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Tentative Assignment of Fundamental Vibrations of Thio- and Selenocarboxylates II. The Dimethyldithiocarbamate Ion

KAI ARNE JENSEN,[a] BRITTA MYNSTER DAHL,[a] PER HALFDAN NIELSEN[a] and GUNNER BORCH[b]

[a] *Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, and* [b] *Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark*

The vibrational spectra of potassium and lead(II) dimethyldithiocarbamate are reported. The fundamentals are assigned on the basis of (1) comparison with the spectra of the deuterated species, and (2) a normal coordinate analysis of the dimethyldithiocarbamate ion with a 24 parameter generalized valence force field.

Currently, much attention is being directed towards the infrared absorption of dithiocarbamate ligands in transition metal chemistry. However, reliable information on the assignment of frequencies and the values of the force constants of the free ligands is not yet available. In the previous paper [1] of this series, the vibrational modes of the dithioacetate ion were described in terms of a generalized valence force field (GVFF). In the present paper, the infrared and Raman spectra of the dimethyldithiocarbamate ion, $(CH_3)_2NCSS^-$ (DDTC), and the perdeuterated species are reported.

The result of a normal coordinate analysis, using a GVFF based upon that for dithioacetate,[1] will be discussed with emphasis on the correlation of the results with spectroscopic evidence.

The experimental results are listed in Table 1. It is assumed that the potassium salt of DDTC is ionic, and accordingly, the infrared and Raman spectra have been taken to represent those of the free ion. It cannot at present be judged how good this approximation is. For example, $\nu_{30}(B_2)$ is placed in the region where the lattice modes occur (Table 1), and the presence of strong coupling between these vibrations cannot be excluded. The selection rules may be quite different for the crystalline state and for solutions, and the static field effect of the metal ion in solid potassium DDTC has also been ignored. However, we feel that the results justify some confidence in the validity of this approximation.

The spectrum of the lead(II) salt has been included for comparison. The deviations from the spectrum of the potassium salt is generally small, but in most cases beyond experimental error.

Table 1. Observed infrared spectra of $(CH_3)_2NCSSK \cdot \frac{1}{2}H_2O$ and $(CD_3)_2NCSSK \cdot \frac{1}{2}H_2O$ in KBr (400–4000 cm^{-1}) and polyethylene (40–400 cm^{-1}), and Raman spectra of aqueous solutions (cm^{-1}). Observed infrared spectra of $[(CH_3)_2NCSS]_2Pb$[d] and $[(CD_3)_2NCSS]_2Pb$[d] in KBr (400–4000 cm^{-1}) and polyethylene (40–400 cm^{-1}). The assignment in column 7 is based on the observed spectra and an assumed potential function.

$(CH_3)_2NCSSK \cdot \frac{1}{2}H_2O$		$[(CH_3)_2NCSS]_2Pb$	$(CD_3)_2NCSSK \cdot \frac{1}{2}H_2O$		$[(CD_3)_2NCSS]_2Pb$	Assignment[b]
Infrared[a]	Raman[a]	Infrared[a]	Infrared[a]	Raman[a]	Infrared[a]	
3008w		2992vw	2261w		2249vw	
2997wsh						
2963m[c]		2962vwsh	2191w[c]	2195vw(DP?)	2177w[c]	$\nu_{16}(B_1),\nu_{25}(B_2)$
2930m	2937vs,P	2920m	2230m	2235vs,P	2217m	$\nu_1(A_1)$
			2148w	2148vs,P	2134m	
			2111w	2124vs,P	2101m	
2890m		2876vwsh	2070m[c]		2059m[c]	$\nu_{17}(B_1)$
2860wsh	2863w (P?)	2842m	2070m[c]	2077vs,P	2059m[c]	$\nu_2(A_1)$
1601m			1601m			H_2O
			1470w			
1498vs		1500vs	1067m[c]	1064w(P?)	1060m[c]	$\nu_3(A_1)$
1464w[c], 1448vw[c]		1454msh[c]	1042m[c]		1034wsh	$\nu_{18}(B_1)$
1464w[c], 1448vw[c]		1454msh[c]	1055m	1054w(DP?)	1045msh	$\nu_{26}(B_2)$
1437m			1400vs	1417s,P	1437vs	$\nu_4(A_1)$
1400m		1397m	1067m[c]		1060m[c]	$\nu_{19}(B_1)$
1361s	1374s,P	1376vs[c]	1115m	1115w	1106m	$\nu_5(A_1)$
1257s		1245s	1240s	1237w,DP	1224s	$\nu_{20}(B_1)$

Table 1. Continued.

