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Spectroscopic and Coordination Behavior of α-Cyanothioacetamide

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α-Cyanothioacetamide (CTAM) complexes of cuprous chloride CuCl–2CTAM and cuprous bromide CuBr–2CTAM have been prepared. The infrared spectra of CTAM and its complexes, and the laser Raman spectrum of CTAM have been recorded. Assignment of the frequencies of the ligand has been made on the basis of a normal coordinate analysis using the Urey-Bradley force field. The copper (I) complexes are inferred to have thiocarbonyl sulfur and amide nitrogen bonded CTAM as evidenced from infrared and electronic spectra.

α-Cyanothioacetamide is a potentially tridentate ligand. The coordination complexes of its oxygen anologue α-cyanoacetamide have been studied recently.[1,2] The results of detailed spectroscopic investigations of thioacetamide[3] and malononitrile[4] are also available. In this connection, we considered it interesting to study in detail the spectroscopic and coordination behavior of α-cyanothioacetamide (CTAM). The location of thiocarbonyl stretching frequency was also of considerable interest. We report here the infrared and laser Raman spectra of CTAM and the assignment of its vibrational frequencies with the aid of a normal coordinate treatment. The complexes of CTAM with cuprous chloride and cuprous bromide are also included. The assignment of the vibrational frequencies and the frequency shifts in metal complexes are discussed.

Experimental

Materials. α-Cyanoacetamide was prepared by reacting ethylcyanoacetate (Boehringer Ingelheim reagent) with liquor ammonia.[5] CTAM was synthesised from α-cyanoacetamide by being refluxed with phosphorus pentasulfide (Fluka) in ethylacetate[6] (BDH reagent). The product was recrystallized from A.R. benzene. The salts $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ were of A.R. grade. Ethanol (99%) was used for the preparation.

Preparations. *CuCl–2CTAM*: An ethanol solution of the ligand was mixed with cupric chloride dihydrate in ethanol when cupric chloride was reduced and a yellow precipitate of the cuprous chloride complex was obtained. It was filtered off, washed with ethanol and dried in a vacuum. Found: Cu, 20.73; S, 20.99%. Calcd for CuCl–2CTAM: Cu, 21.26; S, 21.4%.

CuBr–2CTAM: The above procedure was followed for the preparation of CuBr–2CTAM. The resulting yellow precipitate was filtered, washed with ethanol and dried in a vacuum. Found: Cu, 18.70; S, 18.33%. Calcd for CuBr–2CTAM: Cu, 18.48; S, 18.63%.

Analysis. Copper in the complexes was estimated by the thiosulfate method and sulfur as barium sulfate.

Infrared Spectra. The infrared spectra of CTAM and its complexes were taken in Nujol mull and KBr pellets on a Carl-Zeiss UR 10 spectrophotometer in the range 4000—400 cm^{-1}, and on a Perkin-Elmer 521 grating spectrophotometer in the range 400—250 cm^{-1}.

Raman Spectra. The Raman spectrum of the powdered sample of CTAM sealed in a thin capillary tube was taken on a Cary 81 Raman spectrophotometer equipped with an argon ion laser.[7]

Electronic Spectra. The electronic spectrum of CTAM in acetonitrile was taken on a Unicam SP 700A recording spectrophotometer. The electronic spectra of the complexes were recorded in Nujol mull.

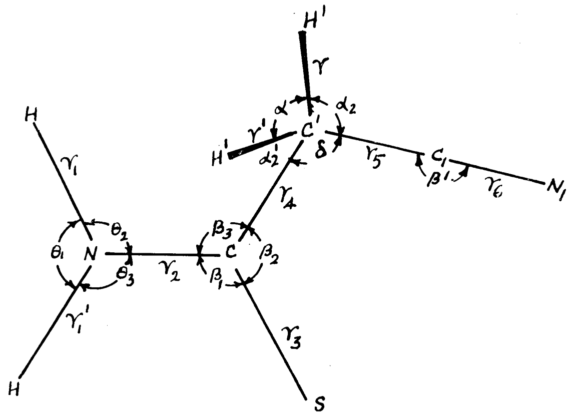

Fig. 1. Internal coordinates.

