agreement with the result of 270 M^{-2} reported here when one considers that previously published figures for β_6 have differed by a factor of 2 × 10^7.

It is suggested, therefore, that there is no conclusive evidence for the existence of the species BiI_5^-, and

$$\frac{[BiI_7^{4-}]}{[BiI_6^{3-}][I^-]} = 1.4\ (\pm 0.1) \times 10^{-1}\ M^{-1}$$

$$\frac{[BiI_6^{3-}]}{[BiI_4^-][I^-]^2} = 2.70\ (\pm 0.05) \times 10^{2}\ M^{-2}$$

$$\frac{[BiI_4^-]}{[BiI_3(\text{solv})][I^-]} = 2.6\ (\pm 0.1) \times 10^{2}\ M^{-1}$$

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Vibrational Spectra and Force Constants of $Zn(NCO)_4^{2-}$, $Zn(NCS)_4^{2-}$, and $Zn(NCSe)_4^{2-}$ [1]

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The Raman spectra and supplementary infrared data are reported for the tetrahedral tetraisocyanate, -isothiocyanate, and -isoselenocyanate complex anions of the type $Zn(NCX)_4^{2-}$, X = O, S, Se. Vibrational assignments are given. A complete vibrational analysis and force constant calculation was carried out *via* Wilson's *F–G* matrix method using a general valence force field. Off-diagonal *F* matrix elements were included in certain cases. A significant increase in the C–X (X = O, S, Se) force constant is observed upon coordination of $N-C-X^-$. The C–N force constant is less affected. The potential energy distribution among the symmetry coordinates was calculated for each species and considerable mixing is evident in the low-energy modes of $Zn(NCSe)_4^{2-}$.

Introduction

There have recently been a number of infrared studies of metal pseudohalide complexes[2-6] in which assignments were made of the bands occurring below 600 cm^{-1}. In order to put these assignments on a firmer basis we have obtained Raman spectra and additional infrared data on zinc complexes of three pseudohalides. With fairly complete vibrational data in hand, we carried out complete vibrational analyses and force constant calculations for these complexes.

Experimental Section

The anions were studied in the form of their tetraethylammonium salts. The preparations of these compounds have been described previously: $[(C_2H_5)_4N]_2[Zn(NCO)_4]$,[7] $[(C_2H_5)_4N]_2[Zn(NCS)_4]$,[4] and $[(C_2H_5)_4N]_2[Zn(NCSe)_4]$.[8] The tetraethylammonium cation was chosen for two reasons: (a) its large size confers on the compounds a high solubility in organic oxy solvents (*i.e.*, about 100% w/w in nitromethane) and (b) it has no absorption in the 700–100-cm^{-1} region in the infrared. The spectra were run in organic solvents to eliminate the solvolysis effects possible in aqueous solutions.

The infrared spectra in the range 3000–200 cm^{-1} were obtained with a Beckman IR 12 spectrophotometer and in the range 200–130 cm^{-1} with a Perkin-Elmer 301 spectrophotometer. Raman spectra were obtained with a Cary 81 spectrophotometer.

Considerable experimental difficulty was encountered in an attempt to obtain the Raman spectrum of the isoselenocyanate complex, since it tended to decompose fairly rapidly in the tube, depositing a thin film of a red material (presumably red elemental selenium or polymeric selenocyanogen) on the walls.

Results

The vibrational frequencies observed are listed in Table I.

The infrared results for $[(C_2H_5)_4N]_2[Zn(NCO)_4]$ were taken from ref 2, except for ν_{11} which was observed in nitromethane solution. (The numbering and descriptions of the fundamental vibrations are those of Miller and Carlson.[9]) The Raman results were obtained on a saturated nitromethane solution. The uncertainty in the position of ν_3 is because of the overlap of ν_3 and ν_{11}.

The data for the isothiocyanato complex are the most complete of the three ions studied. The infrared and Raman spectra for $Zn(NCS)_4^{2-}$ are shown in Figures 1 and 2. We have not observed any combinations which might involve the inactive T_1 modes. The lowest energy E and T_2 fundamentals were also not observed; however, our calculations (*vide infra*) indicate that these N–Zn–N bending modes occur at very low frequencies (<40 cm^{-1}). Some doubt must remain about the assignments of ν_5 and ν_{13}, since the band at 168 cm^{-1} represents a solid-state infrared measurement. It is possible that the band at 150 cm^{-1} observed in the Raman spectrum of a solution is the T_2 mode (Raman and infrared active) shifted from its position in the solid state. However, none of the other T_2 funda-

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF-49(638)-1492.