1400m		1376vs[c]	1208m		1194m	$\nu_7(A_1)+\nu_{23}(B_1)$
1134msh	1135w	1144s	1042m[c]	1037vw(P?)	1034wsh[c]	$\nu_6(A_1)$
1125s	1127wsh	1135ssh	951s	*ca.* 947w	965s, 945m	$\nu_{27}(B_2)$
1099w		1080w				
1049m		1046m	824m		823m	$\nu_{21}(B_1)$
966vs	977w(DP?)	968s	981vs	969m,DP	980s	$\nu_{22}(B_1)$
945w		933vw	787vw	796m,P	780w	$\nu_7(A_1)$
884w	883w(DP?)		843w			$2\nu_{23}(B_1)$?
590w			586w	592vw	558vw	$\nu_{28}(B_2)$
583m	578vs,P	573m	547m	542vs,P	538m	$\nu_8(A_1)$
–	439vs,P	445msh, 439msh	396w	387m,P	386w	$\nu_9(A_1)$
453m		448m	423m		414m	$\nu_{23}(B_1)$
430s,br			430s,br			H_2O
328m		350s	321m	323w,P	339s	$\nu_{10}(A_1)$
264w,br		258m,br	238w,br	236vw(DP?)	234w	$\nu_{29}(B_2)$
142s		148msh	138s		144msh	Lattice mode
123s			88m			$\nu_{30}(B_2)$
106s		106s	104s		104s	Lattice mode
81m			80m			Lattice mode
60w			54w			Lattice mode

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder. The polarisation of a Raman line is indicated by P, depolarisation by DP.

[b] The numbering of the fundamentals refers to the undeuterated compound.

[c] Multiply assigned bands.

[d] In addition to those listed above, the observed infrared spectra of $[(CH_3)_2NCSS]_2Pb/[(CD_3)_2NCSS]_2Pb$ show the following absorptions: 1019w/945m ($\nu_9(A_1)+\nu_{28}(B_2)$ or $\nu_8(A_1)+\nu_{23}(B_1)$),– /288w,br (unassigned) and 129s/127s (lattice mode?). The absorptions 148/144, 129/127, and 106/104 are observed as submaxima of a very broad and strong absorption in the range 80–180 cm^{-1}, and absorption corresponding to $\nu_{36}(B_2)$ observed for the potassium salts is not found for the lead(II) salts.

NORMAL COORDINATE ANALYSIS

The DDTC ion has 12 atoms and has been assumed to belong to the point group C_{2v}. It has accordingly 30 fundamental modes of vibration, which can be described by the representation $10A_1+5A_2+9B_1+6B_2$. All vibrations are Raman active, and all but the vibrations of species A_2 infrared active. From the results listed in Table 1 it is seen that comparison of the infrared and Raman spectra does not allow an assignment of the vibrations of species A_2. This species has accordingly been omitted in the normal analysis. The polarized lines have been assumed to belong to species A_1.

The geometry of the DDTC ion used in the calculations is based upon X-ray investigations of the complexes [2] and the dithiocarbazate ion [3] and an assumed tetrahedral configuration around the carbon atoms of the methyl groups. The following distances have been used: C – H = 1.10 Å, C – N (dimethylamino group) = 1.46 Å, C – N (central bond) = 1.33 Å, and C – S = 1.709 Å. The following angles have been used: H – C – H = H – C – N = 109°28′, C – N – C (dimethylamino group) = 118°, and S – C – S = 123°20′.