Normal Coordinate Analysis. The molecule CTAM belongs to the point group C_s and its 24 fundamental vibrations are distributed as 16 A′ and 8 A″ types. Calculations have been carried out for the A′ vibrations only since the frequencies of interest in the present study belong to this species. The internal coordinates are defined in Fig. 1 and the internal symmetry coordinates are given in Table 1. The molecular parameters of CTAM based on the available structural data for formamide,[8] α-cyanoacetamide,[9] and thioacetamide[10] are given in Table 2. The secular equation of Wilson's GF matrix was solved using Miyazawa's method[11] on a IBM 360/44 computer.

Force Field. Because of its effectiveness for thio-

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TABLE 1. INTERNAL SYMMETRY COORDINATES

Symmetry coordinate	Mode	
$S_1 = (\varDelta r + \varDelta r')/\sqrt{2}$	CH stretching	ν_sCH
$S_2 = (\varDelta r_1 + \varDelta r_1')/\sqrt{2}$	NH sym stretching	ν_sNH
$S_3 = (\varDelta r_1 - \varDelta r_1')/\sqrt{2}$	NH asym stretching	ν_aNH
$S_4 = \varDelta r_6$	C≡N stretching	νC≡N
$S_5 = (\varDelta r_4 + \varDelta r_5)/\sqrt{2}$	CC sym stretching	ν_sCC
$S_6 = (\varDelta r_4 - \varDelta r_5)/\sqrt{2}$	CC asym stretching	ν_aCC
$S_7 = \varDelta r_2$	CN stretching	νCN
$S_8 = \varDelta r_3$	CS stretching	νCS
$S_9 = (2\varDelta\theta_1 - \varDelta\theta_2 - \varDelta\theta_3)/\sqrt{6}$	NH_2 bending	δNH_2
$S_{10} = (\varDelta\theta_2 - \varDelta\theta_3)/\sqrt{2}$	NH_2 rocking	ρNH_2
$S_{11} = (2\varDelta\beta_1 - \varDelta\beta_2 - \varDelta\beta_3)/\sqrt{6}$	NCS bending	δNCS
$S_{12} = (\varDelta\beta_2 - \varDelta\beta_3)/\sqrt{2}$	CCS bending	δCCS
$S_{13} = \varDelta\beta'$	CC≡N bending	δCC≡N
$S_{14} = (5\delta - \varDelta\alpha - \varDelta\alpha_1 - \varDelta\alpha_1' - \varDelta\alpha_2 - \varDelta\alpha_2')/\sqrt{30}$	CCC bending	δCCC
$S_{15} = (4\alpha - \varDelta\alpha_1 - \varDelta\alpha_1' - \varDelta\alpha_2 - \varDelta\alpha_2')/\sqrt{20}$	CH_2 bending	δCH_2
$S_{16} = (\varDelta\alpha_1 + \varDelta\alpha_2' - \varDelta\alpha_2 - \varDelta\alpha_1')/\sqrt{2}$	CH_2 wagging	ωCH_2

TABLE 2. MOLECULAR PARAMETERS

Bond length		Bond angle	
N–H	1.002 Å	HNH	120°
C–H	1.093 Å	HNC	120°
C–N	1.324 Å	NCS	120°
C–S	1.713 Å	SCC′	120°
C–C′	1.540 Å	$C'C_1N$	180°
$C'–C_1$	1.458 Å	Angles around C′ carbon	109°28′
C≡N	1.162 Å		

TABLE 3. UREY-BRADLEY FORCE CONSTANTS (md/Å)

Stretching		Bending		Repulsion	
K_{CH}	4.14	H_{HNH}	0.41	F_{HNH}	0.04
K_{NH}	5.85	H_{HNC}	0.32	F_{HCH}	0.05
K_{CN}	6.45	H_{HCH}	0.39	F_{HNC}	0.44
K_{CS}	3.81	$H_{HC'C}$	0.29	$F_{HC'C}$	0.50
$K_{CC'}$	2.45	$H_{HC'C_1}$	0.31	$F_{HC'C_1}$	0.55
$K_{C'C_1}$	2.90	H_{NCS}	0.22	$F_{NCC'}$	0.70
$K_{C\equiv N}$	18.20	$H_{C'CS}$	0.10	F_{NCS}	1.20
k (intramolecular tension) = −0.05 (md/Å)		$H_{C'CN}$	0.10	$F_{SCC'}$	0.44
		$H_{CC'C_1}$	0.62	$F_{CC'C_1}$	0.42
		$H_{C'C_1N_1}$	0.40	$F_{C'CN_1}$	0.50

