S = 3$.

Recently a ferromagnetic exchange interaction was reported for the corresponding HDMC complex.[5] In the model used

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