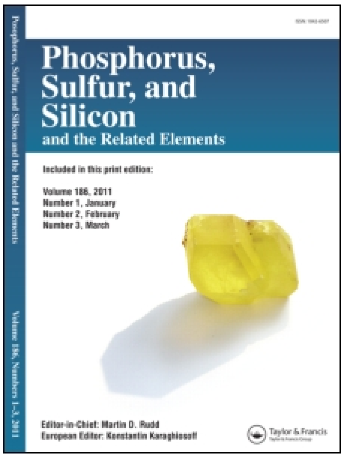


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

RADICAL IONS 52[1]

Judith Giordan[a]; Hans Bock[a]; Manfred Eiser[a]; Herbert W. Roesky[a]
[a] Institutes of Inorganic Chemistry of the Universities of Frankfurt (Main) and Göttingen Niederurseler Hang, Göttingen, West Germany

To cite this Article Giordan, Judith , Bock, Hans , Eiser, Manfred and Roesky, Herbert W.(1982) 'RADICAL IONS 52[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 1, 19 — 24
To link to this Article: DOI: 10.1080/03086648208078978
URL: http://dx.doi.org/10.1080/03086648208078978

Phosphorus and Sulfur, 1982, Vol. 13, pp. 19–24
0308-664X/82/1301-0019/$06.50/0

RADICAL IONS 52[1]

The Formation of the $S_3N_2^{\cdot\oplus}$ Radical Cation via Reaction of Sulfurdiimides, S_4N_4 or $S_3N_2Cl_2$ with $AlCl_3$

JUDITH GIORDAN, HANS BOCK,* MANFRED EISER and
HERBERT W. ROESKY*

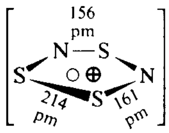
Institutes of Inorganic Chemistry of the Universities of Frankfurt (Main) and Göttingen
Niederurseler Hang, D-6000 Frankfurt (Main) 50 and Tammannstr. 4,
D-3400 Göttingen, West Germany

(*Received November 23, 1981*)

Bei Versuchen, neue S/N-Radikalkationen nachzuweisen, wurden Methylsilyl-Schwefeldiimide $R_{4-n}Si(N{=}S{=}N)_nSiR_{4-n}$ mit $n = 1, 2, 3$ und $R_3Si{-}N{=}S{=}N{-}S{-}N{=}S{=}N{-}SiR_3$ sowie S_4N_4, $S_4N_4 \cdot AlCl_3$ und $[S_3N_2Cl]^{\oplus}Cl^{\ominus}$ mit $AlCl_3$ in H_2CCl_2 umgesetzt. Überraschenderweise beobachtet man in allen Fällen das ESR-Spektrum der bekannten Species $S_3N_2^{\cdot\oplus}$. Die Zeit bis zum Auftreten des ESR-Signals reichte von 2 Tagen für die Schwefeldiimide mit vertikalen ersten Ionisierungsenergien großer als 8 eV über Minuten für $R_3Si{-}N{=}S{=}N{-}S{-}N{=}S{=}N{-}SiR_3$ ($IE_1 = 7.85$ eV) bis zu Sekunden für S_4N_4 oder $[S_3N_2Cl]^{\oplus}Cl^{\ominus}$

In the attempt to detect new S/N radical cations, the silylmethyl sulfurdiimides $R_{4-n}Si(N{=}S{=}N)_nSiR_{4-n}$ with $n = 1, 2, 3$ and $R_3Si{-}N{=}S{=}N{-}S{-}N{=}S{=}N{-}SiR_3$ as well as S_4N_4, $S_4N_4 \cdot AlCl_3$ and $[S_3N_2Cl]^{\oplus}Cl^{\ominus}$ were reacted with $AlCl_3$ in H_2CCl_2. Surprisingly, in each case the ESR spectrum of the well-known $S_3N_2^{\cdot\oplus}$ species was observed. The time required for appearance of the ESR signal varied from 2 days for those sulfurdiimides with vertical first ionization energies above 8 eV to minutes for $R_3Si{-}N{=}S{=}N{-}S{-}N{=}S{=}N{-}SiR_3$ ($IE_1 = 7.85$ eV) and to seconds for S_4N_4 or $[S_3N_2Cl]^{\oplus}Cl^{\ominus}$.