The internal coordinates were chosen as the changes in bond lengths and bond angles, and are shown in Fig. 1. From these, the symmetry coordinates

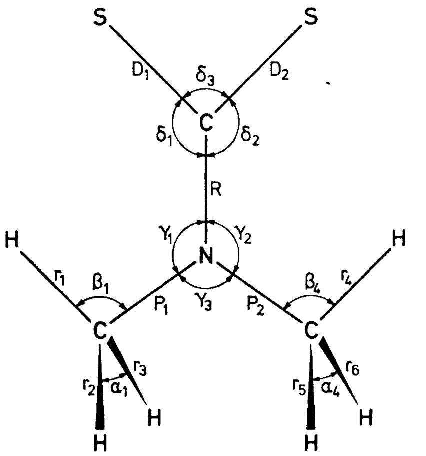

Fig. 1. Internal coordinates for the dimethyldithiocarbamate ion. Additional coordinates are: torsions of methyl groups τ_1 and τ_2, out-of-plane CSS wagging ω_1, and out-of-plane $(CH_3)_2N$ wagging ω_2.

listed in Table 2 were constructed by analogy with those reported for acetone [4] and dimethyl ketone.[5] Normalization of the symmetry coordinates and removal of the redundant ones were effected automatically by the program used for the calculations.

The force field shown in Table 3 (referring to normalized symmetry coordinates) gave the best reproduction of the experimental spectra. The assignment of all observed bands are given in Table 1, but some of these (especially in the νCH/νCD and $\delta CH_3/\delta CD_3$ regions) are open to criticism and may have to be interchanged in the light of future evidence.

The total number of force constants used in calculation of fundamentals is 24, of which K_r, F_r and H_α have been transferred from alkanes.[6] Of the

Table 2. Symmetry coordinates for dimethyldithiocarbamate.

Symmetry coordinate (unnormalized)	Symbol	Description
$S_1(A_1) = 2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6$	ν_{as}CH	Asym. CH stretch
$S_2(A_1) = r_1 + r_2 + r_3 + r_4 + r_5 + r_6$	ν_sCH	Sym. CH stretch
$S_3(A_1) = P_1 + P_2$	ν_sCNC	Sym. CNC stretch
$S_4(A_1) = R$	νCN	CN stretch
$S_5(A_1) = D_1 + D_2$	ν_sCSS	Sym. CSS stretch
$S_6(A_1) = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	$\delta_{as}CH_3$	Asym. CH_3 deformation
$S_7(A_1) = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6$	δ_sCH_3	Sym. CH_3 deformation
$S_8(A_1) = 2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6$	ϱCH_3	In-plane CH_3 rock
$S_9(A_1) = \beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6$	—	Redundant
$S_{10}(A_1) = \delta_1 + \delta_2$	δCSS	CSS deformation
$S_{11}(A_1) = \gamma_1 + \gamma_2$	δCNC	$(CH_3)_2N$ deformation
$S_{12}(A_1) = \delta_3$	—	Redundant
$S_{13}(A_1) = \gamma_3$	—	Redundant
$S_1(B_1) = 2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6$	ν_{as}CH	Asym. CH stretch
$S_2(B_1) = r_1 + r_2 + r_3 - r_4 - r_5 - r_6$	ν_sCH	Sym. CH stretch
$S_3(B_1) = P_1 - P_2$	ν_{as}CNC	Asym. CNC stretch
$S_4(B_1) = D_1 - D_2$	ν_{as}CSS	Asym. CSS stretch
$S_5(B_1) = 2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6$	$\delta_{as}CH_3$	Asym. CH_3 deformation
$S_6(B_1) = \alpha_1 + \alpha_2 + \alpha_3 - \alpha_4 - \alpha_5 - \alpha_6$	δ_sCH_3	Sym. CH_3 deformation
$S_7(B_1) = 2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6$	ϱCH_3	In-plane CH_3 rock
$S_8(B_1) = \beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6$	—	Redundant
$S_9(B_1) = \delta_1 - \delta_2$	ϱCSS	In-plane CSS rock
$S_{10}(B_1) = \gamma_1 - \gamma_2$	ϱCNC	In-plane $(CH_3)_2N$ rock
$S_1(B_2) = r_2 - r_3 + r_3 - r_4$	γCH	CH stretch
$S_2(B_2) = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	δCH_3	CH_3 deformation
$S_3(B_2) = \beta_2 - \beta_3 + \beta_5 - \beta_6$	ϱCH_3	Out-of-plane CH_3 rock
$S_4(B_2) = \tau_1 + \tau_2$	τCH_3	CH_3 torsion
$S_5(B_2) = \omega_1$	ωCSS	CSS out-of-plane wag
$S_6(B_2) = \omega_2$	ωCNC	$(CH_3)_2N$ out-of-plane wag

