Acta Chemica Scandinavica A 29 (1975) 855—860

Microwave Spectrum, Structural Parameters and Nuclear Quadrupole Coupling of *cis*-1-Chlorobuten-3-yne

FRED KARLSSON, MATS GRANBERG and RAGNAR VESTIN

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm,
S-104 05 Stockholm, Sweden

The microwave spectra of the two natural isotopic species of *cis*-1-chlorobuten-3-yne: $CH^{35}ClCHCCH$ and $CH^{37}ClCHCCH$ together with the monodeuterated species: $CH^{35}ClCHCCD$, have been measured and assigned in the region 26 500 – 40 000 MHz. The rotational constants A, B and C for the ground state as well as the centrifugal distortion constants Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K were determined.

The distance between the chlorine atom and the ethynyl hydrogen atom was determined to be 4.679 ± 0.005 Å from the change in moments of inertia due to isotopic substitution. The inertial moments corresponding to the average structure of $CH^{35}ClCHCCH$ were calculated from an estimated valence force field to confirm an electron diffraction investigation of the molecular structure. This force field was also used to predict the centrifugal distortion constants.

The nuclear quadrupole coupling constants χ_{aa} and χ_{bb} were calculated for the $CH^{35}ClCHCCH$ and $CH^{37}ClCHCCH$ species and further used to estimate the symmetry of the field gradient around the C – Cl-bond.

In contrast to *trans*-1-chlorobuten-3-yne,[1] which has a very simple microwave spectrum due to the near degeneracy to an almost prolate symmetric rotor, the spectrum of *cis*-1-chlorobuten-3-yne resisted our attempts at interpretation for nearly two years. Two other chemical isomers: 2-chlorobuten-3-yne[2] and 4-chlorobuten-3-yne[3] were successfully interpreted in the meantime although these investigations started later.

The main reason for our interest in the rotational spectrum of *cis*-1-chlorobuten-3-yne as well as its chemical isomers was to supply additional information for a detailed analysis of the molecular structure of these compounds with electron diffraction in the gas phase.[4] In fact it was the first preliminary structure data of *cis*-1-chlorobuten-3-yne from the electron diffraction experiments that made it possible to predict the rotational constants accurately enough for an assignment of the microwave transitions. On the other hand, the moments of inertia obtained from the analysis of the microwave spectrum have been valuable for confirming the structure obtained with electron diffraction.[5]

EXPERIMENTAL

Incomplete dehydrochlorination of 1,4-dichloro-2-butyne by alkali yields small amounts of *trans*- and *cis*-1-chlorobuten-3-yne.[6] These substances can be isolated from the reaction mixture and purified with gas-liquid chromatography. A mixture of the normal and deuterated species is most conveniently prepared by using D_2O and C_2H_5OD instead of normal water and ethanol in the dehydrochlorination reaction. Due to the strong alkaline milieu the hydrogen-deuterium exchange proceeds rapidly for the ethynyl group.

The microwave spectra were recorded on a Hewlett-Packard model 8460 A R-band spectrometer with a phase stabilized source oscillator. The recordings were made at room temperature or – 15 °C and at a pressure ranging from 10 to 50 mTorr. The frequency region was 26 500 – 40 000 MHz. The precision of the measured transitions was estimated to be 0.05 MHz.

MICROWAVE SPECTRUM

The region 26 500 – 40 000 MHz was swept at a rate of 1 MHz/s in order to assign the spectral transitions. Early calculations of the rotational constants from an assumed structure and calculations of the components of the dipole moments with the CNDO method suggested a spectrum mainly composed of Q-branch transitions active through the μ_b dipole moment.[4] These transitions are strong but very sensitive to the structural parameters of the molecule. The R-branch b-type transitions were hidden effectively among the numerous weak transitions of the spectrum. However, a good preliminary structure obtained from electron diffraction measurements [5] made it possible to guess successfully on the two strongest Q-branch b-type transitions in the region 26 500 – 40 000 MHz: $15_{2,13}\rightarrow15_{3,12}$ and $16_{2,14}\rightarrow16_{3,13}$. The identification was supported by the characteristic nuclear quadrupole hyperfine splitting into doublets for these two transitions.

