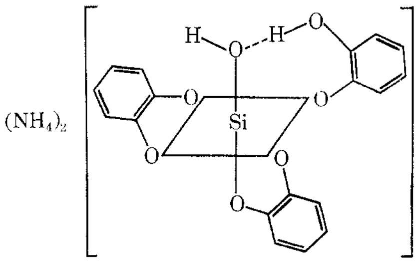

I

under vacuum (<1 Torr) at 60°. Discoloration occurs but X-ray powder diffraction shows that the material is still predominantly the "monohydrate." In the infrared absorption spectrum there is a sharp band at 3545 cm^{-1} which is characteristic of a free or weakly associated –OH group. Also, the nmr spectrum shows aromatic ring protons at τ 3.77 ppm, ammonium ion protons at τ 4.4–5.6 ppm depending on the concentration of the complex and the water content of the solvent, and *two* –OH protons at τ 3.30 and 3.46 ppm relative to TMS. Craddock and Jones[3] assigned this same structure to an arsenic(V) complex with catechol; $H[As(C_6H_4O_2)_3]\cdot H_2O$. Also, "chelation" by catechol through a hydrogen bond, as in structure I, has been established in a nickel(II)–catechol complex by X-ray diffraction.[4] The formula for this compound would be more correctly written as $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$.

Weiss, Reiff, and Weiss[2] suggested a dimeric structure for the $Si(C_6H_4O_2)_3{}^{2-}$ anion. Conductivity studies are being made on the compounds prepared in this work. The one datum available so far (in dimethyl sulfoxide) indicates a monomeric structure for the $Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2{}^{2-}$ ion.

Further evidence for structure I came from attempts to repeat the preparation of anhydrous $(NH_4)_2[Si(C_6H_4O_2)_3]$ from $SiCl_4$ as reported earlier by Rosenheim and Sorge.[5] The first attempts in this laboratory gave the "monohydrate." However, by rigorous exclusion of water a compound that analyzes correctly for $(NH_4)_2[Si(OC_2H_5)(C_6H_5O_2)(C_6H_4O_2)_2]$ was obtained. *Anal.* Calcd for $(NH_4)_2[Si(OC_2H_5)(C_6H_5O_2)(C_6H_4O_2)_2]$: Si, 6.46; C, 55.27; H, 6.03; N, 6.45. Found: Si, 6.49; C, 54.23; H, 6.34; N, 6.42. The structure is probably similar to that shown above for the "monohydrate." That is, the Si–OH group is replaced by an $Si–OC_2H_5$ group and one of the three catechol molecules is attached to the $Si–OC_2H_5$ group by a hydrogen bond. Reexamination of the analytical data presented by Rosenheim and Sorge indicates that they had prepared the "monohydrate" rather than the anhydrous salt. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$: Si, 6.91; $NH_4{}^+$, 8.88. Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]$: Si, 7.23; $NH_4{}^+$, 9.29. Found by Rosenheim and Sorge: Si, 7.04; $NH_4{}^+$, 8.88.

It was mentioned above that $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$ is the *usual* product from the reaction of catechol with silicic acid or colloidal silica in ammonium hydroxide solution after taking the initial colorless crystals to constant weight. In some preparations the X-ray powder diffraction pattern of the product showed the presence of a substantial amount of an impurity even though the infrared absorption spectrum showed nothing amiss. Upon two occasions the product was nearly free of the "monohydrate." Analytical data suggest a compound containing 4 mol of catechol per mole of silicon, *i.e.*, $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_6H_6O_2$. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_6H_6O_2$: Si, 5.44; C, 55.80; H, 5.46; N, 5.42. Found: Si, 5.41, 5.49, 5.52; C, 55.47, 54.84; H, 5.76, 5.58, 5.47; N, 6.39, 5.73, 5.84. The preparation of this compound requires 6–9 mol of catechol per mole of silicon in the reaction medium but it has not yet been obtained completely free from the "monohydrate." It is characterized by a very intense reflection at $2\theta = 9.15°$ in the X-ray powder diffraction pattern whereas structure I is characterized by two strongest reflections at $2\theta = 7.8$ and 15.5°.

