Table IV. Calculated Vibrational Frequencies (cm^{-1}) from 3-21G Optimized Geometries

1 (D_{3h})	**2** (C_{3v})	**3** (D_{4h})	**4** (D_{2d})	**5** (C_{4v})	**5** (C_{2v})
$165i\ \mathrm{e''}$	$218\ \mathrm{e}$	$44i\ \mathrm{b_{1u}}$	$92i\ \mathrm{b_2}$	$34i\ \mathrm{b_2}$	$93\ \mathrm{a_1}$
$214i\ \mathrm{a_2''}$	$274\ \mathrm{a_1}$	$108i\ \mathrm{b_{2u}}$	$143i\ \mathrm{e}$	$220\ \mathrm{a_1}$	$160\ \mathrm{b_1}$
$430\ \mathrm{a_1'}$	$491\ \mathrm{a_1}$	$160i\ \mathrm{e''}$	$146i\ \mathrm{a_2}$	$242\ \mathrm{e}$	$208\ \mathrm{a_1}/237\ \mathrm{b_2}$
$491\ \mathrm{e'}$	$551\ \mathrm{e}$	$164i\ \mathrm{a_{2u}}$	$72\ \mathrm{a_1}$	$268\ \mathrm{b_1}$	$239\ \mathrm{a_2}$
$715\ \mathrm{a_2'}$	$734\ \mathrm{a_2}$	$278\ \mathrm{b_{1g}}$	$212\ \mathrm{b_1}$	$354\ \mathrm{b_1}$	$309\ \mathrm{a_2}$
$870\ \mathrm{e''}$	$862\ \mathrm{e}$	$361\ \mathrm{b_{2g}}$	$459\ \mathrm{b_2}$	$396\ \mathrm{b_2}$	$391\ \mathrm{a_1}$
$970\ \mathrm{a_1''}$	$966\ \mathrm{e}$	$501\ \mathrm{e'}$	$508\ \mathrm{a_1}$	$576\ \mathrm{e}$	$586\ \mathrm{b_2}/592\ \mathrm{b_1}$
$990\ \mathrm{e'}$	$1009\ \mathrm{a_2}$	$504\ \mathrm{a_{1g}}$	$531\ \mathrm{e}$	$577\ \mathrm{a_1}$	$604\ \mathrm{a_1}$
$1059\ \mathrm{a_2''}$	$1165\ \mathrm{a_1}$	$521\ \mathrm{b_{1g}}$	$566\ \mathrm{b_1}$	$617\ \mathrm{a_2}$	$628\ \mathrm{a_2}$
$1189\ \mathrm{e'}$	$1200\ \mathrm{e}$	$563\ \mathrm{a_{2g}}$	$594\ \mathrm{a_2}$	$634\ \mathrm{b_1}$	$649\ \mathrm{a_2}$
$1197\ \mathrm{e''}$	$1216\ \mathrm{e}$	$852\ \mathrm{b_{1u}}$	$754\ \mathrm{e}$	$868\ \mathrm{b_2}$	$808\ \mathrm{b_2}$
$1224\ \mathrm{a_1'}$	$1242\ \mathrm{a_1}$	$879\ \mathrm{e''}$	$818\ \mathrm{a_1}$	$886\ \mathrm{e}$	$816\ \mathrm{b_1}/839\ \mathrm{a_1}$
$1487\ \mathrm{e'}$	$1656\ \mathrm{e}$	$898\ \mathrm{e'}$	$972\ \mathrm{b_1}$	$930\ \mathrm{e}$	$976\ \mathrm{b_1}/985\ \mathrm{b_2}$
$1592\ \mathrm{a_1'}$	$1674\ \mathrm{a_1}$	$902\ \mathrm{a_{1u}}$	$992\ \mathrm{e}$	$987\ \mathrm{a_2}$	$996\ \mathrm{a_2}$
