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Vibrational Spectra of N-Cyanodithiocarbimates

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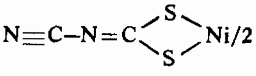
Received December 14, 1970

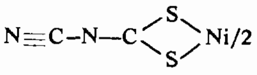
The vibrational spectra of N–cyanodithiocarbimates have been discussed on the basis of a normal coordinate analysis of the infrared spectrum of bis(N–cyanodithiocarbimato)Ni^{II} anion. The potential energy was expressed in terms of a simple Urey Bradley force field except for the C–S, C–S, and M–S, M–S interactions. The vibrational mixing was found to be less when compared with the related systems like dialkyl dithiocarbamates.

Introduction

Vibrational spectra of dialkyl and diaryldithiocarbamates have been widely studied earlier.[1,2] But the closely related system, *viz.* N–Cyanodithiocarbimate, has not been studied much in detail. However, the X-ray crystallographic studies[3] and the infrared spectrum[4] of the nickel complex have been reported. In continuation of our studies[5-7] of the vibrational spectra of metal complexes containing the metal sulfur bond, an attempt has been made in the present paper to understand the infrared spectrum of bis(N–cyanodithiocarbimato)Ni^{II} anion on the basis of normal coordinate analysis. The infrared spectrum of $Cs_2[Ni(C_2N_2S_2)_2]$ has been compared with those of $[(C_3H_7)_4N]_2[Ni(C_2N_2S_2)_2]$ and $K_2(C_2N_2S_2)_2$. As has been suggested by earlier workers[8] the present calculations also support the preponderance of Structure I over Structure II in the nickel complex. The values of the stretching force constants of the C–N bonds indicate that Structure I has a higher contribution than Structure II, in agreement with the values of the bond distances.[3]


$N{\equiv}C{-}N{=}C\langle^{S}_{S}\rangle Ni/2$

(I)


$N{\equiv}C{-}N{-}C\langle^{S}_{S}\rangle Ni/2$

(II)

Experimental Section

The caesium and tetrapropylammonium salts of $[Ni(C_2N_2S_2)_2]^{2-}$ were prepared by the known methods.[5,8] The potassium salt of N–cyanodithiocarbimate was also prepared by a known method.[5] The infrared spectra of the above compounds were recorded on a Perkin-Elmer Model No. 521 diffraction grating double beam spectrophotometer in the region 3500 cm^{-1} to 250 cm^{-1}. Samples were studies as KBr discs. All the spectra were calibrated with polystyrene in the region 700 cm^{-1} to 3500 cm^{-1}. The calibration in the region 250 cm^{-1} to 700 cm^{-1} was carried out with a mixture of 33.3% each by weight of indene, camphor and cyclohexanone.

Calculations

The anion of the nickel complex of N–cyanodithiocarbimate has a planar C_{2h} symmetry.[3] However, the model chosen for the calculations (Figure 1) is one-half of the molecule. This assumption is not very serious except for those vibrations involving the ν(M–S) and δ(S–M–) modes.[9,10] The calculations were performed treating the system as a seven body problem. The present model has a Cs symmetry and the normal modes may be grouped into two classes, $(11A'+4A'')$. In the present paper only the 11 inplane A′ vibrations have been calculated. The internal coordinates are shown in Figure 1 and the structural parameters[3] assumed are listed in Table I. The

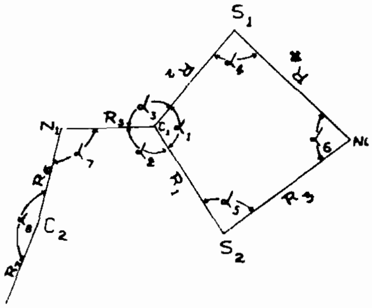


Figure 1 Molecular model used for calculation.

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Table I. Molecular Parameters and Force Constants.

Internal coordinates	Bond distance Å	Stretching force constant md/Å	Internal coordinates	Bond angles (deg)	Bending force constant md/Å	Repulsive force constants md/Å	
R_1	1.75	2.67	L_1	108°	0.11	$S_1...S_2$	0.07
R_2	1.69	3.51	L_2	120°	0.11	$N_1...S_1$	0.20
R_3	2.19		L_3	132°	0.10	$N_1...S_2$	0.11
R_4	2.19	1.22	L_4	85.5°	0.10	$C_1...Ni$	0.10
R_5	1.29	6.40	L_5	87°	0.10	$C_1...C_2$	0.20
R_6	1.34	6.35	L_6	79°	0.10	$N_1...N_2$	0.20
R_7	1.17	15.25	L_7	115°	0.10	C_1—S_1	—0.36
						· C_1—S_2	
			L_8	173°	0.08	M—S_1	—0.18
						· M—S_2	

Table II.