Weiss, Reiff, and Weiss[2] also reported a complex containing 7 mol of catechol and 2 mol of silicon, *i.e.*, $(NH_4)_4[Si_2(C_6H_4O_2)_7]$. They precipitated this compound from a solution in mixed water–ethanol solvent. Compounds were also obtained in this work from a water–ethanol solvent but their nmr spectrum shows one ethyl group per mole of silicon and the compound should be formulated as $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_2H_5OH$. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_2H_5OH$: Si, 5.54; C, 47.42; H, 6.76; N, 5.53. Found (this work): Si, 5.65, 5.77; C, 47.20; H, 6.59; N, 5.87. Found (Weiss, Reiff, and Weiss): Si, 5.67; C, 47.9; H, 6.61; N, 5.50.

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CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY,
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Electron Paramagnetic Resonance Investigations of Some Copper(II) Dialkyldithiophosphate Complexes

BY D. SHOPOV AND N. D. YORDANOV

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Dithiophosphate compounds are important in the inhibition of hydrocarbon oxidation. To clarify the mechanism of their action the investigation of their structure is necessary. In the present paper the structure of the copper(II) dialkyldithiophosphate complexes is studied by means of their epr and electronic spectra.

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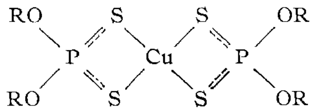
(3) J. H. Craddock and M. M. Jones, *J. Amer. Chem. Soc.*, **83**, 2839 (1961).

(4) L. Sacconi, P. L. Orioli, and M. Di Vaira, *Chem. Commun.*, 849 (1967).

(5) A. Rosenheim and O. Sorge, *Chem. Ber.*, **53**, 932 (1920).

Experimental Section

Complexes with the general formula



were studied, where R is CH_3, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $n\text{-}C_6H_{13}$, $i\text{-}C_8H_{17}$, or $n\text{-}C_{10}H_{21}$.

The complex salts were prepared from the corresponding sodium or potassium dialkyldithiosphosphate and copper(II) chloride in an aqueous solution. The precipitate was extracted by benzene, ether, or chloroform and recrystallized twice.

The epr spectra were obtained with a JEOL epr spectrometer, Model JES-3BS-X, using 100-kc modulation. The magnetic field was calibrated with the epr marker manganese(II) in magnesium(II) oxide with a distance between the third and fourth lines of 86.5 G. The g values were determined using charcoal with $g = 2.0060$ as standard. The low-temperature measurements were carried out using a standard dewar vessel in the spectrometer cavity. All measurements were made in quartz tubes with an inner diameter of 3 mm. The complex concentration was 5×10^{-3} M. The oxygen influence on the line widths was eliminated by evacuation of all investigated samples to 10^{-3} mm.

The electronic spectra were recorded on a Unicam SP 800 spectrometer.

Results and Discussion

The epr spectra of copper(II) dialkyldithiophosphate complexes in a polycrystalline state consisted of asymmetric lines with widths dependent on the alkyl radical size: the greater the alkyl radical, the wider the line. This fact can be explained in terms of decreasing exchange interaction.

The hyperfine splitting of the epr spectra in solution due to the nuclear magnetic moments of the copper isotopes was resolved at room temperature (for ^{63}Cu and ^{65}Cu $I = {}^3/_2$) (Figure 1). The widths of the separate hfs components were in good agreement with McConnell's relaxation mechanism.[1]

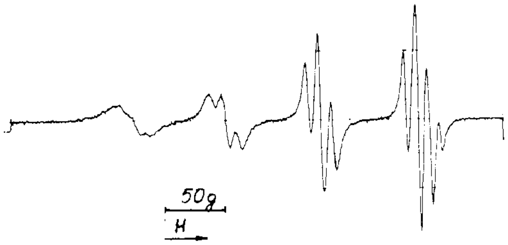


Figure 1.—Epr spectrum, typical for copper(II) dialkyldithiophosphate complexes in solution.

