

Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. IX. The Influence of Metal Complex Formation on the Characteristic Thioamide Bands in 1,2-Dimethyl-3-pyrazolidinethione

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Compounds with a thioamide group often form complexes with metal halides by *S*-coordination. Usually the IR band with maximum CN stretching character moves towards higher frequencies while those with maximum CS stretching character are displaced towards lower frequencies. However, 1,2-dimethyl-3-pyrazolidinethione (DMPT) forms complexes of the type (DMPT)₂ZnBr₂, DMPT·CdI₂, (DMPT)₂CdI₂ and DMPT·HgCl₂ in which the frequencies of the CS bands are unchanged or displaced to higher frequencies on complex formation. The IR spectra of these compounds and five deuterated analogues of DMPT·HgCl₂ were recorded in the region 4000–180 cm⁻¹. Normal coordinate analysis of DMPT·HgCl₂ suggests that one of the reasons for the anomalous shift of the CS stretching bands is due to change in potential energy distribution induced by complex formation. Another reason is an increase in the force constant for CS stretching. From CNDO/2 calculations it is concluded that complex formation increases the weight of the π -character of the thiohydrazide group, N⁺=C–S⁻, with concomitant decrease in the force constant for CS stretching. In addition, the σ -electrons of the CS bond are polarised towards sulfur so as to give an increased σ -density in the CS-region. Apparently the latter effect is pronounced enough to result in an increase in the force constant for CS stretching. The results stress the importance of CNDO/2 calculations as a tool for obtaining qualitative understanding of the changes occurring in ligands on complex formation. An understanding of the importance of the polarisation of the σ -electrons of the CS bond by coordination with metal halides should facilitate

future discussions on the structures of related compounds.

In the early study of Jensen and Nielsen¹ and in the review by Gosavi and Rao,² attention was drawn to the influence of metal complex formation on IR bands characteristic of the thioamide group. Since then a considerable number of papers have appeared on the subject, the most extensive being those by Devillanova and Verani *et al.* on thio- and seleno-ureas,³ Pignedoli and Peyronel *et al.* on dithio-biuret,⁴ Desseyne *et al.* on thioamides,⁵ and by Kedzia *et al.* on mainly thiocarbazates and thiosemicarbazides.⁶ It is generally assumed that *S*-coordination will tend to increase the weight of the canonical structure N⁺=C–S⁻, causing the force constant for ν CN (CN stretching) to increase while that for ν CS to decrease relative to the free ligand values. As a result, bands with ν CN contributions will be displaced towards higher frequencies while bands with ν CS character will be displaced to lower frequencies. *N*-coordination, as a first approximation, will have the opposite effects.

Aarts *et al.*^{7–9} have pointed out that the frequency shifts of these bands on *S*-coordination may be absent or even occur in the opposite direction to that mentioned above. This was attributed principally to the changes in ligand potential energy distribution (PED) following *S*-coordination. Further, back-donation may occur from the metal ion to the empty sulfur d-orbitals or to low-lying anti-

bonding states of the ligand, changing the electron density of the thioamide group. The stereochemistry adopted by the coordination compound¹⁰ or the conformational changes in the ligand¹¹ (e.g. thiosemicarbazides,¹² dithiobiuret¹³) due to complex formation may result in large shifts of the ν_{CN} and ν_{CS} frequencies. However, the rules break down when simultaneous *N,S*-coordination occur.¹⁴

In order to assess the relative importance of these factors, reliable normal coordinate analyses (NCA's) of thioamide coordination compounds are needed. This requires that at least (i) the site of coordination (N and/or S) and the conformation of the ligand are known, (ii) the fundamentals are identified, and (iii) the force field is determined by a least-squares iterative procedure for both the ligand and the complex. For example, the force constant for ν_{CN} increases strongly in *S*-coordinated thioacetamide,¹⁵ but the band with maximum ν_{CN} character exhibits only a negligible shift. The anomalous small shift can therefore be attributed unambiguously to changes in PED following complex formation in this case. Similar investigations have not been reported for metal complexes of thioamides with anomalous shifts of ν_{CS} bands.

