bei der Reaktion des Nickel(II) mit dem Malonat-
anion Nickel(II) ein Wassermolekül weniger frei-
setzt als Co²⁺ und Zn²⁺.

Da C₂O₄²⁻ und CH₂C₂O₄²⁻ in den meisten Kom-
plexen zweizähnig sind, wird die Bildung der Kom-
plex [Co₂C₂O₄]; [Ni₂C₂O₄]; [CoCH₂C₂O₄];
[ZnCH₂C₂O₄] von der Freisetzung zweier H₂O-
Moleküle begleitet. Mn²⁺ und Co²⁺ spalten bei der
gleichen Reaktion je drei Wassermoleküle ab, was
damit verbunden ist, daß die Koordinationszahl des
Mangans von sieben im Aquokomplex auf sechs
übergeht, Kupfer dagegen ändert seine Koordina-
tionszahl unter dem Einfluß beider Liganden von
zehn auf fünf. Im Komplex [NiCH₂C₂O₄] ist der
Ligand offenbar einzähnig, da bei der Bildung die-
es Komplexes ein Wassermolekül freigesetzt wird.
Die Zusammensetzung dürfte folgende sein:

\[\text{Co(H}_2\text{O)}_4(\text{C}_2\text{O}_4)\]; \[\text{Ni(H}_2\text{O)}_4(\text{C}_2\text{O}_4)\];
\[\text{Mn(H}_2\text{O)}_4(\text{C}_2\text{O}_4)\]; \[\text{Cu(H}_2\text{O)}_5(\text{C}_2\text{O}_4)\];
\[\text{Co(H}_2\text{O)}_4(\text{CH}_2\text{C}_2\text{O}_4)\]; \[\text{Zn(H}_2\text{O)}_4(\text{CH}_2\text{C}_2\text{O}_4)\];
\[\text{Mn(H}_2\text{O)}_4(\text{CH}_2\text{C}_2\text{O}_4)\];
\[\text{Cu(H}_2\text{O)}_5(\text{CH}_2\text{C}_2\text{O}_4)\]; \[\text{Ni(H}_2\text{O)}_5(\text{CH}_2\text{C}_2\text{O}_4)\].

Abschließend soll vermerkt werden, daß die er-
haltenen Resultate uns hoffen lassen, daß die Aus-
nutzung der hier angewandten Methode beim Vorlie-
gen zuverlässiger Entropiewerte eine Hilfe darstellt
bei der Aufklärung des schwierigen Mechanismus
der Anlagerung von nicht nur vielfältigen, sondern
auch einzähnigen Liganden an Metallionen und bei
der Bestimmung der Zusammensetzung und manch-
mal auch der Struktur der Komplexionen auf den
sukzessiven Stufen der Komplexbildung.

Ich danke Herrn Professor Dr. habil. H. Koch für
sein an dieser Arbeit gezeigtes Interesse.

Molecular Force Field for Seleninyl Fluoride

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A modified U.B.F.F. containing terms directly related to lone pair electrons, has been used to
evaluate the potential constants of SeOF₂. The value obtained for the Se—O stretching constant
supports the double bond character of the bond. The lone pair-bond pair repulsion bears a fixed
ratio to the non-bonded repulsion (\(F_{Eb}/FF = 1.24\)) and this result is in agree-
ment with earlier conclusions.

Many selenium compounds are not subjected to
spectroscopic studies and SeOF₂ is one of those
molecules for which vibrational and rotational spec-
tral data are available. ROLF et al. studied the
R a m a n spectrum of SeOF₂ with a view to deter-
mine the shape of the molecule. They observed six
fundamental vibrations in the R a m a n spectrum of
this molecule. On the assumption of a pyramidal
structure, they have successfully interpreted the ob-
served spectrum. Their assignment is supported by
studies of similar molecules like selenium oxy-
chloride, thionyl fluoride and thionyl chloride, for
which the shapes have been already determined.
Very recently, BOWATER et al. obtained structural
parameters of this molecule, on the basis of an analy-
sis of its microwave spectrum. They concluded that
the Se—O bond shows substantial double bond
character. According to GILLESPIE et al. selenium
oxyfluoride has trigonal pyramidal structure, based
on the arrangement of four bonding pairs of elec-
trons, including a lone pair. Previous investi-
gations indicate that the influence of lone pair

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9 M. G. KRISHNA PILLAI and P. PARAMESWARAN PILLAI, Indian J. Pure Appl. Phys. 6, 404 [1968].

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electrons must also be taken into account in normal coordinate analysis of molecules, having lone pair electrons. Hence it is thought worthwhile to make such an analysis, making use of a modified Urey-Bradley Force Field (U.B.F.F.), which contains terms directly related to lone pair electrons.

