to coincide with the metal–metal vectors. Those appropriate to the tetrahedron were identical with the set used in the normal-coordinate analysis of the P_4 molecule.[21] We give here (Table IX) symmetry coordinates for an octahedral cluster; internal coordinates are defined in Figure 1.

Registry No. $Os_3(CO)_{12}$, 15696-40-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ir_4(CO)_{12}$, 18827-81-1; $Mn_3H_3(CO)_{12}$, 51160-01-1; $Pb_4(OH)_4{}^{4+}$, 31387-73-2; $Bi_6(OH)_{12}{}^{6+}$, 12441-70-2; $Rh_4(CO)_{12}$, 19584-30-6; $Os_3(OCH_3)_2(CO)_{10}$, 41766-82-9; $Co_4(CO)_{12}$, 17786-31-1.

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[21] C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1421 (1958).

Notes

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The X-ray Photoelectron Spectrum of S_2N_2 Gas

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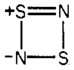
S_2N_2 is a square molecule (D_{2h} symmetry)[2] formed from the interaction of S_4N_4 vapor with silver wool at 150 °C. On warming, condensed S_2N_2 undergoes polymerization (0 °C) to the conducting polymer $(SN)_x$ (polythiazyl).[2,3] Largely as a consequence of the relationship of S_2N_2 with $(SN)_x$ the bonding and charge distribution in S_2N_2 have been a matter of considerable speculation.[4] The bonding in S_2N_2 can formally be represented by valence bond structures I and II.


I


II

These valence bond (VB) structures suggest an S–N bond order of between 1.25 and 1.50 and *formal* S→N charge transfer of between 0 and 0.5 e. Within the valence bond formalism, decreasing S→N charge transfer requires N(pπ)→S(dπ) back-bonding (VB structure II). The extent of participation of sulfur 3d orbitals in the bonding of sulfur compounds has been a controversial issue for several years now.[5a,b] Jolly and co-workers[5c] have utilized X-ray photoelectron spectroscopy (XPS) to evaluate the contribution of sulfur 3d orbitals to the bonding of a variety of sulfur compounds and found that the XPS data could be very satisfactorily explained without the inclusion of S 3d orbitals. In an effort to estimate the charge distribution and extent of S 3d orbital participation in the bonding of S_2N_2, we have obtained core-level binding energies for gaseous S_2N_2 using XPS. The results have been interpreted with the aid of CHELEQ (electronegativity equalization)[5d] and semiempirical MNDO[6] MO calculations.

Table I. Core Level Data for S_2N_2 from X-ray Photoelectron Spectroscopy

	S $2p_{1/2}$	S $2p_{3/2}$	S 2s	N 1s
binding energy, eV[a]	173.64 (10)[c]	172.44 (10)	236.58 (5)	405.86 (5)
FWHM[b]	1.09	1.08	2.15	1.09

[a] Binding energies standardized to a value of 248.62 eV for the Ar $2p_{3/2}$ level of argon gas. [b] Peak full widths at half maxima (FWHM), in eV. [c] Estimated standard deviations (3σ) are given in parentheses.

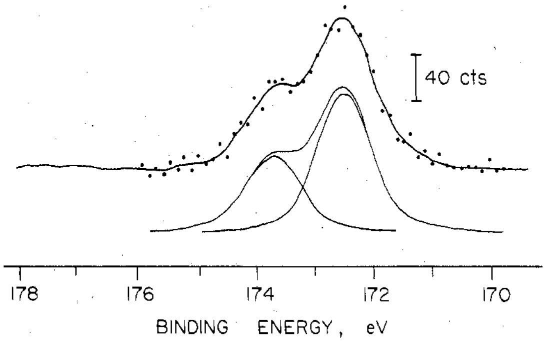


Figure 1. S $2p_{1/2}$, $2p_{3/2}$ spectrum of S_2N_2 gas and the simulated spectrum showing the curve-resolved $2p_{1/2}$ and $2p_{3/2}$ components. The components have 50:50 Gaussian–Lorentzian line shapes.