$2293\ \mathrm{a_2'}$	$2228\ \mathrm{a_2}$	$1120\ \mathrm{e'}$	$1132\ \mathrm{e}$	$1156\ \mathrm{e}$	$1143\ \mathrm{b_1}/1153\ \mathrm{b_2}$
$2402\ \mathrm{e'}$	$2278\ \mathrm{e}$	$1147\ \mathrm{a_{2u}}$	$1146\ \mathrm{b_2}$	$1171\ \mathrm{a_1}$	$1178\ \mathrm{a_1}$
$2752\ \mathrm{e'}$	$2764\ \mathrm{e}$	$1167\ \mathrm{a_{1g}}$	$1180\ \mathrm{a_2}$	$1212\ \mathrm{b_2}$	$1208\ \mathrm{a_1}$
$2762\ \mathrm{a_1'}$	$2776\ \mathrm{a_1}$	$1179\ \mathrm{e''}$	$1186\ \mathrm{e}$	$1243\ \mathrm{b_1}$	$1230\ \mathrm{a_1}$
$2872\ \mathrm{e''}$	$2885\ \mathrm{e}$	$1183\ \mathrm{b_{2g}}$	$1194\ \mathrm{b_2}$	$1258\ \mathrm{e}$	$1241\ \mathrm{b_2}/1252\ \mathrm{b_1}$
$2880\ \mathrm{a_2''}$	$2896\ \mathrm{a_1}$	$1189\ \mathrm{b_{2u}}$	$1208\ \mathrm{a_1}$	$1265\ \mathrm{a_1}$	$1259\ \mathrm{a_1}$
		$1243\ \mathrm{b_{1g}}$	$1258\ \mathrm{a_1}$	$1382\ \mathrm{a_1}$	$1389\ \mathrm{a_1}$
		$1246\ \mathrm{e'}$	$1264\ \mathrm{e}$	$1391\ \mathrm{e}$	$1400\ \mathrm{b_2}/1404\ \mathrm{a_2}$
		$1248\ \mathrm{a_{1g}}$	$1272\ \mathrm{b_1}$	$1393\ \mathrm{b_1}$	$1410\ \mathrm{b_1}$
		$2183\ \mathrm{a_{2g}}$	$2240\ \mathrm{a_2}$	$2110\ \mathrm{a_2}$	$2143\ \mathrm{a_2}$
		$2599\ \mathrm{e'}$	$2574\ \mathrm{e}$	$2457\ \mathrm{e}$	$2442\ \mathrm{b_2}/2474\ \mathrm{b_1}$
		$2655\ \mathrm{b_{2g}}$	$2636\ \mathrm{b_2}$	$2509\ \mathrm{b_2}$	$2508\ \mathrm{a_1}$
		$2762\ \mathrm{e'}$	$2761\ \mathrm{e}$	$2755\ \mathrm{b_2}$	$2752\ \mathrm{a_1}$
		$2763\ \mathrm{a_{1g}}$	$2762\ \mathrm{a_1}$	$2760\ \mathrm{e}$	$2753\ \mathrm{b_2}/2762\ \mathrm{b_1}$
		$2765\ \mathrm{b_{2g}}$	$2762\ \mathrm{b_2}$	$2767\ \mathrm{a_1}$	$2766\ \mathrm{a_1}$
		$2868\ \mathrm{b_{1u}}$	$2871\ \mathrm{a_1}$	$2873\ \mathrm{b_2}$	$2871\ \mathrm{a_1}$
		$2874\ \mathrm{e''}$	$2872\ \mathrm{e}$	$2883\ \mathrm{e}$	$2873\ \mathrm{b_2}/2883\ \mathrm{b_1}$
		$2882\ \mathrm{a_{2u}}$	$2880\ \mathrm{b_2}$	$2894\ \mathrm{a_1}$	$2893\ \mathrm{a_1}$