The vibrational spectra of the thiohydrazide 1,2-dimethyl-3-pyrazolidinethione (DMPT) have previously¹⁶ been thoroughly examined. In the coordination complexes of DMPT, $(\text{DMPT})_2\text{ZnBr}_2$, $\text{DMPT} \cdot \text{CdI}_2$, $(\text{DMPT})_2\text{CdI}_2$ and $\text{DMPT} \cdot \text{HgCl}_2$, the ν_{CS} bands show only very small shifts either towards higher or towards lower frequencies. Since the IR spectra of these coordination compounds are almost identical, $\text{DMPT} \cdot \text{HgCl}_2$ was selected for closer investigation of the anomalously small CS shift. To eliminate errors and gather sufficient material for the NCA, we have prepared the following deuterated derivatives (cf. Ref. 16): $(\text{DMPT-1-}d_3)\text{HgCl}_2$, $(\text{DMPT-2-}d_3)\text{HgCl}_2$, $(\text{DMPT-}d_4)\text{HgCl}_2$, $(\text{DMPT-}d_6)\text{HgCl}_2$ and $(\text{DMPT-}d_{10})\text{HgCl}_2$. The results of the NCA are discussed in relation to the changes in electron density calculated by the CNDO/2 method.

EXPERIMENTAL

The coordination compounds $(\text{DMPT})_2\text{ZnBr}_2$, $(\text{DMPT})_2\text{CdI}_2$ and $\text{DMPT} \cdot \text{HgCl}_2$ were prepared by addition of an ethanolic solution of the ligand to a saturated ethanolic solution of the metal halides. $\text{DMPT} \cdot \text{CdI}_2$ was prepared similarly from a saturated aqueous solution of CdI_2 . The solid

products were freed from metal halides and ligands by washing with the solvent and drying *in vacuo*. Elemental analysis indicated the crude products to be analytically pure and they were used directly for recording the IR spectra without further purification. The solid state spectra were recorded on a Perkin-Elmer model 580 spectrometer in the range 4000–180 cm^{-1} in KBr and/or CsI discs. The spectrum of $(\text{DMPT})_2\text{CdI}_2$ in CHCl_3 and CDCl_3 solution was obtained from saturated solutions in KBr cells of 1 mm thickness. The bands in the low-frequency region sensitive to the halide ion were assumed to originate mainly in vibrations involving the metal halide (Table 2).

NORMAL COORDINATE ANALYSIS

The IR spectra of the four coordination compounds of DMPT (Table 2) are almost identical except in the region below 400 cm^{-1} where vibrations due to the metal-ligand bonds and the metal halide are expected to occur. This indicates (i) that ligand vibrations do not couple significantly with the metal halide vibrations in the range 400–4000 cm^{-1} , (ii) that the ligand spectrum is largely unaffected by the composition (1:1 or 2:1), the symmetry, the crystal structure, and the state of the complex, and (iii) that Zn, Cd and Hg halides coordinate to the same atom(s) of the ligand. These results justify the comparison of the IR results for solid $\text{DMPT} \cdot \text{HgCl}_2$ with CNDO/2 calculations on a DMPT complex with ZnBr_2 . Since we were interested only in the influence of complex formation upon the thiohydrazide bands we did not perform a full NCA including the metal halide molecule. Instead we used the calculations reported previously for DMPT¹⁶ and simply replaced the observed fundamentals with the corresponding values for $\text{DMPT} \cdot \text{HgCl}_2$ and the five deuterated compounds. On the basis of X-ray results for related compounds^{17–19} the geometry of DMPT has been assumed to be unchanged upon *S*-coordination. In summary, a perturbational treatment of the changes in the IR spectrum of DMPT on complex formation is considered adequate for the range 400–4000 cm^{-1} . From Table 2 it is seen that this approximation is liable to fail only in the case of the force constant for the CS in-plane deformation, which is largely determined by the position of the fundamental ν_{43} below 400 cm^{-1} .

The zeroth order values of the force constants were transferred directly from DMPT.¹⁶ As previ-

Table 1. Valence force constants for DMPT · HgCl₂ compared with the values for DMPT.^a