Experimental Section

S_2N_2 was freshly prepared according to the established procedure.[2] Spectra were recorded with a McPherson ESCA-36 photoelectron spectrometer equipped with a Mg Kα (1253.6 eV) X-ray source. The McPherson gas sample cell was fitted with indium gaskets and a 1-mil aluminum window to isolate the sample from the X-ray source. Pressures in the sample chamber ranged from high 10^{-7} to low 10^{-6} torr during data collection. The S_2N_2 was introduced into the gas cell via an evacuated glass vessel. Sufficient S_2N_2 pressure for data collection was maintained by *gently* warming the glass vessel (ca. ≤ 40 °C) with a hot air blower.

Data were collected and processed with a PDP-12 computer. Curve resolution of the S $2p_{1/2}$ and $2p_{3/2}$ levels was achieved by using a Gaussian–Lorentzian curve generation subroutine which is part of the McPherson program package. The simulated and experimental curves were judged equivalent by visual comparison of the curves. Core-level binding energies were standardized to the Ar $2p_{3/2}$ level of argon gas (248.62 eV),[7] spectra of which were recorded immediately before and after data collection for S_2N_2. The two Ar $2p_{3/2}$ binding energies recorded were identical within experimental error.

MNDO calculations on S_2N_2 were performed on the IBM 370/145 computer at Georgetown University using QCPE program no. 353. All geometry parameters were optimized. CHELEQ calculations were performed on the Texas Instruments Advanced Scientific Computer

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(1) (a) Naval Research Laboratory. (b) Georgetown University.
(2) Milkulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358.
(3) (a) Walatka, V. V.; Labes, M. M.; Perlstein, J. H. *Phys. Rev. Lett.* **1973**, *31*, 1139. (b) Greene, R. S.; Grant, P. M.; Street, G. B. *Ibid.* **1975**, *34*, 89.
(4) (a) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039. (b) Yamabe, J.; Tanaka, K.; Fukui, K.; Kato, H. *J. Phys. Chem.* **1977**, *81*, 727. (c) Salaneck, W. R.; Lin, J. W.-p.; Paton, A.; Duke, C. B.; Ceasar, G. P. *Phys. Rev. B: Solid State* **1976**, *13*, 4517. (d) Tanaka, K.; Yamabe, J.; Tachibana, A.; Kato, H.; Kenichi, F. *J. Phys. Chem.* **1978**, *82*, 2121. (e) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Edgell, R. G.; Evans, R. *Inorg. Chem.*, in press.
(5) (a) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174. (b) Noodleman, L.; Mitchell, K. A. R. *Inorg. Chem.* **1978**, *17*, 2710. (c) Jolly, W. L.; Lazarus, M. S.; Glemser, O. *Z. Anorg. Allg. Chem.* **1974**, *406*, 209. (d) Jolly, W. L.; Perry, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442.
(6) Dewar, M. J. S.; Thiel, N. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(7) Johansson, G.; Hedman, J.; Berndstsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 295.

at the Naval Research Laboratory. Details of both calculational procedures are published elsewhere.[5d,6,8]

Results and Discussion

The S_2N_2 core level binding energies and their respective full widths at half maxima (FWHM) are summarized in Table I, while the S $2p_{1/2}$, $2p_{3/2}$ spectrum is shown in Figure 1. The area ratio of the curve resolved $2p_{1/2}$ and $2p_{3/2}$ components of the S 2p level is 1.00:1.90, in close agreement with the ratio predicted by Scofield[9] and by Nefedov et al.[10] (1.00:1.96) and that measured by Banna et al.[11] and Siegbahn and co-workers[12,13] in a number of other sulfur compounds. The $2p_{1/2}$, $2p_{3/2}$ spin–orbit splitting of 1.20 eV also agrees with the value reported previously.[11-13] Line widths of the S $2_{1/2}$, $2p_{3/2}$ and N 1s levels (1.08–1.09 eV) approach the limiting line width for the experimental parameters employed. Thus, these symmetric narrow peaks are consistent with the presence of a single form of sulfur and nitrogen in S_2N_2. The larger line width of the S 2s level (2.15 eV) is undoubtedly due to the more rapid relaxation of the core-hole state which arises from a Coster–Kronig transition.[14]

