glow discharge yields NF_4AsF_6 in high purity while the high-temperature, high-pressure method does not. Because their reported hydrolysis of the glow-discharge product yielded "very large quantities of nitrogen oxides or nitrogen oxygen fluorides," we deduce that their product contained very large quantities of impurities. This is based on the fact that we found unequivocally no nitrogen oxides and only NF_3 and O_2 on hydrolysis of either NF_4AsF_6 or NF_4SbF_6 from our reactor. This evidence and the product analyses make it clear that the reaction under high pressure and elevated temperature yields a product of known high purity and in quantity.

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STAUFFER CHEMICAL COMPANY, RICHMOND, CALIFORNIA 94804

The Difluorochlorate(I) Anion, ClF_2^-. Vibrational Spectra and Force Constants

BY KARL O. CHRISTE, WOLFGANG SAWODNY,[1] AND JACQUES P. GUERTIN

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The vibrational spectra of complexes containing the difluorochlorate(I) anion, ClF_2^-, confirm the linear, centrosymmetric structure of ClF_2^- (point group $D_{\infty h}$) in $NOClF_2$. However, infrared spectra indicate distortion and/or lowering of the site symmetry of ClF_2^- in $RbClF_2$ and $CsClF_2$, the result of crystal field effects. The valence force and coupling constant of ClF_2^-, calculated by using the linear, centrosymmetric structure, are 2.35 and 0.17 mdynes/A, respectively. The bonding in ClF_2^- is best explained by a semiempirical molecular orbital model involving mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center, four-electron $p\sigma$ bond. Valence force constants are confirmed to be generally applicable for the characterization of semiionic 3c–4e (three-center, four-electron) bonds. However, it is suggested that these bonds do not necessarily require unusually high positive values for the coupling constants. There is a correlation between the single-bond order values and the valence force to coupling constant ratio for a series of electronically similar XY_2 groups. The unusually high positive values of the coupling constant of some of the members seem to be due to additional ionic contributions to the over-all potential energy in excess of the amount required for the formation of semiionic bonds.

Introduction

The existence and properties of the difluorochlorate(I) anion, ClF_2^-, have been reported recently.[2-4] Since only one stretching vibration had been observed for this anion in the infrared spectra of its nitrosonium[2] salt, it was suggested that ClF_2^- is linear rather than bent. However, no definite conclusion about the molecular structure could be reached without knowledge of the Raman spectrum. Furthermore, the data available were not sufficient to select the correct bond model.[2-4] Since the knowledge of the Raman spectrum also allows the calculation of force constants and thereby a choice between the different bond models, the recording of this spectrum appeared to be very desirable.

Experimental Section

The preparation of $KClF_2$ and $RbClF_2$ has been previously described.[3] The assays of $KClF_2$ and $RbClF_2$ were 27 and 49%, respectively, the remainder being the corresponding alkali metal fluoride.[3]

Raman spectra of the solids were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 A) as exciting line and a saturated KNO_2 solution as a filter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thickness were used.

Infrared spectra of the solids, $RbClF_2$ and $CsClF_2$, were recorded on a Beckman IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1}. Dry powder and Nujol or hexafluorobenzene mull techniques were used. Samples were placed between AgCl plates held in place by a screw-cap metal cell equipped with neoprene O rings.

Owing to their hygroscopic nature, the ClF_2^- salts were handled in the dry nitrogen atmosphere of a glove box.

Results and Discussion

Figure 1 illustrates the Raman spectrum of solid $KClF_2$. It is very similar to that of solid $RbClF_2$. Both spectra show only one line (very strong intensity) at 475 and 476 cm^{-1}, respectively. Whereas the quality of the infrared spectra of the alkali metal difluorochlorates(I) was somewhat poor, the Raman spectra were of good quality, even that of the $KClF_2$ sample, which contained only 27% difluorochlorate(I) salt,[3] the remainder being KF.

A triatomic ion such as XY_2^- could be either linear or bent, symmetric or asymmetric. Linear sym-

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[1] Visiting Scientist from the Institut für Anorganische Chemie, Technische Hochschule, Stuttgart, Germany.

[2] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 905 (1965).

[3] K. O. Christe and J. P. Guertin, *ibid.*, **4**, 1785 (1965).

[4] K. O. Christe and J. P. Guertin, paper presented at the Third International Fluorine Symposium, Munich, Germany, Aug 1965.