[2] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965).

[3] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

[4] A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).

[5] C. W. Frank and L. B. Rogers, *ibid.*, **5**, 615 (1966).

[6] R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966).

[7] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 2790 (1964).

[8] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 1712 (1965).

[9] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

TABLE I

VIBRATIONAL FREQUENCIES OF THE TETRAPSEUDOHALOZINCATES (CM^{-1})[a]

Zn-$(NCO)_4^{2-}$	Zn-$(NCS)_4^{2-}$	Zn-$(NCSe)_4^{2-}$	Designation[e]		Description
2242	2108	2106	ν_1	A_1	C–N str
1340	836	664	ν_2	A_1	C–X str
~330	255	. . .	ν_3	A_1	M–N str
. . .	466[b]	. . .	ν_4	E	N–C–X def or θ bend
. . .	150	. . .	ν_5	E	Zn–N–C def or π bend
. . .	. . .	. . .	ν_6	E	N–Zn–N def
. . .	. . .	. . .	ν_7	T_1	N–C–X def or θ bend
. . .	. . .	. . .	ν_8	T_1	Zn–N–C def or π bend
2208	2084[d]	2086[d]	ν_9	T_2	C–N degenerate str
1326	831	661	ν_{10}	T_2	C–X degenerate str
326	285	~235	ν_{11}	T_2	M–N degenerate str
624	483[b,d]	434	ν_{12}	T_2	N–C–X def or θ bend
187	168[c]	165[c]	ν_{13}	T_2	Zn–N–C def or π bend
. . .	. . .	. . .	ν_{14}	T_2	N–Zn–N bend

[a] All values are solution measurements in nitromethane unless otherwise noted. [b] Observed in acetone solution. [c] Solid-state measurement. [d] Observed in infrared and Raman spectra. [e] A_1 and E modes are Raman active, T_1 are inactive, and T_2 are both infrared and Raman active.

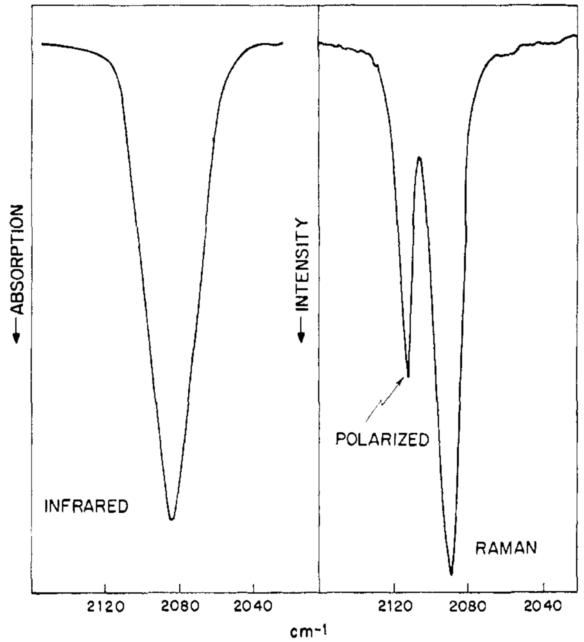

Figure 1.—C–N stretching regions of the infrared and Raman spectra of $Zn(NCS)_4^{2-}$ in nitromethane solution.

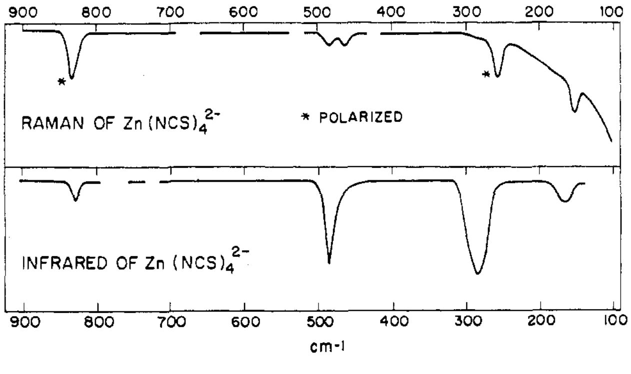

Figure 2.—Low-frequency regions of the infrared and Raman spectra of $Zn(NCS)_4^{2-}$ in nitromethane solution (except for the 400-500-cm^{-1} regions which were recorded in acetone solutions). Base line gaps indicate cation absorptions.

mentals shows solid to solution shifts of more than 5 cm^{-1}.