An additional splitting was observed at the line corresponding to $m_I = -{}^3/_2$, due to the superposition of the two copper isotope lines, which have a slight difference in magnetic moments. The intensity ratio of these two lines is proportional to the copper isotope concentration ratio in the natural mixture. A similar splitting was observed in the epr spectra of copper(II) diethyldithiocarbamate complexes.[2] The hyperfine lines of the epr spectra were additionally split into three components with intensity ratio 1:2:1. This extrahyperfine splitting, due to the ^{31}P ligand atoms ($I_{^{31}P} = {}^1/_2$), suggests strong delocalization of the metal unpaired electron onto the ligand.

The spin Hamiltonian for the investigated complexes in solution is

$$\mathcal{H} = g_0\beta H\hat{S} + A\hat{S}\hat{I} + A^{^{31}P}\hat{S}\hat{I}' \qquad (1)$$

where g_0 is the isotropic g value, β is the Bohr magneton, H is the intensity of the applied magnetic field, A and $A^{^{31}P}$ are the isotropic values of the hyperfine splitting for $^{63,65}Cu$ and ^{31}P, respectively, $\hat{S}$ is the effective spin magnetic moment, and $\hat{I}$ and $\hat{I}'$ are the nuclear spin magnetic moments of $^{63,65}Cu$ and ^{31}P, respectively.

The parameters in eq 1 for the investigated complexes are $g_0 = 2.045 \pm 0.003$, $A = 74.5 \pm 1$ G, $A^{^{31}P} = 9.8 \pm 1$ G. These values are equal to the results for copper(II) diethyl-[3] and dicresyldithiophosphate[4] complexes.

Two absorption bands at 23,700 and 31,000 cm^{-1} were observed in the absorption spectra of all complexes. We relate these bands to the $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz,yz}$ transfers, respectively.

The low-temperature studies (77°K) showed two groups of hyperfine lines around $g_\parallel$ and $g_\perp$, respectively. An isotropic extrahyperfine splitting due to the ^{31}P nuclei (Figure 2) in both the perpendicular and parallel directions was also observed.

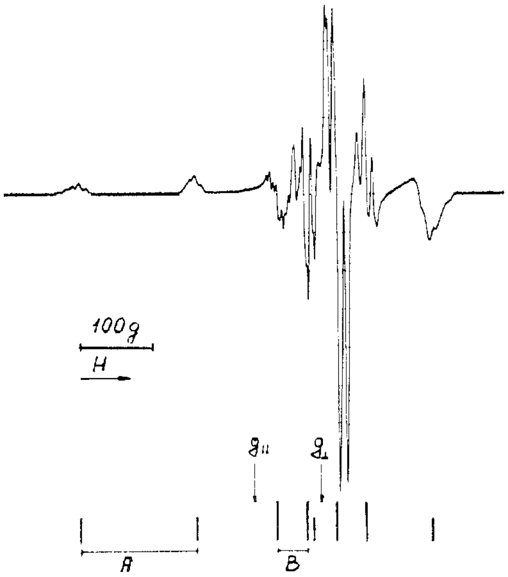


Figure 2.—Epr spectrum, typical for copper(II) dialkyldithiophosphate complexes at 77°K.

The spin Hamiltonian for an axially symmetric complex corresponding to the complexes investigated in the present work is

$$\mathcal{H} = g_\parallel\beta H_zS_z + g_\perp\beta(H_xS_x + H_yS_y) + AI_zS_z + B(I_xS_x + I_yS_y) + A^{^{31}P}(I_x'S_x + I_y'S_y + I_z'S_z) \qquad (2)$$

where $g_\parallel \equiv g_{zz}$ and $g_\perp \equiv g_{xx} \equiv g_{yy}$ are the diagonal

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[1] H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

[2] R. Petterson and T. Vangard, *Ark. Kemi*, **17**, 249 (1961).