Reactions of S_4N_4 under different conditions with various inorganic oxidizing agents have resulted in the formation and isolation of a number S/N containing cations, e.g., $S_3N_2^{\cdot\oplus}$,[2,3] $S_4N_3^{\oplus}$,[4] $S_4N_4^{\oplus\oplus}$,[5] $S_5N_5^{\oplus}$[6] and $S_6N_4^{\oplus\oplus}$.[7] However, $S_3N_2^{\cdot\oplus}$ is the only species fully characterized as a radical cation via ESR[2,3] and, at the same time, the single known S/N radical that has been obtained as a stable crystalline salt.[2,3] Originally, ESR spectra of radicals resulting from treatment of S_4N_4 with concentrated sulfuric acid and also by decomposition of (aminothio)sulfurdiimides[8] were assigned as $SN_2^{\cdot\oplus}$.[8–10] Further ESR investigations led to the conclusion that the observed radical was $S_2N_2^{\cdot\oplus}$[11] in a square planar configuration. Reactions of S_4N_4 with anhydrides[3] and AsF_5[5] also gave ESR signals of radical cations identical to those previously obtained in the sulfuric acid experiments, containing 5 lines (coupling constant $a = 0.315$ mT and g value 2.011) in a ratio of 1:2:3:2:1; consistent with a radical containing 2 equivalent nitrogens. Finally, X-ray studies[2,3,9] clearly demonstrated that the previously assigned $N_2S_2^{\oplus}$ species was indeed $S_3N_2^{\oplus}$:



$(X^{\ominus} = AsF_6^{\ominus}$[2], $F_3CSO_3^{\ominus}$[3]$)$ (1)

---

*To whom correspondence should be directed.

Recently, the combined techniques of PE and ESR spectroscopy have proven fruitful in observing novel radical cations.[12] Compounds with low first ionization potentials of <8 eV in the gas phase as determined by PES have been oxidized to their radical cations using the oxygen-free system of $AlCl_3$ in H_2CCl_2. Main group substituted hydrazines,[13] "strained" five-membered ring disulfides[14] and also open chain amino disulfides[15] have been successfully subjected to this technique. Therefore, due to continued interest in sulfur nitrogen compounds[16] and to the success of the $AlCl_3/H_2CCl_2$ method in generating radical cations,[12] the following sulfur/nitrogen compounds

$$\begin{array}{llll} R_3Si{-}N{=}S{=}N{-}SiR_3 & \mathbf{1} & R_3Si{-}N{=}S{=}N{-}S{-}N{=}S{=}N{-}SiR_3 & \mathbf{4} \\ R_2Si(N{=}S{=}N)_2SiR_3 & \mathbf{2} & S_4N_4 & \mathbf{5} \\ RSi(N{=}S{=}N)_3SiR & \mathbf{3} & S_4N_4 \cdot AlCl_3 & \mathbf{6} \\ & & [S_3N_2Cl]^{\oplus}Cl^{\ominus} & \mathbf{7} \end{array} \tag{2}$$

were studied. The PE spectra of **1–4** will be discussed as well as the ESR results obtained from reaction of $AlCl_3/H_2CCl_2$ with **1–7**.

A. PHOTOELECTRON SPECTRA

Examples of PE spectra for **1–4** are shown in Figure 1.

Due to the large number of ionizations arising from molecules of this size, only broad bands and very little fine structure are observed. However, for each compound at least the first ionization potential, which is important in predicting the applicability of the $AlCl_3/H_2CCl_2$ technique, can be obtained. In general, He(I) photoelectron spectra show *p*-type ionizations, therefore according to a useful rule-of-thumb,[17] the 44 valence *p*-type electrons in the isoelectronic series **1–3** are expected to result in 22 observable ionizations while in **4** 29 ionizations are anticipated.