amides,[3,12–14)] the Urey-Bradley force field (UBFF) was chosen for the calculations. The initial set of force constants were taken from thioacetamide (TAM)[3)] and malononitrile (MNL, set I).[4)] From the results of calculation, the force constants were modified by an iterative procedure so as to get the best fit between the calculated and the observed frequencies. Table 3 shows the final force constants thus obtained. A comparison of the force constants of CTAM with those of TAM and MNL indicates that only three bending force constants differ considerably while all other force constants are nearly the same as those in either TAM or MNL. Thus the transferability of these force constants is good.

TABLE 4. OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES AND THEIR ASSIGNMENTS

Frequencies, cm^{-1}		$\varDelta^{a)}$	Assignments (PED, %)$^{b)}$
Obsd	Calcd		
3375	3375	0	ν_a(NH)(100)
3295	3289	0.18	ν_s(NH)(99)
2895	2898	0.10	ν_s(CH)(99)
2268	2268	0	ν(C≡N)(91)
1630	1627	0.18	$\delta(NH_2)$(77)+ν(CN)(21)
1460	1450	0.69	ν(CN)(41)+$\omega(CH_2)$(27)+ $\delta(NH_2)$(10)
1415	1419	0.28	$\delta(CH_2)$(88)
1385	1386	0.07	$\omega(CH_2)$(59)+ν(CN)(24)
1260	1262	0.16	$\rho(NH_2)$(30)+ν(CS) (17)+ ν_a(CC)(16)+ν_s(CC)(16)+ δ(NCS)(11)
1001	1001	0	$\rho(NH_2)$(49)+ν_s(CC)(20)+ δ(CCC)(14)
955	955	0	ν_a(CC)(63)+ν_s(CC)(13)
760	764	0.53	ν(CS)(63)+δ(CC≡N)(14)
630	629	0.16	ν_s(CC)(35)+δ(CC≡N)(25)+ δ(NCS)(13)
421	421	0	δ(NCS)(77)+δ(CC≡N)(10)
335	333	0.60	δ(CCS)(49)+δ(CC≡N)(27)+ δ(CCC)(10)
105$^{c)}$	102	2.94	δ(CCS)(39)+δ(CCC)(36)+ δ(CC≡N)(20)

a) Percentage deviation.
b) Contribution less than 10 per cent is not included.
c) Taken from Raman data.

The calculated frequencies are compared with the observed ones in Table 4, in which the assignments of the bands based upon the calculated potential energy distribution (PED) are also given.

Results and Discussion

The assignments are compared with those of the closely related TAM and MNL molecules.

3400—2000 cm^{-1} Region. The bands at 3375 and 3295 cm^{-1} in CTAM are due to N–H asymmetric and symmetric stretching vibrations. The CH symmetric and antisymmetric (A″) modes are located at 2895 and 2930 cm^{-1}, respectively. The C≡N stretching occurs at 2268 cm^{-1}.

1650—1000 cm^{-1} Region. The 1630 cm^{-1} band is due to NH_2 bending. The C–N stretching mode is coupled and is distributed in the frequencies at 1630, 1460, and 1385 cm^{-1}, its contribution being maximum (41 per cent) in the 1460 cm^{-1} band. In TAM, NH_2 bending and C–N stretching modes occur, respectively, at *ca.* 1630 and 1400 cm^{-1}. The bands at 1415 and 1385 cm^{-1} due to CH_2 bending and CH_2 wagging, respectively, are compatible with those in MNL[4)] and other related molecules.[15)]

In the 1300—1250 cm^{-1} region, there are two intense absorptions at 1260 and 1295 cm^{-1}. The 1260 cm^{-1}

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Table 5. Observed infrared frequencies[a] (in cm^{-1}) of CTAM and its complexes

