procedure was repeated, starting with **10** and 7-benzoyloxynorbornadiene.

Similar exchange studies in the chromium series indicated a ratio of norbornadienetetracarbonylchromium (**9**) to 7-benzoyloxynorbornadienetetracarbonylchromium (**6**) of 2.3:1 under equilibrium conditions in acetone-d_6. In these studies, however, the time required to reach equilibrium was *ca.* 30 min.

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Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada

The Preparation and Properties of Pentafluorosilicates

By H. C. Clark, K. R. Dixon, and J. G. Nicolson

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The preparation of quaternary ammonium and arsonium pentafluorosilicates is described. It is shown that SiF_5^- is a relatively weak acceptor, forming an unstable 1:1 ammonia adduct and interacting only weakly with other Lewis bases. The infrared and Raman absorptions due to SiF_5^- are not inconsistent with a trigonal-bipyramidal geometry. Many spectroscopic similarities with phosphorus pentafluoride are apparent.

Introduction

Although the chemistry of silicon tetrafluoride and of hexafluorosilicates has been extensively studied, the existence of pentafluorosilicates containing the SiF_5^- ion has not been considered likely. Indeed, it is only recently that five-coordinate derivatives of silicon have been fully characterized.[1-3] Recently, we reported[4] the first formation of a pentafluorosilicate in a complex reaction involving silica, tetrafluoroethylene, and a platinum hydride. We have since been able to show that pentafluorosilicates can be prepared by a simple and convenient method,[5] and we now wish to describe some detailed chemical and spectroscopic investigations of these salts. Since our initial report, several other workers have described studies[3,6,7] leading to the isolation and characterization of pentafluorosilicates.

Synthesis and Properties

For appropriate cations, pentafluorosilicates may be prepared readily by the treatment of a mixture of silica and the appropriate chloride with aqueous hydrofluoric acid. Tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium pentafluorosilicates and tetraphenylarsonium pentafluorosilicate have thus been obtained. Interestingly, the tetramethylammonium salt could not be prepared by this method, the product being the SiF_6^{2-} derivative. Apparently, the cation size required to stabilize SiF_5^- in the solid state is somewhat larger than $(CH_3)_4N^+$ but smaller than $(C_2H_5)_4N^+$, although even the latter gives a rather unstable pentafluorosilicate. Other than this restriction, this general synthetic route should be applicable to the preparation of many additional pentafluorosilicates. It is also somewhat more convenient than the reaction of silicon tetrafluoride with quaternary ammonium fluoride as described[3] by Klanberg and Muetterties and is presumably essentially the same method as that used by Behrends and Kiel.[6] Certainly the dehydrofluorination reactions of Harris and Rudner[7] are less suitable for the synthesis of pentafluorosilicates. It is also surprising that these latter authors claimed to have isolated the trimethylammonium pentafluorosilicate, whereas the above simple reaction led to only tetramethylammonium hexafluorosilicate and not the pentafluorosilicate. This point is discussed in detail later.

While the analytical data for the above quaternary ammonium and tetraphenylarsonium derivatives show the Si:F ratio to be 1:5, further evidence is necessary to establish that discrete, singly charged SiF_5^- ions exist. This is provided first by preliminary X-ray structural studies[8] of tetraphenylarsonium pentafluorosilicate which show that the silicon–silicon distances are too great for the presence of any bridged species, such as $Si_2F_{10}^{2-}$. Second, the conductance data of Table I clearly show that these are 1:1 electrolytes in nitromethane solution although in aqueous solution there is extensive hydrolysis. The conclusion that discrete SiF_5^- ions are present, therefore, is reasonable; it remains to determine their stereochemistry.

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[1] R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Am. Chem. Soc.*, **89**, 5157 (1967).

[2] J. Turley, F. Boer, and C. Frye, *Chem. Eng. News*, **45**, No. 2, 46 (1967).

[3] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **7**, 155 (1968).

[4] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 3360 (1967).

[5] For a preliminary report see H. C. Clark and K. R Dixon, *Chem. Commun.*, 717 (1967).

