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# Low-temperature Ligand-field and Far-infrared Spectra of *Trans*-dichlorotetrakis(5-methylpyrazole)nickel(II) and *Trans*-dibromotetrakis(5-methylpyrazole)nickel(II)

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*Polarized crystal spectra (10 K) and far-infrared spectra (80 K) have been recorded for Ni(MPZ)$_4$X$_2$ (MPZ = 5-methylpyrazole; X = Cl, Br). Reasonable assignments have been made in terms of $D_{4h}$ symmetry. The significance of the various calculated ligand field and orbital angular overlap parameters is discussed.*

## Introduction

Pyrazoles are known to yield the tetragonal species M(ligand)$_4$(anion)$_2$ with divalent transition-metal ions and anions like halide and nitrate [1–4]. In a few cases this has been confirmed by single-crystal X-ray structure determination [5–7]. An interesting feature of these compounds is the presence of intra-molecular hydrogen-bonding between the N–H groups of the equatorial pyrazole ligands and the axial halide ligands. This effect is also deduced from the ligand-field spectra, which show an apparent weakening of the metal–halogen bond as compared, for example, with the same bond in similar pyridine compounds.

In going from pyrazole to 3- or 5-methyl pyrazole, isomers containing 3-methyl pyrazole or 5-methyl pyrazole isomers are to be expected; this has been reasons, however, indicate that only the 5-methyl pyrazole isomers are to be expected; thus has been proved by a single-crystal structure determination [7]. In addition, effects of rhombic ligand fields could be expected to appear. Low-temperature susceptibility and EPR spectra, however, could not detect such rhombic splittings in the ground state of the title compounds [8]. In order to obtain a detailed picture of the excited states of these complexes, we have measured the low-temperature (~10 K) polarized crystal spectra of Ni(MPZ)$_4$X$_2$ (MPZ = 5 methyl pyrazole; X = Cl, Br) and also their far-IR spectra at ~80 K.

## Experimental

### Preparation of the Compounds

The compounds were prepared as described earlier [2]. Single-crystals were obtained after recrystallization from acetonitrile.

### Structure of the Crystals

Although crystal structures are known for Ni(pyrazole)$_4$Cl$_2$ [5] and Ni(pyrazole)$_4$Br$_2$ [6], the structures of the corresponding 5-methyl pyrazole complexes are not known. Vermaas *et al.* [9] note, however, that the X-ray powder diffraction patterns of Ni(MPZ)$_4$X$_2$ (X = Cl, Br) are similar to that of Mn(MPZ)$_4$Br$_2$ for which the crystal structure has been determined [7]. It belongs to the triclinic system, space group $P\bar{1}$, with one molecule per unit cell. The compound consists of *trans*-Mn(MPZ)$_4$Br$_2$ units with approximate $D_{4h}$ symmetry. So Vermaas *et al.* [9] assumed that the Ni(MPZ)$_4$X$_2$ (X = Cl, Br) compounds have the same structure.

### Spectral Measurements

The polarized absorption spectra of single crystals were measured at room temperature (*ca.* 295 K) and at approximately 10 K using an Air Products Displex cryogenic refrigerator and a Cary 14 spectrophotometer. The light was polarized with a pair of Glan-Thompson prisms, and spectra were recorded with the electric vector of the light parallel to two orthogonal extinction axes of the crystal. The extinction axes are not coincident with any prominent edges of the crystal. Because of the low symmetry of the crystals, and because the two observed polarizations are so similar, they probably represent different mixtures of $\sigma$ (electric vector perpendicular to $C_4$) and $\pi$ (electric vector parallel to $C_4$) spectra.

Infrared spectra were recorded at room temperature and ~80 K from 20 to 450 cm$^{-1}$ using a Beck-

TABLE I. Band Positions for *trans*-Ni(MPZ)$_4$X$_2$.[a]