CTAM	CuCl·2CTAM	CuBr·2CTAM
3375 s	3280 mb	3290 m
3295 s	3180 mb	3180 m
3170 sb	—	—
2930 m	2935 m	2935 w
2895 m	2855 vw	2880 w
	2275 vw	2270 vw
2268 m	2190 sb	2200 sb
1740 vw	1750 w	1745 w
1685 shw	1690 w	1695 w
1630 vsb	1632 vs	1618 vs
1460 vsb	1470 vs	1475 vsb
1415 m	—	—
1385 m	1385 s	1385 vs
1295 s	1300 sb	1325 sb
1260 sb	1201 mb	1205 mb
	1090 w	1100 mw
1001 s	1040 mw	1030 m
	1010 mw	
955 s	960 vw	965 vw
905 mw	920 m	925 m
	890 vw	885 sh
855 vw	825 shw	850 wsh
	785 msh	780 sh
760 s	700 s	710 s
715 msh	695 s	700 m
696 vs (695 s)		
630 vsb		
495 mw	525 w	525 w
	480 m	470 vw
421 mw (422 m)	440 w	430 vw
390 w		
380 w	378 vw	380 vw
365 mw	364 w	360 vw
335 s (331 m)	328 vw	328 vw
(145 mw)		
(105 s)		
(92 s)		
(72 m)		

a) Values in parantheses are Raman frequencies. Because of poor signal/noise ratio in the Raman spectrum, only the prominent bands are given.

band has been included in A′ vibrations in preference to the 1295 cm^{-1} one. The 1260 cm^{-1} band has a complicated mode of coupling with a slightly higher contribution from NH_2 rocking (Table 4). The 1295 cm^{-1} band has been assigned to CH_2 twisting (A″) in accordance with the CH_2 twisting mode at 1225 cm^{-1} in MNL.[4] The 1295 cm^{-1} band is not much affected on complex formation with metals while that at 1260 cm^{-1} shows a large red shift (Table 5). The infrared spectra of the deuterated ligand and the reaction product with HCl gas also showed that the 1295 cm^{-1} band is not affected while the 1260 cm^{-1} band showed a large variation. These findings might support the assignments.

The bands at 1001 and 1260 cm^{-1} have, respectively, 50 and 30 per cent NH_2 rocking mode. Comparable frequencies in TAM appear at 1310, 1030, and 965 cm^{-1} having, respectively, 50, 20, and 16 per cent contribution from NH_2 rocking vibration.[3]

950—700 cm^{-1} Region. The asymmetric C–C stretching mode in CTAM is observed at 955 cm^{-1} while the symmetric mode is distributed amongst 1001, 955, and 630 cm^{-1} bands. The asymmetric mode is comparable with the 985 cm^{-1} band in MNL.[4] The symmetric C–C stretching in MNL occurs as a pure band around 890 cm^{-1}. The symmetric C–C vibration in CTAM is comparable with the C–C stretching mode in TAM, where it is distributed in the bands in the 1400—700 cm^{-1} region.[3]

The band at 760 cm^{-1} is of considerable interest and is due, mainly, to C=S stretching in agreement with an earlier empirical assignment.[16] The C=S stretching occurs at 720 cm^{-1} in TAM.[3] Occurrence of C=S stretching at a higher frequency in CTAM could be attributed to the electron withdrawing effects of the CN group. This band shifts to lower frequency in metal complexes (where sulfur is presumed to be the donor) which may be taken as a support to the above assignment.

650—100 cm^{-1} Region. The CCC bending mode is observed at 580 cm^{-1} in MNL, while in the present case, it is highly coupled and appears in the bands at 1001, 335, and 105 cm^{-1}, the contribution being the largest (36 per cent) in the 105 cm^{-1} band.

The assignment of bands at 421 and 335 cm^{-1} to predominantly NCS and CCS bending modes needs some comment. The corresponding bands in TAM have been observed at 470 and 390 cm^{-1}. One would be inclined therefore to assign empirically the 495 and 421 cm^{-1} in CTAM to NCS and CCS bending vibrations, respectively. The frequencies obtained from the initial trial set were very close to 420 and 330 cm^{-1}. To raise these bands to 495 and 420 cm^{-1}, it was necessary to employ unusually large bending force constants. When this was done, the assignments obtained for some of the higher frequencies were of "unacceptable" nature. Hence, the present assignments for 421 and 335 cm^{-1} were preferred. The lowering of NCS and CCS bending frequencies in CTAM may be attributed to its coupling with CC≡N bending. The CC≡N "in-plane" bending modes in MNL[4] occur at 365 and 165 cm^{-1}.