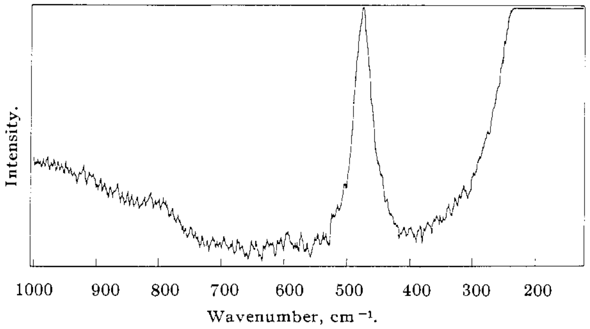

Figure 1.—Raman spectrum of solid $KClF_2$.

metric XY_2^- has symmetry $D_{\infty h}$. The three normal modes of vibration are classified as $\Sigma_g^+ + \pi_u + \Sigma_u^+$. Since linear symmetric XY_2^- has a symmetry center, it follows the rule of mutual exclusion. Therefore, π_u and Σ_u^+ will be only infrared active and Σ_g^+ only Raman active. Bent symmetric XY_2^- has symmetry C_{2v}. The three normal modes of vibration are classified as 2 $A_1 + B_1$. All three modes will be active in both the infrared and Raman spectra. Similarly, for asymmetric XY_2^-, whether linear or bent, all three normal modes of vibration are expected to be active in both the infrared and Raman spectra.

The observed vibration spectra of difluorochlorate(I) salts are listed in Table I along with their assignment.

TABLE I

VIBRATIONAL SPECTRA OF SOLID DIFLUOROCHLORATE(I) SALTS AND THEIR ASSIGNMENT

Frequencies obsd, cm⁻¹					Assignment (symmetry $D_{\infty h}$)	
Infrared			Raman			
$NOClF_2$[2]	$CsClF_2$[3]	$RbClF_2$	$KClF_2$	$RbClF_2$		
635 vs	636 m	661 m	...	...	ν_{asym}	ν_3 (Σ_u^+)
...	510 w 478 mw	470 s	475 vs	476 vs	ν_{sym}	ν_1 (Σ_g^+)
Not observed (probably lower than 400 cm⁻¹)			...	...	δ	ν_2 (π_u)

The observed Raman spectrum of ClF_2^- is quite consistent with the suggested linear structure[2-4] for the following reasons: (i) only one Raman band has been observed in agreement with the selection rules for $D_{\infty h}$, and (ii) the rule of mutual exclusion is followed for $NOClF_2$; *i.e.*, the Raman-active band is not infrared active and *vice versa*. The appearance of the symmetric stretching vibration, ν_1, as a band of relatively high intensity in the infrared spectrum of solid $RbClF_2$ and $CsClF_2$ and the doublet nature of this band in the latter's spectrum indicate a distortion of ClF_2^- and/or crystal field effects and vibrational coupling between two or more anions in the unit cell (the crystal structure of these salts is not known), respectively. Similar effects were observed in the infrared spectrum of other linear anions, such as $BrCl_2^-$ [5] and ICl_2^-.[6] The absence of the deformation vibration (ν_2) in the infrared spectrum can be easily explained. The spectrum was measured only in the range 4000–400 cm⁻¹ and ν_2 may be expected at a wavenumber lower than 400 cm⁻¹ (the bending mode of ClF_3[7] in the species A_1 was observed at 326 cm⁻¹). Thus, the infrared-active band at about 640 cm⁻¹ corresponds to the asymmetric stretching vibration (ν_3) and the Raman-active band at about 475 cm⁻¹ corresponds to the symmetric stretching mode (ν_1). The slight variation of the frequencies of ClF_2^- with the nature of the cation is not surprising and was also found for spectra of similar compounds such as $BrCl_2^-$ salts.[5,6] Assigning the infrared-active band at about 640 cm⁻¹ to a combination vibration is most unlikely owing to its high relative intensity and to the fact that the infrared spectrum of $NOClF_2$ shows no other band for ClF_2^- above 400 cm⁻¹. No data are available on the far-infrared spectrum of $NOClF_2$, owing to the lack of suitable window material for the low-temperature infrared cell (AgCl begins to absorb at 400 cm⁻¹). Also, experimental difficulties prevented the recording of any far-infrared spectra for the alkali metal difluorochlorates(I).

Summarizing, the linear centrosymmetric structure of ClF_2^- in $NOClF_2$ (point group $D_{\infty h}$) is confirmed, whereas distortion and/or lowering of the site symmetry of ClF_2^- in $RbClF_2$ and $CsClF_2$ by crystal field effects are indicated in the solid state. Since the frequency of ν_1 does not vary appreciably with change of cation and since the frequency of ν_3 of undistorted ClF_2^- is known from the $NOClF_2$ spectrum, it seems reasonable to assume 476 and 635 cm⁻¹ as frequencies of ν_1 and ν_3, respectively, of linear, centrosymmetric ClF_2^-.