Symbol	DMPT · HgCl ₂	DMPT	Symbol	DMPT · HgCl ₂	DMPT
	<i>CH₃/CH₃</i>			<i>Ring</i>	
<i>K_r</i>	4.76	4.72	<i>K_D</i>	3.85	3.76
<i>F_{rr}</i>	0.01	0.01	<i>K_{L2}</i>	3.59	3.88
<i>H_α</i>	0.51	0.51	<i>K_{L1}</i>	4.71	4.59
<i>H_β</i>	0.82	0.76	<i>K_{B1}</i>	3.77	3.97
<i>F_β</i>	-0.04	-0.04	<i>K_A</i>	5.56	5.35
<i>K'_r</i>	4.77	4.80	<i>K_{B2}</i>	8.56	7.51
<i>F'_{rr}</i>	-0.08	-0.13	<i>K_{P1}</i>	4.48	4.64
<i>H'_α</i>	0.51	0.51	<i>K_{P2}</i>	5.07	5.07
<i>H'_β</i>	0.76	0.72	<i>H_{μ1}</i>	0.41	0.58
<i>F'_β</i>	-0.03	-0.03	<i>H_{μ2}</i>	1.59	1.77
	<i>CH₂</i>		<i>H_{μ3}</i>	0.79	0.82
<i>K_d</i>	4.71	4.80	<i>H_{ε1} = H_{ε2}</i>	1.40	1.27
<i>F_{dd}</i>	0.04	0.03	<i>H_{θ1} = H_{θ2}</i>	2.65	2.42
<i>f_y</i>	0.05	0.06	<i>H_{ε3} = H_{θ3}</i>	0.68	0.75
<i>F'_γ</i>	0.08	0.08	<i>H_Δ</i>	0.34	0.35
<i>H_{δ2}</i>	0.48	0.47	<i>F_{Dμ1} = F_{Dμ2}</i>	0.55	0.42
<i>H_{γ3} = H_{γ4}</i>	0.54	0.59	<i>F_{L1γ1} etc.</i>	0.35	0.35
<i>H_{γ3}^o = H_{γ4}^o</i>	0.69	0.69	<i>F_{L2w2} etc.</i>	0.76	0.74
<i>F_{γ3γ4}</i>	-0.31	-0.32	<i>F_{P1β} = F_{P2β}</i>	0.65	0.66
<i>F_{γ3γ4}^o</i>	0.07	0.08			
<i>H_{δ1}</i>	0.41	0.43			
<i>H_{γ1} = H_{γ2}</i>	0.78	0.78			
<i>H_{γ1}^o = H_{γ2}^o</i>	0.69	0.66			
<i>F_{γ1γ2}</i>	-0.21	-0.14			
<i>F_{γ1γ2}^o</i>	0.12	0.09			

^aFor interpretation of symbols, units, and force field for DMPT, see Ref. 15. The values of *H_v*, *F_{DL2}*, *F_{DB2}*, *F_{B2μ2}*, *F_{B2μ3}*, *F_{L2μ3}* = *F_{Aε3}*, *H_w*, and *F_w* are the values of DMPT (see text).

ously, the interaction constants *F_{DL2}*, *F_{DB2}*, *F_{B2μ2}* and *F_{B2μ3}* were fixed. The values of *H_v*, *H_w* and *F_w* are mainly determined by the fundamentals below 180 cm⁻¹, the position of which have not been recorded for the coordination compounds. Since these force constants can hardly be expected to vary to a significant degree on complex formation they were likewise equated to the values found for DMPT. Inspection of the correlation matrix indicated *F_{L2μ3}* = *F_{Aε3}* to be highly correlated and therefore they were also transferred from DMPT. A simultaneous least-squares adjustment was then made for DMPT · HgCl₂ and its deuterated derivatives. By fitting the remaining 43 force constants to ca. 250 observed frequencies, the final set (reported

in Table 1) was obtained. The force constants pertaining to the CH₃, CH₃' and CH₂ - CH₂ groups show only small changes. This result supports the expectation that complex formation does not notably influence these parts of the DMPT molecule. The most important changes are observed in the force constants of the thiohydrazide skeleton (N - N - C - S). The force constants for CS in-plane and out-of-plane deformations (*H_{μ1}*, *H_{μ2}*, *H_Δ*) decrease on complex formation. This is related to the lowering of *ν₃₈*, *ν₄₀* and *ν₄₃* frequencies which originate to a considerable degree in these modes (Table 2). The upward trends in *ν₁₁*, *ν₂₀* and *ν₃₉* frequencies reflect to a large degree the increase in the force constants for *ν*CS (from 3.76 to 3.85