Revealing the Q-branch part of the spectrum gave us two relations between the rotational constants: the differences A – C and the asymmetry parameter $\varkappa$.[7] The remaining relation, which is necessary for identifying the R-branch transitions can be obtained by assuming the inertial defect to be zero for a planar molecule. However, due to vibrational effects this is far from being true and we obtained a much closer estimate by calculating the inertial defect from a simple estimated force field.

The strongest Q-branch and R-branch b-type transitions for the two isotopic species $CH^{35}ClCHCCH$ and $CH^{37}ClCHCCH$ were measured with high resolution and, for the most abundant species $CH^{35}ClCHCCH$, the strongest lines of the weak R-branch a-type transitions were also observed and measured with high resolution: see Tables 1 and 2. The lines from

Table 1. The observed rotational transitions for *cis*-1-chlorobuten-3-yne, $CH^{35}ClCHCCH$, are given as $\nu_{obs} = \nu_{center} + \Delta\nu_i$ (in MHz) where ν_{center} is the center of the hypothetical unsplit line and $\Delta\nu_1$, $\Delta\nu_2$, $\Delta\nu_3$, and $\Delta\nu_4$ are the observed nuclear quadrupole hyperfine splitting of the rotational transition.

$CH^{35}ClCHCCH$							ν_{center}	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$
J'	K_{-1}'	K_{+1}'	J	K_{-1}	K_{+1}	μ	$J'_{K_{-1}'K_{+1}'}\leftarrow J_{K_{-1}K_{+1}}$	$F=J+\frac{3}{2}$	$F=J+\frac{1}{2}$	$F=J-\frac{1}{2}$	$F=J-\frac{3}{2}$
7	1	7	6	1	6	a	29 544.85	–	–	–	–
7	0	7	6	0	6	a	30 246.78	0.86	– 0.87	– 0.87	0.86
8	0	8	7	0	7	a	34 201.40	0.70	– 0.70	– 0.70	0.70
9	1	9	8	1	8	a	37 722.27	–	–	–	–
9	0	9	8	0	8	a	38 133.61	0.58	– 0.59	– 0.59	0.58
7	0	7	6	1	6	b	27 724.80	– 0.91	1.63	0.84	– 1.74
6	1	6	5	0	5	b	28 757.19	2.36	– 3.63	– 2.22	3.81
7	1	7	6	0	6	b	32 066.76	1.92	– 2.71	– 1.88	2.82
8	0	8	7	1	7	b	32 381.36	– 0.64	0.95	0.56	– 0.95
8	1	8	7	0	7	b	35 467.33	1.44	– 1.88	– 1.39	1.92
9	0	9	8	1	8	b	36 867.61	– 0.33	0.32	0.32	– 0.33
9	1	9	8	0	8	b	38 988.17	1.22	– 1.22	– 1.22	1.22
10	3	7	10	2	8	b	26 864.20	1.79	– 2.41	– 1.82	2.47
15	3	12	15	2	13	b	27 507.74	– 1.68	2.05	1.67	– 2.08
9	3	6	9	2	7	b	28 098.72	2.25	– 3.05	– 2.25	3.09
13	2	11	13	1	12	b	29 397.22	– 4.42	5.60	4.39	– 5.63
16	3	13	16	2	14	b	29 768.30	– 2.41	2.85	2.41	– 2.87
7	3	4	7	2	5	b	30 634.90	2.55	– 3.73	– 2.46	3.72
17	3	14	17	2	15	b	32 831.92	– 2.95	3.51	3.01	– 3.57
18	4	14	18	3	15	b	33 379.66	0.20	– 0.20	– 0.20	0.20
19	4	15	19	3	16	b	33 640.27	– 0.46	0.46	0.46	– 0.46
17	4	13	17	3	14	b	33 863.14	0.94	– 0.94	– 0.94	0.94
20	4	16	20	3	17	b	34 739.56	– 1.16	1.16	1.16	– 1.16
16	4	12	16	3	13	b	34 955.74	1.56	– 1.56	– 1.56	1.56
15	4	11	15	3	12	b	36 485.94	1.99	– 1.99	– 1.99	1.99
18	3	15	18	2	16	b	36 646.13	– 3.51	4.00	3.47	– 3.98
21	4	17	21	3	18	b	36 731.12	– 1.84	1.84	1.84	– 1.84
14	4	10	14	3	11	b	38 258.91	2.33	– 2.33	– 2.33	2.33
15	2	13	15	1	14	b	38 457.29	– 4.65	5.80	4.65	– 5.81
22	4	18	22	3	19	b	39 622.47	– 2.43	2.42	2.42	– 2.43

Table 2. The observed rotational transitions for *cis*-1-chlorobuten-3-yne, $CH^{37}ClCHCCH$, given as in Table 1.