The infrared spectrum of the $Zn(NCO)_4^{2-}$ ion was previously[2] interpreted on the basis of T_d symmetry. This was because of the lack of splitting of the T_2 modes. Recently it has been found[10] that in the isoelectronic $Zn(N_3)_4^{2-}$ ion the degeneracy of the T_2 modes has been lifted, presumably because the Zn–N–N angle is considerably less than 180°. The infrared spectra of $Zn(NCS)_4^{2-}$ and $Zn(NCSe)_4^{2-}$ resemble $Zn(NCO)_4^{2-}$ rather than $Zn(N_3)_4^{2-}$, and we have therefore assigned the spectra on the basis of T_d symmetry. Of course, this is not to say that the Zn–N–C–X groups are rigorously linear. Small deviations might not produce splittings of the T_2 modes large enough to be detected in the infrared spectra.

Calculations.—Vibrational analyses were carried out for the three ions using the standard Wilson *F–G* matrix method.[11] The symmetry coordinates for a T_d $M(XYZ)_4$ species were obtained and, along with expressions for the symmetry force constants in terms of the internal valence force constants, have been deposited with the ADI.[12] The meanings of the principal internal valence force constants are obvious from Figure 3. The only interaction force constants of importance here for which the notation is not obvious are those of the type $f'_{XY,YZ}$ and $f''_{XY,YZ}$, etc., where the single prime refers to interactions within the same MXYZ group while the double primes refer to interactions between different MXYZ groupings.

The *G*-matrix elements were calculated by means of a computer program developed by Schachtschneider.[13] The bond distances used in the computation were: for $Zn(NCO)_4^{2-}$, Zn–N = 2.00 A, N–C = 1.18 A, C–O = 1.18 A; for $Zn(NCS)_4^{2-}$, Zn–N = 2.00 A, N–C = 1.15 A, C–S = 1.75 A; for $Zn(NCSe)_4^{3-}$, Zn–N = 2.00 A, N–C = 1.15 A, C–Se = 1.75 A.[14]

The secular equation was then solved with a computer program also developed by Schachtschneider.[13] The calculation used the Jacobian method to obtain the best set of force constants for the observed frequencies.

Some assumptions are necessary in solving the secular determinant. Since the lowest energy E and T_2 modes have not been observed for any of the anions, it is necessary to estimate the E and T_2 *F*-matrix elements. Both of these modes are essentially N–Zn–N

(10) D. Forster and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1510 (1966).

(11) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(12) Document No. 9229, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(13) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 117 (1963).

(14) $Ni(CO)_4$ was used as a test problem for the *G*-matrix program and a small error was found in the published *G*-matrix of an $M(XY)_4$ species. Element G_{78} should read

$$-2^{1/2}\left[\frac{8\mu_M}{3x^2} + \mu_X\left(\frac{1}{x^2} + \frac{1}{xy}\right)\right]$$

[See H. Murata and K. Kawai, *J. Chem. Phys.*, **26**, 1355 (1957).]

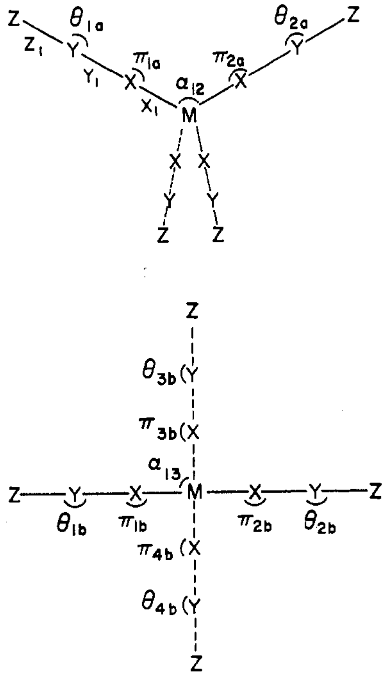

Figure 3.—Internal coordinates of $M(XYZ)_4$.