Table 2. IR spectra (cm^{-1}) of metal complexes $(\text{DMPT})_2\text{ZnBr}_2$, $(\text{DMPT})_2\text{CdI}_2$, $(\text{DMPT})_2\text{CdI}_2$ and $(\text{DMPT})_2\text{HgCl}_2$ of 1,2-dimethyl-3-pyrazolidimethione (DMPT). Calculated frequencies, tentative assignments, description of the fundamentals and frequency shift relative to DMPT for the complex $(\text{DMPT})_2\text{HgCl}_2$.^a

$(\text{DMPT})_2\text{ZnBr}_2$		$(\text{DMPT})_2\text{CdI}_2$		$(\text{DMPT})_2\text{HgCl}_2$		Assignment and description (PED, %) ^f	
Observed IR, disc ^b	Observed IR, disc ^b	Observed, IR disc ^b	DMPT-shift ^d IR, disc ^b	DMPT-shift ^d solid solut. ^c	Calc. ^e		obs. calc.
2991m	3002m	3003m	3008m	+18 +15	3000m	3001 +15 +13	$\nu_1, \nu_{\text{as}}\text{CH}_3(99)$
2971m	2988m 2977m	2987m 2973m	2980m	+15	2971m	2998 +15 +13	$\nu_2, \nu_{\text{as}}\text{CH}_3(99)$
		2960vw,sh 2940vw,sh	2965w,sh 2945vw,sh	(-21) (-20)	2968m,sh 2949w,sh	2976 +10 +9	$\nu_3, \nu_{\text{as}}\text{CH}_3(99)$
2935w,sh	2935w,sh	2931w,sh	2940w,sh	-7 +4	2913m	2972 +10 +8	$\nu_4, \nu_{\text{as}}\text{CH}_3(99)$
2914m	2908m	2908m	2920m		2913m	2968 -17 -3	$\nu_5, \nu_{\text{as}}\text{CH}_2(99)$
2858m	2867m 2857m	2870w,sh 2861m	2878m	(+9) +18	2869m	2954 -12 -4	$\nu_6, \nu_{\text{as}}\text{CH}_2(99)$
1560vs,br	1560vs,br	1562vs,br	1550vs,br	+62 +57	1571vs,br	2928 +1 -1	$\nu_7, \nu_{\text{as}}\text{CH}_3(98)$
1459ms	1462m,sh	1461m,sh	1467m,sh	+1 +1	1462m,sh	2927 +1 -3	$\nu_8, \nu_{\text{as}}\text{CH}_2(97)$
1450m,sh	1450ms	1446ms	1454ms 1448w,sh	-3 0	1450ms	2915 -2 -3	$\nu_9, \nu_{\text{as}}\text{CH}_2(99)$
1440vw,sh		1438w,sh 1432w,sh	1418ms	0	1430w	2867 +17 +5	$\nu_{10}, \nu_{\text{as}}\text{CH}_3(100)$
1420ms	1420ms	1421ms	1418ms		1420m,sh	1565 +71 +67	$\nu_{11}, \nu\text{C}^3\text{N}(81), \delta_{\text{as}}\text{CH}_2(7)$
1416m,sh	1412m,sh	1416w,sh	1416w,sh		1413ms	1462 +2 -3	$\nu_{12}, \delta_{\text{as}}\text{CH}_3(41), \delta_{\text{as}}\text{CH}_3(32), \delta\text{CH}_2(17)$
1389m	1396m	1399m	1399m		1395m	1457 +1 -2	$\nu_{13}, \delta_{\text{as}}\text{CH}_3(57), \delta_{\text{as}}\text{CH}_3(27)$
1349w	1352w,sh	1354w,sh	1354w,sh		1354w	1453 +1 -2	$\nu_{14}, \delta_{\text{as}}\text{CH}_3(99)$
1340w	1347ms	1346ms	1350mw	+6 +6	1348w	1439 -10 -4	$\nu_{15}, \delta_{\text{as}}\text{CH}_3(87)$
1318s	1319s	1319s	1319s	+6 +6	1318s	1431 -10 0	$\nu_{16}, \delta_{\text{as}}\text{CH}_3(15), \delta\text{CH}_2(67)$
1260w,sh	1253w	1265vw,sh	1260m	-5 +1	1249m	1421 (+4) +6	$\nu_{17}, \delta_{\text{as}}\text{CH}_3(68), \delta\text{CH}_2(26)$
1246m	1244m	1244m	1248m	+4 +5	1233mw	1411 (-9) -10	$\nu_{18}, \delta\text{CH}_2(63), \delta_{\text{as}}\text{CH}_3(25)$
1235m,sh	1233mw	1235m,sh	1238w,sh	+8 +8	1193s	1397 +6 +6	$\nu_{19}, \delta_{\text{as}}\text{CH}_3(99)$
1192s	1195s	1195s	1193s		1178m,sh	1353 +10 +6	$\nu_{20}, \nu\text{NN}(29), \nu/\delta\text{ring}(54)$ and $\nu_{34} + \nu_{37}$
1185s,sh	1133vs	1130vs	1133vs	0 0	1130vs	1324 +5 +7	$\nu_{21}, \text{tCH}_2(68), \omega\text{CH}_2(26)$
1130vs	1115m,sh	1118s	1115m,sh		1120s,sh	1314 +1 +5	$\nu_{22}, \omega\text{CH}_2(26), \nu\text{ring}(34), \delta\text{ring}(24)$
						0	$\nu_{33} + \nu_{41}$
						1238 +2 +5	$\nu_{35} + \nu_{37}$
						1204 +6 +6	$\nu_{23}, \nu/\delta\text{ring}(43), \omega/\text{tCH}_2(35), \rho\text{CH}_3(29)$
						1164 +2 -4	$\nu_{24}, \text{tCH}_2(37), \omega\text{CH}_2(18), \rho\text{CH}_3(22)$
						1137 +9 0	$\nu_{25}, \rho\text{CH}_3(56), \nu\text{ring}(20), \omega/\text{tCH}_2(25)$
							$\nu_{26}, \rho\text{CH}_3(30), \nu\text{ring}(41)$ and $\nu_{36} + \nu_{38}$