$CH^{37}ClCHCCH$							ν_{center}	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$
J'	K_{-1}'	K_{+1}'	J	K_{-1}	K_{+1}	μ	$J'_{K_{-1}'K_{+1}'} \leftarrow J_{K_{-1}K_{+1}}$	$F=J+\frac{3}{2}$	$F=J+\frac{1}{2}$	$F=J-\frac{1}{2}$	$F=J-\frac{3}{2}$
7	0	7	6	1	6	b	27 136.85	−0.71	1.24	0.70	−1.35
7	1	7	6	0	6	b	31 565.52	1.45	−2.18	−1.39	2.23
8	0	8	7	1	7	b	31 724.43	−0.44	0.74	0.41	−0.78
9	0	9	8	1	8	b	36 144.98	−0.28	0.28	0.28	−0.28
9	1	9	8	0	8	b	38 339.32	0.95	−0.95	−0.95	0.95
15	3	12	15	2	13	b	27 029.35	−1.35	1.34	1.34	−1.35
16	3	13	16	2	14	b	29 103.73	−1.94	1.93	1.93	−1.94
17	3	14	17	2	15	b	31 961.42	−2.48	2.48	2.48	−2.48
18	4	14	18	3	15	b	33 226.55	—	—	—	—
19	4	15	19	3	16	b	33 314.06	—	—	—	—
17	4	13	17	3	14	b	33 836.88	0.83	−0.84	−0.84	0.83
20	4	16	20	3	17	b	34 198.86	−0.79	0.78	0.78	−0.79
16	4	12	16	3	13	b	35 007.97	1.27	−1.27	−1.27	1.27
18	3	15	18	2	16	b	35 562.47	−2.74	2.74	2.74	−2.74
21	4	17	21	3	18	b	35 941.44	−1.32	1.31	1.31	−1.32
15	4	11	15	3	12	b	36 569.18	1.68	−1.68	−1.68	1.68
22	4	18	22	3	19	b	38 560.42	−1.79	1.79	1.79	−1.79

Table 3. The observed rotational transitions for *cis*-1-chlorobuten-3-yne, $CH^{35}ClCHCCD$, given as in Table 1.

$CH^{35}ClCHCCD$							ν_{center}	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$
J'	K_{-1}'	K_{+1}'	J	K_{-1}	K_{+1}	μ	$J_{K_{-1}'K_{+1}'} \leftarrow J_{K_{-1}K_{+1}}$	$F=J+\frac{3}{2}$	$F=J+\frac{1}{2}$	$F=J-\frac{1}{2}$	$F=J-\frac{3}{2}$
7	1	7	6	0	6	b	30 631.32	1.97	−2.80	−2.08	3.06
8	0	8	7	1	7	b	30 857.18	−0.84	0.87	0.87	−0.84
8	1	8	7	0	7	b	33 870.41	1.61	−2.05	−1.59	2.12
9	0	9	8	1	8	b	35 144.75	−0.46	0.46	0.46	−0.46
9	1	9	8	0	8	b	37 223.25	1.25	−1.25	−1.25	1.25
10	0	10	9	1	9	b	39 295.14	−0.22	0.22	0.22	−0.22
16	3	13	16	2	14	b	28 333.92	−2.48	2.91	2.49	−2.92
17	3	14	17	2	15	b	31 181.81	−3.05	3.59	3.07	−3.60
18	4	14	18	3	15	b	32 065.09	0.26	−0.27	−0.27	0.26
19	4	15	19	3	16	b	32 229.20	−0.41	0.40	0.40	−0.41
17	4	13	17	3	14	b	32 594.76	1.05	−1.05	−1.05	1.05
20	4	16	20	3	17	b	33 180.50	−1.13	1.13	1.13	−1.13
16	4	12	16	3	13	b	33 686.88	1.65	−1.65	−1.65	1.65
18	3	15	18	2	16	b	34 749.03	−3.80	3.80	3.80	−3.80
21	4	17	21	3	18	b	34 974.17	−1.85	1.84	1.84	−1.85
22	4	18	22	3	19	b	37 623.15	−2.43	2.42	2.42	−2.43
24	5	19	24	4	20	b	39 525.94	—	—	—	—
23	5	18	23	4	19	b	39 856.32	−0.67	0.67	0.67	−0.67