remaining 21 force constants, those referring to the dimethylamino group have been chosen so as to correspond as closely as possible to those previously reported for methyl amines [7] and *N*-methylacetamide.[8] Thus, the value for K_p (4.67) and H_β (0.73) are close to the counterparts for amines (4.627 and 0.797) and *N*-methylacetamide (4.704 and 0.757). The local force field for the dithiocarboxylate group (Table 3) was initially chosen as that used for dithioacetate,[1] *i.e.* $K_D = 3.50$, $F_D = 0.95$, $H_\delta = 1.15$, $H_{\delta'} = 1.60$, and $H_{\omega_1} = 0.41$. The value of the force constant K_R for stretching of the central CN bond depends heavily on the number of interaction constants used in the calculations. Different selections or values of interaction force constants turned out to have the effect that K_R had to be increased to *ca.* 6 mdyn/Å as compared to 4.8 mdyn/Å in Table 3. Accordingly, the present calculations are not decisive as regards the double bond character of the central CN bond. The validity of the final force field (Table 3) has been ascertained by carrying out preliminary normal coordinate analyses on the dimethyldiselenocarbamate ion and

Table 3. Final valence force constants for dimethyldithiocarbamate.

Force constant	Group	Coordinate(s) involved	Atoms common to interacting coordinates	Value[a]
		Stretch		
K_r	CH_3	C–H	–	4.699[b]
K_P	CH_3–N	C–N	–	4.67
K_R	N–CS_2	N–C	–	4.80
K_D	CS_2	C–S	–	3.95
		Stretch-stretch		
F_r	CH_3	C–H, C–H	C	0.043[b]
F_P	CH_3–N–CH_3	C–N, C–N	N	0.83
F_D	S–C–S	C–S, C–S	C	0.95
F_{PR}	CH_3–N–CS_2	C–N, N–C	N	0.178
F_{RD}	N–C–S	N–C, C–S	C	0.234
		Bend		
H_α	CH_3	∠HCH	–	0.54[b]
H_β	CH_3–N	∠HCN	–	0.73
H_γ	CH_3–N–$C'S_2$	∠CNC′	–	1.40
$H_{\gamma'}$	CH_3–N–CH_3	∠CNC	–	1.40
H_δ	N–C–S	∠NCS	–	0.80
$H_{\delta'}$	S–C–S	∠SCS	–	1.80
H_{ω_1}	N–CS_2	∠NCS_2	–	0.57
H_{ω_2}	$(CH_3)_2$N–C′	∠C_2NC'	–	0.167
		Stretch-bend		
$F_{P\beta}$	CH_3–N	C–N, ∠HCN	C–N	0.318
$F_{P\gamma}$	CH_3–N–$C'S_2$	C–N, ∠CNC′	C–N	0.347
$F_{R\gamma}$	CH_3–N–$C'S_2$	C′–N, ∠CNC′	C′–N	0.283
$F_{R\delta}$	N–C–S	N–C, ∠NCS	N–C	0.283
		Bend-bend		
F_β	CH_3–N	∠HCN, ∠HCN	C–N	–0.04
$F_{\omega_1\omega_2}$	C_2N–CS_2	∠C_2NC, ∠NCS_2	N–C	0.10
		Torsion		
H_τ	CH_3–N	C–N	–	0.0335

[a] In units of mdyn/Å (stretch constants), mdyn/rad (stretch-bend interaction constants), and mdyn Å/(rad)^2 (bending and torsion constants). [b] Values transferred from Ref. 6.

