Infrared Spectrum and Normal Vibrations of *N,N*-Dimethylthioacetamide

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Infrared spectrum of *N,N*-dimethylthioacetamide (DMTA) has been recorded in the region 250—4000 cm^{-1}. Normal vibration analysis has been carried out employing Urey-Bradley force field and assignments are made and supported by comparison with related molecules. The complexes of DMTA with cobalt(II), copper(I), and mercury(II) chlorides have been prepared and their infrared spectra recorded. The frequency shifts in metal complexes are in accord with the assignments of C=S and C–N frequencies.

Although the normal vibrations of primary and secondary thioamides have been well investigated,[1,2] no detailed study of tertiary thioamides seems to have been made. It is only recently we made a normal vibration analysis of *N,N*-dimethylthioformamide (DMTF) to know the detailed nature of the vibrations.[3] It was considered worthwhile to study the normal vibrations in the next higher thioamide, *N,N*-dimethylthioacetamide (DMTA). In this paper, the normal coordinate treatment of DMTA employing Urey-Bradley force field (UBF) is reported. The preparation of the complexes of DMTA with the chlorides of cobalt(II), copper(I), and mercury(II) and their infrared spectra are also included. The assignment of the infrared frequencies are discussed by comparison with related molecules and also from frequency shifts in metal complexes.

Experimental

Materials Employed. *N,N*-Dimethylthioacetamide was synthesized by treating "high purity" *N,N*-dimethylacetamide (obtained from National Chemical Laboratory, Poona, India) with phosphorus pentasulphide (Merck) in benzene (A. R. Grade) according to the general procedure of Hofmann.[4] It was repeatedly recrystallized from *n*-hexane. $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $HgCl_2$ were of A. R. Grade quality. Distilled ethanol (99%) was used.

Preparation of Complexes. *Dichlorobis(DMTA) Cobalt-(II)*: It was prepared by mixing ethanol solutions of DMTA and cobalt(II) chloride according to the reported procedure[5] (Found: Co, 17.03; S, 18.66%. Calcd for $CoCl_2 \cdot 2DMTA$: Co, 17.54; S, 19.05%.).

Chloro-(DMTA) Copper(I): An ethanol solution of DMTA was mixed with copper(II) chloride in ethanol, when copper-(II) gets reduced to copper(I) and an yellow precipitate of the cuprous complex was obtained. It was filtered off, washed thoroughly with ethanol followed by carbon disulphide and dried in vacuum (Found: Cu, 31.23; S, 14.90%. Calcd for CuCl·DMTA: Cu, 31.43; S, 15.84%.).

Dichlorotetrakis(DMTA) Mercury(II): The above method was followed for its preparation. The resulting white precipitate was filtered, washed with ethanol and dried in vacuum (Found: Hg, 30.30; S, 18.41%. Calcd for $HgCl_2 \cdot 4DMTA$: Hg, 29.34; S, 18.72%.).

Analysis. The complexes were analysed for metal and sulfur by standard methods.

Infrared Spectra. The infrared spectra of DMTA 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 grating spectrophotometer, 521 in the range 400—250 cm^{-1}.

Normal Coordinate Treatment

The molecule DMTA belongs to the point group C_s and its 39 fundamental vibrations are classified as 24 A′ and 15 A″ vibrations. The secular equation of the Wilson's GF matrix was solved for A′ vibrations only, which were of interest in the present study. Further, the six C–H stretching modes were split off for simplification. The internal coordinates are defined in Fig. 1 and the symmetry coordinates are listed in Table 1. The structural parameters were taken from DMTF.[3] The C–C′ bond length was assumed to be 1.54 Å and the angles around carbon, tetrahedral. An IBM computer 360/44 was used.

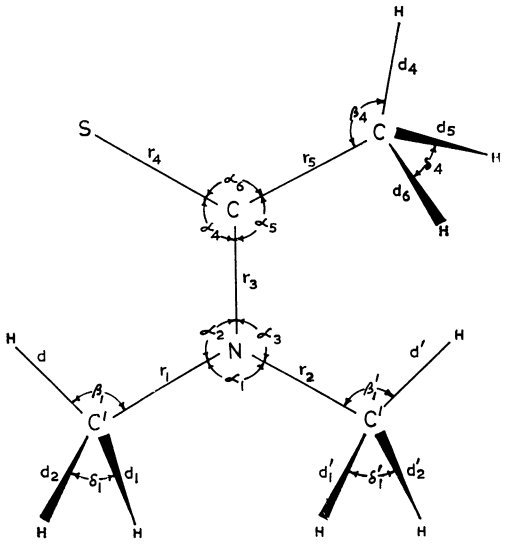

Fig. 1. Internal coordinates for DMTA.