In large molecules such as those studied here, the assignment of specific molecular orbitals to radical cation states is usually difficult if not impossible.[18] However, MNDO calculations using parameters from the X-ray structure of **3**[19] allow for a straightforward assignment—via Koopman's Theorem, $IE_n^v = -\epsilon_j^{SCF}$,—of the ionizations in the tris-sulfurdiimide (**3**) (Figure 1). Interestingly, previous PE studies on alkyl substituted —N=S=N— systems[20,21] repeatedly assigned the first low energy cation states to an orbital sequence $\pi_{nb} < n_{\dot{S}} < n_N^-$. Silicon substitution, however, appears to scramble the ordering of these orbitals (Figure 1). As has been demonstrated e.g. for the blue azo compound, $(H_3C)_3Si{-}N{=}N{-}Si(CH_3)_3$,[22] a tremendous shift of electron density from silicon to nitrogen centers occurs. No wonder, therefore, that a MNDO calculation for bis(dimethylsilyl) sulfurdiimide (cf. **1**) predicts the 3 lowest radical cation states with predominant nitrogen contributions, represented by the orbitals:

$$\begin{array}{llll} & \pi_{nb}(a_2) & n_N^-(b_2) & n_N^+(a_1) \\ \epsilon_j^{MNDO} & -\ 9.0\ eV & -9.5\ eV & -10.4\ eV \end{array} \tag{3}$$

The next four $M^{\cdot\oplus}$ states, which presumably fall under the second hump in the PE spectrum (Figure 1), according to the MNDO wave function are of σ_{SiC} type.

The MNDO calculation for the cage compound **3** suggests that the first $M^{\cdot\oplus}$ states are also essentially of nitrogen lone pair n_N character (Figure 1: A_1'' and E''). The fol-