[3] N. S. Garif'yanov and B. M. Kozyref, *J. Struct. Chem.* (USSR), **6**, 773 (1965).

[4] P. M. Solojeikin, N. U. Kopitzia, and N. P. Loseva, *Teor. Eksp. Khim.*, **4**, 708 (1968).

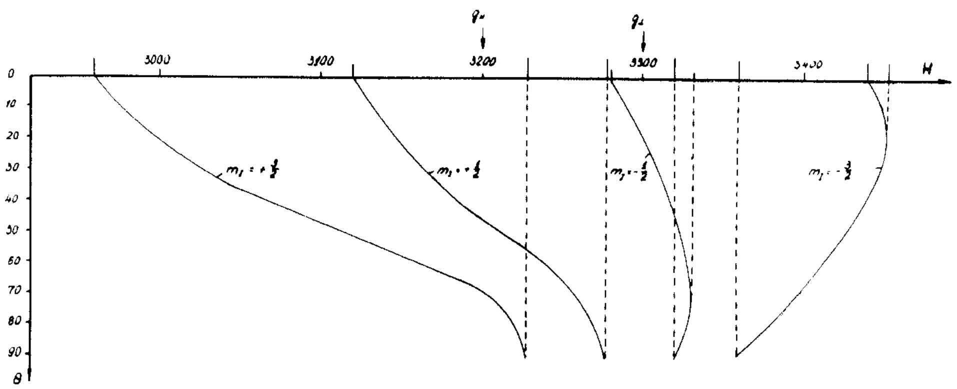

Figure 3.—A stick theoretical spectrum of copper(II) dialkyldithiophosphate complexes.

values of the g tensor, β is the Bohr magneton, H_x, H_y, and H_z are the components of the external magnetic field, S_x, S_y, and S_z are the components of the electron spin magnetic moment, I_x, I_y, and I_z are the components of the nuclear spin magnetic moment of ^{63,65}Cu ions, and I_x', I_y', and I_z' are the components of the nuclear spin magnetic moment of the ^{31}P atoms. $A^{^{31}\mathrm{P}}$ is the isotropic value of the ehfs constant due to the ^{31}P ligand atoms.

The parameters in eq 2 for the investigated complexes are $g_\parallel = 2.078 \pm 0.002$, $g_\perp = 2.023 \pm 0.002$, $A = 164 \pm 2$ G, $B = 41 \pm 2$ G, and $A^{^{31}\mathrm{P}} = 11 \pm 1$ G.

We suppose a high complex symmetry, owing to which the peak of the extra absorption in the epr spectra at 77°K overlaps with the $m_I = -{}^3/_2$ line for a parallel orientation.[5] In order to verify this superposition the angular dependence of the hyperfine line position was calculated. Neglecting the ehfs and the difference between the magnetic moments of the two copper isotopes, the transition energy corresponding to the spin Hamiltonian in eq 2 for an ideal solid state can be expressed as[6]

$$h\nu = g\beta H - m_I K/g \qquad (3)$$

where

$$g = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}$$
$$K^2g^2 = A^2g_\parallel^2\cos^2\theta + B^2g_\perp^2\sin^2\theta \qquad (4)$$

It follows from eq 3 that

$$H = h\nu/g\beta - m_I K/\beta g^2 \qquad (5)$$

The graphical solution of eq 5 is given in Figure 3. The following values are used for the parameters: $A = 160$ G, $B = 41$ G, $g_\parallel = 2.09$, $g_\perp = 2.02$, $\nu = 9.4 \times 10^9$ c. These spin Hamiltonian parameters fit all experimental data for copper(II) dialkyldithiophosphate complexes closely. It can be seen from Figure 3 that the distance between the line corresponding to $m_I = -{}^3/_2$ in a parallel orientation and the peak of the extra absorption is 15 G. On that account these two lines overlap partially. The peak of the extra absorption corresponding to the line with $m_I = -{}^1/_2$ is not observed owing to its low intensity and its position on the magnetic field axis.