Force Field. It is noteworthy that the UBF has been found to be very effective in the vibrational analysis of thioamide derivatives.[1-3,6] It is for this reason that UBF was chosen for our calculations.

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Table 1. Symmetry coordinates for DMTA

Symmetry coordinate	Description[a]
$S_1=(r_1+r_2)/\sqrt{2}$	Sym C'N str
$S_2=(r_1-r_2)/\sqrt{2}$	Asym C'N str
$S_3=r_3$	CN str
$S_4=r_4$	CS str
$S_5=r_5$	CC' str
$S_6=(2\alpha_1-\alpha_2-\alpha_3)/\sqrt{6}$	C'NC' bend
$S_7=(\alpha_2-\alpha_3)/\sqrt{2}$	C'NC bend
$S_8=(2\alpha_4-\alpha_5-\alpha_6)/\sqrt{6}$	NCS bend
$S_9=(\alpha_5-\alpha_6)/\sqrt{2}$	CCS bend
$S_{10}=(\delta_4+\delta_5+\delta_6-\beta_4-\beta_5-\beta_6)/\sqrt{6}$	Sym (C)CH_3 def
$S_{11}=(2\delta_4-\delta_5-\delta_6)/\sqrt{6}$	Asym (C)CH_3 def
$S_{12}=(2\beta_4-\beta_5-\beta_6)/\sqrt{6}$	(C)CH_3 rock
$S_{13}=(2\delta_1-\delta_2-\delta_3+2\delta_1'-\delta_2'-\delta_3')/\sqrt{12}$	Asym (N)CH_3 def
$S_{14}=(2\delta_1-\delta_2-\delta_3-2\delta_1'+\delta_2'+\delta_3')/\sqrt{12}$	Asym (N)CH def
$S_{15}=(\delta_1+\delta_2+\delta_3-\beta_1-\beta_2-\beta_3+\delta_1'+\delta_2'+\delta_3'-\beta_1'-\beta_2'-\beta_3')/\sqrt{12}$	Sym (N)CH_3 def
$S_{16}=(\delta_1+\delta_2+\delta_3-\beta_1-\beta_2-\beta_3-\delta_1'-\delta_2'-\delta_3'+\beta_1'+\beta_2'+\beta_3')/\sqrt{12}$	Sym (N)CH_3 def
$S_{17}=(2\beta_1-\beta_2-\beta_3+2\beta_1'-\beta_2'-\beta_3')/\sqrt{12}$	(N)CH_3 rock
$S_{18}=(2\beta_1-\beta_2-\beta_3-2\beta_1'+\beta_2'+\beta_3')/\sqrt{12}$	(N)CH_3 rock

a) Sym is symmetric, asym is asymmetric and def is deformation.

Table 2. Force constants (in md/Å) for DMTA

Stretching		Bending		Repulsion	
$K_{C'N}$	3.40	$H_{C'NC'}$	0.180	$F_{C'C'}$	0.25
K_{CN}	5.75	$H_{C'NC}$	0.20	$F_{CC'}$	0.55
K_{CS}	3.74	H_{SCN}	0.150	F_{NC}	0.75
K_{CC}	2.85	$H_{C'CN}$	0.390	F_{NS}	1.45
Intramolecular tension (md Å)		$H_{C'CS}$	0.390	F_{SC}	0.60
k_{CCH3}	−0.056	$H_{HC'N}$	0.30	F_{NH}	0.55
k_{NCH3}	−0.050	$H_{HC'(N)H}$	0.425	F_{CH}	0.50
		$H_{HC'C}$	0.255	F_{HH}	0.05
		$H_{HC'(C)H}$	0.410	F'	−0.1F

The initial set of UBF constants were taken from thioacetamide (TAM), *N*-methylthioacetamide (NMTA), and DMTF.[1-3] The force constants were progressively improved by an iterative procedure. Some of the bending force constants in DMTA differ from, and the stretching and repulsion force constants remain nearly the same as those in TAM, NMTA, and DMTF. Thus, the force field appears to be satisfactorily transferrable among related thioamide molecules. The frequency fit is satisfactory except the rocking frequencies which show comparatively large deviations as are usually the case in the UBF. The final set of force constants is given in Table 2.