Because there is only one normal vibration in each species for triatomic XY_2^- of symmetry $D_{\infty h}$, the valence force constant and the corresponding coupling constant can be evaluated unequivocally from the two observed frequencies. They have the values, f_r = 2.35 and f_{rr} = 0.17 mdynes/A, respectively, assuming ν_1 = 476 cm⁻¹ and ν_3 = 635 cm⁻¹.

The structure of ClF_2^- is closely related to that of ClF_3. In ClF_3, the equatorial fluorine atom has a shorter bond distance than the two axial fluorine atoms. Since the coupling between the equatorial and the two axial bonds is negligible[8] (the bond angle between them is approximately 90°), the vibrations of the nearly linear F–Cl–F part of ClF_3 should be comparable to those of ClF_2^-. In the latter, a lowering of the asymmetric and symmetric stretching vibrations is observed, resulting in a decrease of the valence force constant. This effect may be caused by the additional free-electron pair on the central chlorine atom,[9] thus increasing the contribution of the ionic structures F^- Cl–F and F–Cl F^- to the over-all potential energy.

The linear structure of ClF_2^- conforms with that established for other similar triatomic poly- and inter-

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[5] J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44**, 4356 (1966).

[6] W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *ibid.*, **35**, 908 (1961).

[7] H. H. Claassen, B. Weinstock, and J. G. Malm, *ibid.*, **28**, 285 (1958).

[8] D. A. Long and D. T. L. Jones, *Trans. Faraday Soc.*, **59**, 273 (1963).

[9] J. Goubeau, *Angew. Chem.*, **69**, 77 (1957).

halogen anions of the type X_3^-, XY_2^-, and XYZ^- [6,10–17] and with that of the isoelectronic XeF_2[18] and KrF_2.[19,20] On the basis of force constants now available, it can be decided for ClF_2^- whether the hybridization or the semiempirical molecular orbital model (involving mainly a delocalized p-electron pair of the chlorine atom for the formation of a semiionic 3c–4e pσ bond[16,18,21–25]) is more favorable. According to a theory proposed for polyhalide ions such as ICl_2^-, ICl_4^-, $BrCl_2^-$, and Br_3^-,[6] the valence force constant, f_r, of a semiionic 3c–4e pσ bond should be roughly half that of a covalent single bond, and the interaction constant, f_{rr}, should have an unusually large positive value. Comparison of the valence force constant of ClF_2^- with that of ClF and ClF_2^+ (Table II) does indeed show that f_r of ClF_2^- (2.35 mdynes/A) is about half that of ClF_2^+ [26] (4.77 mdynes/A) and of ClF[27] (4.36 mdynes/A), indicating that the bonding in ClF_2^- should be interpreted in terms of the semiionic 3c–4e pσ bond model. However, the interaction constant, f_{rr}, in ClF_2^-, is only about 7% of f_r, much smaller than earlier predicted.[6] Meanwhile, more data have become available on linear symmetric triatomic XY_2^- or XY_2 species, electronically comparable to ClF_2^- and ICl_2^- (having formally one electron pair in excess of the corresponding noble gas configuration). The semiionic 3c–4e bond model was suggested for these species. In addition to the valence force and interaction constants of XY_2 species, the valence force constants, f_r, of the mainly covalent XY molecules are given. Assuming a bond order of about 1 for XY, the ratio $n = f_r(XY_2)/f_r(XY)$ will represent approximately the single-bond order of XY_2. Furthermore, the ratio f_{rr}/f_r is listed, to show whether the predictions made for f_{rr} in semiionic 3c–4e bonds[6] are generally applicable. The XY_2^- and XY_2 species listed in Table II are not quite analogous. They can be separated into three subgroups: (i) HCl_2^- and HF_2^-, both having [s–p]σ bonds, (ii) ICl_2^-, $BrCl_2^-$, and ClF_2^-, having mainly [p–p]σ bonds and a formal oxidation number of +1 for X, the central atom, and (iii) XeF_2 and KrF_2, having mainly [p–p]σ bonds and a formal oxidation number of +2 for X.