The fact that the values of A, B, $g_\parallel$, and $g_\perp$ averaged according to the equations

$$g_0 = \frac{2g_\perp + g_\parallel}{3} \qquad (6)$$

$$a = \frac{A + 2B}{3} \qquad (7)$$

fit closely to all experimental data for solution shows that the complexes do not undergo any changes at low temperature. (It is reported in ref 4 that in the epr spectrum of the copper(II) dicresyldithiophosphate no ehfs from ^{31}P ligand atoms is observed in vitreous state.)

The fact that the spin-Hamiltonian parameters are equal for all complexes investigated indicates that the energy state of the copper(II) ion in the chelate is independent of the alkyl radical shape and size.

To calculate the metal–ligand bond parameters, the molecular orbital theory developed for planar copper(II) complexes[7,8] and the structural analogy of the dithiophosphate- and dithiocarbamate–copper(II) complexes were used.

The structural investigations of the copper(II) diethyldithiocarbamate complexes[9,10] show that the molecule is planar. The S atoms form a square around the copper(II) ion and the latter lies 0.26 Å above the plane defined by the S atoms. This structure corresponds to C_{4v} symmetry. A similar structure could be expected for the copper(II) dialkyldithiophosphate complexes. In the calculations of the metal–ligand bond parameters we assume that the rhombic deformation is slight and the deviation from the D_{2h} symmetry to C_{4v} is insignificant. In that case the following antibonding molecular orbitals formed from the 3d orbitals of the copper(II) ion and the corresponding ligand orbitals are written

$$\psi_{b_{1g}} = \alpha^2 d_{x^2-y^2} - (\alpha'/2)(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})$$
$$\psi_{b_{2g}} = \beta_1 d_{xy} - (\beta_1'/2)(\rho_y^{(1)} + \rho_x^{(2)} - \rho_y^{(3)} - \rho_x^{(4)})$$

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[5] D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 156 (1961).

[6] B. Bleany, *Phil. Mag.*, **42**, 441 (1951).

[7] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

[8] D. Kivelson and R. Neiman, *ibid.*, **35**, 194 (1961).

[9] G. Peyronel and A. Pignedoli, *Ric. Sci.*, **29**, 1505 (1959).

[10] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 886 (1965).

$$\psi_{e_g} = \begin{vmatrix} \beta d_{xz} - (\beta'/\sqrt{2})(\rho_z^{(1)} - \rho_z^{(3)}) \\ \beta d_{yz} - (\beta'/\sqrt{2})(\rho_z^{(2)} - \rho_z^{(4)}) \end{vmatrix}$$

where

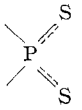
$$\sigma^{(i)} = np^{(i)} + (1 - n^2)^{1/2}S^{(i)}$$

$$\alpha^2 - 2\alpha\alpha'S + \alpha'^2 = 1$$

We do not take into account the molecular orbital including the d_{z^2} atomic orbital of the copper(II) ion as it is influenced only by the solvent.

The metal–ligand bond parameters are calculated according to Kivelson and Neiman's[8] method with the use of the parameters in eq 2 and the optical spectral data. The coefficients of the molecular orbitals are $\alpha^2 = 0.56$, $\beta_1^2 = 0.53$, and $\beta^2 = 0.70$; *i.e.*, the σ and π metal–ligand bonds in the xy plane, characterized with α^2 and β_1^2, respectively, are strongly covalent, while the π bonds in the xy and yz plane (β^2) have less covalent character.

It follows from our studies that both in solution and in a vitreous state the alkyl radical does not exert appreciable influence on the spin-Hamiltonian parameters. The strongly covalent character of both the σ and π metal–ligand bonds is determined exclusively from the fragment



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Negative Ion–Molecule Reactions and the Determination of the Heats of Formation of Inorganic Anions

BY J. C. J. THYNNE AND K. A. G. MACNEIL

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Lattice energies of compounds may be used as criteria of bond types, for the determination of electron affinities, and in discussions of the stabilities of hypothetical compounds.[1] The usual methods of evaluating the lattice energies of inorganic compounds involve Born–Haber cycles, the Born–Landé or Born–Mayer equations,[2] or extended classical calculations[3] involving the use of several experimental parameters.