Table 4. Calculated (ν_{calc}, cm^{-1}) and observed (ν_{obs}, cm^{-1}) frequencies and potential energy distribution for the dimethyldithiocarbamate ion from a 24-parameter valence force field.

No.	$(CH_3)_2NCSS^-$			$(CD_3)_2NCSS^-$		
	ν_{calc}	ν_{obs} IR/Raman	Description[a]	ν_{calc}	ν_{obs} IR/Raman	Description[a]
A_1 ν_1	2965	2930/2937	$\nu_{as}CH(100)$	2224	2230/2235	$\nu_{as}CD(100)$
ν_2	2884	2860/2863	$\nu_sCH(100)$	2081	2070/2077	$\nu_sCD(100)$
ν_3	1474	1489/–	$\delta_{as}\mathit{CH_3}(61),\varrho CH_3(22),\nu CN(10),\nu_sCNC(6)$	1054	1067/1064	$\nu_{as}CD_3(91)$
ν_4	1429	1437/–	$\delta_{as}\mathit{CH_3}(28),\mathit{\nu CN}(24),\nu_sCNC(20)$	1404	1400/1417	$\mathit{\nu CN}(46),\nu_sCNC(24)$
ν_5	1381	1361/1374	$\delta_sCH_3(91)$	1119	1115/1115	$\delta_s\mathit{CD_3}(46),\nu_sCNC(21)$
ν_6	1116	1134/1135	$\varrho\mathit{CH_3}(32),\mathit{\nu CN}(25),\nu_sCSS(21)$	1009	1042/1037	$\delta_s\mathit{CD_3}(37),\varrho CD_3(21),\nu_sCSS(16)$
ν_7	946	945/–	$\nu_s\mathit{CNC}(47),\delta CH_3(35)$	770	787/796	$\varrho\mathit{CD_3}(58),\nu_sCNC(32)$
ν_8	575	583/578	$\delta\mathit{CNC}(31),\nu_sCNC(29),\nu_sCSS(22),\nu CN(14)$	524	547/542	$\nu_s\mathit{CSS}(42),\nu_sCNC(22),\nu CN(22)$
ν_9	446	–/439	$\nu_s\mathit{CSS}(50),\delta CNC(37)$	415	396/387	$\delta\mathit{CNC}(36),\nu_sCSS(28)$
ν_{10}	319	328/–	$\delta\mathit{CSS}(67),\delta CNC(18),\nu CN(15)$	301	321/323	$\delta\mathit{CSS}(55),\delta CNC(30),\nu CN(16)$
B_1 ν_{16}	2961	2963/–	$\nu_{as}CH(100)$	2213	2191/2195	$\nu_{as}CD(100)$
ν_{17}	2882	2890/–	$\nu_sCH(100)$	2075	2070/–	$\nu_sCD(100)$
ν_{18}	1461	1464/–	$\delta_{as}CH_3(89)$	1046	1042/–	$\delta_{as}CD_3(77)$
ν_{19}	1386	1361/–	$\delta_sCH_3(94)$	1069	1067/–	$\nu_s\mathit{CD_3}(58),\nu_{as}CNC(28)$
ν_{20}	1257	1257/–	$\varrho\mathit{CNC}(27),\nu_{as}\mathit{CNC}(24),\nu_{as}CSS(14),\varrho CSS(12)$	1244	1240/1237	$\varrho\mathit{CNC}(35),\nu_{as}\mathit{CSS}(23).\nu_{as}\mathit{CNC}(21),\varrho CSS(18)$
ν_{21}	1054	1049/–	$\varrho\mathit{CH_3}(56),\nu_{as}CSS(29)$	792	824/–	$\varrho CD_3(81)$
ν_{22}	965	966/977	$\nu_{as}\mathit{CNC}(71),\nu_{as}CSS(13)$	961	981/969	$\nu_{as}\mathit{CSS}(39),\nu_{as}\mathit{CNC}(33)$
ν_{23}	445	453/–	$\varrho\mathit{CNC}(53),_{as}\nu\mathit{CSS}(42)$	409	423/–	$\varrho\mathit{CNC}(44),\nu_{as}\mathit{CSS}(37)$
ν_{24}	179	–/–	$\varrho\mathit{CSS}(72),\varrho CNC(24)$	168	–/–	$\varrho\mathit{CSS}(72),\varrho CNC(28)$
B_2 ν_{25}	2960	2963/–	$\nu CH(100)$	2209	2191/2195	$\nu CD(100)$
ν_{26}	1464	1464/–	$\delta CH_3(87)$	1049	1055/1054	$\delta CD_3(90)$
ν_{27}	1120	1125/1127	$\varrho CH_3(85)$	896	951/947	$\varrho CD_3(84)$
ν_{28}	590	590/–	$\omega CSS(89)$	585	586/592	$\omega CSS(93)$
ν_{29}	263	264/–	$\omega CNC(85)$	238	238/236	$\omega CNC(87)$
ν_{30}	123	123/–	$\tau CH_3(80)$	88	88/–	$\tau CD_3(79)$