[6] K. Behrends and G. Kiel, *Naturwissenschaften*, **54**, 537 (1967).

[7] J. J. Harris and B. Rudner, *J. Am. Chem. Soc.*, **90**, 515 (1968).

[8] P. W. R. Corfield and J. A. Ibers, private communication.

TABLE I

CONDUCTANCE DATA FOR FLUOROSILICATE AND FLUOROBORATE SALTS

	Solvent	Molar conductance, ohm^{-1} cm^2
$[(CH_3)_4N]_2SiF_6$	Water	450
$(n\text{-}C_3H_7)_4NSiF_5$	Water	450
$[(CH_3)_4N]_2SiF_6$	CH_3NO_2	149
$(C_2H_5)_4NSiF_5$	CH_3NO_2	103
$(C_2H_5)_4NBF_4$	CH_3NO_2	108
$(n\text{-}C_3H_7)_4NSiF_5$	CH_3NO_2	96
$(n\text{-}C_3H_7)_4NBF_4$	CH_3NO_2	98
$(C_6H_5)_4AsSiF_5$	CH_3NO_2	87
$(C_6H_5)_4AsBF_4$	CH_3NO_2	92

Since silicon tetrafluoride is a strong electron-pair acceptor and forms complexes of the type $SiF_4 \cdot 2$(donor) with donors such as ammonia,[9] trimethylamine,[10] and pyridine,[11] thus completing an octahedral configuration about silicon, the SiF_5^- ion should be a somewhat weaker acceptor forming octahedral complex ions of the type (donor)SiF_5^-. Reactions of tetra-*n*-propylammonium pentafluorosilicate with a variety of donors were investigated, but only with ammonia could a complex be isolated. Its stability was low, ammonia being lost on standing under vacuum at 25°, but analyses indicated an approximately 1:1 stoichiometry, $(NH_3)SiF_5^-$. From dissociation pressure measurements in the temperature range −80–40° (Figure 1), the dissociation energy for the process

$$[(n\text{-}C_3H_7)_4N][(NH_3)SiF_5](s) \longrightarrow NH_3(g) + [(n\text{-}C_3H_7)_4][SiF_5](s)$$

is calculated to be 7.9 kcal mol^{-1}. This may be compared with $\Delta H = 18.2$ kcal mol^{-1} obtained previously[9] for the dissociation

$$SiF_4 \cdot 2NH_3(s) \longrightarrow SiF_4(g) + 2NH_3(g)$$

For other Lewis bases, a qualitative study of the extent of complex formation, $SiF_5 \cdot B^-$, was made by observing the intensity of the 874-cm^{-1} infrared absorption band, characteristic of the SiF_5^- ion, in acetonitrile solutions with varying concentrations of the bases (Figure 2). From the extent that this absorption lost intensity in the presence of a particular base, it was possible to conclude that the order of donor interaction with SiF_5^- was $(C_2H_5)_2NH > (C_2H_5)_3N > (n\text{-}C_3H_7)_3N > C_5H_5N \sim (C_2H_5)_3P$.

Infrared and Raman Spectroscopic Studies

We[4,5] have previously reported that the SiF_5^- ion is characterized by strong infrared absorptions at approximately 870, 790, 480, and 450 cm^{-1}, in contrast to the absorptions at 740 and 480 cm^{-1} which characterize[12] hexafluorosilicates. Hence, the fact that Harris and Rudner[7] apparently did not observe the very characteristically intense band at about 870 cm^{-1}, together with our observation that cations larger than $(CH_3)_4N^+$ are necesary to stabilize SiF_5^-, forces us to the conclusion that the material described by Harris and Rudner[7] was not a simple pentafluorosilicate.