Table 2. Continued.

1092m	1094m	1096m	1098m	+2	+3	1091w	1101	-3	-1	$\nu_{27}, \rho\text{CH}_2(96)$
1078m	1080m	1080m	1080mw	+4	+4	1076m	1084	0	-2	$\nu_{28}, \nu_{as}\text{NCS}(13), \rho\text{CH}_3(41), \nu/\delta\text{ring}(37)$
1063w,sh	1062vw,sh	1059w,sh	1049w	0			1063		+3	$\nu_{29}, \nu\text{CC}(43), \rho\text{CH}_2(30)$
1043w	1042w	1042w	1039vw	-3	-4	1043w	1037	-2	-9	$\nu_{30}, \nu_{as}\text{NCS}(8), \text{vring}(49), \rho\text{CH}_3(24)$
1009m	1008m	1010m	1008m	+4	+4	1007m	997	+1	+1	$\nu_{31}, \rho\text{CH}_2(64), \nu\text{CC}(16)$ and $2 \cdot \nu_{38}$
980w	970w	968vw	968w	-2	-3	976vw	947m	+6	+5	
942m	944m	945m	946m	+3	+6	947m	944	+5	-5	$\nu_{32}, \rho\text{CH}_2(59), \nu\text{NN}(7), \text{vring}(24)$ and $\nu_{37} + \nu_{38}$
930w,sh	932vw,sh	932w,sh	(890m)	-6	(-1)	939m	899	+11	-5	$\nu_{33}, \nu\text{NN}(15), \nu\text{CS}(6), \text{vring}(39), \rho\text{CH}_2(19)$
880m	885m	887m	—			882m	794	-11	-6	$\nu_{34}, \nu\text{CS}(43), \nu\text{NN}(6), \nu/\delta\text{ring}(60)$
787m	785m	789m	—			780m	694	-9	+3	$\nu_{35}, \nu\text{C}^3\text{N}(8), \text{vring}(21), \delta\text{ring}(54)$
688mw	689mw	690mw	—			690mw	634	0	-4	$\nu_{36}, \nu\text{NN}(13), \nu/\delta\text{ring}(100)$ and $\nu_{39} + \nu_{45}$
638w	635w	640vw	(641w)	0		639w	562	-1	+9	$\nu_{37}, \Delta\text{CH}_3 - \text{N} < (58), \text{vring}(23)$ and $\nu_{42} + \nu_{45}$
592mw	595mw	598mw	600w	0	+1	596mw	487	-2	-3	$\Delta\text{CS}(23), \Delta\text{CH}_3 - \text{N} < (26), \text{vring}(18)$
547m	543m	550m	550mw	+2	+8	553m	433	+7	+4	$\nu_{38}, \nu\text{CS}(23), \nu\text{NN}(13), \Delta\text{CS}(18), \delta\text{ring}(32)$
515vw	515vw	515vw	518w	-7	+1	515vw	414	-3	-7	$\nu_{39}, \nu\text{CS}(23), \nu\text{NN}(13), \Delta\text{CS}(18), \delta\text{ring}(32)$
490m	490m	490m	491m	-1	+4	488m	378	+6	0	$\nu_{40}, \Delta\text{CS}(34), \nu\text{NCS}(16), \Delta\text{CH}_3 - \text{N} < (43), \text{vring}$
434f	436ms	435ms	437m	+5	+5	436m		-9		$\nu_{41}, \nu/\delta\text{ring}(59), \rho\text{CH}_2(46)$
416m	410m	418m	420ms	-4	-3	413m		+3		DMPT-metal halide
378vw	375w,sh	378vw	—	+2		379vw	335		-3	$\nu_{42}, \delta\text{CH}_3 - \text{N} < / \text{CH}_3 - \text{N} < (43), \nu/\delta\text{ring}(74)$
356m	360m	358m	358m			359mw	251	-10	-17	DMPT-metal halide
320m	340w,sh	340w,sh	338vw,sh	-10	-11	340m		-15		$\nu_{43}, \delta\text{CS}(72), \delta\text{CH}_2 - \text{N} < (17)$
248w,sh	318m	310m	310m	-15		282mw	199		-3	DMPT-metal halide
220m	230m	255vw,sh	229m			255w,sh	170		-1	DMPT-metal halide
200m		200vw	200vw			238m	114		-4	DMPT-metal halide
							68		+1	$\nu_{44}, \tau\text{CH}_2'(69)$
							21		-1	$\nu_{45}, \tau\text{CH}_3(91)$
										$\nu_{46}, \delta\text{ring}$
										$\nu_{47}, \delta\text{ring}$
										$\nu_{48}, \delta\text{ring}$

