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)$_2$ZnBr$_2$, DMPT·CdI$_2$, (DMPT)$_2$CdI$_2$ and DMPT·HgCl$_2$ 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·HgCl$_2$ were recorded in the region 4000–180 cm$^{-1}$. Normal coordinate analysis of DMPT·HgCl$_2$ 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 $\pi$-character of the thiohydrazide group, $N^+ = C - S^-$, with concomitant decrease in the force constant for CS stretching. In addition, the $\sigma$-electrons of the CS bond are polarised towards sulfur so as to give an increased $\sigma$-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 $\sigma$-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 Nielsen$^1$ 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 dithiobiuret,$^4$ Desseyn 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 $\nu$CN (CN stretching) to increase while that for $\nu$CS to decrease relative to the free ligand values. As a result, bands with $\nu$CN contributions will be displaced towards higher frequencies while bands with $\nu$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 compound\(^{10}\) or the conformational changes in the ligand\(^{11}\) (e.g. thiosemicarbazides,\(^{12}\) dithiobiuret\(^{13}\)) due to complex formation may result in large shifts of the \(\nu CN\) and \(\nu CS\) 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 \(\nu CN\) increases strongly in \(S\)-coordinated thiocetamide,\(^{15}\) but the band with maximum \(\nu CN\) 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 \(\nu CS\) bands.

The vibrational spectra of the thiourea derivative 1,2-dimethyl-3-pyrazolidinethione (DMPT) have previously\(^{16}\) been thoroughly examined. In the coordination complexes of DMPT, (DMPT)\(_2\)ZnBr\(_2\), DMPT·CdI\(_2\), (DMPT)\(_2\)CdI\(_2\) and DMPT·HgCl\(_2\), the \(\nu CS\) bands show only very small shifts either towards higher or towards lower frequencies. Since the IR spectra of these coordination compounds are almost identical, DMPT·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): (DMPT-\(1-d_3\))HgCl\(_2\), (DMPT-\(2-d_3\))HgCl\(_2\), (DMPT-\(d_2\))HgCl\(_2\), (DMPT-\(d_0\))HgCl\(_2\), and (DMPT-\(d_{10}\))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 (DMPT)\(_2\)ZnBr\(_2\), (DMPT)\(_2\)CdI\(_2\) and DMPT·HgCl\(_2\) were prepared by addition of an ethanolic solution of the ligand to a saturated ethanolic solution of the metal halides. DMPT·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 \textit{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 (DMPT)\(_2\)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 DMPT·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 thiourea bands we did not perform a full NCA including the metal halide molecule. Instead we used the calculations reported previously for DMPT\(^{16}\) and simply replaced the observed fundamentals with the corresponding values for DMPT·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 \(\nu_{43}\) 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·HgCl$_2$ compared with the values for DMPT.$^a$

<table>
<thead>
<tr>
<th>Symbol</th>
<th>DMPT·HgCl$_2$</th>
<th>DMPT</th>
<th>Symbol</th>
<th>DMPT·HgCl$_2$</th>
<th>DMPT</th>
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<tr>
<td></td>
<td>$CH_3/CH'_3$</td>
<td>$CH_3$</td>
<td></td>
<td>$CH_3/CH'_3$</td>
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</tr>
<tr>
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<td>4.71</td>
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<td>3.85</td>
<td>3.76</td>
</tr>
<tr>
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<td>0.01</td>
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<td>3.88</td>
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<td>0.51</td>
<td>$K_{l1}$</td>
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<td>4.59</td>
</tr>
<tr>
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<td>$K_{B1}$</td>
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<td>-0.04</td>
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</tr>
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<td>4.64</td>
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<td>0.51</td>
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<td>-0.03</td>
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<td>etc.</td>
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<tr>
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<td>0.66</td>
<td>$F_{p1p2}$</td>
<td>etc.</td>
<td></td>
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</table>

$^a$For interpretation of symbols, units, and force field for DMPT, see Ref. 15. The values of $H_{e1}, H_{D_{12}}, F_{D_{12}}, F_{B_{2u2}}, F_{B_{2u3}}$, $F_{L_{2w3}}=F_{A_{3}}, H_{w}$, and $F_{w}$ are the values of DMPT (see text).

ously, the interaction constants $F_{DL_{2}}, F_{DB_{2}}, F_{B_{2u2}}$, and $F_{B_{2u3}}$ were fixed. The values of $H_{e1}, H_{e2}$ and $H_{e3}$ were 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 $F_{L_{2w3}}=F_{A_{3}}$ to be highly correlated and therefore they were also transferred from DMPT. A simultaneous least-squares adjustment was then made for DMPT·HgCl$_2$ 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 $CH_3, CH_3$ and $CH_2-CH_2$ 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 ($H_{u1}, H_{u2}, H_{u3}$) decrease on complex formation. This is related to the lowering of $v_{38}, v_{40}$ and $v_{43}$ frequencies which originate to a considerable degree in these modes (Table 2). The upward trends in $v_{11}, v_{20}$ and $v_{39}$ frequencies reflect to a large degree the increase in the force constants for $vCS$ (from 3.76 to 3.85
Table 2. IR spectra (cm⁻¹) of metal complexes (DMPT)₂ZnBr₂, DMPT·CdI₂, (DMPT)₂CdI₂ and DMPT·HgCl₂ of 1,2-dimethyl-3-pyrazolidinethione (DMPT).

Calculated frequencies, tentative assignments, description of the fundamentals and frequency shift relative to DMPT for the complex DMPT·HgCl₂.