| | X = Cl | | X = Br | |
|---|---|---|---|---|
| | calc. | obs. | calc. | obs. |
| $^3B_{1g}$ | 0.00 | | 0.00 | |
| $^3E_g$ | 8.53 | 8.56 | 7.66 | 7.65 |
| $^1A_{1g}$ | 11.33 | | 10.05 | |
| $^3B_{2g}$ | 11.40 | 11.40 | 11.05 | 11.05 |
| $^1B_{1g}$ | 13.24 | 13.24 | 13.03 | 13.03 |
| $^3A_{2g}$ | 13.74 | 13.68 | 12.19 | 12.22 |
| $^3E_g$ | 16.75 | 16.71 | 16.20 | 16.20 |
| $^1E_g$ | 21.26 | 21.43 | 20.10 | 20.36 |
| $^1A_{2g}$ | 23.48 | 23.27 | 21.46 | 21.38 |
| $^1A_{1g}$ | 23.59 | | 23.94 | |
| $^1B_{2g}$ | 24.24 | | 23.68 | |
| $^3A_{2g}$ | 25.44 | | 24.63 | 24.17[c] |
| $^3E_g$ | 26.46 | 26.46 | 25.97 | 25.98 |
| $^1E_g$ | 28.80 | | 28.90 | |
| $^1A_{1g}$ | 33.67 | 32.04[b] | 32.03 | 32.13 |
| $^1E_g$ | 34.30 | | 32.86 | |
| $^1B_{1g}$ | 35.09 | | 34.36 | |
| $^1B_{2g}$ | 35.49 | | 34.76 | |
| $^1A_{1g}$ | 57.36 | | 55.90 | |
| DQ | 26.82 | | 25.33 | |
| DS | −5.98 | | −8.25 | |
| DT[d] | −3.82 | | −4.27 | |
| B | 0.822 | | 0.822 | |
| $\gamma = C/B$ | 4.28 | | 4.16 | |
| RMS | 0.10 (8 bands) | | 0.17 (10 bands) | |

[a] All data in kK. [b] Omitted in calculation of RMS deviation; this is the first of a four band progression in *ca.* 1.00 kK. [c] Not used in getting best fit of the triplet bands. [d] The sign of DT follows the convention in [18]; it is the opposite of that given earlier in [10].

man FS-720 Interferometer operating under standard conditions. Samples were recorded as pressed discs in polythene.

### *Calculations*

In calculating the band positions, we have assumed $D_{4h}$ symmetry for the complexes, and have used symmetry adapted functions and a normalized spherical harmonic (NSH) Hamiltonian for $D_{4h}$ [10]. A fitting program was used to minimize the differences between observed and calculated band positions for the spin-allowed bands. For both compounds the position of the upper $^3A_{2g}$ state was varied so as to give the best fit. After this was done, the choice of a suitable value of C permitted the fitting of the spin-forbidden bands.

## Results and Discussion

### *Ligand Field Spectra*

The polarized spectra for Ni(MPZ)$_4$Cl$_2$ and Ni(MPZ)$_4$Br$_2$ at 10 K are shown in Fig. 1. In general detail they are similar to the diffuse reflectance and CH$_2$Cl$_2$ solution spectra of these compounds previously reported [8]. They are also similar to the spectra of the corresponding pyrazole complexes reported by Reimann [11]. But the use of low-temperature polarized crystal spectroscopy brings out certain new, and possibly significant, features.

The spectra of both compounds show the expected blue shift of the maxima on cooling. This is due to depopulation at low temperature of vibrational levels associated with the ground electronic state. The bands also show considerable diminution in size

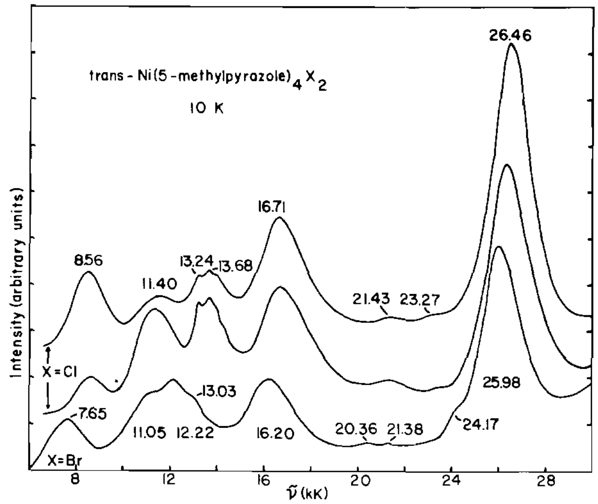

Fig. 1. Polarized crystal spectra of *trans*-Ni(5-methylpyrazole)$_4$X$_2$ (X = Cl, Br) at 10 K. Two orthogonal polarizations of the chloro complex are shown, but only one polarization of the bromo complex, since both polarizations are nearly identical. Weak bands also appear at 32.04 kK (Cl) and 32.13 kK (Br) which are not shown here. The maxima for the chloro complex are the average of the two polarizations.

on cooling. This indicates that vibronic coupling is significant as an intensity-gaining mechanism (see below).