The simplest method is that involving thermochemical cycles but, because of the limited number of gaseous anions for which heat of formation data are available, few Born–Haber cycles may be used to evaluate cycle lattice energies and consequently few diatomic or polyatomic ionic salts may be studied.

Ion–molecule reactions occurring in the gas phase have received considerable attention.[4,5] The requirement that, for such a reaction to occur, the reaction must be thermoneutral or exothermic has enabled an upper limit to be deduced for many bond energies. In addition, the heats of formation of several organic and inorganic positive ions have been determined in this manner.

This situation suggests that a study of the negative ion–molecule reactions which occur with inorganic compounds may offer a relatively simple route to obtaining heat of formation data for some gaseous anions. Clark and Dixon[6] have recently reported stabilization of the SiF_5^- ion by the formation of tetraphenylarsonium pentafluorosilicate. We decided to examine negative ion formation in silicon tetrafluoride in order to see if thermochemical data could be determined for the SiF_5^- ion.

Experimental Section

The experimentas were carried out using a Bendix time-of-flight mass spectrometer, Model 3015. The pressure of silicon tetrafluoride in the ion source was varied from <1 to 10^{-6} to $\sim 8 \times 10^{-5}$ Torr. The electron energy was read on a digital voltmeter and the electron current was kept constant over the energy range by automatic regulation.

Use of two channels of the mass spectrometer analog output scanners enabled two mass peaks (*e.g.*, SiF_3^- and SiF_5^-) to be monitored simultaneously so that no switching between peaks was necessary.

Discussion

Our experiments showed that, at low ion source pressures ($<10^{-6}$ Torr), the primary ions F^-, F_2^-, and SiF_3^- were formed by dissociative attachment processes, *e.g.*

$$SiF_4 + e^- \longrightarrow F^- + SiF_3 \qquad (1)$$

$$\longrightarrow SiF_3^- + F \qquad (2)$$

When the pressure of silicon tetrafluoride in the ion source was raised to $>10^{-5}$ Torr, formation of the ion SiF_5^- was observed as a result of an ion–molecule reaction.

Possible ion–molecule reactions leading to SiF_5^- ion formation were

$$F^- + SiF_4 \longrightarrow SiF_5^- \qquad (3)$$

$$F_2^- + SiF_4 \longrightarrow SiF_5^- + F \qquad (4)$$

$$SiF_3^- + SiF_4 \longrightarrow SiF_5^- + SiF_2 \qquad (5)$$

The identity of the reactant ion was established by comparing the dependence of the primary ion current upon electron energy with that obtained for SiF_5^-. It is apparent from Figure 1 that the normalized electron energy profiles for SiF_3^- and SiF_5^- are identical, hence the ion–molecule reaction responsible for SiF_5^- formation is reaction 5.

Recently, Page and Goode,[7] using the magnetron technique, have measured the electron affinity of SiF_3

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(1) D. A. Johnson, "Some Thermodynamic Aspects of Inorganic Chemistry," Cambridge University Press, Cambridge, England, 1968.

(2) D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **4**, 8 (1957).

(3) T. E. Brackett and E. B. Brackett, *J. Phys. Chem.*, **69**, 3611 (1965).

(4) F. W. Lampe, F. H. Field, and J. L. Franklin, *Progr. React. Kinet.*, **1**, 67 (1961).

(5) P. Ausloos, Ed., *Advan. Chem. Ser.*, **No. 58** (1966).

(6) H. C. Clark and K. R. Dixon, *Chem. Commun.*, 717 (1967).

(7) F. M. Page and G. C. Goode, "Negative Ions and the Magnetron," Wiley, New York, N. Y., 1969.