bending. Now in $Ni(CO)_4$ the C–Ni–C bending force constant is 0.23 mdyne-A/radian^2,[15] and since the Zn–N bond distance is expected to be longer than the 1.83-A Ni–C distance, a slightly smaller force constant (0.20) has been assumed in this work. Also it is necessary to estimate values for the off-diagonal N–C, C–X (X = O, S, Se) interaction constants since it would require data from isotopically substituted molecules to determine these constants accurately. The free-ion values of 1.34[16] and 0.9[17] mdynes/A for the isocyanate and isothiocyanate complexes, respectively, have been taken as reasonable approximations. Unfortunately, no value is available for the free selenocyanate ion since the reported study[18] of the vibrational spectrum of this ion did not include isotopic substitution. We have therefore carried out the calculation on the $Zn(NCSe)_4^{2-}$ ion in two ways: (i) with an estimated $f'_{NC,CSe}$ interaction constant of 0.5 mdyne/A and (ii) without an interaction constant, in order to obtain a comparison with the reported free-ion stretching force constants.

$Zn(NCO)_4^{2-}$.—A solution was attempted neglecting all off-diagonal elements except $f'_{NC,CO}$ ($f''_{NC,CO}$ being set equal to zero). Perfect agreement between the calculated and observed frequencies can be obtained with the set of force constants (rounded off to two decimal places) listed in Table II (approximation A). The distribution of the potential energy among the symmetry coordinates is given in Table V and shows that the original assignments[2] are correct, although the low-energy bending modes are considerably mixed, and therefore the calculated value of F_π of T_2 is not expected to be very accurate. In this case ν_3 and ν_{11} appear to be fairly accurately described as metal–nitrogen stretching modes. This solution is not entirely satisfactory because of the comparatively large, negative $f'_{CO,CO}$ interaction constant necessary. In view of the number of bonds separating the C–O bonds, it is much more likely that $f'_{CO,CO}$ is negligible. Therefore a solution was attempted in which F_{CO} of A_1 was set equal to F_{CO} of T_2 (approximation B). The force constants listed in Table II give the frequencies also in Table II which are in good agreement with the observed values.

TABLE II

FORCE CONSTANTS FOR $Zn(NCO)_4^{2-}$

	Approx A[a]	Approx B[b]
f_{CN}, mdynes/A	14.435	14.57
f_{CO}, mdynes/A	12.61	12.50
f_{MN}, mdynes/A	1.80	1.77
f_θ, mdyne-A/radian^2	0.59	0.59
f_π, mdyne-A/radian^2	0.24	0.24
f_α, mdyne-A/radian^2	0.20[c]	0.20[c]
$f'_{NC,CO}$, mdynes/A	1.35[c]	1.35[c]
$f'_{CN,CN}$, mdyne/A	0.275	0.13
$f'_{CO,CO}$, mdyne/A	−0.22	0
$f'_{MN,MN}$, mdyne/A	0.40	0.37

[a] This set of force constants reproduces the observed frequencies exactly. [b] Using this approximation, the following set of frequencies (cm^{-1}) was obtained: A_1: 2246, 1359, 324; E (approximate values, see text): 624, 192, 37; T_1 (approximate values, see text): 621, 164; T_2: 2209, 1320, 624, 326, 187, 42. [c] Assumed value.

The values calculated for the E and T_1 modes were obtained simply by using the T_2 *F*-matrix elements and therefore must be considered as only very approximate. The calculated value of ν_{14}, the N–Zn–N bending mode, is probably a reasonable approximation since changing f_α from 0.20 to 0.23 mdyne-A/radian^2 changes the calculated value of ν_{14} by only 1 cm^{-1}.

The principal force constants obtained by both procedures appear to be reasonable. Comparison of the C–N and C–O force constants with the reported values of the free ion are not meaningful since the frequencies of $Zn(NCO)_4^{2-}$ have not been corrected for anharmonicity. If the free-ion values are calculated without an anharmonicity correction, but keeping $f'_{CN,CO}$ equal to 1.35 mdynes/A, one obtains f_{CN} = 14.99 and f_{CO} = 11.01 mdynes/A. Comparison of these values with f_{CN} and f_{CO} of the complexed isocyanate indicates a considerable increase in the C–O force constant on coordination of the ion.