<table>
<thead>
<tr>
<th>(DMPT)₂ZnBr₂</th>
<th>DMPT·CdI₂</th>
<th>(DMPT)₂CdI₂</th>
<th>DMPT·HgCl₂</th>
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<tr>
<td><strong>Observed IR, disc</strong></td>
<td><strong>Observed, IR</strong></td>
<td><strong>DMPT-shift</strong></td>
<td><strong>Observed IR, disc</strong></td>
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<td></td>
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<td>solut.</td>
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<tr>
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<td>3002m</td>
<td>3003m</td>
<td>+ 18</td>
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<tr>
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<tr>
<td>1560vs,br</td>
<td>1560vs,br</td>
<td>1562vs,br</td>
<td>1550vs,br</td>
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</tr>
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<td>1454ms</td>
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</table>

*The following abbreviations have been used: s, strong; m, medium; w, weak; b, broad; sh, shoulder. Weak and very weak bands not assigned to fundamentals have many instances in the spectra. Approximate values are in parentheses. The values in the table are considered significant. * Shifts based on all six isotopic species of DMPT·HgCl_2. * Abbreviations: \nu = stretch; \delta = deformation; \Delta = out-of-plane deformation; \rho = rock; \omega = wag; \tau = twist; \tau = torsion; \nu = symmetric; \nu = antisymmetric. Vibrations believed to originate mainly in the metal halide are designated DMPT-metal halide. The potential energy distribution (PED, x_{3k} = 100F_{k}/L_{k}^2/L_{k}) is stated only for significant contributions. The PED referring to the thiohydrazide group is given in bold type.
Fig. 1. The IR spectra of 1,2-dimethyl-3-pyrrozolindethione 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 HgCl₂) are indicated as DMPT·HgCl₂.

mdyn/Å, vCN (from 7.51 to 8.56 mdyn/Å) and vNN (from 5.35 to 5.56 mdyn/Å). The force constants for three of the bonds adjacent to the N—N—C—S grouping (K₁₁, K₁₂, and K₁₃) decrease on complex formation. This feature appears to be indirectly connected with the decrease in ν₃₃.

RESULTS AND DISCUSSION

The IR spectra of DMPT (liquid) and DMPT·HgCl₂ (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 DMPT·HgCl₂ 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 DMPT·HgCl₂ 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, ν(DMPT·HgCl₂)−ν(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 DMPT·HgCl₂, 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 DMPT·HgCl₂ with the following reservations. Firstly, strong intensity changes may occur as in ν₃₅, 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. ν₃₆ followed by ν₃₉+ν₄₅ 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. ν₁₇ and ν₁₈ have interchanged positions, ν₃₉ has an increased contribution from ΔCS).

All these complications have been described in some detail in the previous paper \textsuperscript{10} 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.\textsuperscript{16} The fundamentals $v_{21}$ and $v_{24}$, 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\textsubscript{2} and CH\textsubscript{3} groups. As a matter of fact, most of the shifts observed on complex formation of DMPT are 10 cm\textsuperscript{-1} or less, and without the results of the NCA it would be extremely difficult to locate the contributions from the thiolythyrazide group. These results also explain the problems encountered by Devillanova and Verani\textsuperscript{21} in identifying the thioamide bands in heterocyclic thiones with complex formation with CdCl\textsubscript{2}.

The fundamental $v_{11}$ of DMPT, mainly due to the C\textsuperscript{3}N stretching vibration, is displaced by 60–70 cm\textsuperscript{-1} towards higher frequencies on complex formation. We therefore expect $v_{34}$ and $v_{39}$, with the highest contributions from CS stretching to shift towards lower frequencies. Nevertheless, $v_{34}$ shows a downwards shift by only 0–9 cm\textsuperscript{-1} and $v_{39}$ even shifts 4–6 cm\textsuperscript{-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 HgCl\textsubscript{2}. It is seen that the PED of $v_{34}$ shows an increased contribution from sCS (from 31 to 43 3\% ) at the expense of ring stretching and deformation vibrations. By contrast, the sCS contribution of $v_{39}$ decreases from 32 to 23 3\% while ACS increases from 4 to 18 3\%.

However, the NCA also indicates the force constant for CS stretching to increase from 3.76 to 3.85 mdyr/\textring. 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 structure\textsuperscript{19} 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 N\textsuperscript{+} = C\textsuperscript{-} S\textsuperscript{-} 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 DMPT·ZnBr\textsubscript{2}·H\textsubscript{2}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. (DMPT)\textsubscript{2}ZnBr\textsubscript{2} or DMPT·HgCl\textsubscript{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\textsubscript{2}/CH\textsubscript{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 $\pi$-bond relative to the NCS group of DMPT since the zinc atom is assumed to lie in the NCS plane). In addition weak $\pi$-bonding arises as a result of electron donation from the $p_x$- and $d_x$-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 $\pi$-density of the NCS group corresponding to an increased weight of the structures N\textsuperscript{+} = C\textsuperscript{-} S\textsuperscript{-}.

\textbf{Fig. 2.} The CNDO/2 charge density for DMPT·ZnBr\textsubscript{2}·H\textsubscript{2}O and, in parentheses, for DMPT.
and C\(^+\)–S\(^-\), i.e. the \(\pi\)-density (and force constant) of the CN bond increases while the \(\pi\)-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 \(\sigma\)-density of the NCS group. The electron-deficient sulfur atom polarises the CS bond with the result that \(\sigma\)-density is removed from the carbon atom and transferred to the region closer to sulfur with subsequent increase in the \(\sigma\)-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 \(\pi\)-density but an increase in \(\sigma\)-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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