chromium(VI) in a 3 *M* perchloric acid solution as temperature was changed from 17 to 32°. From the present data the ΔH and ΔS of the first dissociation of chromic acid were -8.5 kcal and -26 eu, respectively. The ΔS value was of the same order of magnitude as ΔS values of other weak acids.[17,18]

Acknowledgment.—This work was supported by the United States Atomic Energy Commission through Contract AT(11-1)-687.

[17] E. L. King, *J. Chem. Educ.*, **30**, 71 (1953).

[18] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y. 1958, p 667.

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The Exchange Rates of Water and Thiocyanate Ion With Nickel(II)–Thiocyanate Complexes by Oxygen-17 and Nitrogen-14 Nuclear Magnetic Resonance[1,2]

By R. B. Jordan, Harold W. Dodgen, and John P. Hunt[3]

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Water and thiocyanate exchange rates have been measured for aquothiocyanato complexes of nickel(II) ($[Ni(NCS)_4(H_2O)_2]^{2-}$ presumably) in concentrated aqueous thiocyanate solutions. These exchanges proceed independently over the temperature range studied. In *ca.* 8 *M* KNCS, ΔH^* for water exchange is 6.0 ± 0.6 kcal/mole while ΔH^* for thiocyanate exchange is 9.2 ± 0.6 kcal/mole. In 3.5 *M* NaNCS plus 4.5 *M* $NaClO_4$, ΔH^* for water exchange is 7.4 ± 0.5 kcal/mole. The scalar coupling constant A/h for H_2O^{17} in $[Ni(NCS)_4(H_2O)_2]^{2-}$ is 2.0×10^7 cps. Substitution of water in $[Ni(H_2O)_6]^{2+}$ by thiocyanate results in a labilizing of the remaining water ligands.

Introduction

Some preliminary results were reported earlier on H_2O^{17} exchange with a presumed $[Ni(NCS)_4(H_2O)_2]^{2-}$ species.[4] These suggested that water and thiocyanate exchange proceeded independently and led us to investigate the matter in more detail. Such studies may give new insight into the mechanisms of substitution reactions in complex ions.

Experimental Section

The nmr techniques and equipment previously described have been used.[4,5] Using a static field of 9270 gauss, the O^{17} nmr line in H_2O was observed at *ca.* 5.35 Mc/sec while the N^{14} line in aqueous KNCS solution occurs at *ca.* 2.85 Mc/sec. Much better control of the sample temperature in the nmr probe than was previously possible was achieved by circulating thermostated isooctane or pentane through the probe rather than nitrogen gas. Sample temperatures were constant to ±0.1° throughout the sample.

Solutions were prepared using water containing 1.19 atom % O^{17} (*ca.* 17% O^{18} and "normalized" in H content) obtained from Bio-Rad Laboratories. Water redistilled from alkaline permanganate gave the same results as the water used as supplied. Other reagents used were Fisher Scientific Co. CP $Ni(NO_3)_2 \cdot 6H_2O$, Baker Analyzed KNCS, and $NaClO_4$ prepared by the method of Willard and Smith.[6]

Measurements of O^{17} chemical shifts (*S*) were made using, for reference purposes, a small sample tube containing KNCS in H_2O^{17} placed inside the usual sample tube and solution.

Treatment of Data and Results

The basic theoretical treatment is found in the detailed paper of Swift and Connick.[7] Some modifications of this treatment were subsequently introduced by our group.[8] The details are somewhat involved and will not be repeated here except in outline. We are concerned with line broadenings for the free H_2O^{17} and $N^{14}CS^-$ nmr absorption signals produced by the addition of paramagnetic Ni(II). Line broadening results are reported in terms of the quantity $T_{2p}'' = 2\ m(\mathrm{Ni})/\gamma\Delta'$ where m(Ni) is the total molality of Ni(II), γ is the magnetogyric ratio (3628 gauss^{-1} sec^{-1} for O^{17} and 1934 gauss^{-1} sec^{-1} for N^{14}), and Δ' is the line broadening in gauss, measured at half-maximum absorption using the full line widths, produced by added Ni(II). That is, Δ' is $(W_{\mathrm{obsd}} - W_0)$ where W_{obsd} is the line width observed in the presence of Ni(II) and W_0 is the line width observed at the same temperature and other conditions except with no added nickel. Values for Δ', T_{2p}'', and W_0 as a function of temperature and composition of the solutions are given in Table I. Values of Δ' are the average of three or four measurements and have a precision of ±5–10%. A semilogarithmic plot of TT_{2p}'' (T = absolute temperature) *vs.* $10^3/T$ is given in Figure 1.