In qualitative accord with the simple valence bond picture for S_2N_2 (valence bond structures I and II) and straightforward electronegativity arguments, we find that the recorded S 2p, S 2s, and N 1s binding energies are indicative of charge transfer from sulfur to nitrogen. For example, the S $2p_{3/2}$ binding energy of 172.44 eV in S_2N_2 is 1.8–1.9 eV higher than that reported for S_8 vapor.[11a] Conversely, the N 1s binding energy of S_2N_2 (405.86 eV) is 4.1 eV lower than that of N_2.[7]

The bonding and charge distribution of S_2N_2 can be examined in greater detail by comparison of the observed core level binding energies of S_2N_2 with those of other sulfur- and/or nitrogen-containing molecules, including S_4N_4, and by using the atomic charges calculated according to the electronegativity equalization method. The atomic charges and core level binding energies can then be correlated by using the point-charge potential model[12]

$$E_B = kQ + V + l$$

where E_B is the measured binding energy, Q is the ground-state charge of the core ionized atom, V is the Coulomb potential due to all the other atoms in the molecule, and k and l are constants. We have used the CHELEQ program written by Jolly and Perry[5d] for this purpose. The atomic charges calculated depend on the weighting of the plausible valence bond structures selected. The structure and valance bond representations (I and II) for S_2N_2 have already been discussed. S_4N_4 has a cage structure (D_{2d} symmetry)[15] comprised of a bisphenoid of sulfur atoms and a square of nitrogen atoms. The S–N bond distances in S_4N_4 (1.616 and 1.642 Å) are very similar to those in S_2N_2 (1.657 and 1.651 Å). A notable additional feature in the topology of S_4N_4 is the short S–S distance (~2.58 Å) from which one can infer a significant S–S bonding interaction.

Table II. Variance of Calculated and Experimental Core-Level Binding Energies for S_2N_2 and S_4N_4 According to the CHELEQ Method

valence bond structure	E_B(calcd) – E_B(exptl), eV S $2p_{3/2}$	N 1s	charge transfer,[a] e (S→N)
II, S_2N_2	−0.58	−0.20	0.19
III, S_4N_4	−1.0	0.0	0.19
IV, S_4N_4	+0.5	−4.6	0.43
80% III + 20% IV	−0.6	−0.7	0.24

[a] CHELEQ method. [b] Best fit for both S $2p_{3/2}$ and N 1s E_B's.

Table III. Calculated Charge Transfer (S→N) in S_2N_2 and S_4N_4

method	charge transfer, e (S→N) S_2N_2	S_4N_4	ref
MNDO	0.402	0.53	this work
SCF-Xα	0.48	0.55	4a
INDO-type ASMO-SCF	0.201	0.709	4b,d
CNDO-S		0.47	4c

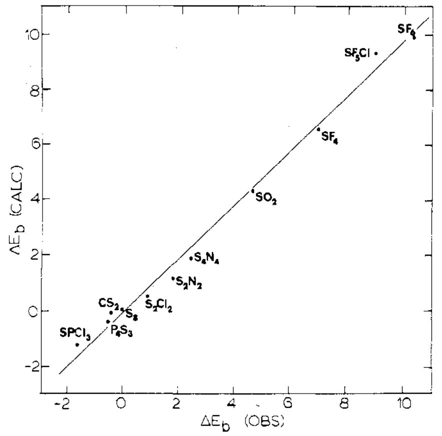
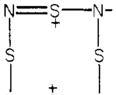


Figure 2. A plot of the CHELEQ calculated vs. experimental S $2p_{3/2}$ binding energies.

On the basis of its structure, possible valence bond representations for S_4N_4 are given (III–VI). As in the case for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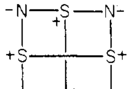
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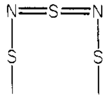
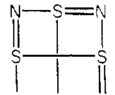

V


VI

S_2N_2, N(pπ)→S(dπ) back-bonding and decreased S→N charge transfer (valence bond forms V and V1) may be significant in the bonding of S_4N_4.