^a The following abbreviations have been used: s, strong; m, medium; w, weak; br, broad; sh, shoulder. Weak and very weak bands not assigned to fundamentals have in many instances been omitted from the table. ^b Best values from KBr/CsI discs. ^c From spectra run in CHCl_3 and CDCl_3 solutions. ^d Shifts of corresponding bands from DMPT to complex compound in the IR spectra. Approximate values are given in parentheses. The values in bold types are considered significant. ^e Iteration based upon all six isotopic species of $\text{DMPT} \cdot \text{HgCl}_2$. ^f Abbreviations: ν = stretch; δ = deformation; Δ = out-of-plane deformation; ρ = rock; ω = wag; t = twist; τ = torsion; s = symmetric; as = antisymmetric. Vibrations of the pyrazolidine ring and the attached carbon atoms are designated 'ring' or using the following nomenclature: $\text{N}^1 - \text{CH}_3$, $\text{N}^2 - \text{CH}_2$, C^3s . Vibrations believed to originate mainly in the metal halide are designated DMPT-metal halide. The potential energy distribution (PED, $x_{ik} = 100F_{ij}L_{ik}^2/\lambda_k$) is stated only for significant contributions. The PED referring to the thiohydrazide group is given in bold types.

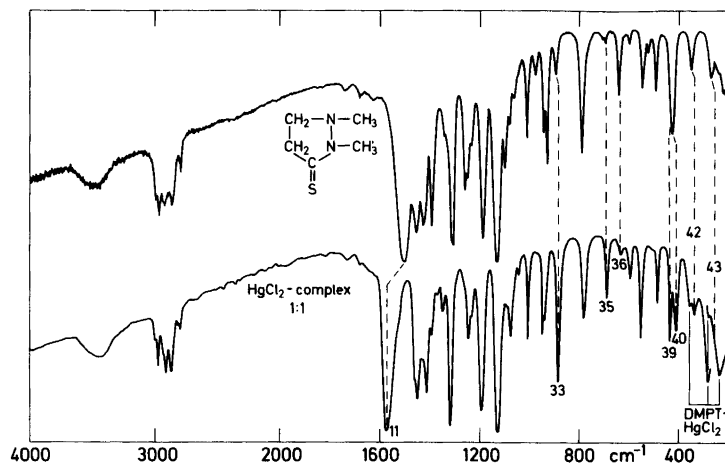


Fig. 1. The IR spectra of 1,2-dimethyl-3-pyrazolidinethione in the liquid state (upper) and the mercury(II) chloride complex in the solid state (lower). Corresponding bands are indicated by dotted lines. The three bands below 400 cm^{-1} (believed to originate from the coordinated HgCl_2) are indicated as $\text{DMPT}\cdot\text{HgCl}_2$.