TABLE II

VALENCE FORCE CONSTANTS, f_r, INTERACTION CONSTANTS, f_{rr}, SINGLE-BOND ORDERS, n, AND INTERACTION TO VALENCE FORCE CONSTANT RATIO, $f_{rr},/f_r$, FOR A SERIES OF LINEAR SYMMETRIC XY_2^- OR XY_2, SPECIES[a]

Ion or molecule		f_r, mdynes/A		f_{rr}, mdynes/A	$n = f_r(XY_2)/f_r(XY)$	$f_{rr}(XY_2)/f_r(XY_2)$
HCl_2^- [b]		0.80		0.61	0.16	0.76
	HCl[c]		5.15			
HF_2^- [6]		2.31		1.72	0.24	0.74
	HF[6]		9.67			
$BrCl_2^-$ [5]		1.02		0.47	0.36	0.46
	BrCl[6]		2.83			
ICl_2^- [5,6]		1.00		0.36	0.42	0.36
	ICl[6]		2.38			
ClF_2^-		2.35		0.17	0.55	0.07
	ClF[27]		4.36			
	ClF_2^+ [26]		4.77			
XeF_2[20]		2.84		0.13		0.05
KrF_2[20]		2.46		−0.20		−0.08

[a] X_3^- ions such as Br_3^-,[6] Cl_3^- (J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44,** 3638 (1966)) or XY_3 molecules such as ClF_3 or BrF_3 could also be included in this table if certain assumptions are made. In the latter case, only the axial Y–X–Y group should be taken into consideration, and the coupling between the two axial bonds and the shorter equatorial X–Y bond should be neglected since their bond angle is almost 90°. [b] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **70,** 11 (1966). [c] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 175.

While it is not possible to give a quantitative explanation for the correlations indicated in Table II without detailed numerical calculations, the nature of the bonding in all of these XY_2^- or XY_2 species appears to be sufficiently similar to allow the following qualitative statements.

(i) The single-bond orders, n, for the series are about 0.5 or smaller, thus confirming earlier predictions[6] and indicating that the XY_2^- or XY_2 species listed in Table II contain a large semiionic 3c–4e bond contribution.

(ii) The occurrence of single-bond orders having values considerably smaller than 0.5 indicates ionic contributions in excess of that required for the formation of semiionic bonds.

(iii) Semiionic bonds are not necessarily accompanied by unusually high interaction constants as previously predicted.[6] The interaction constants may have small positive values or even slightly negative values as in the case of KrF_2. A theoretical explanation for the latter has recently been given.[28] According to this explanation the contribution of the no-bond structure to the over-all potential energy increases, if the stability of XF_2 decreases. Thus, the increasing influence of the no-bond structure on the stretching vibrations with decreasing stability of XF_2 may cause relatively small or even negative values for the coupling force constant, f_{rr}. Whereas this effect may account for the difference between f_{rr} of KrF_2 and XeF_2,[28] it does not account for f_{rr} of ClF_2^- compared to f_{rr} of $BrCl_2^-$ and ICl_2^-. Instead of showing considerably lower stability, $CsClF_2$[3] actually is more stable than either $CsICl_2$ or $CsBrCl_2$.[29] The unusually high coupling constants found for some of the compounds can-

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(10) R. M. Bozort and L. Pauling, *J. Am. Chem. Soc.*, **47**, 1561 (1925).

(11) R. C. L. M. Slater, *Acta Cryst.*, **12**, 187 (1959).

(12) E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 724 (1959).

(13) F. A. Cotton and B. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 309.

(14) R. W. G. Wyckoff, *J. Am. Chem. Soc.*, **42**, 1100 (1920).

(15) R. C. L. Mooney, *Z. Krist.*, **100**, 519 (1939).

(16) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

(17) R. C. L. Mooney, *Z. Krist.*, **98**, 324 (1938).

(18) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

(19) J. J. Turner and G. C. Pimentel, *Science*, **140**, 974 (1963).

(20) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, **42**, 1229 (1965).

(21) G. C. Pimentel, *ibid.*, **19**, 446 (1951).

(22) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).

(23) R. E. Rundle, *ibid.*, **85**, 112 (1963).

(24) F. Schreiner, J. G. Malm, and J. C. Hindman, *ibid.*, **87**, 25 (1965).

(25) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 158 (1961).

(26) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(27) A. H. Nielsen and E. A. Jones, *J. Chem. Phys.*, **19**, 1117 (1951).

(28) C. A. Coulson, *ibid.*, **44**, 468 (1966).