$Zn(NCS)_4^{2-}$.—When a solution was attempted neglecting all off-diagonal *F*-matrix elements except $f'_{NC,CS}$, a good fit between the calculated and observed frequencies could not be obtained for the bending modes. The potential energy distribution (see Table V) indicates a considerable amount of mixing between θ and π modes. Therefore a small (0.1 mdyne-A/radian^2) off-diagonal $F_{\pi\theta}$ interaction constant was introduced.

Perfect agreement between calculated and observed frequencies could then be obtained with the force constants listed in Table III (approximation A). The calculated value of f_θ using this procedure is quite close to the free-ion NCS bending force constant which adds

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(15) L. H. Jones, *J. Mol. Spectry.*, **5**, 133 (1960).
(16) A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959).
(17) L. H. Jones, *ibid.*, **25**, 1069 (1956).
(18) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

TABLE III

FORCE CONSTANTS FOR $Zn(NCS)_4{}^{2-}$

	Approx A[a]	Approx B[b]	Approx C[c]
f_{CN}, mdynes/A	15.57	15.57	15.63
f_{CS}, mdynes/A	5.46	5.46	5.29
f_{MN}, mdynes/A	1.67	1.68	1.68
$f_{\theta} + f'_{\theta,\theta}$, mdyne-A/radian^2	0.57	0.59	0.59
$f_{\pi} + f'_{\pi,\pi}$ mdyne-A/radian^2	0.20	0.18	0.18
f_{α}, mdyne-A/radian^2	0.20[d]	0.20[d]	0.20[d]
$f'_{CN,CS}$, mdyne/A	0.90[d]	0.90[d]	0.90[d]
$f'_{\theta,\pi}$, mdyne-A/radian^2	0.10[d]	0.10[d]	0.10[d]
$f'_{CN,CN}$, mdyne/A	0.07	0.07	0.02
$f'_{CS,CS}$, mdyne/A	−0.16	−0.16	0.00[d]
$f'_{MN,MN}$, mdyne-A/radian^2	0.40	0.39	0.39
$f''_{\theta,\theta}$, mdyne-A/radian^2	0.018	0.00[d]	0.00[d]
$f''_{\pi,\pi}$, mdyne-A/radian^2	−0.041	−0.016	−0.016

[a] This set of force constants reproduces the observed frequencies exactly. [b] This set of force constants reproduces the observed frequencies exactly except for $\nu_5 = 156$ and $\nu_{13} = 160$ cm^{-1}. [c] This set of force constants produces the frequencies (cm^{-1}): A_1: 2108, 855, 256; E: 465, 156, 22; T_1: 479, 136; T_2: 2084, 811, 483, 285, 160, 29. Values for E and T_1 were obtained using the T_2 F-matrix elements and therefore were not expected to be very accurate. [d] Assumed values.

some justification for the introduction of the π,θ interaction constant. The other principal force constants also appear to be quite reasonable but some of the interaction constants seem unrealistic. It is most likely that $f'_{\theta\theta}$ and $f''_{\theta\theta}$ will be negligible because of the large nonbonded separations and therefore a solution to the secular equation was attempted setting $F_{\theta}{}^{E} = F_{\theta}{}^{T_2}$. Agreement between the calculated and observed values was then obtained for all except the E and T_2 π bends for which values of 156 and 160 cm^{-1} were obtained with the force constants listed in Table III (approximation B). The value of f_{θ} which results is quite close to the free-ion value[17] of 0.30 mdyne/A which seems reasonable.

Further as with the isocyanate complex it seems likely that $f'_{CS,CS}$ will be negligible. Therefore the secular equation was solved setting $F_{CS}{}^{A_1} = F_{CS}{}^{T_2}$. With this assumption, the frequencies listed in Table III are obtained with the force constants given (approximation C).