[a] Abbreviations (*cf.* Table 2): ν= stretching, δ= deformation, ϱ= rocking, ω= wagging, τ= torsion, and, as subscripts, s= symmetric, as= antisymmetric. The rounded percentage potential energy distribution values are shown in parentheses; small values have been neglected. In cases where several vibrations contribute significantly, the most important is printed in italics.

nickel(II) dimethyldithio- and dimethyldiselenocarbamate. These results will be published shortly.

The calculated fundamentals and their description in the symmetry coordinates is given in Table 4. The overall agreement is considered fairly good, except that some of the calculated frequencies associated with the methyl rocking and symmetrical deformation modes (ν_6, ν_{19}, ν_{21}, and ν_{27}) deviate considerably from the experimental values. This is a phenomenon previously noted when using similar force fields for methyl groups attached to unsaturated systems,[4,5] and its origin has not been clarified. Within the framework of the force field chosen for the present work, exploratory calculations showed that the discrepancy could not be removed.

DISCUSSION

From Table 1 is seen that the experimental spectrum of the DDTC ion in the region 1400 – 1500 cm^{-1} is dominated by the presence of the strong broad $\nu_3(A_1)$ at 1489 cm^{-1}. A counterpart to this band is found in metal complex compounds of differently substituted dithiocarbamates (see references in part I [1]), and is generally assumed to originate mainly in the stretching vibration of the central CN bond which has attained some double bond character. This interpretation does not apply for the DDTC ion. From Table 4 is seen that the A_1 fundamentals in the region 1400 – 1500 cm^{-1},ν_3 and ν_4, arise from coupling between asymmetric CH_3 deformation and a skeletal mode, which according to the L-matrix is due to an out-of-phase combination of νCN and ν_sCNC. In the deuterated compound, the frequency of the deformation mode is lowered with the result that the almost pure $\delta_{as}CD_3$ vibration is observed at 1054 cm^{-1}, while the out-of-phase combination of νCN and ν_sCNC becomes the main component of the strong band at 1400 cm^{-1}. The strong mixing of νCN and ν_sCNC is quite reasonable in view of the similar values of the stretching force constants K_R and K_P (Table 3).

In the infrared region 1200 – 1400 cm^{-1} of DDTC, the two strong fundamentals $\nu_5(A_1)$ and $\nu_{20}(B_1)$ occur at 1361 cm^{-1} and 1257 cm^{-1}, respectively. The former of these is due to δ_sCH_3 stretching, but the latter band is only displaced by *ca.* 20 cm^{-1} on deuteration, and must accordingly originate mainly from a skeletal motion. From Table 4 and the L-matrix values it can be concluded that it arises from approximately equal amounts (as measured by the contribution to the potential energy) of skeletal stretching (out-of-phase combination of ν_{as} CSS and ν_{as}CNC) and skeletal rocking modes. If the GVFF treatment adopted here is not gravely in error, it can be concluded that bands occurring in what is commonly described as the CN stretching region may contain a considerable contribution from skeletal rocking modes usually placed at much lower frequencies.