The shift data for H_2O^{17} are given in Table II and are plotted in Figure 1. The quantity $TSm(\mathrm{H_2O})/m(\mathrm{Ni})$ is used where S is the change in frequency divided by the original frequency and $m(\mathrm{H_2O})$ is the molality of the water.

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[2] Purchase of O-17 used was made possible by funds granted by the Washington State University Research Committee.

[3] To whom inquiries may be addressed.

[4] R. Murray, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **3**, 1576 (1964).

[5] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 206 (1965).

[6] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **44**, 2817 (1922).

[7] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[8] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965).

TABLE I

LINE-BROADENING DATA FOR H_2O^{17} EXCHANGE

t, °C	Δ', gauss	$10^6T_{2p}''$, m sec	W_0, gauss
(A) 0.281 *m* Ni; 13.3 *m* KNCS			
31.1	0.50	30.8	0.36
20.8	0.63	24.4	0.39
9.2	0.75	20.6	0.43
4.3	0.87	17.7	0.45
2.4	0.93	16.6	0.46
−9.5	0.79	19.5	0.51
−14.8	0.93	16.6	0.54
(B) 0.363 *m* Ni; 13.3 *m* KNCS			
29.5	0.51	39.3	0.36
16.4	0.73	27.4	0.40
8.1	1.02	19.6	0.43
−8.0	1.18	17.0	0.50
−9.0	1.11	18.0	0.51
−12.0	1.13	17.7	0.52
−15.1	1.18	17.0	0.54
−19.3	1.12	17.9	0.56
−24.0	0.82	24.4	0.59
−28.0	0.66	30.4	0.63
−31.4	0.58	34.5	0.65

t, °C	Δ', gauss	$10^6T_{2p}''$, m sec	W_0, gauss
(C) 0.565 *m* Ni; 12.9 *m* KNCS			
30.5	0.94	33.1	0.36
26.7	1.19	25.8	0.37
18.9	1.43	21.7	0.39
−15.7	1.77	17.5	0.54
−19.0	1.65	18.8	0.56
−21.1	1.46	21.4	0.58
−26.7	1.14	27.4	0.62
(D) 0.318 *m* Ni; 5.4 *m* NaNCS; 7.0 *m* $NaClO_4$			
26.7	0.77	22.6	0.45
13.9	1.29	13.4	0.50
6.0	1.58	11.0	0.60
−10.8	1.20	14.4	1.25
−15.5	1.08	16.0	1.75
−19.3	0.74	23.2	2.25
−23.5	0.60	28.8	3.30