Table 3. Observed and calculated frequencies of DMTA and their assignments

Frequencies, cm^{-1}			PED,[b] %
Obsd	Calcd	Δ[a]	
1540	1536	0.26	$S_3(46)$, $S_{13}(16)$, $S_{17}(15)$
1470	1475	0.34	$S_{14}(80)$, $S_{18}(19)$
	1462	0.54	$S_{13}(42)$, $S_{11}(30)$, $S_{12}(11)$
	1429	2.11	$S_{15}(50)$, $S_{11}(28)$, $S_{13}(10)$
1430	1422	0.56	$S_{16}(96)$
	1405	1.75	$S_{15}(44)$, $S_3(18)$, $S_{11}(15)$
1370	1373	0.22	$S_{10}(91)$
1284	1279	0.39	$S_5(28)$, $S_4(17)$, $S_8(15)$, $S_2(11)$, $S_7(10)$
1185	1154	2.62	$S_{17}(36)$, $S_{15}(14)$, $S_{16}(12)$
1130	1133	0.27	$S_2(26)$, $S_{18}(26)$, $S_5(24)$
1060	1004	5.28	$S_2(39)$, $S_{18}(38)$
1020	998	2.16	$S_{12}(38)$, $S_{17}(22)$, $S_3(11)$
870	867	0.34	$S_1(37)$, $S_4(24)$, $S_{12}(15)$
656	661	0.76	$S_1(44)$, $S_4(25)$, $S_5(17)$
495	495	0	$S_8(40)$, $S_7(21)$, $S_2(16)$
444	446	0.40	$S_9(59)$, $S_6(12)$, $S_4(10)$
300	300	0	$S_6(79)$, $S_9(13)$
—	202	—	$S_7(59)$, $S_8(33)$

a) $\Delta=|\nu\text{calc}-\nu\text{obs}|\times 100/\nu\text{obs}$; ν denotes frequency in cm^{-1}.
b) Contribution less than 10% is not included.

Table 4. Infrared frequencies in the range 250—1800 cm^{-1} for DMTA complexes and their assignment

$CoCl_2$ 2DMTA	CuCl DMTA	$HgCl_2$ 4DMTA	DMTA	Assignment[a]
1580 vs	1590 vs	1610 vs	1540 vs	ν(C–N)+δ_a(N–CH_3)+r(N–CH_3)
1465 s	1470 vs	1470 s	1470 s	δ_a(CH_3)N,C
1430 s	1430 vs	1410 s	1430 s	δ_s(N–CH_3)
1385 vs	1385 s	1370 s	1370 s	δ_s(C–CH_3)
1285 vs	1262 vs	1270 vs	1284 vs	ν(C–C′)+ν_a(C′–N)+ν(C=S)+δ(NCS)
1192 vs	1190 m	1195 m	1185 s	r(N–CH_3)+δ(N–CH_3)
—	—	—	1160 vw	r(N–CH_3);(A″)
1130 s	1115 s	1130 s	1130 s	ν_a(C′N)+ν(C–C)+r(N–CH_3)
1060 s	1085 sh	1050 w	1060 w	ν_a (C′–N)+r(N–CH_3)
1030 vs	1025 s	1015 m	1020 vs	r(CH_3)N,C
862 s	845 m	860 vw 845 m	870 s	ν_s(C′–N)+ν(CS)
655 vs	635 s	640 s	656 s	ν_s(C′–N)+ν(C=S)+ν(C–C′)
542 vw	540 vw	535 w	540 vw	π(C–C′);(A″)
498 m	485 w	498 w	495 m	δ(NCS)+δ(CNC′)
448 m	435 m	451 m	444 m	δ(CCS)
428 vw	400 w	428 w	402 vw	—
378 w	368 w	364 s	370 vw	—
336 vw 325 vw	340 vw	350 m	349 vw	π(C′NC′);(A″)
290 w	306 sh	284 sh	300 sh	δ(C′NC′)

a) ν means stretching, δ=bending, r=rocking, π=out-of-plane bending; s=symmetric and a=asymmetric; A″ vibrations are tentatively assigned.