**Modified Urey-Bradley Force Field for SeOF₂**

Seleninyl fluoride belongs to the point group Cs and has 4 $A'$ + 2 $A''$ normal modes of vibration. All the six fundamental vibrations are both Raman and infrared active. The lone pair electrons occupy a position on the symmetry axis as shown in Fig. 1.

![Diagram of SeOF₂ molecule](image)

The expression for the potential energy based on the Urey-Bradley model was written in the usual way, in terms of the internal coordinates defined in Fig. 1. The expression obtained for the valence force constants therefrom are given below.

\[
\begin{align*}
    f_{a} &= K_a + (t_{gg}^{2} F_{gg} + S_{gg}^{2} F_{gg}) + (t_{gy}^{2} F_{gy} + S_{gy}^{2} F_{gy}) \\
    f_{R} &= K_R + 2 (t_{o}^{2} F_{o} + S_{o}^{2} F_{o}) + (t_{oe}^{2} F_{oe} + S_{oe}^{2} F_{oe}) \\
    f_{D} &= K_D + 2 (t_{o}^{2} F_{oe} + S_{o}^{2} F_{oe}) + (t_{o}^{2} F_{oe} + S_{oe}^{2} F_{oe}) \\
    f_{a} &= H_a - S_{gg}^{2} F_{gg} + t_{gg}^{2} F_{gg} \\
    f_{R} &= H_R - S_{o}^{2} F_{o} + t_{o}^{2} F_{o} \\
    f_{D} &= H_D - S_{o}^{2} F_{oe} + t_{o}^{2} F_{oe} \\
    f_{a} &= S_{gg}^{2} F_{gg} - t_{gg}^{2} F_{gg} \\
    f_{R} &= S_{o}^{2} F_{o} - t_{o}^{2} F_{o} \\
    f_{D} &= S_{o}^{2} F_{oe} - t_{o}^{2} F_{oe} \\
    f_{a} &= t_{gg}^{2} F_{gg} + t_{gg}^{2} F_{gg} \\
    f_{R} &= t_{o}^{2} F_{o} + t_{o}^{2} F_{o} \\
    f_{D} &= t_{o}^{2} F_{oe} + t_{o}^{2} F_{oe} \\
\end{align*}
\]

where $S_{ij} = r_{ij} - r_{ij} \cos 2\eta_{ij}$ and $t_{ij} = r_{ij} \sin 2\eta_{ij}$.

$D$, $R$ and $a$ are internuclear distances and $\alpha$, $\beta$, $\gamma$ and $\eta$ are the interbond angles. $Y$, stands for $F$ atoms. Here the subscripts refer to pairs of atoms; $q$ $S$ represent the nonbonded distances; the symbols $K$, $H$ and $F$ have their usual meaning. The constants $F'_{11}$ are set equal to $-0.1$ times the corresponding $F$ values, assuming that the energies associated with repulsion between non-bonded atoms are proportional to $q^{-9}$.

The following set of symmetry coordinates was then defined.

**$A'$ species:**

- $S_1 = \frac{\Delta a_1 + \Delta a_2}{2}$  
- $S_2 = \Delta R$  
- $S_3 = \frac{\Delta a + \Delta \beta_1 + \Delta \beta_2}{3}$  
- $S_4 = \frac{\Delta a - \Delta \beta_1 - \Delta \beta_2}{6}$  
- $S_5 = \Delta D$  
- $S_6 = \Delta \eta$  
- $S_7 = \Delta a_1 + \Delta \beta_1 + \Delta \beta_2 + B(\Delta \gamma_1 + \Delta \gamma_2) = 0$  

**$A''$ species:**

- $S_8 = \frac{1}{2} (\Delta a_1 - \Delta a_2)$  
- $S_9 = \frac{1}{2} (\Delta \beta_1 - \Delta \beta_2)$  
- $S_{19} = \frac{1}{2} (\Delta \gamma_1 - \Delta \gamma_2)$  

where

- $A = \frac{1}{\sqrt{3+2N^2}}$  
- $B = \frac{N}{\sqrt{3+2N^2}}$  

and

- $N = \frac{a \sin \gamma + 2 R \sin \eta}{2 R \sin \eta}$.

Coordinate $S_7$ is kept redundant. Coordinates $S_3$ and $S_4$ are not orthogonal.