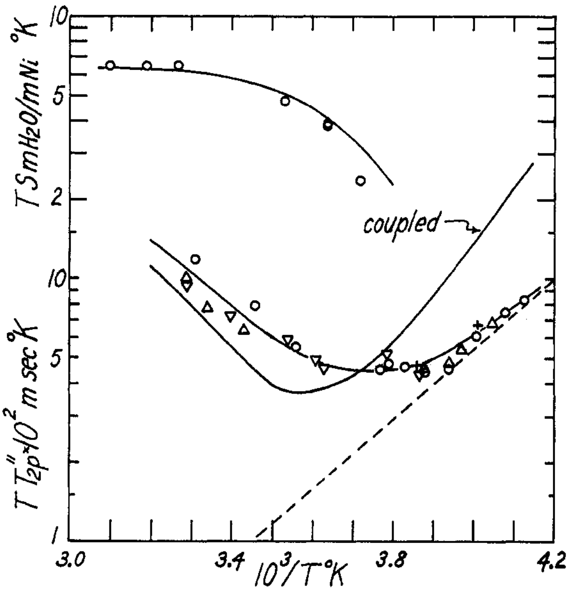

Figure 1.—Plot of TT_{2p}'' *vs.* $1/T$ and $TSm(H_2O)/m(Ni)$ *vs.* $1/T$ for H_2O^{17}: ▽, 0.281 *m* Ni, 13.3 *m* KNCS; ○, 0.363 *m* Ni, 13.3 *m* KNCS; △, 0.565 *m* Ni, 12.9 *m* KNCS; +, redistilled H_2O. The solid curves are calculated curves. The curve labeled "coupled" is discussed in the text. The dashed line gives $m(Ni)P_LT_{\tau M}/P_M$ *vs.* $1/T$ from which the rate parameters are derived.

TABLE II

CHEMICAL SHIFT DATA FOR H_2O^{17} WITH 13.3 *m* KNCS

m(Ni)	t, °C	Shifts (S), ppm	$TSm(H_2O)/m(Ni)$
0.363	50.0	133	6.50
0.363	41.0	136	6.46
0.363	32.6	139	6.44
0.363	2.0	94	3.90
0.565	10.5	176	4.76
0.565	2.3	146	3.84
0.565	−4.0	92	2.36

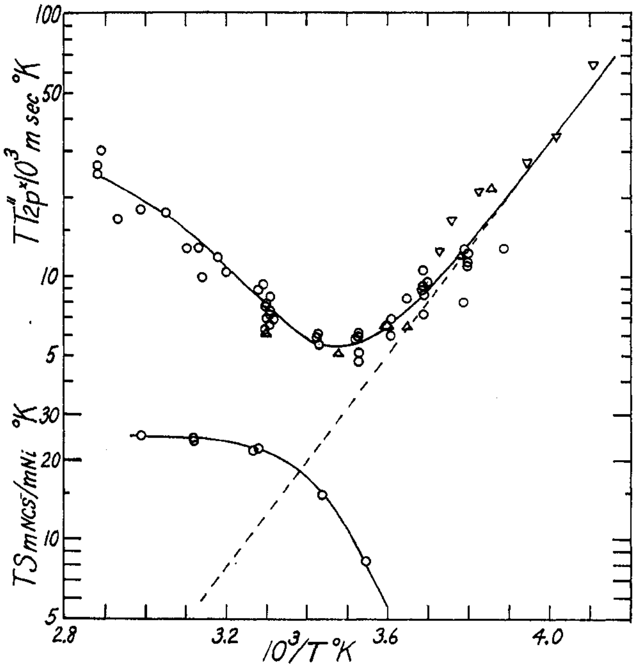

Figure 2.—Plot of TT_{2p}'' *vs.* $1/T$ and $TSm(NCS^-)/m(Ni)$ *vs.* $1/T$ for $N^{14}CS^-$: △, 0.0163 *m* Ni, 13.7 *m* KNCS; ▽, 0.198 *m* Ni, 13.7 *m* KNCS; ○, 15.5 *m* KNCS, recalculated from data in ref 4. The solid curves are calculated curves. The dashed line gives $m(Ni)P_LT_{\tau M}/P_M$ *vs.* $1/T$ from which the rate parameters are derived.

Some additional measurements were made on the thiocyanate exchange, particularly in the important low-temperature range. These results and those of Murray,[4] *et al.*, were calculated on a molal basis and are shown in Figure 2. The agreement between the earlier and present data is satisfactory. In order to extract the information of chemical interest from the data, a curve-fitting procedure is followed. Upon examination of Figures 1 and 2 and attempts at curve fitting, it became clear that the following approach provided the best fit for all of the data.

The basic equation[7] (modified by our definition of T_{2p}'') is

$$T_{2p}'' = T_{2p}m(\mathrm{Ni}) = \frac{m(\mathrm{Ni})P_{\mathrm{L}}}{P_{\mathrm{M}}}\left[\frac{1/\tau_{\mathrm{M}} + \Delta\omega_{\mathrm{M}}^2\tau_{\mathrm{M}}}{1/T_{2\mathrm{M}}\tau_{\mathrm{M}} + \Delta\omega_{\mathrm{M}}^2}\right]$$