structure is more compact than the D_{3h} structure: the B–B distance is contracted from 2.351 to 2.256 Å, and the angle at the bridge hydrogen is reduced from 128.5 to 118.9° (Table III).

Vibrational frequencies (Table IV) for B_3H_9 indicate that the C_{3v} structure is at a minimum, since all are positive and real. The three negative frequencies for the D_{3h} structure indicate that it is not a candidate for the transition state between interconverting C_{3v} structures. Although the negative frequency of 214*i* cm^{-1} of the imaginary mode having a_2'' symmetry could interconvert C_{3v} structures, the 65*i* cm^{-1} frequency belongs to an imaginary mode in which two bridge hydrogens move in one direction and the third moves in the other direction out of the major plane of the molecule. Thus, the correct transition state is probably one in which one bridge "flips" first, followed by the other bridge hydrogens.

For B_4H_{12}, we find that the D_{2d}, C_{4v}, and C_{2v} structures are all more stable than the D_{4h} structure at all levels of computation (Table III). The C_{2v} structure is more stable than the D_{4h} structure by 6.8 kcal/mol at the [MP3/6-31G*] + ZPC level and is only 2.2 kcal/mol (3.5 kcal/mol) more stable than the C_{4v} (D_{2d}) structure at this level (Table II). If ZPC corrections are omitted, the C_{2v} structure is 9.8 kcal/mol more stable than the D_{4h} structure and is 3.5 kcal/mol more stable than the D_{2d} structure at the [MP3/6-31G*] level. Both of these lower symmetry structures are slightly more compact than the D_{4h} structure, as indicated by the shortening of B–B distances and decrease in the bond angle about the bridge hydrogens (Table III).

The vibrational frequencies (Table IV) reveal five imaginary modes for the D_{4h} structure, four imaginary modes for the D_{2d} structure, one imaginary mode for the C_{4v} structure, and no imaginary modes for the C_{2v} structure. Distortion of the C_{4v} structure to C_{2v} is indicated in **5**, where diagonal borons are displaced 0.26 Å closer to (+) or further (−) form the plane containing the four bridge hydrogens while the average displacement is nearly identical with that found in the C_{4v} structure. Because of its negative eigenvalues, the D_{4h} structure cannot be the transition state for interconversion of C_{2v} structures, and we suggest that some sequence of consecutive or nonsimultaneous flips occurs during the interconversion such that the barrier remains below 6.8 kcal/mol. Both B_3H_9 and B_4H_{12} are therefore double-minimum vibrational problems and should show the expected splitting of rotational lines.

Reduced symmetry[2] appears in BH_5, $B_2H_7^-$, B_4H_8, and B_5H_{11} and, here, in B_3H_9 and B_4H_{12}. There are two main effects. The first is a tendency for low-coordinated boron to raise its coordination number, particularly if underuse of boron orbitals by bridge hydrogens occurs. The second is the conversion of terminal hydrogens to bridge hydrogens as long as strain is not excessive. This latter effect is primarily due to correlation: the pair of electrons in a bridge bond are separated by a nucleus, while these electrons show comparatively greater repulsion effects if they are in a single terminal bond.

Acknowledgment. We thank the National Science Foundation (Grants CHE-82-10536 and PCM-77-11398) and Auburn University (Grant 82-54) for support. Computer time was donated by the Auburn University Computer Center.

Registry No. B_3H_9, 36350-66-0; B_4H_{12}, 60349-62-4.

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Vibrational Study of Ionic Association in Aprotic Solvents. 8. Copper(I) Thiocyanate in Soft Donor Solvents

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Received September 24, 1984

Copper(I) thiocyanate is insoluble in water and in most usual solvents, but it is readily soluble in *N*,*N*-dimethylthioformamide (DMTF), which is highly polar, donating through the soft S atom. This salt is also slightly soluble (($\sim$1–4) × 10^{-2} M) in tetrahydrothiophene (THT), dimethyl sulfoxide (Me_2SO), and hexamethylphosphoric triamide (HMPT). The existing species and the bonding mode of SCN can be identified by infrared spectroscopy.

Experimental Section

THT was distilled on a 20-plate column, and DMTF was distilled under reduced pressure. Other solvents were of the best commercial grade. All solvents were stored on 4-Å molecular sieves. Solutions were prepared in a drybox. IR spectra were recorded on an interferometric Bruker IFS 45 spectrometer and Raman spectra on a Coderg T 800 spectrometer.