Results and Discussion

The observed and calculated frequencies along with the assignments from potential energy distribution (PED) are given in Table 3. The infrared frequencies of DMTA and its complexes in the region 250—1800 cm^{-1} and their assignments are presented in Table 4. A brief discussion of the assignment of the frequencies is given below.

C–N and C=S Stretching Modes. From valence bond concept, on coordination of the thiocarbonyl sulfur to metal, the C–N stretching frequency is expected to increase while the C=S stretching frequency show a decrease. The C–N stretching frequency occurring at 1540 cm^{-1} in DMTA increases to 1580 to 1610 cm^{-1} in metal complexes and the increase is apparently related to the metal ion. The C–N stretching frequency has been reported to increase to 1600 cm^{-1} on *S*-methylation as expected.[7] A band at 1560 cm^{-1} in DMTF has a similar assignment.[3]

Two bands at 870 and 656 cm^{-1} have large C=S stretching contribution, about 25% in each case. These frequencies decrease to 862—845 and 652—635 cm^{-1}, respectively, in metal complexes. The decrease in the 870 and 656 cm^{-1} bands is substantial in the case of copper(I) and mercury(II), while it is nominal in the case of cobalt(II). This is understandable since copper(I) and mercury(II) are known to form stronger coordination bonds with sulfur donors than cobalt(II). The 870 and 656 cm^{-1} bands have been found to shift to lower frequencies on "selenation", *i.e.*, in *N,N*-dimethylselenoacetamide,[7] to 834 and 606 cm^{-1}, respectively. Similar downward shift in these two frequencies has been noted on *S*-methylation.[7] These findings support the larger contribution from C=S stretching to 870 and 656 cm^{-1} bands. An earlier assignment[8] of C=S stretching for a band near 1100 cm^{-1} is thus not favoured.

Significant contribution of C=S stretching is seen in the 1284 cm^{-1} band also. This band also shows smaller shift to a lower frequency by 10—15 cm^{-1} in metal complexes except in the cobalt complex.

C′–N and C–C′ Stretching Modes. The asymmetric C′–N stretching, unlike in DMTF and DMF[3] (*N,N*-dimethylformamide), is highly coupled and is distributed in the frequencies at 1284, 1130, and 1060 cm^{-1}. The C′–N symmetric stretching has contributions in the 870 and 656 cm^{-1} bands. Their occurrence is comparable with those of DMF and DMTF.[3]

Similarly, the C–C′ stretching is highly mixed with other vibrations and has contributions in the frequencies at 1284, 1130, and 656 cm^{-1}. The assignment is comparable to that in NMTA[1] and *N*-methylacetamide.[9] The C–C stretching has been located at 954 cm^{-1} in *N,N*-dimethylacetamide.[10]

Skeletal Bending Modes. The bands at 495 and 444 cm^{-1} are predominantly due to NCS and CCS bending vibrations, respectively. The corresponding bands in thioacetamide have been found[1] at 470 and 380 cm^{-1}. No gradual change in frequencies has been

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observed for these bands in complexes, probably because of their possible different structures.

C–CH_3 and N–CH_3 Bending Modes. The symmetric and asymmetric deformations at 1370 and 1470 cm^{-1}, respectively, and the rocking mode at 1020 cm^{-1} for C–CH_3 group compare well with those in related molecules.[1,9,12] Similarly, the symmetric and asymmetric bending modes of the N–CH_3 group are easily located at 1430 and 1470 cm^{-1}, respectively and the rocking modes at 1185 and 1060 cm^{-1}.[9–12]

Frequency Shifts in Metal Complexes. Although cobalt(II) complexes were known earlier,[5] no infrared study concerning DMTA has been reported. The complexes of copper(I) and mercury(II) chlorides are new. The effect of complex formation on C=S and C–N stretching frequencies was pointed out earlier. It is satisfying to note that the expected frequency shifts have been realised. The NCS bending frequency may be expected to show a small increase on coordination to metals. However, this band is nearly stationary, except for 3 cm^{-1} raise in mercury and cobalt complexes. This may be attributed to the complicated nature of coupling in the 495 cm^{-1} frequency and also to the different structures of the complexes.

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