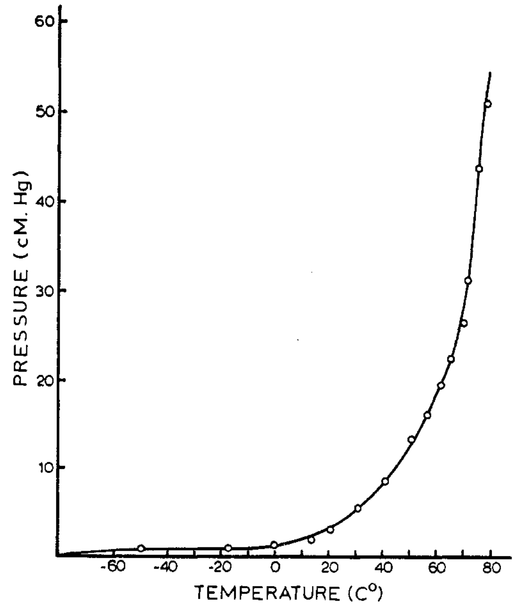

Figure 1.—Dissociation pressure of $(n\text{-}C_3H_7)_4N^+H_3NSiF_5^-$.

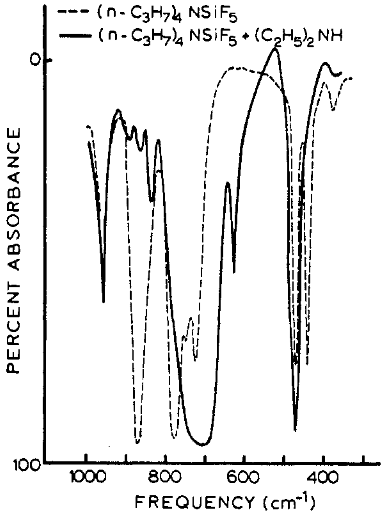

Figure 2.—Infrared spectra (acetonitrile solutions).

Infrared and Raman spectroscopic studies should also provide a distinction between the trigonal-bipyramidal and the square-pyramidal geometries for SiF_5^-. The tetra-*n*-propylammonium pentafluorosilicate has been chosen for these studies; all other pentafluorosilicates showed the same anion absorptions, with the exception of tetraphenylarsonium pentafluorosilicate for which, instead of the 785-cm^{-1} peak, two bands at 794 and 776 cm^{-1} were observed. This may be a solid-state effect, perhaps a factor group splitting.

The infrared and Raman spectra of tetra-*n*-propyl-

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[9] D. M. Miller and H. H. Sisler, *J. Am. Chem. Soc.*, **77**, 4998 (1955).

[10] C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 927 (1953).

[11] U. Wannagat and R. Schwarz, *Z. Anorg. Allgem. Chem.*, **277**, 73 (1954).

[12] D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc., A*, 100 (1967).

Table II

Absorption Bands and Assignments for PF_5 and SiF_5

		PF_5[a]			SiF_5^-		
		ν, cm^{-1}	Ir	Raman	ν, cm^{-1}	Ir	Raman
ν_5	E′	1026	vs	vw	874	vs	w
ν_3	A_2''	945	vs	. . .	785	vs	. . .
ν_1	A_1'	817	. . .	vs, pol	708	. . .	vs, pol
ν_2	A_1'	640	. . .	w, pol	519	. . .	w
ν_4	A_2''	575	m	. . .	481	s	
ν_6	E′	533	m	vw	449	s	
ν_8	E″	514	. . .	w			
ν_7	E′	300	vw	Not obsd			

[a] Reference 13.

ammonium pentafluorosilicate in the solid state and in acetonitrile solution were essentially identical. The process of dissolution in acetonitrile has, therefore, not affected the geometry of SiF_5^-. The Raman spectrum (200–1000 cm^{-1}) was recorded for both solid and solution; however, below 400 cm^{-1}, there was considerable absorption due to the cation. The infrared spectrum (80–4000 cm^{-1}) showed no absorptions below 400 cm^{-1}, and only bands attributable to the cation were observed above 1000 cm^{-1}. The spectra in the 400–1000-cm^{-1} region are shown in Figures 3 and 4. Bands assignable to SiF_5^- in the infrared spectrum are those at 874 (vs), 785 (vs), 481 (s), and 449 (s) cm^{-1}, and in the Raman spectrum bands assignable to SiF_5^- are at 880 (w), 708 (vs), and 519(w) cm^{-1}. Moreover, in acetonitrile solution, the strong Raman absorption at 708 cm^{-1} was polarized and must therefore be assigned to an A_1 mode. The fact that this mode is infrared inactive is consistent with D_{3h} but not C_{4v} symmetry. A consideration of the remaining frequencies in terms of both D_{3h} and C_{4v} symmetry also supports the conclusion that the former is probably the correct symmetry. This is supported by the similarities with the infrared and Raman spectra[13] of PF_5 (Table II).