The band assignments for the spin-allowed bands are the same as those made for the room temperature reflectance spectra [8]. They also correspond well with those for the analogous pyrazole complexes [11] and with those for a series of *trans*-Ni(sym-diethylethylenediamine)$_2$X$_2$ (X = Cl, Br, $H_2O$, *etc.*) complexes [12]. The observed and calculated band positions together with the parameters used in obtaining the best fit are listed in Table I.

Because of work done on similar compounds the assignments are rather straightforward, except for the bands in the 12–13 kK region in the bromide and in the 13–14 kK region in the chloride. A suitable fit can be obtained if the principal broad band in these regions is assigned to the $^3B_{1g} \rightarrow {}^3A_{2g}$ transition. One of the other shoulders or spikes is probably the transition to $^1B_{1g}$, which is calculated to appear near the $^3A_{2g}$ state. It seems that considerable mixing of the two states augments the intensity of the singlet. The band positions we have chosen represent what we feel is the best of several choices; therefore the calculated parameters do not, a priori, represent a unique set. Other sets calculated do not, however, alter the arguments given below.

A significant advantage of low-temperature crystal spectroscopy is seen in studying the intense band *ca.* 26 kK, which is assigned to $^3B_{1g} \rightarrow {}^3A_{2g} + {}^3E_g$. Even at low temperature the $^3A_{2g}$ component is almost never [9, 11] observed as a discrete band, but it is seen as a shoulder on the low-energy side of the band, when it can be discerned at all. In the chloro complex it is not seen at all, but in the bromo complex, it appears clearly as a shoulder. An unusual feature is that at 10 K this shoulder shows two weak overlapping progressions in 185 ± 5 cm$^{-1}$, the two progressions being separated by 90–100 cm$^{-1}$. The 185 cm$^{-1}$ frequency probably represents $\nu$(Ni–Br) ($a_{1g}$), a symmetric stretching frequency of the molecule in the $^3A_{2g}$ excited state. The Raman spectrum shows a weak, broad band at 190 cm$^{-1}$ [13]. While this is a rather low value for the ground state Ni–Br stretch, it can be rationalized on the basis of a long Ni–Br bond distance in this compound. In Ni(Pz)$_4$Cl$_2$ and Ni(Pz)$_4$Br$_2$ (Pz = pyrazole) the Ni–Cl and Ni–Br bond lengths are 2.507 and 2.682 Å as compared with 2.38 and 2.58 Å in the analogous pyridine complexes. These exceptionally long Ni–X bonds are due to hydrogen-bonding between the halogen and the proton on N(2) of pyrazole [11]. It seems likely that such an effect is operative here also.

The 90–100 cm$^{-1}$ spacing may reflect the splitting of the $^3A_{2g}$ state into its spin–orbit components, $\bar{A}_{1g} + \bar{E}_g$. Since the ground-state splitting is 5.3 cm$^{-1}$ [9], both spinor states ($\bar{B}_{2g}$ and $\bar{E}_g$) will be significantly occupied even at 10 K, and transitions from both components of the ground state to both components of $^3A_{2g}$ are allowed in both polarizations by coupling with the various odd vibrations of the chromophore. (An exception to this is that $\bar{B}_{2g} \rightarrow \bar{A}_{1g}$ is not allowed in $\pi$ since there is no $b_{1u}$ vibration of the NiN$_4$X$_2$ chromophore). It is to these spinor components plus $u$ vibration that the $a_{1g}$ progression is added. Alternatively, the second progression which lies 90–100 cm$^{-1}$ above the first could result from the coupling of a low-frequency $g$ vibration to the electronic level. No such vibration is, however, observed in the Raman spectrum of the molecule [13].

As noted above, the band intensities in general decrease on cooling. Measurements of the area of the 26 kK band in the chloro complex indicate that at 10 K it is only about 42% of its size at room temperature. According to the hyperbolic cotangent law [14] this would indicate an enabling vibration of about 185 cm$^{-1}$. This may correspond to the ground state odd vibration which appears in the IR spectrum at 180 cm$^{-1}$. The symmetry and exact nature of this vibration cannot at present be further specified (see below). The selection rules indicate, however, that the $^3B_{1g} \rightarrow {}^3E_g$ transition is vibronically allowed in $\sigma$ by coupling of $^3E_g$ with an $a_{2u}$ or $b_{2u}$ vibration and in $\pi$ by coupling of $^3E_g$ with an $e_u$ vibration. It is harder to estimate the shrinkage in the bromo complex due to the evident composite nature of the 26 kK band and a poorer baseline. But the band shrinkage appears to be of similar magnitude.