Results and Discussion

The CuSCN solutions in pure DMTF were first investigated in the ν(CN) and ν(CS) regions of SCN. In both regions two absorption bands were observed at 2055 and 2076 cm^{-1} (Figure 1b) and at 737 and 780 cm^{-1}. The bands at 2055 and 737 cm^{-1} are characteristic of the SCN^- ion. They appeared at the same frequency in spectra of NBu_4SCN solutions (Figure 1a). This assignment was confirmed by dilution effects on the relative intensities in the ν(CN) region. The other two bands were assigned to the isothiocyanate ion pair CuNCS because the frequency shift of ν(CS) relative to SCN^- is positive while it is negative for thiocyanate complexes such as AgSCN.[1,2] The frequency shifts (27 and 43 cm^{-1}) of ν(CN) and ν(CS) are in the same ratio as for LiNCS (14 and 30 cm^{-1}) and somewhat larger, which indicates that the structures of both ion pairs are similar. The isothiocyanate structure of CuNCS was also proved by the variation in integrated intensity between SCN^- and CuNCS. This variation was more easily measured in THT where the integrated intensity of ν(CN) rises from 17 100 in NBu_4SCN to 20 700 mol^{-1} L cm^{-2} in CuNCS.

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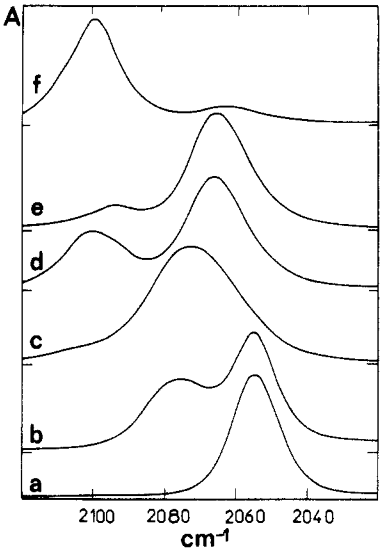

Figure 1. Infrared spectra of SCN^- and CuSCN aggregates in soft donor solvents: NBu_4SCN 1.16 M in DMTF (a); CuSCN 0.17 M in DMTF (b), 0.2 M in 80% THT + 20% DMTF (c), 0.034 M in THT (d), 0.0034 M in THT (e), and 0.0034 M in 90% CS_2 + 10% THT (f). Absorbances (A) are in arbitrary units.

Such an increase in integrated intensity of ν(CN) is characteristic of isothiocyanate complexes.[3]

The proportion of CuNCS ion pair was found to increase when the less polar THT was added to DMTF solutions. For instances, the spectrum of a 0.2 M solution of CuSCN in a mixed solvent containing 80% THT showed the peak of CuNCS only (Figure 1c). The band of SCN^- appeared again by dilution in the same solvent. A shift of the SCN^- band, due to a dielectric effect,[4] from 2055 cm^{-1} in pure DMTF to 2051 cm^{-1} in pure THT, was observed. The shift of the CuNCS band was more important (from 2076 to 2066 cm^{-1}). Such a behavior has never been observed in LiNCS aggregates.

The IR spectrum of a saturated solution of CuSCN (0.037 M) in THT exhibited two weak bands at 2101 and 2093 cm^{-1} in addition to the main band of CuNCS at 2066 cm^{-1} (Figure 1d). The first of them disappeared on dilution (Figure 1e) and was therefore assigned to an aggregate $(CuNCS)_p$. The ratio of the height of the CuNCS band to that of the 2093-cm^{-1} band ($\sim$6) was not dependent on dilution down to 10^{-4} M, and consequently this absorption was assigned to the isomer species CuSCN. Such a type of isomerism has been found between AuNCS and AuSCN.[5] For these two species the ratio of the frequency shifts relative to SCN^- is equal to 26/70, or 0.37, which is very close to the same ratio 15/42, or 0.36, for CuNCS and CuSCN. In THT the AgSCN band was observed at the same frequency as for CuSCN. The polarizing powers of Cu^+ and Ag^+ ions toward the sulfur end of SCN^- appear to be the same, but the interaction of the smaller and harder Cu^+ must be less covalent than that of Ag^+.