Proceeding towards lower frequencies in the infrared spectrum of the DDTC ion, the next strong, characteristic band is found at 966 cm^{-1}. This has been assigned to the fundamental $\nu_{22}(B_1)$ and is hardly influenced by deuteration. According to the L-matrix elements, it originates from in-phase combinations of ν_{as}CSS and ν_{as}CNC in different proportions in the undeuterated and the deuterated compounds. A similar origin would be expected for the counterpart observed in metal complex compounds of dithiocarbamates (between 900 cm^{-1} and 1000 cm^{-1}, see references in part I [1]), which is generally assumed to arise chiefly from ν_{as}CSS.

The fundamentals $\nu_8(A_1)$ and $\nu_{28}(B_2)$ are observed partly superimposed at 583 and 590 cm^{-1}, respectively, in the infrared spectrum of the DDTC ion. The former of these bands is also the strongest band in the Raman spectrum, with a depolarization ratio of *ca.* 0.1. According to the L-matrix, the main contribution is from a skeletal stretching motion, in which all five bonds stretch in phase: a "skeletal breathing motion". The correspondence between the Raman results and the GVFF description as regards this fundamental supports the validity of the treatment adopted in the present work.

The remaining fundamentals will be discussed in some detail in connection with the dimethyldiselenocarbamate ion. In the present context, we shall only point out that the asymmetrical and the symmetrical CSS stretching modes in the DDTC ion are both strongly coupled to other vibrational modes. The δCSS scissoring mode is found at slightly lower frequencies in DDTC (*ca.* 325 cm^{-1}) than in dithioacetate (*ca.* 370 cm^{-1}). The wagging mode, ωCSS, shows the opposite trend (*ca.* 590 cm^{-1} in DDTC, 450 cm^{-1} in dithioacetate). The CSS rocking mode, which gives rise to very weak absorption in dithioacetate near 325 cm^{-1}, has not been observed for the DDTC ion. According to the calculations, it should be located below 200 cm^{-1} where the strong, broad absorption from the lattice modes dominates the spectrum.

EXPERIMENTAL

The experimental details of obtaining the spectra and performing the normal coordinate analyses were described in part I of this series.[1] We thank Dr. Kjeld Rasmussen and Dr. O. Faurskov Nielsen for providing us with the far-infrared and the Raman data, respectively.

Potassium dimethyldithiocarbamate hemihydrate. To a suspension of powdered potassium hydroxide (2×10^{-2} mol) in dioxane (25 ml) was added dimethylammonium chloride (2×10^{-2} mol), and the reaction mixture was stirred for 1 h at room temperature. The solution containing the free amine was separated from potassium chloride by centrifugation and added to another suspension of powdered potassium hydroxide (2×10^{-2} mol) in dioxane (15 ml). Into this vigorously stirred mixture was dropped a solution of carbon disulfide (2×10^{-2} mol) in dioxane (25 ml) over a period of 1 h at room temperature. The colourless precipitate was isolated by filtration, washed successively with dioxane and dry ether, and dried *in vacuo*. More salt could be obtained by adding dry ether to the mother liquor. Total yield: 95 %. The salt was purified by one recrystallization from dioxane, followed by one from dry acetone. (Found: C 21.76; H 4.40; N 8.52. Calc. for $C_3H_6NS_2K \cdot \frac{1}{2}H_2O$: C 21.40; H 4.19; N 8.32.)

The perdeuterated salt was prepared in an identical manner, using *C*-deuterated dimethylammonium chloride.

Lead(II) dimethyldithiocarbamate. On mixing the calculated amounts of aqueous solutions of lead(II) acetate and potassium dimethyldithiocarbamate, colourless lead(II) dimethyldithiocarbamate precipitated in excellent yield. (Found: C 16.25; H 2.76; N 6.31. Calc. for $C_6H_{12}N_2S_4Pb$: C 16.10; H 2.70; N 6.26.)

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