The above set of symmetry coordinates gives a non-orthogonal $U$-matrix. The unsymmetrized $G$-matrix was constructed by standard methods. Then the matrices were symmetrized by the following transformations:

$$F = (U^{-1})^T f U^{-1};$$

$$g = U G U'.$$

Some of the $g$ elements are infinite owing to the presence of the atom (electron) of negligible mass. The rows and columns containing these elements are now dropped from $g$ and the residue $g^0$ is taken with modified $F^0$ to give for each symmetry block a reduced secular equation. The elements of this modified $F^0$ matrix obtained, following the method given by Pariseau and Overend, are given below.

$A'$ species:

$$F_{11}^0 = f_a + f_{aa} + \frac{2}{3} f_{aa} f_a,$$

$$F_{12}^0 = \sqrt{2} \left( f_{aa} f_a - \frac{2}{3} f_{aa} f_a \right),$$

$$F_{13}^0 = \sqrt{2/3} \left( f_{aa} f_a + f_{aa} f_a - \frac{2}{3} f_{aa} f_a \right),$$

$$F_{14}^0 = \frac{3}{2} \left( f_{aa} f_a + f_{aa} f_a \right).$$

$A''$ species:

$$F_{25}^0 = f_a - f_{aa} - \frac{2}{3} f_{aa} f_a,$$

$$F_{26}^0 = f_{aa} f_a,$$

$$F_{27}^0 = f_{aa} f_a.$$

For the convenience of calculation, the $F^0$ matrix obtained above is modified to a new matrix through the transformation:

$$F = U F^0 U.$$

Where $U$ is the matrix of transformation from real internal coordinates (excluding the lone pair) to the symmetry coordinates.

The modified $F$ elements are:

$$f_a = f_a - \frac{2}{3} f_{aa} f_a - \frac{1}{2} f_t,$$

$$f_R = f_R - \frac{2}{3} f_{aa} f_a - \frac{1}{2} f_t,$$

$$f_{aa} = f_{aa} + \frac{1}{2} A^2 f_t - \frac{1}{2} f_t,$$

$$f_{aR} = f_{aR} - \frac{1}{2} A^2 f_t - \frac{1}{2} f_t,$$

$$f_{aR} = f_{aR} + \frac{1}{2} A^2 f_t - \frac{1}{2} f_t.$$

The rows and columns containing these elements are now dropped from $g$ and the residue $g^0$ is taken with modified $F^0$ to give for each symmetry block a reduced secular equation. The elements of this modified $F^0$ matrix obtained, following the method given by Pariseau and Overend, are given below.

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$$F_{13}^0 = \sqrt{2/3} \left( f_{aa} f_a + f_{aa} f_a - \frac{2}{3} f_{aa} f_a \right),$$

$$F_{14}^0 = \frac{3}{2} \left( f_{aa} f_a + f_{aa} f_a \right).$$

$A''$ species:

$$F_{25}^0 = f_a - f_{aa} - \frac{2}{3} f_{aa} f_a,$$

$$F_{26}^0 = f_{aa} f_a,$$

$$F_{27}^0 = f_{aa} f_a.$$

For the convenience of calculation, the $F^0$ matrix obtained above is modified to a new matrix through the transformation:

$$F = U F^0 U.$$

The force constants in eqs. (6 - 17) were adjusted in the usual way using the molecular parameters and frequencies given in Table 1 and with the assumption that the lone pair electrons are located at a point 0.59 Å, which is the average radii of the outer electronic orbits of M and N shells from the nucleus.

The set of force constants which gave the best reproduction of frequencies was obtained. The results thus obtained are shown in detail in Table 2. For comparison the calculated frequencies are given in Table 1 along with observed frequencies.

**Discussion**

Table 2 provides a summary of the modified Urey-Bradley force constants of SeOF₂. A comparison of the values obtained for the main constants with those obtained for SOF₂ from a similar study, shows that they are in order. The value obtained for Se – O (\(K = 7.4915\) mdyn/Å) in the present investigation is nearly twice the value (\(K = 3.652\) mdyn/Å) obtained by Purushothaman for Se – O in the case of SeO₃. This supports the conclusion drawn by Bowater et al. from a microwave study of the molecule about the double bond character of the Se – O bond in the molecule. On scrutiny of the values obtained for the repulsive forces, it is found that the lone pair-bond pair repulsion is greater than the bond pair-bond pair repulsion. This is in agreement with the electron repulsion theory put forth by Gillespie et al. In addition the ratio between the lone pair-bond pair repulsion force constants seems to be a constant \(F_{FE}/F_{OF} = 1.24\) and \(F_{FF}/F_{OOC} = 1.23\). This conclusion is in conformity with our earlier results.

13 C. Purushothaman, Proceedings of the Seminar on Raman and Infrared Spectroscopy, University of Kerela, 1964, 204.