the species $CH^{35}ClCHCCD$ in the spectrum of the deuterated samples were identified and measured with high resolution: see Table 3.

The rotational constants and five centrifugal distortion parameters were fitted to the observed spectrum by the least squares method: see Tables 4 and 5.

CENTRIFUGAL DISTORTION

The five centrifugal distortion parameters Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K were included in the least square fitting process of the rotational constants:[8,9] see Table 5. This was necessary to obtain a good fit. These constants were also calculated from the assumed structure

Table 4. Observed rotational constants in MHz for three isotopic species of *cis*-1-chlorobuten-3-yne.

	A	B	C
$CH^{35}ClCHCCH$	8942.40 ± 0.01	2572.271 ± 0.004	1994.994 ± 0.003
$CH^{37}ClCHCCH$	8857.50 ± 0.02	2519.494 ± 0.005	1958.967 ± 0.005
$CH^{35}ClCHCCD$	8569.43 ± 0.02	2450.872 ± 0.010	1903.284 ± 0.009

Table 5. Measured and calculated centrifugal distortion constants for three isotopic species of *cis*-1-chlorobuten-3-yne in kHz.

	$CH^{35}ClCHCCH$		$CH^{37}ClCHCCH$		$CH^{35}ClCHCCD$	
	obs.	calc.	obs.	calc.	obs.	calc.
Δ_J	2.20 ± 0.02	2.81	2.16 ± 0.05	2.72	2.07 ± 0.05	2.61
Δ_{JK}	−17.8 ± 0.1	−20.9	−17.8 ± 0.2	−20.4	−16.3 ± 0.5	−19.7
Δ_K	53. ± 1.	56.2	56. ± 2.	55.1	45. ± 5.	54.5
δ_J	0.700 ± 0.002	0.893	0.661 ± 0.005	0.859	0.672 ± 0.009	0.832
δ_K	3.3 ± 0.1	4.20	3.7 ± 0.2	4.09	2.3 ± 0.4	3.98

Table 6. The absolute values of the coordinates for the chlorine atom and the ethynyl hydrogen atom calculated with Kraitchman's equations and the distance between these atoms compared with the coordinates and the distance obtained from an electron diffraction investigation of the structure.[5] Conversion factor 505 376 (MHz) (au Å^2).

	Microwave spectroscopy (Å)		Electron diffraction (Å)	
Atom	|a|	|b|	|a|	|b|
Cl	1.4493	0.5345	1.454	0.535
H	3.1004	1.6263	3.113	1.627
Distance Cl−H	4.679		4.667	

and a simple estimated valence force field with force constants estimated from similar bonds in smaller molecules.[7]

The following symbols are used for the force constants according to Gribov.[10] K_i is the force constant for the stretching of the bond i, K_{ij} is the bending of the angle between the bonds i and j, ϱ_k^{ij} is the bending of the bond k out of the plane spanned by the bonds i and j, χ_{kl}^{ij} finally is the torsion between the planes spanned by the bonds i and j, and k and l, respectively.

The values of the constants are with the bond numbers of Fig. 1: $K_1 = 3.85$, $K_2 = 9.10$, $K_3 = 4.62$, $K_4 = 15.69$, $K_5 = 6.31$, $K_6 = 6.31$, $K_7 = 5.64$, $K_{12} = 0.85$, $K_{23} = 0.84$, $K_{26} = 0.53$, $K_{27} = 0.53$, $K_{34} = 0.32$, $K_{45} = 0.23$, $\varrho_2^{17} = 0.312$, $\varrho_2^{36} = 0.286$ and $\chi_{36}^{17} = 0.512$ in md/Å mdÅ and for stretching and bending constants, respectively. The same force constants were assumed for bending in plane and out of plane for the linear acetylenic group.