$\text{mdyn}/\text{\AA}$), νCN (from 7.51 to $8.56\text{ mdyn}/\text{\AA}$) and νNN (from 5.35 to $5.56\text{ mdyn}/\text{\AA}$). The force constants for three of the bonds adjacent to the $\text{N}-\text{N}-\text{C}-\text{S}$ grouping (K_{L_2} , K_{B_1} and K_{P_1}) decrease on complex formation. This feature appears to be indirectly connected with the decrease in ν_{33} .

RESULTS AND DISCUSSION

The IR spectra of DMPT (liquid) and $\text{DMPT}\cdot\text{HgCl}_2$ (solid) are compared in Fig. 1. Some of the more important shifts and some shifts which are difficult to observe are indicated with dotted lines. The bands which are believed to originate mainly in vibrations of the coordinated metal halide (below 400 cm^{-1}) have also been indicated on Fig. 1. The frequencies of the vibrational modes of interest are listed in Table 2 in a manner similar to that used for DMPT¹⁶ and the selenium analogue (DMPS)²⁰ in previous papers in this series. The complete list of the frequencies observed for the isotopic derivatives has been omitted to save space. Generally speaking, the frequencies listed for $\text{DMPT}\cdot\text{HgCl}_2$ in Table 2 are similar to those of DMPT.¹⁶ Therefore, a systematic description of the spectra can be dispensed with, and the discussion will be restricted to some features of general interest.

In the present context, *i.e.* when the IR spectrum of $\text{DMPT}\cdot\text{HgCl}_2$ is treated as a perturbed spectrum of DMPT, the following theoretical framework

seems appropriate (*cf.* DMPS²⁰). Coordination of DMPT involves (i) geometrical change, which is probably small, and (ii) a change in force field due to electronic and steric effects of the metal halide. The complex formation results in (i) a change in position of bands, $\nu(\text{DMPT}\cdot\text{HgCl}_2) - \nu(\text{DMPT})$ (DMPT-shift in Table 2), (ii) a change in PED of the normal vibrations; and as long as the changes are small we will make use of corresponding bands in DMPT and $\text{DMPT}\cdot\text{HgCl}_2$, *i.e.* the concept of group frequencies will be applied, (iii) a partial breakdown of the perturbational treatment below 400 cm^{-1} due to coupling effects between DMPT and the metal halide, (iv) changes in intensity and profile of the bands especially as a result of different Fermi interactions with overtones and combination modes.

From the spectra shown in Fig. 1 it appears that there is a close correspondence between DMPT and $\text{DMPT}\cdot\text{HgCl}_2$ with the following reservations. Firstly, strong intensity changes may occur as in ν_{35} , for example due to the different symmetry of the coordination compounds. Secondly, an intensity reversal may occur between a fundamental and the accompanying Fermi-enhanced combination mode (*e.g.* ν_{36} followed by $\nu_{39} + \nu_{45}$ at slightly lower frequency). Thirdly, some bands which by virtue of their position, form, and intensity seem to be corresponding, have nevertheless quite different PED's (*e.g.* ν_{17} and ν_{18} have interchanged positions, ν_{39} has an increased contribution from ΔCS).

All these complications have been described in some detail in the previous paper²⁰ and will not be discussed further here.

In qualitative discussions of the vibrational spectra of coordination compounds it is usually assumed that once the above correspondence with the spectrum of the free ligand has been established, the bands which show a frequency shift have important contributions from vibrations of the parts of the ligand involved in complex formation. This assumption is not correct, as can be seen from a comparison of the results in Table 2 with those reported for DMPT.¹⁶ The fundamentals ν_{21} and ν_{24} , for example, display small but definite shifts towards higher frequencies. Nevertheless, the NCA reveals that the shifts arise merely from a change in PED of vibrations of the CH_2 and CH_3 groups. As a matter of fact, most of the shifts observed on complex formation of DMPT are 10 cm^{-1} or less, and without the results of the NCA it would be extremely difficult to locate the contributions from the thiohydrazide group. These results also explain the problems encountered by Devillanova and Verani²¹ in identifying the thioamide bands in heterocyclic thiones by complex formation with CdCl_2 .