All of these procedures lead to very similar values for the principal stretching force constants f_{CN}, f_{CO}, and f_{MN} which is gratifying. The C–N and C–S force constants may be compared with the free-ion values of 15.51 and 4.98 mdynes/A, respectively (calculated from Jones' data[17] without correcting for anharmonicity and setting $f'_{NC,\ CS} = 0.9$ mdyne/A). The difference between the C–N force constant for the free and complexed thiocyanate is probably not significant. However the apparent increase in the C–S force constant on coordination is probably meaningful and can be rationalized in terms of canonical structures. Of the structures (a) $N{\equiv}C{-}S^-$, (b) $N{=}C{=}S$, and (c) $^{2-}N{-}C{\equiv}S^+$, Jones[17] calculated that form a contributes 71% in the free ion, and it seems probable that, when an isothiocyanate complex is formed, there will be an electron drift toward the nitrogen favoring forms b and c. The calculated Zn–N force constant is smaller than in the isocyanate complex. However we do not attach much significance to this difference. Thus the calculated Zn–N stretches are only 5 and 10 cm^{-1} too high for the A_1 and T_2 modes, respectively, if one uses the isocyanate force constant values. It seems likely that the difference arises mainly from differing amounts of coupling between the Zn–N and C–X stretching modes. In order to obtain an idea of the magnitude of this coupling in the isothiocyanate complex, the secular equations were solved using the isocyanate values of f_{MN} and $f'_{MN,MN}$ and varying $F_{ZnN,CS}{}^{A_1}$ and $F_{ZnN,CS}{}^{T_2}$ to obtain agreement with the observed values. Good agreement between the calculated and observed frequencies could be obtained with $f'_{ZnN,CS} = -0.265$ and $f''_{ZnN,CS} = 0.106$ mdyne/A. These interaction constants seem quite reasonable in view of the mixing evident in the potential energy distribution (see Table V).

$Zn(NCSe)_4{}^{2-}$.—This is the least satisfactory case of the three ions studied. Of course the experimental data are less complete, but, apart from this, it rapidly became obvious during the course of the calculations that several off-diagonal elements would be necessary in order to reproduce the observed frequencies.

It appears to be essential to have an off-diagonal $f_{\theta,\pi}$ interaction constant of about 0.15 mdyne-A/radian.^{2} It is then possible to reproduce the observed bending mode frequencies with a value of f_{θ} about the same as the free-ion value of 0.25 mdyne/A.[18] The force constants in Table IV yield the frequencies listed.

TABLE IV

FORCE CONSTANTS FOR $Zn(NCSe)_4{}^{2-}$

Approximation A[a]

f_{CN}	= 15.67 mdynes/A	f_{α}	= 0.20 mdyne-A/radian^2 (assumed value)
f_{CSe}	= 4.055 mdynes/A	$f'_{\theta\pi}$	= 0.15 mdyne-A/radian (assumed value)
f_{MN}	= ∼1.5 mdynes/A	$f'_{CN,CSe}$	= 0.50 mdyne/A (assumed value)
f_{θ}	= 0.52 mdyne-A/radian^2	$f'_{CN,CN}$	= 0.06 mdyne/A
f_{π}	= 0.28 mdyne-A/radian^2	$f'_{CSe,CSe}$	= −0.245 mdyne/A
		$f'_{MN,MN}$	= 0.4 mdyne/A (assumed value)

[a] Using this approximation the following set of frequencies (cm^{-1}) is obtained: A_1: 2106, 664, 166; E: 434, 175, 17; T_1: 427, 149; T_2: 2088, 652, 433, 244, 152, 22. The values for E and T_1 are rough estimates only; the corresponding T_2 F-matrix elements were used for the E and T_1 blocks.

An unrealistically large f_{π} force constant would be required to fit the observed value of 165 cm^{-1} for the π-bending mode. This probably arises because there is appreciable interaction between the T_2 M–N stretch (ν_{11}) and the T_2 π bend (ν_{13}) as evidenced by the potential energy distribution (Table V). In order to determine the effect of this interaction we have introduced an off-diagonal $F_{MN,\pi}$ interaction constant of 0.1 mdyne/radian which is the same value as that used in $Ni(CO)_4$.[15] The main difference from the frequencies

TABLE V

POTENTIAL ENERGY DISTRIBUTION (IN PER CENT)

$Zn(NCO)_4^{2-}$ calculated from force constants in Table II (Approx. B)

	A_1			E			T_2					
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}
$V_{CN,CN}$	69	25	7				67	30	4			
$V_{CO,CO}$	39	59	1				43	57	1			
$V_{CN,CO}$	-10	7	3				-11	8				
$V_{MN,MN}$	2	9	89				1	5	85		8	
$V_{\theta,\theta}$				84	14	2			2	84	13	2
$V_{\pi,\pi}$				15	51	34			3	15	53	29
$V_{\alpha,\alpha}$				1	35	64			5	1	26	69