Observed	Calculated	Percent contribution of predominant coordinates
cm^{-1}	cm^{1-}	18.5%νC_2—N_1+81.3%νC_2≡N_2
2160	2161	78.55%νC_1=N_1+5.4%νC_2—N_1
1425	1427	41%νC_1=N_1+71.5%νC_2—N_1+14.5%νC_2=N_2
1025	1024	37.5%ν_1—S_1+43.8%νC_2—S_2+4.7%δL_2+5%δL_3
965	964	47.9%νC_1—S_1+30.9%νC_1—S_2+9.7%νC_1=N_1
525	525	39.9%νM—S_1+43.3%νM—S_2+5.3%δL_4+4.5%δL_5
345	345	35.8%νM—S_1+37.6%νM—S_2+11.1%δL_1+3.5%δL_2
335	334	+1.3%δL_3+3.2%δL_4+4.0%δL_5
290	289	7%νC_1—S_1+13%νNi—S_2+6%δL_3+6%δL_5+42%δL_7
—	230	Skeletal deformation
—	135	δN_2—C_2—N_1
—	122	Skeletal deformation

potential energy was expressed in terms of a simple U.B.F. field except for the introduction of two interaction constants (one between the two C–S bonds and the other between the two (M–S) bonds in the sense of a generalized valence force field. The force constants were transferred from the reported work on related systems.[11,12] The inplane GF-matrix was symmetrized by the standard procedure[13] and diagonalized. The best set of force constants obtained after several trials is listed in Table I. In Table II the calculated frequencies are compared with the observed ones and an approximate description of each frequency has been given.

Results and Discussion

In the spectrum of $Cs_2[Ni(C_2N_2S_2)_2]$, the band at 2160 cm^{-1} may be assigned to the ν(C_2≡N_2) mode. This band apears at 2185 cm^{-1} in the corresponding tetrapropylammonium salt.[4] The lowering of the frequency in the case of the caesium salt may be attributed to the difference in the interactions of the two cations in question with the anion of the $[Ni(C_2N_2S_2)_2]^{2-}$. In the case of the nickel complex the cation has a closest approach to the anion only from the nitrogen end of the anion. The caesium ion is smaller in size than the tetrapropyl ammonium ion and thus the former will be able to polarize the electron density of the C_2≡N_2 bond towards the nitrogen to a greater extent than the latter. This kind of interpretation has been proposed earier by Cotton[3] and coworkers to interpret the spectra of N–cyanodithiocarbimate and its salts with potassium and tetraphenylarsonium ions. The ν(C_2—N_1) and ν(C_1—N_2) modes are coupled and give rise to two absorptions at 1425 cm^{-1} and 1025 cm^{-1}. The potential energy distribution shows that the normal coordinates of these frequencies do not have any appreciable contribution from any of the ν(C—S) modes. This supports the predominance of Structure I. The two (C—S) bonds are close to each other and interact strongly. The bond order of these bonds is appreciably higher than one (this will be one only if there is no contribution from Structure II) and thus two absorptions are expected,[5,14,15] one in the range 900 cm^{-1} to 1000 cm^{-1} and the other in the range 500 cm^{-1} to 600 cm^{-1}. Thus the absorptions at 965 cm^{-1} and 525^{-1} in the caesium salt of the nickel complex may be assigned to these ν(C—S) modes. The assignment of the 525 cm^{-1} band to a ν-(C—S) mode may be equivocal because of the presence of another band at 570 $^{-1}$. However, the assignment of the 570 $^{-1}$ band to the ν(C—S) mode may be ruled out as follows: When a metal ion is coordinated to the sulfur, the ν(C—S) mode is expected to shift to lower wave numbers, with reduced intensity compared to the uncoordinated case.[16] This feature is found in the behaviour of the 525 cm^{-1} band (rather than the 570 cm^{-1} band) of the nickel complex $Cs_2[(C_2N_2S_2)_2]$, as this may be identified with the 550 cm^{-1} band of the uncoordinated potassium salt of the ligand. The bands at 345 cm^{-1} and 335 cm^{-1} of the

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nickel complex are not present in the potassium salt of the ligand and thus they may be assigned to ν(M–S) modes.[5,8,16] The deformation modes, being very weak could not be characterized well. However, a weak absorption at 290 cm^{-1} in the spectrum of the caesium salt has been tentatively assigned to $\delta(C_1–N_1–C_2)$ mode. The other deformation modes could not be observed but some tentative assignments have been made to the calculated frequencies on the basis of our calculations. The results are shown in Table II.

Force Constants

The $K(C_2–N_2)$ force constant (15.25 md/Å) indicates an appreciable contribution from the resonance structure II. The same trend is also shown by the close values of $K(C_1–N_1)$ and $K(C_2–N_1)$. If the structure of the anion were to be completely represented by any one of the two resonance structures, the values of these stretching force constants will be by far different. The separation between the two ν(C–N) modes is not because of much of a difference between these force constants, but it results from a strong interaction between the two bonds. The relative values of the K(C–S) force constants are quite in agreement with the bond distances. Two interaction constants were introduced in the sense of a generalized valence force field *viz.* (C–S, C–S, –0.36 md/Å) and (M–S, M–S, –0.18 md/Å).

Acknowledgments. The authors thank the Director, Indian Institute of Technology, Kanpur for providing the facilities. One of the authors (PBR) thanks the Council of Scientific and Industrial Research (India) for the financial assistance.