if $1/T_{2\mathrm{M}}$ is small compared to $1/\tau_{\mathrm{M}}$. In this equation P_{L} and P_{M} are the fractions of relevant nuclei present in the free ligand and bound in the metal complex, respectively, τ_{M} is the mean lifetime for a bound ligand with respect to exchange with free ligand, $\Delta\omega_{\mathrm{M}}$ is the resonant frequency of the nucleus when bound *minus* the frequency found for the nucleus in the free ligand in the absence of Ni(II), and $(T_{2\mathrm{M}})^{-1} = (S(S+1)/3)\cdot(A/h)^2T_{1\mathrm{e}}$ where S is the resultant electron spin for Ni(II) ($S = 1$ here), A/h is the scalar coupling constant, and $T_{1\mathrm{e}}$ is the electron spin relaxation time. $T_{1\mathrm{e}}$ is used here because it is very small compared to τ_{M}. Previously[4] we had used the limiting case $T_{2p}'' = (m(\mathrm{Ni})P_{\mathrm{L}}/P_{\mathrm{M}})(1/\Delta\omega_{\mathrm{M}}^2\tau_{\mathrm{M}} + \tau_{\mathrm{M}})$. A better fit for the total data can be obtained by using the equation

$$T_{2p}'' = (m(\mathrm{Ni})P_{\mathrm{L}}/P_{\mathrm{M}})[(1/\Delta\omega_{\mathrm{M}}^2\tau_{\mathrm{M}} + \tau_{\mathrm{M}})/(1 + 1/T_{2\mathrm{M}}\tau_{\mathrm{M}}\Delta\omega_{\mathrm{M}}^2)]$$

The right-hand portion of the curves (of major interest here) is not affected by this change, but the left-hand portion can be fitted more satisfactorily. It is not necessary to suppose that a new complex species is involved at higher temperatures, and all the data can be rationalized in terms of a single complex, presumably $[\mathrm{Ni(NCS)_4(H_2O)_2}]^{2-}$.

The parameters derived from the curve-fitting processes are shown in Table III. The k_1 values are calculated from the rate laws $R(\mathrm{H_2O}) = 2k_1[\mathrm{Ni(II)}]$ and $R(\mathrm{NCS^-}) = 4k_1[\mathrm{Ni(II)}]$. The ΔS^* values are based on k_1 defined above. The errors shown are estimated based on the range of values allowed by the curve-fitting process. The $T_{1\mathrm{e}}$ value is reasonable in magnitude and is below the upper limit set for the aquo complex[7] but is uncertain by some 50%. E_{a} is the activation energy associated with the temperature variation of $T_{1\mathrm{e}}$. The same values of $T_{1\mathrm{e}}$ were used for fitting the $\mathrm{O^{17}}$ and $\mathrm{N^{14}}$ data. This corresponds to assuming the same complex species is involved for both $\mathrm{H_2O}$ and $\mathrm{NCS^-}$.

Table III

	$\mathrm{H_2O^{17}}$	$\mathrm{N^{14}CS^-}$ [b]
Exchange rate (25°), m sec^{-1} [a]	$(2.2 \pm 0.2) \times 10^6$ [c]	$(2.1 \pm 0.2) \times 10^6$ [c]
Exchange rate (−23°), m sec^{-1} [a]	$(2.5 \pm 0.1) \times 10^5$	$(9 \pm 0.5) \times 10^4$
k_1 (25°), sec^{-1}	$(1.1 \pm 0.1) \times 10^6$ [c]	$(5.3 \pm 0.5) \times 10^5$ [c]
ΔH^*, kcal/mole	6.0 ± 0.6	9.2 ± 0.6
ΔS^*, cal/mole deg	-11 ± 3	-1.4 ± 3
A/h, cps	2.0×10^7	2.2×10^7
$T_{1\mathrm{e}}$ (25°), sec	2.7×10^{-12}	
E_{a}, kcal/mole	1.2	

[a] In hypothetical 1 m Ni(II) solution. [b] 13.7 m KNCS. [c] Extrapolated values.