The theoretically obtained centrifugal distortion constants were valuable for the identification of the spectral lines. Especially some of the Q-branch transitions are strongly displaced by the centrifugal distortion.

MOLECULAR STRUCTURE

Nothing has been found that indicates a deviation from planarity in the molecular structure. The inertial defect for $CH^{35}ClCHCCH$ is 0.34 ± 0.02 au Å^2 and we obtained 0.39 au Å^2 with a theoretical calculation assuming planarity and using the previously mentioned force field.

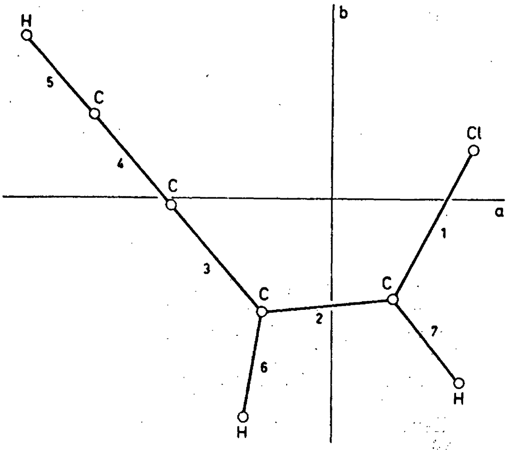

Fig. 1. Assumed structure of *cis*-1-chlorobuten-3-yne with principal axes of inertia.

The Cartesian coordinates for the chlorine atom and the ethynyl hydrogen atom were calculated in the principal axis system of the $CH^{35}ClCHCCH$ molecule from the change in the moments of inertia I_b and I_c on isotopic substitution:[11,12] see Table 6. These coordinates were in good agreement with those calculated from the electron diffraction study of the structure: see Table 6. The chlorine and the ethynyl hydrogen atom are well away from the principal axes and the moments of inertia are accurately determined, so that the main source of uncertainty is in the vibrational effects. Change in inertial defect and the effect of change in effective bond length with isotopic substitution will be most critical for the position of the hydrogen atom.[13] Therefore we expect the error of the hydrogen-chlorine distance to be about ±0.005 Å.

Throughout the entire investigation of the chlorobutenyne structures we have used the principal moments of inertia obtained from microwave spectroscopy to confirm the electron diffraction measurements.[4] The moments of inertia obtained with microwave spectroscopy derives from the effective rotational structure r_0.[14,15] For $CH^{35}ClCHCCH$: $I_a^0 = 56.514$, $I_b^0 = 196.471$ and $I_c^0 = 253.322$ au Å². Using the force field above, these moments were transformed to the corresponding average structure parameters: $I_a^z = 56.604$, $I_b^z = 196.855$ and $I_c^z = 253.405$ au Å². This was in good agreement with the values from the electron diffraction structure and this removed some remaining uncertainties there.[5]

QUADRUPOLE COUPLING

The rotational transitions are split into four observable peaks by the interaction of the rotation with the quadrupole moment of the chlorine nucleus.[7] However, in many cases the components overlap partially or completely so that only a doublet or a single line can be distinguished.

A least squares fitting of the quadrupole coupling constants χ_{aa} and χ_{bb} to the observed splittings into quartets or doublets was made with the LETAGROP method.[3,16] In order to avoid systematic errors, only splitting values greater than 0.70 MHz were accepted. The values obtained are for ^{35}Cl in $CH^{35}ClCHCCH$: $\chi_{aa} = 16.3 \pm 0.4$ and $\chi_{bb} = -46.8 \pm 0.2$ MHz and for ^{37}Cl in $CH^{37}ClCHCCH$: $\chi_{aa} = 11.8 \pm 0.8$ and $\chi_{bb} = -36.2 \pm 0.4$ MHz.

These constants can be transformed to the principal axis system of the quadrupole coupling tensor if we assume that one of these tensor axes coincides with the C–Cl bond and if we know the direction of the C–Cl bond in the principal axis system of the inertial moments: see Fig. 1. The coordinates of the chlorine atom could be calculated from the difference in the moments of inertia for the two isotopic species with ^{35}Cl and ^{37}Cl as described above but that was not possible for the carbon atom in the C–Cl bond due to the low natural abundance of the ^{13}C and the high costs of preparing ^{13}C enriched samples. However, since the coordinates of the chlorine and the ethynyl hydrogen atom are so close to the coordinates calculated from the electron diffraction structure it is reasonable to expect that the position of the carbon atom in the C–Cl bond obtained with electron diffraction is significant enough for the transformation of the coupling constants: see Table 6.