It is of interest to note that in contrast to the solution Raman spectrum, the solid-state Raman spectrum showed the 708 cm^{-1} to be not polarized. This is not readily explained, but in view of the paucity of Raman spectroscopic data for solids, this may be a solid-state effect.

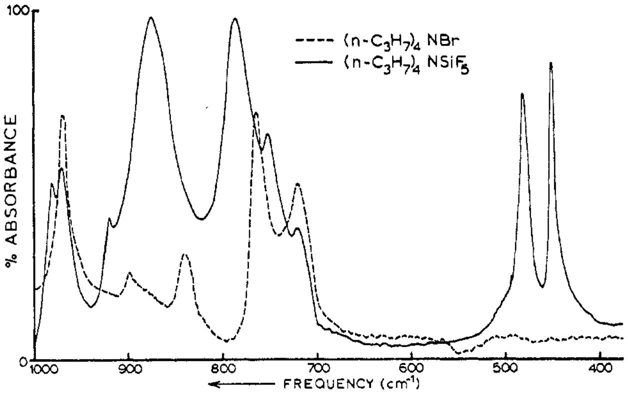

Figure 3.—Infrared spectra (Nujol mulls).

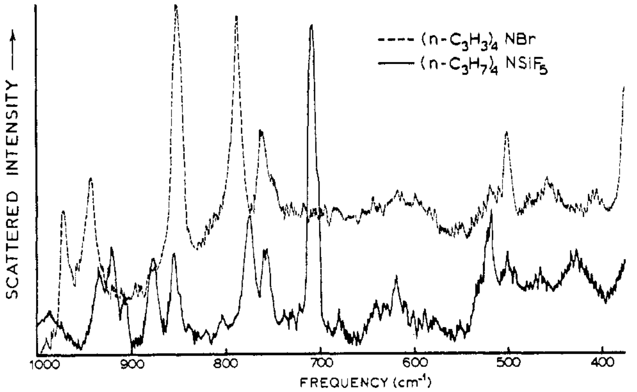

Figure 4.—Raman spectra (solid samples).

Experimental Section

Preparation of Pentafluorosilicates.—The general method required the treatment of silica and the appropriate chloride with aqueous hydrofluoric acid. The yields were generally variable, because of the tendency to lose silicon in varying amounts during the evaporation steps.

(a) When tetramethylammonium chloride (2.075 g) and silica (1.102 g) were dissolved in a methanol–aqueous hydrogen fluoride solution in a platinum dish, repeated evaporations with methanol, followed by recrystallization from aqueous ethanol, gave only tetramethylammonium hexafluorosilicate, $[(CH_3)_4N]_2SiF_6$. *Anal.* Calcd for $C_8H_{24}N_2F_6Si$: C, 33.2; H, 8.28. Found: C, 33.5; H, 8.34. The infrared spectrum (Nujol mull) showed the characteristic SiF_6^{2-} absorptions.[11]

(b) Tetraethylammonium chloride (1.998 g) and silica (0.731 g) were dissolved, in a platinum dish, in a methanol–aqueous hydrogen fluoride solution. The solution was evaporated, methanol was added, and the evaporation from methanol was repeated several times until no hydrogen fluoride was evolved. The product was dissolved in chloroform and then precipitated as fine crystals by the addition of ethyl acetate. Further recrystallization was achieved from methanol. The yield of white crystals was 2.3 g, approximately 70%. *Anal.* Calcd for $C_8H_{20}NF_5Si$: C, 38.0; H, 7.95; Si, 11.1; F, 37.6. Found: C, 38.2; H, 7.92; Si, 12.1; F, 38.8. The infrared absorptions characteristic of SiF_5^- were observed at 875 (vs, b), 785 (vs, b), 482 (s), and 448 (s) cm^{-1}. The compound is rather difficult to purify and crystallize as shown by the fact that recrystallization from an acetonitrile–ethyl acetate mixture gave a nicely crystalline product, but its infrared spectrum showed the typical SiF_6^{2-} absorptions[12] at 720 (vs, b) and 470 (s) cm^{-1}.