The fundamental ν_{11} of DMPT, mainly due to the C^3N stretching vibration, is displaced by $60\text{--}70\text{ cm}^{-1}$ towards higher frequencies on complex formation. We therefore expect ν_{34} and ν_{39} , with the highest contributions from CS stretching to shift towards lower frequencies. Nevertheless, ν_{34} shows a downwards shift by only $0\text{--}9\text{ cm}^{-1}$ and ν_{39} even shifts $4\text{--}6\text{ cm}^{-1}$ towards higher frequencies. The results of the NCA leaves no doubt that one of the reasons for the anomalous shifts of these bands stems from a change in PED. By comparison of the last column in Table 2 with the results published previously for DMPT we can estimate the changes in the composition of the bands following conversion of DMPT to $\text{DMPT} \cdot \text{HgCl}_2$. It is seen that the PED of ν_{34} shows an increased contribution from νCS (from 31 to 43%) at the expense of ring stretching and deformation vibrations. By contrast, the νCS contribution of ν_{39} decreases from 32 to 23% while ΔCS increases from 4 to 18%.

However, the NCA also indicates the force constant for CS stretching to increase from 3.76 to 3.85 $\text{mdyn}/\text{\AA}$. Even if we take all possible errors into account we may safely state that the anomalous shifts of these bands are partly due to the fact that

the force constant for CS stretching does not decrease as expected. The reason must be found in the electronic displacements following complex formation, since the phenomenon is observed (Table 2) in Zn, Cd and Hg complexes with different stoichiometry and structure¹⁹ and both in the solid state and in solution. As the metals in question do not have external d-electrons readily available for back-donation to DMPT such an explanation seems excluded.

The possibility remains that the electronic redistribution induced in DMPT on complex formation does not correspond to an increased weight of the structure $\text{N}^+ = \text{C} - \text{S}^-$ but is rather associated with an increased electronic density of both the NC and the CS bond. We therefore calculated the electronic density for DMPT and the (hypothetical) complex $\text{DMPT} \cdot \text{ZnBr}_2 \cdot \text{H}_2\text{O}$ (with the water molecule added in order to retain the tetrahedral structure around Zn) by the CNDO/2 method. The available program did not permit calculations on *e.g.* $(\text{DMPT})_2\text{ZnBr}_2$ or $\text{DMPT} \cdot \text{HgCl}_2$, but there are no grounds for believing that such calculations would significantly alter the conclusions. The principal changes (Fig. 2) are that a density of 0.51e is removed from DMPT mainly from the hydrogen atoms of the CH_2/CH_3 groups (0.15e) and the sulfur atom (0.30e). The Zn-S bond is mainly of the donor-acceptor type and is established between the vacant orbitals of the metal cation and one of the lone-pairs of sulfur (*i.e.* a σ -bond relative to the NCS group of DMPT since the zinc atom is assumed to lie in the NCS plane). In addition weak π -bonding arises as a result of electron donation from the p_π - and d_π -orbitals of sulfur to those of zinc. The calculated bond order and electron density contributions from the individual atomic orbitals show, in line with classical theory, that the electron-deficient sulfur atom induces a change in the π -density of the NCS group corresponding to an increased weight of the structures $\text{N}^+ = \text{C} - \text{S}^-$

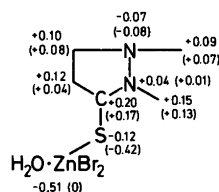


Fig. 2. The CNDO/2 charge density for $\text{DMPT} \cdot \text{ZnBr}_2 \cdot \text{H}_2\text{O}$ and, in parentheses, for DMPT.

and $C^+ - S^-$, i.e. the π -density (and force constant) of the CN bond increases while the π -density (and force constant) of the CS bond decreases. However, in addition to the changes predicted by classical theory, the CNDO/2 calculations also reveal a change in the σ -density of the NCS group. The electron-deficient sulfur atom polarises the CS bond with the result that σ -density is removed from the carbon atom and transferred to the region closer to sulfur with subsequent increase in the σ -bond order (and force constant) of the CS bond. In summary, the changes in the thiohydrazide group amount to an increased strength of the NC bond, while the CS bond (with a decrease in π -density but an increase in σ -density) does not necessarily become weaker on complex formation but may very well be unchanged or become stronger as indicated by the results of the NCA.

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