With the quadrupole tensor axis z parallel to the C–Cl bond and y perpendicular to the molecular plane we obtained the following principal values for ^{35}Cl in $CH^{35}ClCHCCH$: $\chi_{xx} = 39.3 \pm 0.7$ and $\chi_{yy} = 30.5 \pm 0.7$ MHz. The uncertainty limits are estimated from the measured deviation of the constants χ_{aa} and χ_{bb} and the assumption that the error in the coordinates of the carbon atom in the C – Cl bond is less than ± 0.005 Å.

According to Goldstein et al.[17] the difference $\chi_{xx}-\chi_{yy}$ is related to the numbers of electrons lost from chlorine as a result of double bonding δ, with $\delta=(\chi_{xx}-\chi_{yy})/164.6$. The value δ may be regarded as approximately defining the double bond character of the C – Cl bond. We obtained $\delta=0.05\pm0.01$. This value is comparable with $\delta=0.04$ obtained for vinyl chloride.[18] So the presence of the acetylene group does not seem to have any major effect on the double bond character of the C – Cl bond.

The principal components of the chlorine quadrupole coupling tensor for the $CH^{35}ClCHCCH$ molecule above are of course very uncertain due to the necessary assumptions but we were able to test them to some extent by calculating the χ_{aa} and the χ_{bb}-values for the $CH^{35}ClCHCCD$ molecule. The change in direction of the C – Cl bond in the principal axis system of inertial moments due to the deuterium substitution was estimated from the electron diffraction structure and the transformation yielded: $\chi_{aa}=19.2$ and $\chi_{bb}=-49.7$ MHz. The calculated hyperfine splitting of the rotational transitions for $CH^{35}ClCHCCD$ using the above constants agreed with those observed within the error of measurement.

Acknowledgements. We thank all those who have contributed to this paper and especially Dr. Stig Ljunggren and Mr. Hasse Karlsson for pleasant cooperation and valuable discussions.

REFERENCES

1. Karlsson, F. and Vestin, R. *Acta Chem. Scand.* *27* (1973) 3033.
2. Karlsson, F., Granberg, M. and Vestin, R. *Acta Chem. Scand. A* *28* (1974) 206.
3. Karlsson, F., Granberg, M. and Vestin, R. *Acta Chem. Scand. A* *29* (1975) 111.
4. Karlsson, F. *Chem. Commun Univ. Stockholm* (1974) No. 1.
5. Almenningen, A., Gundersen, G., Borg, A., Granberg, M. and Karlsson, F. *Acta Chem. Scand. A* *29* (1975) 395.
6. Vestin, R., Borg, A. and Lindholm, T. *Acta Chem. Scand.* *22* (1968) 687.
7. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Interscience, New York 1970.
8. Watson, J. K. G. *J. Chem. Phys.* *46* (1967) 1935.
9. Kirchhoff, W. H. *J. Mol. Spectrosc.* *41* (1972) 333.
10. Gribov, L. A. *Vvedenie v teoriyu i raschët kolebatelnȳkh spektrov mnogoatomnȳkh molekul*, Istadelstvo Leningradskogo Universita, 1965.
11. Kraitchman, J. *Amer. J. Phys.* *21* (1953) 17.
12. Costain, C. C. *J. Chem. Phys.* *29* (1958) 864.
13. Laurie, V. W. and Herschbach, D. R. *J. Chem. Phys.* *37* (1962) 1687.
14. Herschbach, D. R. and Laurie, V. W. *J. Chem. Phys.* *37* (1962) 1668.
15. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* *36* (1962) 1108.
16. Sillén, L. G. *Acta Chem. Scand.* *16* (1962) 159.
17. Goldstein, J. H. and Bragg, J. K. *Phys. Rev.* *75* (1949) 1453.
18. Gerry, M. C. L. *Can. J. Chem.* *49* (1971) 255.

Received April 3, 1975.