(29) F. Ephraim, *Ber.*, **50**, 1069 (1917).

not be explained satisfactorily by the no-bond structure contribution alone. They are probably due to some extent to the ionic contribution in excess of the amount required for the formation of the semiionic 3c–4e bonds. This seems plausible if we consider the contribution of the following structures to the over-all potential energy

$$\underset{\text{I}}{\text{Y}\text{–}\bar{\text{X}}\text{–Y}} \longleftrightarrow \underset{\text{II}}{\text{Y}^-\ \text{X–Y}} \longleftrightarrow \underset{\text{III}}{\text{Y–X}\ \ \text{Y}^-}$$

The migration of the negative charge in II and III results in a shortening of the bond length of the remaining X–Y part causing a strong coupling effect. Therefore, an additional increase of the relative contribution of the ionic structures II and III should decrease the valence force constant, f_r, and, thereby, the bond order, n (since valence force constants represent only the covalent contribution to the over-all bond energy) and should increase the coupling constant, f_{rr}, over that of a pure semiionic 3c–4e bond.

(iv) The relative ionic bond contribution to the over-all potential energy should increase in the order anion > neutral molecule > cation, if otherwise comparable anions, neutral molecules, and cations are considered. This is due to a decrease in the amount of negative charge on the central atom resulting in a reduction of the electronegativity of this atom.

(v) The relatively low mass of the central atom in HCl_2^- and HF_2^- should further enhance the coupling effect in these anions.

(vi) The electronegativity difference between the X atom and the Y atom does not seem to be the dominating effect, since it does not agree with the observed orders: $HCl_2^- > HF_2^-$ and $BrCl_2^- > ICl_2^- > ClF_2^-$.

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(30) After completing this paper we learned about the work of A. G. Maki and R. Forneris on the infrared and Raman spectra of some trihalide ions: ICl_2^-, IBr_2^-, I_3^-, I_2Br^-, and $BrICl^-$, to be published in *Spectrochim. Acta.* We are indebted to Dr. Maki for making a preprint of their paper available to us. Their findings on these anions are in good agreement with our results on ClF_2^-. Their observations on the infrared and Raman spectra of $RbICl_2$ are very similar to those made by us for $RbClF_2$ and $CsClF_2$. Their interpretation of the large interaction constants as being due to an unusually flat bottom of the potential well for the central atom of the trihalide ions parallel ours (which uses the bond order n) since both explanations assume that the interaction constant increases as the central atom to ligand bond strength decreases. Therefore, both Maki's interpretation and ours disagree with Coulson's prediction[28] for this type of molecules: "the greater the bond energy the larger f_{rr} would be, and only when the bond energy was very small would we expect negative f_{rr}."

CONTRIBUTION FROM THE METALS AND CERAMICS DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

Lower Oxidation States of Bismuth. Bi^+ and $[Bi_5]^{3+}$ in Molten Salt Solutions[1a]

BY NIELS J. BJERRUM, CHARLES R. BOSTON, AND G. PEDRO SMITH[1b]

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Principal items reported here are the preparation, identification, and absorption spectra of Bi^+ and $[Bi_5]^{3+}$ contained in dilute solutions in the molten salt eutectics composed of 63 mole % $AlCl_3$–37 mole % NaCl and 72 mole % $ZnCl_2$–28 mole % KCl and equilibrium quotients for equilibria involving Bi^+ and $[Bi_5]^{3+}$. Topics of less significance, or else treated in less detail, are the following: procedures for preparing high-purity $AlCl_3$–NaCl and $ZnCl_2$–KCl mixtures suitable as spectrophotometric solvents, the density of the molten $ZnCl_2$–KCl eutectic as a function of temperature, and the absorption spectrum of Bi^{3+} in the $AlCl_3$–NaCl eutectic. The investigation consisted of spectrophotometric measurements on equilibrium reaction mixtures that involved bismuth metal (as a separate liquid phase), Bi^{3+}, Bi^+, and $[Bi_5]^{3+}$ in various combinations and concentrations. The data were insufficient to give any information on ligands coordinated to these entities.

Introduction

Bismuth metal reacts with dilute solutions of $BiCl_3$ in liquid eutectic mixtures of $AlCl_3$–NaCl or $ZnCl_2$–KCl to form colored melts. In a recent short communication[2] we asserted that the reaction products formed under most conditions are Bi^+ and $[Bi_5]^{3+}$ with a third (unidentified) product formed under special conditions. In the present paper we give the evidence upon which these claims are based. We have since prepared Bi^+ by hydrogen reduction of $BiCl_3$ in the $AlCl_3$–NaCl eutectic.

The designations Bi^+ and $[Bi_5]^{3+}$ are intended to specify the oxidation states and numbers of bismuth atoms per molecular unit of the reaction products. We do not intend these designations to imply anything regarding coordination between bismuths and surroundings atoms.

Previous studies of oxidation states of bismuth between zero and 3+ have produced only a few firm facts regarding molecular entities although partially supported speculations have been numerous. Much

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(2) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965).