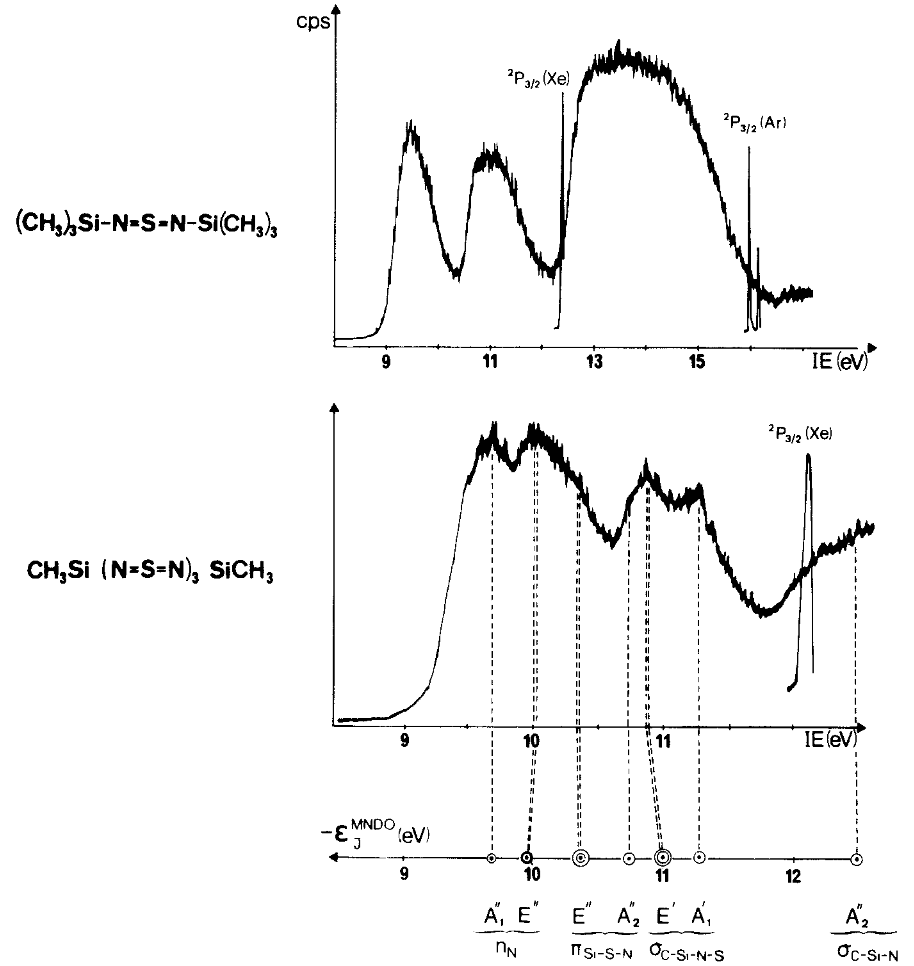


FIGURE 1 He(I) PE spectra between 8 and 18 eV for bis(*N,N'*-trimethylsilyl)sulfurdiimide **1** and between 8 and 12 eV for bis(*N,N'*-methylsilyl)tris(sulfurdiimide) **3**.

lowing 3 orbitals also contain predominant n_N contributions (A_2'' and E″) but both silicon and sulfur centers participate. The next 3 are "cage" orbitals σ_{CSiNS} (E′ and A_1').

For S_4N_4 a first ionization energy of 9.47 eV[23] has been determined. In all the compounds studied, only **4** exhibited a first IE of 7.85 eV, i.e. lower than the 8 eV limit associated with easy oxidation using $AlCl_3$ in CH_2Cl_2.[12-15]

B. ELECTRON SPIN RESONANCE SPECTRA

The results obtained from reaction of **1–7** with $AlCl_3$ in CH_2Cl_2 are summarized in Figure 2. Interestingly, sulfurdiimides **1–3**, with first ionization energies of greater than 8 eV, as well as **4**, with an IE_1^v of 7.85 eV, react to form $S_3N_2^{\oplus}$. The time required for observance of the ESR signal is, however, considerably shorter for **4** as for **1–3**.

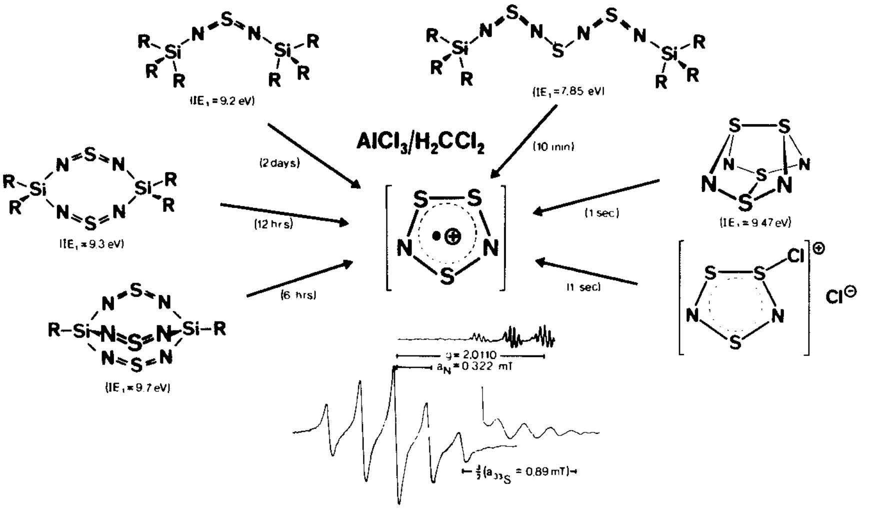


FIGURE 2 ESR results on treatment of S/N compounds (**1–5,7**) with $AlCl_3$ in H_2CCl_2 including the reaction time required until the radical signal appeared (see text).

Persistent ESR signals from **1–3** are obtained by allowing the prepared ESR tube (see Experimental Section) to remain at 0°C until an ESR spectrum develops. In the case of **1**, two days are required, for **2** approximately 10 hours and for **3** about 6 hours. Although a radical signal from **4** is not seen immediately, after 10 minutes at 0°C the same signal as from **1–3** appears.