In the CHELEQ program, a least-squares fit of the observed binding energies for a given atom with the calculated values of Q and V provides values of k and l. These parameters are then used along with the calculated Q and V to yield calculated binding energies. On the assumption that lesser deviations of E_B (calcd) from E_B (obsd) reflect a more accurate view of the bonding in a given molecule, we find that the bonding in S_2N_2 is best described by VB structure II while the best description for S_4N_4 involves a mixture of 80% VB structure III and 20% VB structure IV.[16] Results for the best fits of E_B (calcd) to E_B (exptl) are summarized in Table II and the least-squares fit of observed and calculated S $2p_{3/2}$ binding energies for

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(8) Jolly, W. L.; Perry, W. B. *Inorg. Chem.* **1974**, *13*, 2686.
(9) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.
(10) Nefedov, V. I.; Sergushin, N. P.; Band, I. M.; Tryhaskovaskaya, M. B. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 383.
(11) (a) Banna, M. S.; Frost, D. C.; McDowell, C. A.; Wallbank, B. *Chem. Phys. Lett.* **1976**, *43*, 426. (b) Banna, M. S.; Frost, D. C.; McDowell, C. A.; Wallbank, B. *J. Chem. Phys.* **1977**, *66*, 3509.
(12) Siegbahn, K.; Nordling, C; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, J.; Karlsson, S. E.; Lindgren, I.; Lindberg, B. "ESCA; Atomic, Molecular, and Solid State Structure Studies by Means of Electronic Spectroscopy"; Almquist and Wiksells: Uppsala, Sweden, 1967.
(13) Saethre, L. J.; Svensson, S.; Martensson, N.; Gelius, U.; Malmquist, P. Å; Basilier, E.; Siegbhan, K. *J. Chem. Phys.* **1977**, *20*, 431.
(14) Erman, P.; Bergstrom, I.; Chu, Y. Y.; Emergy, G. T. *Nucl. Phys.* **1965**, *62*, 401.
(15) Delucia, M. L.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336.
(16) The values of k and l obtained from the plot of E_B S $2p_{3/2}$ (obsd) = $kQ_S + V_S + l$ are 17.37 eV/charge and 170.60 eV while those obtained from a similar plot for N 1s binding energies is 31.45 eV/charge and 410.55 eV. These parameters are nearly identical with those published by Jolly et al.[5c,d]

sulfur compounds is shown in Figure 2.

Two important conclusions can be drawn on the basis of the above results. First, the XPS data for S_2N_2 and S_4N_4 are best interpreted without invoking $N(p\pi)\rightarrow S(d\pi)$ back-bonding. Second, the greater $S\rightarrow N$ charge transfer in S_4N_4 arises from a significant contribution (20%) of valence bond structure IV in which sulfur–sulfur bonds are present. Thus, the XPS data are indicative of a modest S–S bonding interaction, consistent with the S–S distance in the S_4N_4 structure and in accord with a recent UV photoelectron spectroscopic study.[4c]

For comparison we have also calculated atomic charges for S_2N_2 and S_4N_4 by the parameterized MNDO molecular orbital method. The $S\rightarrow N$ charge transfer according to this method is 0.402 e for S_2N_2 and 0.53 e for S_4N_4.[17] The charge transferred calculated by the MNDO MO method is compared with those calculated by other molecular orbital methods in Table III. In agreement with the CHELEQ analysis of the XPS results, all of the methods predict greater $S\rightarrow N$ charge transfer in S_4N_4 than in S_2N_2.

Summary

XPS results, interpreted with the aid of the CHELEQ procedure, show that $N(p\pi)\rightarrow S(d\pi)$ back-bonding is not necessary for a clear understanding of the bonding and charge distribution in S_2N_2 or its precursor S_4N_4. Semiempirical MNDO MO calculations are in agreement with this view. XPS also shows $S\rightarrow N$ charge transfer to be greater in S_4N_4 than in S_2N_2.

Acknowledgment. P.B. would like to thank the National Research Council for the award of a postdoctoral fellowship.

Registry No. S_2N_2, 25474-92-4; S_4N_4, 28950-34-7.

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(17) The minimum energy geometry for S_2N_2 obtained from the MNDO calculations is essentially square with S–N bond lengths of 1.621 Å (1.62 Å experimental) and SNS and NSN angles of 95.0° (92.0° experimental) and 85.0° (88.0° experimental), respectively. The minimum energy geometry of S_4N_4 is largely the same as that which has been experimentally determined except that the MNDO S–S distances are 0.50 Å greater than those reported in the X-ray crystal structure determination. Detailed results of the MNDO calculations will be published elsewhere.