Discussion and Conclusions

The experiments were undertaken to determine the extent of coupling of water and thiocyanate exchange in *ca.* 8 M KNCS through an equilibrium of the type

$$[\mathrm{Ni(NCS)_4(H_2O)_2}]^{2-} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Ni(NCS)_3(H_2O)_3}]^{-} + \mathrm{NCS^-}$$

If the entry of a thiocyanate into the first coordination sphere of nickel were always accompanied by the expulsion of a water and *vice versa*, then the *rates* of exchange of these ligands would be equal at all temperatures. Since $\tau_{\mathrm{H_2O}} = m(\mathrm{H_2O})/R(\mathrm{H_2O})$, $\tau_{\mathrm{NCS^-}} = m(\mathrm{NCS^-})/R(\mathrm{NCS^-})$, and $R(\mathrm{H_2O}) = R(\mathrm{NCS^-})$ at each temperature for the completely coupled case, one has $\tau_{\mathrm{H_2O}} = \tau_{\mathrm{NCS^-}}[m(\mathrm{H_2O})/m(\mathrm{NCS^-})]$. This relation, along with the observed high-temperature shift of the $\mathrm{H_2O^{17}}$ resonance and $\tau_{\mathrm{NCS^-}}$ values obtained from $\mathrm{N^{14}}$ data, permits the calculation of the expected values of TT_{2p}'' *vs.* T for $\mathrm{H_2O}$,[17] assuming a completely coupled mechanism. Strictly speaking, the completely coupled exchange mechanism requires use of three-site equations. However, it can be shown that the three-site equations take the form of the two-site equations used in this paper if the parameters are properly redefined and that in the low-temperature limit T_{2p} becomes equal to τ_{M} as expected. The dashed curve labeled "coupled" in Figure 1 is the result of this calculation. This calculated curve does not agree with the experimental points, especially in the low-temperature range. The experimental results at 250°K, a temperature at which both rates are measured directly, show that water exchanges *ca.* 2 times faster than thiocyanate. Because of the difference in ΔH^*, the rates would become equal near room temperature and then diverge again with thiocyanate exchanging at a faster rate.

Since the water exchange rate at the lower temperatures is greater than for thiocyanate, it would seem possible that all of the thiocyanate exchange proceeds through the coupled path while the water exchange proceeds through the coupled path plus an additional path which, when added to the rate of the coupled path, would give the observed rate. This would mean that $1/\tau_{\mathrm{H_2O}} = 1/\tau_{\mathrm{H_2O(C)}} + 1/\tau_{\mathrm{H_2O(X)}}$, where $\tau_{\mathrm{H_2O(C)}}$ is the mean life of a $\mathrm{H_2O}$ for exchange through the coupled path whereas $\tau_{\mathrm{H_2O(X)}}$ is the same quantity for the other path. An attempt was made to fit the data using for $\tau_{\mathrm{H_2O(C)}}$ the values which would be consistent with $\tau_{\mathrm{NCS^-}}$ as described above and values for $\tau_{\mathrm{H_2O(X)}}$ which would give agreement with the observed TT_{2p}'' *vs.* T curve for $\mathrm{H_2O^{17}}$ at the lowest temperatures. The resulting TT_{2p}'' *vs.* T curve was unsatisfactory, giving too small values of TT_{2p}'' in the region of the minimum in the curve. We conclude from this that, at most, only a minor part of the thiocyanate exchange can be occurring through the coupled path and that an even smaller fraction of the $\mathrm{H_2O^{17}}$ exchange can be occurring through a coupled path. Although the data are not very precise, the differences found are outside experimental error. The data are consistent with the treatment of the nmr effects as being controlled by chemical

TABLE IV

WATER AND THIOCYANATE EXCHANGE DATA

System	k_1 (25°), sec^{-1}	ΔH^*, kcal/mole	ΔS^*, cal/mole deg	A/h, cps
$[Ni(H_2O)_6]^{2+}$–H_2O^{17} [a]	2.7×10^4	11.6	0.6	4.3×10^7
$[Ni(NCS)_4(H_2O)_2]^{2-}$–H_2O^{17} [b]	1.1×10^6	6.0	−11	2.0×10^7
$[Ni(NCS)_4(H_2O)_2]^{2-}$–H_2O^{17} [c]	*ca.* 1.5×10^5	7.4	−5	*ca.* 3×10^7
$[Ni(NCS)_4(H_2O)_2]^{2-}$–NCS^- [b]	5.3×10^5	9.2	−1	2.2×10^7 (N^{14})