Although it is known that tetrasulfur tetranitride reacts with $AlCl_3$ to form a 1:1 adduct,[24] the structures of the two 4 sulfur plus 4 nitrogen containing species are different, indicating that rearrangement of the S_4N_4 skeleton must take place.[16,18] In addition, it has been proposed that upon reaction of S_4N_4 in the presence of $SOCl_2$ and $AlCl_3$ or $FeCl_3$ to form $[S_3N_2Cl]^{\oplus} A^{\ominus}$, the first step is the fission of the tetrasulfur tetranitride ring giving both NSN and S_3N_2 fragments.[25] Therefore, S_4N_4 was allowed to react with $AlCl_3/H_2CCl_2$, to demonstrate whether an $S_3N_2^{\cdot\oplus}$ fragment could be detected. Instantly, upon insertion of the sample tube into the pre-cooled ESR cavity, the signal for $S_3N_2^{\cdot\oplus}$ developed. If indeed, the $S_4N_4 \cdot AlCl_3$ adduct arises through rearrangement of tetrasulfur tetranitride via $S_3N_2^{\cdot\oplus}$, then the adduct itself might be expected to give rise to this moiety. $S_4N_4 \cdot AlCl_3$ **6** dissolved in CH_2Cl_2 showed no ESR signal, however, upon addition of extra $AlCl_3$, the familiar 5 line ESR pattern of the $S_3N_2^{\cdot\oplus}$ radical cation developed immediately. Finally, the "parent" compound $[S_3N_2Cl]^{\oplus}$ $Cl^{\ominus}$[25] was reacted with $AlCl_3$ in H_2CCl_2 (cf. Exp. Part) and yielded—in an unknown way—again $S_3N_2^{\cdot\oplus}$.

C. CONCLUSION

Two categories of compounds have been studied; those with a "preformed" S_3N_2 fragment and/or first ionization potential below 8 eV such as S_4N_4 or **4**, and those with a first IE greater than 8 eV, e.g. **1–3**. Type 1 molecules reacted quickly with $AlCl_3$ to give rise to an ESR signal, while type 2 species reacted very slowly. Although no mechanism for these reactions can be proposed simply from the results obtained, especially since radical concentrations as low as 10^{-5} mole/l are enough to give ESR signals, it is important to note that for each compound except $[S_3N_2Cl]^{\oplus}$ $Cl^{\ominus}$, the formation of $S_3N_2^{\cdot\oplus}$ requires transfer of a N=S=N fragment and for **1-4** the breaking of Si—N bonds.

A number of reactions, nucleophilic as well as thermal, have been described recently involving movement of an N=S=N unit,[26–28] although attempts to detect this species have been, to date, unsuccessful. Calculations indicate that although the lowest energy N_2S unit has a linear NNS configuration,[27,28] two metastable species NSN (90° dihedral angle) and NSN (linear) may also exist.[28] Therefore, transfer or movement of such a fragment during the complicated process of forming the $S_3N_2^{\cdot\oplus}$ radical cation observed here is possible. Silicon-heteroatom bonds are known to be labile in the presence of $AlCl_3$.[29,30] Azidosilanes, for example, have been reported to react quantatively with $AlCl_3$ to form chlorosilanes.[31] Therefore, while the breaking of Si—N bonds in **1-4** in conjunction with the transfer of N=S=N moieties as is necessary in **1-7** to ultimately form the $S_3N_2^{\cdot\oplus}$ species in the presence of $AlCl_3$ was not expected, results reported previously for reactions involving sulfur/nitrogen and silicon/nitrogen systems indicate that the overall scheme proposed is plausible.

EXPERIMENTAL SECTION

Compounds used for study

Bis (*N-N'*-trimethylsilyl)sulfurdiimide (**1**),[32] bis (*N-N'*-dimethylsilyl)di(sulfurdiimide)[33] (**2**), bis (*N-N'*-methylsilyl)tris(sulfurdiimide)[34] (**3**), bis(trimethylsilylsulfurdiimide)sulfide[8] (**4**), tetrasulfur tetranitride (**5**), tetrasulfur tetranitride aluminium chloride (**6**)[22] and 1-chloro-1,2,4-trithia-3,5-diazacyclopentahetranenium chloride (**7**)[38] were prepared according to literature procedures. IR and NMR data, where applicable, were comparable to literature values.

Photoelectron Spectra

The He(I) spectra were recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system. Spectra were calibrated by the $^2P_{3/2}$ ionizations of Xe and Ar.