$Zn(NCS)_4^{2-}$ calculated from force constants in Table III (Approx. C)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}
$V_{CN,CN}$	93	2	7				94	3	3			
$V_{CS,CS}$	10	76	14				11	82	7		1	
$V_{CN,CS}$	-6	2	2				-6	3	1			
$V_{MN,MN}$	3	20	77				1	11	75		12	
$V_{\theta,\theta}$				109	3				2	100	6	
$V_{\pi,\pi}$				19	37	57			4	27	41	38
$V_{\theta,\pi}$				-30	7	-2				-29	9	2
$V_{\alpha,\alpha}$				2	53	45			8	2	31	60

$Zn(NCSe)_4^{2-}$ calculated from force constants in Table IV

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}
$V_{CN,CN}$	94		7				94	3	3		1	
$V_{CSe,CSe}$	6	62	33				8	77	10		5	
$V_{CN,MSe}$	-3		1				-3	2				
$V_{MN,MN}$	3	38	59				1	18	49		30	1
$V_{\theta,\theta}$				106	12				6	106	6	
$V_{\pi,\pi}$				44	35	40			10	46	31	33
$V_{\theta,\pi}$				-53	15	1			6	-55	11	1
$V_{\alpha,\alpha}$				3	38	59			16	3	16	65

calculated by approximation A is that ν_{11} and ν_{13} are moved to 233 and 160 cm^{-1}, respectively.

The approximations described above used a C–N, C–Se stretch–stretch interaction constant which was essentially a guess but which gives a reasonable C–N force constant in comparison with the isothiocyanate complex. If the calculation is carried out without this interaction constant, one can fit the observed frequencies fairly well with $f_{CN} = 15.08$, $f'_{CN,CN} = 0.075$, $cf_{Se} = 4.29$, and $f'_{CSe,CSe} = -0.31$ mdyne/A, with the other force constants remaining as in Table IV. These C–N and C–Se force constants can be compared with the calculated[18] free-ion values of 15.10 and 3.88 mdynes/A, respectively. The C–N force constants both for the free and complexed ion, calculated without an $f'_{CN,CSe}$ interaction are appreciably less than the C–N force constant of the free or complexed thiocyanate ion. In view of the fact that the C–N stretching frequencies for both the free and complexed selenocyanate ion are almost coincident with the corresponding values for thiocyanate, this is not reasonable. In fact the C–N force constant in the selenocyanate should, if anything, be slightly greater than that in the thiocyanate ion. It is for this reason that we have included a stretch–stretch interaction in the calculation indicated in Table IV.

The Zn–N force constant obtained is less than in the isothiocyanate complex. However the value must not be regarded as very accurate because we have not included the $f'_{ZnN,\alpha}$ or $f'_{CSe,ZnN}$ interaction constants although the potential energy distribution (Table V) indicates appreciable mixing between ν_{10}, ν_{11}, and ν_{13} in the T_2 block. This problem is much more important in this case than in the cyanate case because now the five lowest T_2 fundamentals are much closer together in energy.

Conclusions.—In all three cases treated there appears to be an increase in the C–X force constant upon coordination. According to the canonical structures given for NCS^- (*vide supra*), this should be accompanied by a decrease in the CN force constant. This has been observed for the isocyanate complex but not for the other complexes. This may be connected with the lack of an off-diagonal $f'_{MN,CN}$ interaction constant.

The metal–nitrogen stretching force constant of $Zn(NCO)_4^{2-}$ is probably the most reliable of the three ions studied, since the potential energy distribution indicates that the description of "metal–nitrogen" stretch becomes less adequate as the pseudohalide becomes heavier. Thus for the isoselenocyanate complex, in particular, an accurate metal–nitrogen force constant could be obtained only if several off-diagonal elements were known. Nevertheless, it appears safe to say that the zinc–nitrogen force constant in the complexes studied is slightly higher than the zinc–carbon force constant (1.30 mdynes/A) in $Zn(CN)_4^{2-}$.[19]

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[19] L. H. Jones, *Spectrochim. Acta*, **17**, 188 (1961).