TABLE II. Derived Parameters for *trans*-[$Ni(MPZ)_4X_2$] and *trans*-[$Ni(s\text{-}Et_2en)_2X_2$] (ref. 12) (data in kK).

| | $Ni(MPZ)_4X_2$ | | $Ni(s\text{-}Et_2en)_2X_2$ | |
|---|---|---|---|---|
| | X = Cl | X = Br | X = Cl | X = Br |
| $d\sigma$ | −1.81 | −2.36 | −1.70 | −2.06 |
| $d\pi$ | −0.58 | −0.98 | −0.28 | −0.64 |
| DQ(axial) | 17.77 | 15.22 | 17.16 | 16.80 |
| DQ(equatorial) | 31.35 | 30.38 | 32.76 | 32.36 |
| B | 0.822 | 0.822 | 0.864 | 0.845 |
| $e'_{\sigma X}$ (axial) | 1.54 | 0.80 | 1.71 | 1.18 |
| $e'_{\pi X}$ (axial) | −0.42 | −0.82 | −0.28 | −0.64 |
| $e'_{\sigma N}$ (equatorial) | 3.95 | 3.95 | 3.97 | 3.92 |
| $e'_{\pi N}$ (equatorial) | 0.16 | 0.16 | 0.00 | 0.00 |
| Ds | 0.85 | 1.18 | 0.72 | 0.97 |
| Dt | 0.28 | 0.32 | 0.32 | 0.32 |
| 10 Dq | 11.40 | 11.05 | 11.91 | 11.77 |

Another interesting feature in the spectrum of $Ni(MPZ)_4Cl_2$ is the appearance in one polarization at 10 K of four weak bands which seem to be a progression in ~1.00 kK beginning at 32.04 kK. Spin forbidden bands are calculated to appear in this region (Table I). However, the bands could also represent a vibronic progression built on the forbidden $n \rightarrow \pi^*$ transition on the MPZ ligands. No such band, however, has been reported for MPZ; the lowest reported absorption is at 219 nm (45. 7 kK) with $\log \epsilon = 3.51$ [15].

### *Infrared Spectra*

Of the 15 normal vibrations of $NiN_4X_2$ in $D_{4h}$, only two $a_{2u}$ (Ni–X stretch and $NiN_4$ out-of-plane bend) and three $e_u$ (Ni–N stretch, $NiN_4$ in-plane bend, and XNiX bend) vibrations are IR active. Since, in fact, five bands are found below 400 $cm^{-1}$ in the IR spectra of both compounds (see Table III), one is tempted to make a one to one correlation. But this is not feasible. The band around 370 $cm^{-1}$ is insensitive to X and is clearly too high to be a $NiN_4$ bending vibration. The Ni–N stretch, in analogy to similar compounds, must be below 300, and probably below 250 $cm^{-1}$. So the band at 370 $cm^{-1}$ has been assigned to a ligand vibration, most probably the $C\text{–}CH_3$ in-plane deformation [13].

The band at about 235 $cm^{-1}$ is also insensitive to X and may be assigned as principally $\nu$(Ni–N). This agrees with the assignment of the (M–py) stretch to values between 287 and <200 $cm^{-1}$ [16] and with that of $\nu$(Ni–N) in $Ni(imidazole)_2Br_2$ to a band at 262 $cm^{-1}$ [17].

TABLE III. Infrared Bands (450–20 $cm^{-1}$) at 80 K of $Ni(MPZ)_4X_2$ (X = Cl, Br).

| Absorption ($cm^{-1}$) | | Ratio (Cl/Br) |
|---|---|---|
| X = Cl | X = Br | |
| 371 | 370 | |
| 236 | 234 | |
| 205 | 175 | 1.17 |
| 180 | 139 | 1.29 |
| 143 | 115 | 1.24 |
| | 108 | 1.32 |

A likely order for the remaining vibrations is

$$\underset{(e_u)}{\nu(M\text{–}X)} > \underset{(a_{2u})}{\delta(MN_4 \text{ in-plane})} > \underset{(e_u)}{\delta(MN_4 \text{ out-of-plane})} > \underset{(a_{2u})}{\delta(XMX)}$$

Since there are only three bands between 100 and 220 $cm^{-1}$ and all three are sensitive to X, we must conclude that there is extensive mixing of the two $e_u$ vibrations and/or of the two $a_{2u}$ vibrations. The lowest vibration (143 and 108/115) is probably largely $\delta$(XMX) and the highest (205 and 175) is largely $\nu$(M–X). In addition, some of the frequencies must overlap, since there are too few bands. Finally, it must be remembered that the actual symmetry is lower than $D_{4h}$ and further splitting of $e_u$ vibrations is possible. Without a normal coordinate analysis, however, no further elucidation seems possible.