Electron Spin Resonance spectra were recorded on a Varian E 9 instrument and calibrated from the perylene radical anion.[35] Values are considered correct to within 1%.

Generation of Radical Cations

The samples for study were all prepared by first evacuating an ESR tube and, under a stream of dry N_2, adding the compound of interest. The tube, continually under N_2, was then placed in a −196°C bath and water-free $AlCl_3$ was added. H_2CCl_2 that was dried and kept over $AlCl_3$ was condensed in and the tube sealed off under vacuum. The solid solvent (H_2CCl_2) was not allowed to melt into the sample until immediately before the tube was placed into a pre-cooled (−60°C) ESR cavity. If a signal did not instantaneously develop, the sample was held at 0°C and checked every 10 min. for the first hour, every half hour for the next 3 hours, every hour for the next 3 hours and then every 5 or 6 hours until a signal was observed. All spectra were recorded at −60°C and a temperature study showed expected broadening of the $M \neq O$ high field nitrogen lines at lower temperatures.[36]

The MNDO calculations were performed at the Hochschul-Rechenzentrum Frankfurt using the program kindly given to us by M. J. S. Dewar and W. Thiel.[37]

ACKNOWLEDGMENTS

This work has been supported by Land Hessen, Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. We would like to thank Margret Pohlenz for recording the PE spectra. One of us (J. G.) is indebted to the Alexander von Humboldt-Stiftung for a Fellowship during this time.