(c) Tetra-*n*-propylammonium bromide (10.13 g) and silica (2.613 g) were dissolved in a methanol–aqueous hydrogen fluoride solution in a platinum dish. Repeated evaporations with methanol removed all traces of hydrogen fluoride, to give a product which was recrystallized from chloroform and ethyl acetate. The final product consisted of white needles; mp 207.5–208.5° (uncor). *Anal.* Calcd for $C_{12}H_{28}NF_5Si$: C, 46.6; H, 9.1; N, 4.5; Si, 9.1; F, 30.7. Found: C, 46.8; H, 9.1; N, 4.6; Si, 9.1; F, 30.8. The infrared spectrum showed the absorptions characteristic of SiF_5^-.

(d) A similar reaction with tetra-*n*-butyl bromide and silica gave an oily product which showed infrared absorptions characteristic of SiF_5^- at 875 (vs, b), 780 (vs, b), 480 (s), and 447 (s) cm^{-1}. This product could not be obtained in a crystalline form.

(e) Tetraphenylarsonium chloride (1.94 g) and silica (0.30 g) were treated as in (a)–(c) above. The solid product was recrystallized from acetonitrile and washed with ethyl acetate and finally ether, to give finally long, needlelike crystals. *Anal.*

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(13) J. E. Griffiths, R. P. Carter, and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

Calcd for $C_{24}H_{20}AsF_5Si$: C, 56.9; H, 4.0; As, 14.8; Si, 5.6; F, 18.8. Found: C, 56.6; H, 4.0; As, 14.7; Si, 5.6; F, 19.0. The infrared spectrum, in addition to absorptions characteristic of the cation, showed SiF_5^- peaks at 875 (vs, b), 776 (vs), 794 (vs) (doublet), 476 (s), and 448 (s) cm^{-1}.

Preparation of Tetrafluoroborates.—The tetrafluoroborates containing the tetramethylammonium, tetraethylammonium, tetra-*n*-propylammonium, and tetraphenylarsonium cations were obtained by treating a saturated methanol solution of the corresponding quaternary ammonium halide with an aqueous methanol solution of fluoroboric acid.

Reactions of the Pentafluorosilicate Ion with Donor Molecules.—Excess dry ammonia was condensed onto tetra-*n*-propylammonium pentafluorosilicate at −78° and allowed to stand for 1 hr. Removal of the ammonia at −78° left a white solid smelling strongly of ammonia, which could only be handled under dry nitrogen. The infrared spectrum of this solid did not show the characteristic 874-cm^{-1} band of SiF_5^- but rather bands characteristic of six-coordinate silicon[12] at 720 (vs, b) and 478 (s) cm^{-1}. When a sample of this product was kept under vacuum for 18 hr at 25°, only partial recovery of the ammonia was achieved, but the resulting solid showed the characteristic SiF_5^- infrared absorptions together with N-H absorptions at *ca.* 3300 cm^{-1}. Samples of the ammonia adduct, prepared by removal of excess ammonia from the pentafluorosilicate at −95°, were sealed under vacuum and then opened under concentrated sulfuric acid for determination of total nitrogen by the Kjeldahl method. The product from 0.1635 g of tetra-*n*-propylammonium pentafluorosilicate thus contained 0.0149 g of nitrogen (0.0148 g is required for the 1:1 adduct). The vapor pressure of the adduct in the temperature range −80–40° was determined, giving the data shown in Figure 1. The reversibility of this dissociation was also established by measurements of the vapor pressure during both cooling and warming cycles.