Out-of-plane Vibrations. Mention should be made of the A″ vibrations although no calculations have been carried out to assign the frequencies to these modes. There are 8 A″ vibrations. The CH_2 antisymmetric stretching occurs at 2930 cm^{-1}. A band at 1295 cm^{-1} is assigned to CH_2 twisting. The CH_2 rocking mode is assigned at 905 cm^{-1} in comparison with that at 936 cm^{-1} in MNL.[4] A strong band at 695 (715) cm^{-1} is assigned to NH_2 wagging in agreement with that in TAM[3] and acetamide,[17] while a very weak band at 855 cm^{-1} is assigned to NH_2 torsional vibration in comparison with that around 800 cm^{-1} in acetamide.

Of the remaining four modes, the band at 495 cm^{-1}

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may be due to C–C out-of-plane bending and is compatible with that at 530 cm^{-1} in TAM.[3] An out-of-plane C–C≡N bending mode is assigned to 365 cm^{-1} in comparison with the one at 371 cm^{-1} in MNL.[4] The C=S out-of-plane bending is tentatively placed at 380, 390 cm^{-1}. The bands below 150 cm^{-1} in Raman spectrum (excepting 105 cm^{-1}) may be due to lattice modes.

Metal Complexes. Except for the copper(I) complexes, the initial efforts to prepare complexes of other metals were unsuccessful. The cuprous complexes are insoluble in most solvents, thus restricting the studies. The site of coordination of CTAM in the complexes were inferred from the infrared data based on the assignments for the ligand bands discussed above. The changes in the infrared frequencies of CTAM on coordination to copper(I) can be seen in Table 5.

A strong band at 760 cm^{-1} due mainly to C=S stretching is lowered by 50 to 60 cm^{-1} in the complexes. This large red shift clearly indicates the coordination of CTAM through sulfur.

The NH_2 stretching modes are found to shift to lower frequencies by about 100 cm^{-1} in the complexes. No perceptible variation is observed in the NH_2 bending frequency. The NH_2 rocking frequencies at 1260 and 1001 cm^{-1} are affected differently. The 1260 cm^{-1} band which has considerable C=S stretching decreases to ~1200 cm^{-1} while the 1001 cm^{-1} shows two or three bands at higher frequencies at 1030—1100 cm^{-1}. Similar variations in the $-NH_2$ group frequencies have been noted in the case of (glycine[18]), urea[19] and thiourea[20] complexes of metals when coordination is said to have taken place through nitrogen. This indicates that in CTAM the bonding to copper(I) through amide nitrogen is likely.

The decrease in C≡N stretching frequency at 2268 cm^{-1} to ~2200 cm^{-1} in metal complexes is puzzling. Normally, coordination through the nitrogen of the cyanide group should increase the C≡N frequency, as has been observed in almost all the cases, including α-cyanoacetamide.[1,21] A decrease in C≡N stretching frequency has been found in cases where the coordination to the metal is through the π-bonding of the CN group.[21] Such a possibility is not thought of seriously in this case, although it cannot be completely ruled out. The intense broad band at 630 cm^{-1} in CTAM disappears in the complexes or appears as a weak band at 525 cm^{-1}. If the latter is the case, the unusually large shift is rather difficult to explain, if CN group is not coordinated.

The complexes of α-cyanothioacetamide are likely to be polymeric and may have complicated stereochemistry.

Electronic Spectra. The electronic spectrum of CTAM in acetonitrile shows bands at 270 mμ (ε 10000) and at 358 mμ (ε 200). These are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the C=S chromophore. The electronic spectra of the complexes in solid state give a well-defined peak ~225 mμ. This band may correspond to the π—π^* transition at 270 mμ of the ligand. This blue shift may be attributed to the coordination of the thiocarbonyl sulfur to the metal.

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