REFERENCES

1. Part 51 cf. J. Giordan and H. Bock, *Chem. Ber.*, in print.
2. R. J. Gillespie, P. R. Ireland and J. E. Vekris, *Can. J. Chem.*, **53,** 3147 (1975).
3. H. W. Roesky and A. Hamza, *Angew. Chem.*, **88,** 226 (1976); *Angew. Chem. Int. Ed. Engl.*, **15,** 226 (1976) vgl. hierzu auch B. Krebs, G. Henkel, S. Pohl and H. W. Roesky, *Chem. Ber.*, **113,** 226 (1980).
4. P. Friedman, *Inorg. Chem.*, **8,** 692 (1969) and references cited therein.
5. R. J. Gillespie, D. R. Slim and J. D. Tyrer, *JCS Chem. Comm.*, 253 (1977).
6. a) A. J. Banister and H. G. Clarke, *JCS, Dalton Trans.*, 2661 (1972); b) A. C. Hazell and P. G. Hazell, *Acta Chem. Scand.*, **26,** 1287 (1972); c) H. W. Roesky, W. G. Böwing, I. Rayment and H. M. M. Shearer, *JCS Chem. Comm.*, 735 (1975).
7. A. J. Banister, H. G. Clarke, I. Rayment and H. M. M. Shearer, *Inorg. Nucl. Chem. Lett.*, **10,** 647 (1974).
8. I. Ruppert, V. Bastian and R. Appel. *Chem. Ber.*, **107,** 3426 (1974).
9. H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, **22,** 239 (1979) and references therein.
10. D. Chapman and A. G. Massey, *Trans. Farady Soc.*, **58,** 1291 (1962).
11. R. Appel, M. Montenarh and I. Ruppert, *Chem. Ber.*, **108,** 582 (1975); S. A. Lipp, J. J. Chang and W. L. Jolly, *Inorg. Chem.*, **9,** 1970 (1970); D. A. C. McNeil, M. Murray and M. C. R. Symons, *J. Chem. Soc. A*, 1019 (1967).
12. H. Bock and W. Kaim, *Acc. Chem. Res.*, **14,** (1981).
13. H. Bock, W. Kaim, H. Nöth and A. Semkow, *J. Amer. Chem. Soc.*, **102,** 442 (1980).
14. H. Bock, U. Stein and A. Semkow, *Chem. Ber.*, **113,** 3208 (1980), cf. also H. Bock, G. Brähler, D. Dauplaise and J. Meinwald, *Chem. Ber.*, **114,** 2622 (1981).
15. H. Bock, W. Schulz and U. Stein, *Chem. Ber.*, **114,** 2632 (1981).
16. R. Gleiter, *Angew. Chem.*, **93,** 442 (1981); *Angew. Chem. Int. Ed. Engl.*, **20,** 444 (1981).
17. H. Bock and B. Ramsey, *Angew. Chem.*, **85,** 773 (1973); *Angew. Chem. Int. Ed. Engl.*, **16,** 633 (1977).
18. H. Bock, *Angew. Chem.*, **89,** 63 (1977); *Angew. Chem. Int. Ed. Engl.*, **16,** 633 (1977).
19. H. W. Roesky, M. Witt, B. Krebs, G. Henkel and H.-J. Korte, *Chem. Ber.*, **114,** 201 (1981).
20. J. Kroner, W. Strack and F. Holsboer, *Z. Naturforsch.*, **28b,** 188 (1973).
21. B. Solouki, H. Bock and O. Glemser, *Z. Naturforsch.*, **33b,** 284 (1978).
22. H. Bock, K. Wittel, M. Veith and N. Wiberg. *J. Amer. Chem. Soc.*, **98,** 109 (1976).
23. Vgl. z.B. W. R. Salaneck, J. W. Lin, A. Paton, C. B. Duke and G. P. Ceasar, *Phys. Rev. B*, **13,** 4517 (1976).
24. C. H. Chan and F. P. Olsen, *Inorg. Chem.*, **11,** 2836 (1972); K. Wynne and W. L. Jolly, *Inorg. Chem.*, **6,** 107 (1967) and references cited therein.
25. A. J. Banister and P. J. Dainty, *J.C.S., Dalton Trans.*, 2658 (1972).
26. T. Chivers and R. T. Oakley, *J.C.S. Chem. Comm.*, 752 (1979); J. Bojes and T. Chivers, *J.C.S. Chem. Comm.*, 453 (1977); *Inorg. Chem.*, **17,** 318 (1978); T. Chivers, R. T. Oakley, A. Wallace and P. Swepston, *J.C.S., Chem. Comm.*, 35 (1978); A. Golloch and M. Kuss, *Z. Naturforsch.*, **27B,** 1280 (1972); J. Bojes, T. Chivers, A. W. Cordes, G. Maclean and R. T. Oakley, *Inorg. Chem.*, **20,** 16 (1981).
27. M. P. S. Collins and B. J. Duke, *J.C.S. Chem. Comm.*, 277 (1978).
28. W. G. Laidlaw and M. Trsic, *Inorg. Chem.*, **20,** 1792 (1981).
29. Cf. D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Amer. Chem. Soc.*, **68,** 77 (1946); F. C. Whitmore, L. H. Sommer and J. Gold, *J. Amer. Chem. Soc.*, **69,** 1976 (1947); F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, *J. Amer. Chem. Soc.*, **69,** 2108 (1947); A. Y. Yakubovich and G. V. Motsarer, *Zhur. Obshchez. Khim.*, **23,** 771 (1953); *Doklady Akad. Nauk. SSR*, **88,** 87 (1953).
30. W. R. Peterson, Reviews on Silicon, Germanium, Tin and Lead Compounds I (**3**) (1974) and references therein.
31. N. Wiberg and B. Nemda, *Chem. Ber.*, **99,** 740 (1966).
32. U. Wannagat and H. Kuckertz, *Angew. Chem.*, **74,** 117 (1962); *Angew. Chem. Int. Ed. Engl.*, **1,** 113 (1962).
33. H. W. Roesky and H. Wiezer, *Chem. Ztg.*, **97,** 661 (1973).
34. H. W. Roesky and H. Wiezer, *Angew. Chem.*, **86,** 130 (1974); *Angew. Chem. Int. Ed. Engl.*, **13,** 146 (1974).
35. K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz," Springer-Verlag, Berlin, 1970.
36. M.-Y. Ahn and C. S. Johnson, Jr., *J. Chem. Phys.*, **50,** 632 (1968).
37. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, **99,** 4907 (1971).
38. W. J. Jolly, K. D. Maguire and D. Rabinovich, *Inorg. Chem.*, **2,** 1304 (1963).