In solid CuSCN the SCN groups are in bridging positions[6] between one nitrogen and three sulfur atoms. The ν(CN) absorption at 2173 cm^{-1} is located 122 cm^{-1} higher than for SCN^-.[7] This difference can be compared to the value calculated by applying an additivity rule to the shifts observed in both ion pairs: $15 + (3 \times 42) = 141$ cm^{-1}. It seems that such a rule gives an upper limit of the observed shifts and generally a rough estimation of them. When CS_2 was added to CuSCN–THT solutions, we observed an increase of the relative intensity of the $(CuNCS)_p$ band at 2101 cm^{-1} (Figure 1f). In solutions containing 90% CS_2 the ion-pair absorption at 2065 cm^{-1} disappeared almost completely. The frequency shift of the 2101 cm^{-1} band relative to that of SCN^- is 50 cm^{-1} which can be compared to 42 cm^{-1} for CuSCN and 14 cm^{-1} for CuNCS in the same solvent. If the approximate additivity rule is followed, this band must be assigned to a bridging NCS group. The same assignment has been made for $AgNCSAg^+$.[8] Therefore, the aggregate $(CuNCS)_p$ is probably a centrosymmetric dimer.

The addition of a large excess (5/1) of triphenylphosphine (Ph_3P) to a saturated solution of CuSCN in THT caused the bands at 2093 and 2101 cm^{-1} to disappear and the band at 2066 cm^{-1} to shift slightly to 2064.5 cm^{-1}. At the same time the integrated intensity of this band increased from 20 700 to 27 600 cm^{-1}. These changes arise from a preferential solvation of Cu^+ by Ph_3P. We did not observe any difference between the ν(CN) IR and Raman frequencies of these solutions. Therefore the formation of a centrosymmetric dimer is unlikely in this case even though some solid compounds of Ph_3P with copper(I) salts are dimerized.[9] On the other hand the compound $(Bu_3P)_2$ CuNCS has been found to exhibit a ν(CN) band at 2077 cm^{-1}.[10] Hence, the addition of Ph_3P does not seem to induce an important change in aggregation of CuNCS, but the strong increase in intensity due to the addition of Ph_3P has not been yet interpreted.

The IR spectra of saturated solutions ($\sim 10^{-2}$ M) of CuSCN in Me_2SO and in HMPT were also investigated. The main band (at 2089 cm^{-1} in Me_2SO and 2085 cm^{-1} in HMPT) gradually shifted to 2076 cm^{-1} when DMTF was added to the solutions and no splitting was observed. Consequently, this band was assigned to CuNCS. There is little ionization of CuNCS in these solvents because their ability to solvate Cu^+ through the oxygen atom is poor. On the contrary, the relatively strong Cu–NCS interaction induces a large frequency shift on ν(CN) (31 cm^{-1} in Me_2SO compared to 21 cm^{-1} in DMTF).

The mixtures of CuSCN and NBu_4SCN were studied by Job's method. A new band at 2075 cm^{-1} was attributed to $Cu(NCS)_2^-$. The Raman frequency of this species was observed at 2086 cm^{-1}. $Cu(NCS)_2^-$ is probably centrosymmetric even though the Raman band at 2086 cm^{-1} appeared as a shoulder in the IR spectrum and vice versa. This complex is of the isothiocyanate type because its ν(CS) IR band was observed at 791 cm^{-1} instead of 737 cm^{-1} for SCN^-. The difference between Raman and IR ν(CN) frequencies is nearly the same as for $Cu(CN)_2^-$ (2137 and 2125 cm^{-1}),[11] as expected for similar groups coupled through the same Cu^+ ion.

In conclusion, Cu^+ generally acts as a hard cation toward SCN^-, contrary to Ag^+ and Au^+, which are known to be softer.[12] Consequently, Cu^+ should be considered, like Cd^{2+}, as being in a borderline position between hard and soft cations.

Acknowledgment. We thank Didier Legoff for his technical assistance with the IR spectrometry.

Registry No. $Cu(NCS)_2^-$, 60896-41-5; CuNCS, 1111-67-7; SCN^-, 302-04-5; Cu^+, 17493-86-6.

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Raman Spectroscopic Evidence for the Existence of TiO^{2+} in Acidic Aqueous Solutions

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Received November 19, 1984

The existence of solid vanadium(IV) oxo complexes containing a true vanadyl (V=O) moiety is well established.[1,2] The vi-

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