[a] T. W. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962). [b] *Ca.* 8.0 *M* KNCS. [c] *Ca.* 3.5 *M* NaNCS, 4.5 *M* $NaClO_4$.

exchange. It would, of course, be desirable to have some independent method to check on the rate data. Assuming that the results are correctly interpreted, there seems to be no way of distinguishing between processes involving independent water and thiocyanate exchange with the same species of nickel complex or with independent processes involving different nickel species. The predominant species are not necessarily the kinetically significant ones. The shift data, however would be more difficult to reconcile with effects due to minor species, requiring rather large values for the scalar coupling constants. We plan to turn to systems which seem to be better defined, such as the $Ni^{II} \cdot NH_3(aq)$ and $Co^{II} \cdot NH_3(aq)$ complexes, in order to pursue these exchange studies and to see how general such results are. Use of higher O^{17} enrichments and higher magnetic fields will be of considerable aid in obtaining more precise data.

Some data for comparisons are collected in Table IV. Substitution of water by thiocyanate in $[Ni(H_2O)_6]^{2+}$ appears to labilize the remaining water with a quite large decrease in ΔH^*. It may be that a *trans*-tetrathiocyanatodiaquonickel species with stretched Ni–O bonds is involved. This idea is consistent with the lower A/h value per water molecule in the substituted species. A plot of ΔH^* *vs.* A/h for the water data is linear (including the origin). This fact may not be significant but is consistent with the notion that replacement of water by thiocyanate results in weaker bonding (due to stretched bonds) with the remaining water.

We do not attach a large amount of significance to the NaNCS–$NaClO_4$ data as they are limited in number, and uncertainties about species and medium effects are considerable. The apparent difference in ΔH^* between the 8 *M* KNCS and the 3.5 *M* NaNCS–4.5 *M* $NaClO_4$ mixtures might be real and due to the importance of species such as the trithiocyanato at lower thiocyanate concentration. More work is needed before such effects can be clearly understood.

It seems to us rather significant that the water and thiocyanate exchanges should proceed independently and that further studies of this general nature will be of great interest in this field.

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Bonding in Crystalline Potassium Dicyanocuprate(I)[1,2]

BY JACK D. GRAYBEAL AND GARY L. McKOWN

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Using the known structure of $KCu(CN)_2$ and the experimentally determined electric field gradient tensor components and asymmetry parameter a model of the bonding, using sp^2-hybrid σ-bonding orbitals and d–π^* bonding, is developed. This model shows substantial agreement with experimental evidence. Other possible contributions to the bonding are discussed and their omissions justified.

Introduction

The determination of the components of the electric field gradient (EFG) tensor and asymmetry parameter at the copper nuclei,[3] the assignment of the infrared and Raman spectra,[4-6] and the previously determined crystal structure[7] of potassium dicyanocuprate(I), $KCu(CN)_2$, have provided a sufficient experimental basis for the development of a model for the bonding in the compound. The first prediction of the type bonding in $KCu(CN)_2$ was by Kruger and Meyer-Berkhout[8] following their initial observation of the nuclear quadrupole resonance (nqr) spectrum of a polycrystalline sample. Their assumption was that of a structure containing linear (NC–Cu–CN) units in which the Cu atom employed $p_z d_z$-hybrid orbitals for bonding. The subsequent crystal structure determination has shown this to be incorrect. The dia-

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(2) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(3) G. L. McKown and J. D. Graybeal, *J. Chem. Phys.*, **44**, 610 (1966).

(4) G. Moreau, H. Poulet, and J. P. Mathieu, *Bull. Soc. Franc. Mineral. Crist.*, **88**, 6 (1965).

(5) M. J. Reisfeld and L. H. Jones, *J. Mol. Spectry.*, **18**, 222 (1965).

(6) D. Cooper and R. A. Plane, *Inorg. Chem.*, **5**, 16 (1966).

(7) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).

(8) H. Kruger and U. Meyer-Berkhout, *Z. Physik*, **132**, 171 (1952).