### *Calculated Parameters*

The parameters listed in Table I are in large part comparable to those calculated by Vermaas *et al.* [9]. The differences can be attributed mostly to the fact that their spectra were diffuse reflectance and were recorded at much higher temperatures (110 K minimum).

The NSH parameters listed in Table I can be converted by standard equations [18] to the more usual tetragonal parameters (Dq, Ds, Dt) and to other parameters which have more chemical significance. Some of these are listed in Table II for the two compounds studied here as well as for the analogous sym-diethylethylenediamine ($Et_2en$) complexes [12]. The McClure parameters, $d\sigma$ and $d\pi$, give the difference in $\sigma$- and $\pi$-antibonding effects between the axial M–X and equatorial M–N ligands [19]. The negative values indicate that the halogens have weaker $\sigma$- and $\pi$-antibonding effects with the metal orbitals than do the nitrogens. The spectrochemical series indicates that nitrogen sets up a stronger ligand field than chlorine or bromine, so this effect is expected. The $d\sigma$ and $d\pi$ values for the four compounds form a consistent set: $d\sigma(Br) < d\sigma(Cl)$ and $d\pi(Br) < d\pi(Cl)$ for both pairs, and the values for all parameters are more negative in the MPZ pair than in the $Et_2en$ pair.

B is slightly less for the MPZ compounds than for the $Et_2en$ complexes. This also may be a reflection of longer M–X bonds in the former, which allow for lowered interelectronic repulsion and smaller B.

The three NSH parameters (DQ, DS, DT) can also be related to four orbital angular overlap parameters: $e'_\sigma$ and $e'_\pi$ for the axial and equatorial ligands [18]. $e'_\sigma$ and $e'_\pi$ represent respectively the $\sigma$-antibonding and $\pi$-antibonding (or bonding) effects exerted on the d orbitals of the metal by interaction with the ligand orbitals [20]. The subscripts X and N refer to the halogen and nitrogen ligands. For the $Et_2en$ pair the $e'_\sigma$ and $e'_\pi$ parameters could be calculated using the assumption that $e'_{\pi N} = 0$ [12]. In lieu of making the extended calculations that Hitchman [21] did, we have made the assumption that for the MPZ set $e'_\sigma$ for the four equatorial nitrogens has the same average value as for the equatorial nitrogens in the $Et_2en$ set, namely, 3.95 kK. The values for $e'_\sigma$ and $e'_\pi$ listed in Table II were calculated under this assumption. The $e'_{\sigma X}$ parameters for the MPZ pair are slightly smaller than those for the $Et_2en$ pair; this again may reflect longer Ni–X bond lengths in the MPZ pair.

All the $e'_\pi$ parameters in the two pairs are not very large when compared to the case of Cr(III), in which $d\pi$ can have rather large values [22]. As has been pointed out [12], this is explicable if the $\pi$-interaction is principally L → M donation, for Cr(III) has a half-filled $t_{2g}$ ($O_h$) shell, whereas that of Ni(II) is full.

### *Rhombic distortion*

The compound *trans*-$Ni(Pz)_4(NO_3)_2$ has been shown by low-temperature heat capacity and paramagnetic susceptibility measurements to have a considerable rhombic distortion [23]. In addition, magnetic susceptibility measurements and Mössbauer spectra of $Fe(MPZ)_4Cl_2$ and $Fe(MPZ)_4Br_2$ could be interpreted in terms of a point symmetry lower than tetragonal with a small rhombic component present [24]. It was hoped that low-temperature optical spectra might give some indication about such distortions in $Ni(MPZ)_4X_2$ (X = Cl, Br). The 26 kK and 16 kK bands in the spectra of the chloro complex indeed show some differences in the position of the maxima in the two polarizations. But these differences, which are only *ca.* 150 cm$^{-1}$, lie near the limits of precision of the spectral measurements. Even if they are real, however, it would be hazardous to attribute them to rhombic distortion, since other factors could also cause such small differences. So we conclude that the present spectra offer no sure indication of rhombic distortion.

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