For other donor molecules, adducts could not be isolated, but infrared studies were conducted of acetonitrile solutions which were approximately 0.1 *M* in tetra-*n*-propylammonium pentafluorosilicate with varying concentrations of the base. Observations were made of the relative intensity of the 874-cm^{-1} band, characteristic of the SiF_5^- ion, at various concentrations of the base concerned. Only for diethylamine was the 874-cm^{-1} band destroyed completely at a 1:1 amine:silicon ratio. For pyridine, little interaction was apparent at the 1:1 ratio and five-coordinate silicon was still present at a 10:1 ratio of pyridine to silicon. The order of interaction with SiF_5^- was thus established as: $(C_2H_5)_2NH > (C_2H_5)_3N > (n\text{-}C_3H_7)_3N > C_5H_5N \sim (C_2H_5)_3P$.

Conductivity Measurements.—Conductances were measured at 25° using a dip-type cell of constant 0.1 cm^{-1} connected to a conductivity bridge, Model RC 18, Industrial Instruments Inc. Nitromethane (Fisher Scientific Co.) with a specific conductance of 25×10^{-7} ohm^{-1} cm^{-1} was used without further purification.

Infrared and Raman Spectroscopic Measurements.—Infrared spectra were measured on a Beckman IR 10 spectrometer and, through the courtesy of Dr. A. Lane, on an RIIC interferometer in the low-frequency region. Raman spectra of solutions were obtained on a Cary 81 Raman spectrometer, through the kindness of Dr. D. E. Irish of the University of Waterloo, and of solids on a laser Raman spectrometer, through the kindness of Dr. R. J. Gillespie of McMaster University. Infrared spectra were calibrated against water vapor and polystyrene, and carbon tetrachloride was used to calibrate Raman spectra. Frequencies were measured to an accuracy of ±3 cm^{-1}.

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CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURGH,
DEPARTMENT OF CHEMISTRY, PITTSBURGH, PENNSYLVANIA 15213

Mössbauer Spectra of Some Ferric Hydroxamates

BY L. M. EPSTEIN AND DAREL K. STRAUB

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A variety of tris(hydroxamato)iron(III) complexes were prepared and their Mössbauer spectra were obtained. In many cases relaxation effects precluded a straightforward interpretation of peak positions even at room temperature. Otherwise most isomer shifts and quadrupole splittings were confined to a range of values typical of high-spin iron(III) with little covalent bonding. The trisodium salt of tris(benzohydroxamato)iron(III) was prepared pure in two hydrated forms, the higher hydrate apparently displaying a large relaxation effect. Unusually large splittings occurred in tris(salicylhydroxamato)iron(III) and tris(nicotinylhydroxamato)iron(III).

Introduction

Hydroxamic acids are rather weak acids ($pK_a \approx 9$) which have the general formula RCON(R′)OH, where R and R′ are hydrogen or some organic group.[1] In acid solution hydroxamic acids form deeply colored 1:1 complexes with iron(III), a reaction which has been known for a long time and which has been used for both qualitative and quantitative determinations of hydroxamic acids or active acyl compounds which can be converted to hydroxamic acids. In neutral solutions a tris(hydroxamato)iron(III) complex is formed, the hydroxamate anion acting as a bidentate ligand. These are very stable complexes in general, as indicated, for example, by the value of 28.3 for log β_3 for acetylhydroxamate (R = CH_3).[1] Iron(III) complexes of the primary hydroxamic acids (*i.e.*, R′ = H) can be further deprotonated by loss of the nitrogen proton in strongly basic solution. On the basis of visible spectroscopy, Aksnes has proposed the equilibria[2]

$$\underset{\text{medium acidic}}{Fe(RCONHO)^{2+}} \rightleftharpoons \underset{\text{weakly acidic}}{Fe(RCONHO)_2^{+}} \rightleftharpoons$$

$$\underset{\text{neutral}}{Fe(RCONHO)_3} \rightleftharpoons \underset{\text{strongly alkaline}}{Fe(RCONO)_3^{3-}}$$

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(1) J. B. Neilands, *Struct. Bonding* (Berlin), **1**, 59 (1966).

(2) G. Aksnes, *Acta Chem. Scand.*, **11**, 710 (1957).