(18) Perry, W. B.; Schaaf, T. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 4899.

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State University of New York at Buffalo,
Buffalo, New York 14214

Synthesis and Molecular Geometry of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$

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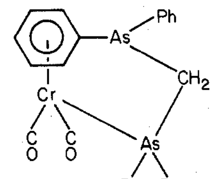
Received April 22, 1980

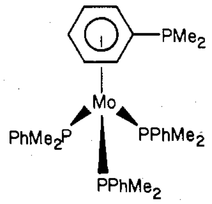
The preparation and structural chemistry of η^6-arene complexes have been investigated thoroughly; in particular, definitive structural studies of $(\eta^6\text{-}C_6H_6)_2Cr$[1] and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$[2] have appeared. A number of complexes have been reported in which a $(\eta^6\text{-arene})\rightarrow$metal linkage arises by interaction of the phenyl (or substituted phenyl) ring of (inter alia) an arylphosphine or an arylarsine ligand with the metal atom. Another unexpected class of molecules thus obtained consists of $[(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]Ru[P(OMe)_3]_2$[3] and related $[(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$Ru-containing complexes.[4]

The ligand $Ph_2AsCH_2AsPh_2$ reacts with $Cr(CO)_6$ in decane yielding the chelate complex I, the crystal structure of which has been reported.[5]



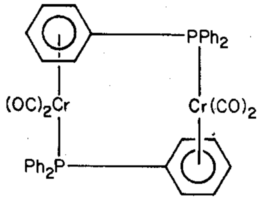
I

A rather less direct route has led to the production of $(PPhMe_2)_4Mo$ which has been shown[6] to have structure II. This appears to be the only nonchelating monomeric complex based upon an η^6-arylphosphine or -arsine to be characterized structurally to date.



II

The reaction of $Cr(CO)_6$ with various triarylphosphine ligands (L) at high temperature has been shown[7] to give rise to two series of complexes of stoichiometry $[Cr(CO)_2L]_2$ and $Cr(CO)_3L$. A structural study of the dimeric species $\{[(\eta^6\text{-}C_6H_5)P(C_6H_5)_2]Cr(CO)_2\}_2$ has revealed[8] the configuration III.



III (schematic, only)

We now report the preparation of a $Cr(CO)_3L$ derivative (L = triphenylarsine), its crystallographic characterization as $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$, and its reaction with $(NMe_3)Cr(CO)_5$.

Experimental Section

Preparation of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$. A mixture of $Cr(CO)_6$ (1.0 g) and $As(C_6H_5)_3$ (3.0 g) in decane (50 mL) was refluxed under argon for 8 h. The resulting orange solution was concentrated and passed down a Florisil column with hexane as eluant. The yellow band was collected, reduced in volume, and cooled to −20 °C overnight, yielding 0.5 g of yellow crystals of $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ (25% yield), which were washed with pentane and dried in vacuo; mp 119–120 °C. IR(hexane): ν(CO) 1978 (s), 1914 (s) cm^{-1}. ^1H NMR (CCl_4): δ 7.3 (H, aryl), 5.1–5.0 (H, π-arene); ratio 2:1. Anal.

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(1) Kenlen, E.; Jellinek, F. *J. Organomet. Chem.* **1966**, *5*, 490–492.

(2) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2516–2528.

(3) Nolte, M. J.; Gafner, G.; Haines, L. M. *Chem. Commun.* **1969**, 1406–7.

(4) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339–2343. See also: Albano, P.; Aresta, M.; Manassero, M. *Ibid.* **1980**, *19*, 1069–1072.

(5) (a) Robertson, G. B.; Whimp, P. O.; Colton, R.; Rix, C. J. *Chem. Commun.* **1971**, 573–574. (b) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 1047–1053.

(6) Mason, R.; Thomas, K. M.; Heath, G. A. *J. Organomet. Chem.* **1975**, *90*, 195–202.

(7) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1971**, *24*, 2471–2480.

(8) Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *60*, C11–C13.

0020-1669/80/1319-2831$01.00/0